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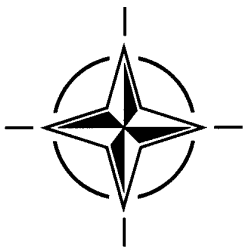
# Environmental Aspects of Rocket and Gun Propulsion

(les Aspects environnementaux de la propulsion par fusée et des canons)

*Papers presented at the Propulsion and Energetics Panel (PEP) 84th Symposium held in Aalesund, Norway, 29 August - 2 September 1994.*

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AGARD CP 392, January 1986

**Advanced Instrumentation for Aero Engine Components**
AGARD CP 399, November 1986

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AGARD CP 400, March 1987

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AGARD AR 275, July 1990

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**Terminology and Assessment Methods of Solid Propellant Rocket Exhaust Signatures** *(Results of Working Group 21)*
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AGARD R 745, November 1987

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AGARD R 775, June 1990

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# Environmental Aspects of Rocket and Gun Propulsion

Environmental issues associated with the use of missile and gun propulsion are becoming increasingly demanding. Concerns are frequently expressed over the environmental effects of rocket exhaust on people, land and the upper atmosphere. Major demilitarization initiatives have resulted in significant quantities of surplus propellant needing safe and environmentally proper disposal. Work has been aggressively started to develop new "clean" propellants, new manufacturing methods, and new disposal procedures and facilities. Efforts involve both the development of new technologies to minimize future environmental impacts as well as engineering methods to safely dispose of propellant or reuse propellant ingredients. This Symposium addresses a topic of particular concern today; it will act as a focus for the discussion of relevant research and engineering solutions to these difficult problems, and allows this knowledge to be shared amongst the NATO research community.

# Thème

# Les aspects environnementaux de la propulsion par fusée et des canons

Les questions d'environnement associées à l'activation des systèmes de propulsion des missiles et des canons sont de plus en plus préoccupantes. Des inquiétudes sont souvent exprimées concernant les effets environnementaux des jets de propulseur sur les populations, sur les terres et sur la haute atmosphère. Suite aux récentes initiatives de démilitarisation importantes, il est nécessaire d'identifier des moyens d'évacuation sûrs et écologiquement acceptables pour les quantités importantes de propergols qui en ont résulté.

Des travaux ont été lancés avec promptitude en vue du développement de nouveaux propergols "propres", de nouvelles méthodes de fabrication, de nouvelles procédures d'évacuation et de nouvelles installations de traitement. Les efforts y consacrés comprennent le développement de nouvelles technologies afin de réduire au minimum l'impact environnemental à l'avenir, ainsi que le développement de procédés industriels soit pour l'élimination des propergols en toute sécurité, soit pour le recyclage de leurs ingrédients.

Le sujet de ce symposium suscite de nombreuses préoccupations aujourd'hui. La réunion doit servir de forum pour la discussion des travaux de recherche pertinents qui sont en cours, ainsi que des éventuelles solutions technogéniques à ces problèmes difficiles. Il favorise ainsi la mise en commun des connaissances des membres de la communauté de recherche de l'OTAN.

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* Due to circumstances beyond the Authors' control they were unable to present this paper during the Symposium but the paper was available in time for distribution

# RAPPORT D'EVALUATION TECHNIQUE

**(English version follows)**

**par Alain Davenas ***

## Introduction

Le 84ème Symposium du Propulsion and Energetics Panel s'est tenu à Aalesund (Norvège) du 29 août au 2 septembre 1994 avec pour thème : les aspects environnementaux des systèmes de propulsion des fusées et canons. L'annonce de ce symposium stipulait que "ce sujet suscite de nombreuses préoccupations aujourd'hui". La réunion devait servir "de forum pour la discussion des travaux de recherche pertinents qui sont en cours ainsi que les éventuelles solutions technologiques à ces problèmes difficiles". Il devait ainsi "favoriser la mise en commun des connaissances des membres de la communauté de recherche de l'OTAN".

Les thèmes des sessions étaient les suivants :

1. Propergols propres
2. Développement de propergols
3. Mesures
4. Elimination
5. Récupération et recyclage
6. Contamination

## Résumé et commentaires

Le programme prévu était très dense puisqu'il comportait 44 exposés. Toutefois 35 seulement ont été présentés. Les objectifs ont cependant été globalement atteints, particulièrement la mise en commun des connaissances sur ce sujet délicat dont le professeur Clark Hawk a rappelé dans son discours d'introduction qu'elle devait être développée dans la communauté aérospatiale ainsi que la collaboration avec la communauté scientifique. Les discussions ont été relativement fournies et ouvertes, tant pendant qu'après les sessions. Un problème particulier s'est posé à ce niveau avec les orateurs russes, le problème de langue rendant la discussion très difficile. Seule la procédure des questions/réponses écrites a permis d'améliorer un peu les échanges avec ceux-ci.

Les aspects relatifs à la propulsion pour armes à tubes n'ont pratiquement pas été traités à l'exception d'un exposé, d'ailleurs utile et pertinent sur la toxicologie de l'ergol XM 46 pour canon à ergol liquide. Il est clair cependant que la plupart des données présentées à propos des propergols solides sont transposables aux poudres pour arme.

Le programme ne comportait par ailleurs aucun exposé tourné vers les technologies nouvelles de production présentant un impact plus réduit sur l'environnement par réduction des déchets (procédés continus par exemple) ni sur les études de nouveaux produits énergétiques conçus dès l'origine pour favoriser leur élimination ou leur recyclage. Ces points pourraient devenir importants à l'avenir. Ce Symposium comportait en fait deux grandes parties de nature technique assez différente.

La première traitait de l'impact de la propulsion (essentiellement propulsion fusée et jets de propulseur) sur l'environnement, de son évaluation et de sa mesure et de la recherche de nouveaux propergols solides susceptibles de réduire cet impact. Elle faisait donc, pour l'essentiel, suite aux polémiques du début

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des années quatre vingt dix sur l'effet des lanceurs ou des missiles sur la couche d'ozone stratosphérique qui protège la terre du rayonnement ultraviolet du soleil ainsi que sur les risques de pluies acides ou de pollutions aux alentours des sites d'essai ou de lancement.

La seconde partie traitait de l'impact des opérations de production, de destruction ou d'élimination des moteurs fusées à propergol solide ou liquide sur l'environnement. Ce dernier point devient de plus en plus critique, compte tenu de législations de plus en plus contraignantes (l'interdiction de détruire les composants énergétiques selon la méthode traditionnelle du brûlage à l'air libre tendant à se généraliser) et de l'évolution de la situation internationale qui conduit à la nécessité de détruire des stocks considérables de vieilles munitions.

Enfin la restructuration des industries de Défense obligeant à la fermeture de nombreux sites entraîne la recherche de moyens efficaces et économiques de décontamination ou de dépollution.

On peut considérer que ce symposium venait à point nommé car il a montré que sur un certain nombre de questions un consensus peut être considéré comme acquis, alors qu'il y a encore deux ou trois ans ces points étaient l'objet de controverses importantes au sein de la communauté scientifique internationale. Par ailleurs une expérience de quelques années dans la mise en oeuvre de systèmes de destruction des poudres ou propergols respectant les nouvelles contraintes d'environnement permet de tirer des premières leçons.

## Evaluation *

Impact de la propulsion fusée sur l'environnement

Le problème est clairement et avant tout celui des lanceurs. A titre d'illustration un lancement de navette représente, pour les seuls propergols solides, l'équivalent de l'émission gazeuse de trente tirs de missiles stratégiques français M4 ou de 30 000 missiles air-air Magic ou Sidewinder.

Le discours d'ouverture du Professeur Clark Hawk avait pour titre : "Effets des propergols solides sur l'environnement, perceptions et réalités". En cette matière, perception et communication sont certainement essentiels, particulièrement vis-à-vis de la presse, des communautés locales et des associations écologiques. La communication concernant l'impact de l'activité industrielle sur l'environnement est délicate. L'histoire récente a montré que la communication en matière d'évènements liés aux lancements est très délicate. La communication en matière de lancements et de leur impact sur l'environnement l'est donc au carré ! Une politique de communication ouverte, très bien préparée, associée à des procédures adaptées et à un contrôle rigoureux de la réalisation des lancements ou des essais au banc peut conduire à des succès auprès de l'opinion comme le montrent les exemples des actions de communication menées au Kennedy Space Center ou au Centre Spatial Guyanais de Kourou.

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*Les chiffres entre parenthèses renvoient aux numéros des exposés dans le programme du symposium.

Il n'est toutefois possible de bien communiquer que si l'on dispose de données et d'éléments validés sur lesquels s'appuyer et sur lesquels la communauté scientifique internationale s'accorde. Une première étape importante fut franchie en 1991 avec l'élaboration par un groupe de travail de l'AIAA d'un rapport de synthèse sur les effets sur l'atmosphère de la propulsion chimique. Cette synthèse, dont C. Hawk et A.J. Mac Donald, participants actifs au Symposium, furent à l'époque des chevilles ouvrières, a servi de base pour l'ensemble de la communauté aérospatiale à une communication rationnelle et à une réévaluation de ces problèmes. Ce rapport concluait en particulier, compte tenu des éléments alors disponibles, à un impact de la propulsion extrêmement faible et négligeable par rapport aux autres sources de composés susceptibles de réagir avec l'ozone. A.J. Mac Donald (1) a présenté une mise à jour détaillée des connaissances sur ces problèmes et confirmé les analyses et ordres de grandeurs précédents.

Ces conclusions ne sont pas susceptibles d'être remises en cause, ni par une augmentation importante du nombre de lancements (dans les limites actuellement concevables), ni par la réduction des autres émissions.

A. Tishin (2) semble globalement d'accord avec ces conclusions bien qu'il considère la propulsion liquide comme moins "polluante" que la propulsion solide (et donc les lanceurs russes comme moins polluants que les lanceurs occidentaux). Son exposé portait sur une critique d'études russes précédentes qui prévoient, sur les lanceurs, des taux d'oxydes d'azote supérieurs à ses propres estimations. Mac Donald et Tishin s'accordent d'ailleurs sur la nécessité de perfectionner les modèles cinétiques de recombinaison du jet avec l'atmosphère et de développer des méthodes de mesure expérimentales plus précises des espèces dans les jets et le long de la trajectoire lors des lanceurs.

L'élément le plus nouveau à sans doute été apporté par A. J. Mac Donald. Des expérimentations récentes effectuées aux USA, en liaison avec des études préliminaires liées aux projets de transport supersoniques à haute altitude ont montré que le cycle de l'hydrogène -qui passe par les radicaux H, OH, $HO_2$- joueraient un rôle beaucoup plus important que prévu dans la consommation d'ozone, ce qui pourrait conduire à une réévaluation de l'impact relatif solides/liquides (les oxydes d'azote auraient eux un rôle moins important que prévu).

Dans ces conditions rien ne justifie à court terme le remplacement, pour les questions liées à l'environnement, des propergols actuels de la grosse propulsion par de nouveaux propergols qui supposent des investissements, de développement et de qualification considérables. Seule une amélioration d'ensemble des caractéristiques fonctionnelles et des performances énergétiques en particulier, à condition que l'incidence sur le coût du propergol reste acceptable serait justifiée. L'application pourrait alors être envisagée lors du développement de systèmes entièrement nouveaux qui devront intégrer les contraintes d'environnement et toutes les connaissances alors disponibles relatives à l'impact sur celui-ci du futur lanceur.

Enfin E.Y. Krasilnikov dans sa communication intitulée "Rocket Engines and Ecology Problems" (23) a présenté des corrélations qu'il a observées entre les dates de certains lancements et de certains phénomènes atmosphériques ou sismiques importants. Il a présenté des modèles atmosphériques qui pourraient expliquer ces corrélations. Ces informations ne peuvent être valablement appréciées que par des spécialistes de météorologie et de géophysique.

Propergols à haute énergie améliorés

Un débat s'est instauré au cours du symposium sur le qualificatif de propergols "propres" qui constitue le titre d'une des sessions. Il est certain que ce vocable, inventé à une époque où les données rappelées ci-dessus étaient peu disponibles ou peu connues, a comme conséquence de faire apparaitre, sans aucune nuance, les propergols au perchlorate d'ammonium d'aujourd'hui comme sales. A.J. Mac Donald a proposé le vocable de "propergol alternatif", ce qui convient sans doute davantage si l'on vise le remplacement du propergol dans un système déjà existant.

C. Beckman (6) a présenté l'ensemble des solutions concevables à court ou moyen terme pour remplacer les propergols composites actuels dans des applications à des gros propulseurs en éliminant le gaz chlorhydrique des gaz de combustion. Les propergols à capteur de chlore incorporé dans la composition ont l'avantage de conserver les principales caractéristiques des composites industriels ainsi que l'essentiel des technologies de base. L'impulsion spécifique volumique est améliorée mais l'impulsion spécifique est diminuée, ce qui se traduirait malheureusement par une perte de performances au niveau de la plupart des applications. L'exposé de C. Pérut (4) montre que cette technologie conduit bien au but recherché, l'élimination du gaz chlorhydrique des gaz de combustion. Elle peut être considérée comme pratiquement disponible si elle devait être mise en oeuvre.

La voie intéressante des propergols au magnésium dans laquelle la neutralisation de l'acide chlorhydrique s'effectue par $Mg(OH)_2$ non pas dans la chambre mais dans le jet, selon des processus cinétiques fonction des conditions ambiantes, conduit à une élimination de celui-ci incomplète et variable, en fonction des conditions d'ambiance et de fonctionnement. Elle est en cours d'abandon.

La voie des propergols nouveaux comportant un oxydant liquide en solution ne conduit pas non plus à une augmentation des performances énergétiques. Elle a cependant le mérite de laisser espérer des améliorations de coûts de fabrication. Bien qu'ayant fait déjà l'objet d'un essai de démonstration à une échelle élevée,le changement technologique très important qu'elle représente et les méconnaissances qui en résultent (reproductibilité vieillissement ...) supposeraient un investissement lourd qui ne semble pas clairement décidé.

Finalement un accroissement significatif de l'énergie par rapport aux propergols solides actuels implique l'utilisation de nouveaux composés énergétiques sans chlore. Ces composés et les performances accessibles ont fait l'objet de présentations par S. DeMay(15) et G.B. Manelis (13) (principalement CL 20, ADN et autres dérivés de l'ion dinitramide) et J. Mul (HNF) (11). L'accès à des performances élevées suppose à notre avis également l'emploi de nouveaux liants énergétiques. Dans ces conditions il nous semble que deux questions fondamentales vont se poser qui étaient peu traitées dans ces présentations, et n'ont pu être qu'abordées dans les discussions :

- Celle des caractéristiques de détonabilité et plus généralement de sécurité de ces candidats potentiels à la succession des propergols actuels

- Celle des coûts de ces nouveaux ingrédients à l'échelle industrielle et de leur incidence sur le coût des moteurs les utilisant, particulièrement critique pour les gros lanceurs compte tenu des tonnages correspondants.

Propergols discrets pour missiles à signature réduite

La suppression des fumées secondaires liées au gaz chlorhydrique dans les jets de moteurs de missiles tactiques implique la suppression du perchlorate d'ammonium. Le besoin de propergols permettant la réalisation de munitions insensibles ou à risque atténué a entraîné des recherches sur des composés moins sensibles que l'hexogène ou l'octogène utilisés jusque là dans les propergols discrets. Ce domaine sur lequel portent des recherches importantes dans plusieurs pays a fait l'objet de nombreux exposés (7, 8, 9, 14, 15, 16, 17).

Des progrès importants ont été enregistrés ces dernières années. La mise au point de premières générations de propergols insensibles et discrets parait pratiquement acquise. Ces formulations utilisent pour l'essentiel le nitrate d'ammonium (NA) comme solide oxydant et des polymères énergétiques, PAG ou Poly NIMMO en particulier, comme base du liant. Le PAG peut être aujourd'hui considéré comme pratiquement industriel ; le développement du Poly NIMMO progresse. Dans ces conditions ce type de formulation pourrait certainement rentrer en phase de développement exploratoire, voire de développement industriel, si le problème du nitrate d'ammonium était résolu. Compte-tenu de ce qui a été exposé il ne nous semble pas que ce soit le cas. Les diverses solutions explorées pour supprimer les transitions de phase de ce composé reposent soit sur des "stabilisants" posant des problèmes de toxicité (Ni) ou de fumée (Zn) soit sur des solutions dont la viabilité risque d'être limitée au laboratoire (NA ultra sec). Un effort important et résolu sur ce point nous parait nécessaire, faute de quoi toutes les recherches effectuées sur ces propergols l'auront été en vain.

De nombreux ingrédients nouveaux et prometteurs pour l'accroissement de l'énergie de ces propergols ont été présentés par May Chan et Susan DeMay (9 et 15). Ils permettront un accroissement de l'énergie des propergols, particulièrement l'ADN et le CL 20. Le coût de ces composés même s'il est un facteur un peu moins critique pour les moteurs de missiles que pour les très gros propulseurs sera une des clés du passage à l'application. Un effort important doit être conduit par les chimistes sur ce point tant au niveau de la recherche des voies de synthèse les plus économiques que pour la prédiction des prix à l'échelle industrielle.

Conclusion sur le problème de l'interaction des jets de propulseur avec l'environnement.

L'ensemble des exposés et des discussions conduit aux conclusions suivantes :

1. Il n'y a aucun besoin et aucune raison, à court terme, de remplacer, pour des raisons liées à l'environnement, les propergols composites actuels dans les lanceurs existants ou actuellement en cours de développement.

2. Des travaux de recherche doivent être poursuivis en laboratoire sur de nouveaux propergols exempts de chlore, au cas où de nouvelles découvertes remettraient en cause les conclusions actuelles, où bien pour disposer de solutions si des décisions politiques étaient prises en raison de pressions psychologiques irrationnelles.

3. Les recherches doivent se poursuivre sur les mécanismes de consommation de l'ozone stratosphérique, sur la modélisation des phénomènes d'interaction du jet du lanceur avec l'atmosphère et surtout sur la mesure de ces effets.

4. Dans ces conditions, le seul objectif raisonnable est celui des propergols de performances supérieures à celles des propergols actuels avec des coûts acceptables. Ils ne devraient être appliqués

que lorsque leur maturité aura été démontrée, à l'occasion du développement d'un nouveau système. Le choix du type de propergol pourra dépendre des résultats des recherches indiquées au point 3.

5. Compte-tenu de l'examen des solutions possibles la caractérisation détonique et de sécurité des propergols envisageable devrait être une des actions prioritaires, préalable à un développement approfondi des compositions correspondantes. Dans ce contexte un échange d'information plus détaillé sur les caractéristiques des propergols à l'ADN qui auraient été développés industriellement en Russie, et qui n'a pas pu réellement avoir lieu au cours de ce symposium, serait extrêmement utile à la communauté aérospatiale.

6. Les travaux de recherche sur les propergols à signature réduite pour la propulsion tactique qui ont leur propre justification, outre le fait que leurs résultats contribuent à la réduction de la toxicité des émissions gazeuses ont un tronc commun et des retombées importantes, par exemple au niveau des composés énergétiques de base ou des mécanismes de combustion, sur le développement de nouveaux propergols à haute énergie.

Industrie de la propulsion et environnement

L'évolution de plus en plus contraignante des législations ne peut que conduire l'industrie à un effort d'adaptation considérable ; c'est pour celle-ci une question de survie. Deux exposés (20 et 21) ont montré l'adaptation des installations d'essai et les investissements que SNPE et DASA ont du réaliser sur leurs sites pour réduire les nuisances sonores sur l'environnement. Sans ces mesures l'exploitation de leurs installations serait devenu impossible. S. DeMay (9) et A.J. Mac Donald (37) ont rappelé l'évolution de la législation et des réglementations aux USA au niveau des émissions et des rejets et comment elles affectent l'industrie de la propulsion. JM. Tauzia (32) a montré que la législation en Europe évolue, avec un décalage dans le temps, dans le même sens : interdiction possible du brûlage à l'air libre en France à partir de 1996-97 et élaboration en cours d'une directive européenne spécifique aux matériaux énergétiques définissant des niveaux maxima de rejets gazeux admissibles.

Substances qui appauvrissent la couche d'ozone

Quatre exposés ont traité en détail des conséquences du protocole de Montréal et des restrictions ou interdictions d'utilisation à très court terme de ces substances (37, 38, 42, 43). Les conséquences sont considérables au niveau de la production des moteurs à propergol solide qui utilise en particulier des solvants chlorés pour le nettoyage, le dégraissage et la préparation des collages à divers stades de la production, tant pour les applications militaires que pour la navette spatiale. B. Goldberg (28) a présenté une stratégie et une méthodologie de hiérarchisation des priorités pour la qualification de produits et procédés de remplacement. Outre l'ampleur de la tâche, une des difficultés tient à la prolongation de l'existence de systèmes (exemples du SRM de la navette et du Minuteman) alors qu'une requalification à l'occasion du développement de nouveaux systèmes serait plus aisée. L'ensemble des informations échangées sera utile à la communauté aérospatiale qui a certainement intérêt à limiter au strict minimum (cas des collages intervenant de façon critique dans la fiabilité des moteurs par exemple) les demandes de dérogation. En outre, comme le montrent des exemples vécus en France, notre industrie a intérêt à développer ses propres solutions plutôt que de se reposer sur les produits de remplacement -souvent très onéreux- proposés par l'industrie chimique.

Un point important a été souligné (37), celui du contrôle industriel de la propreté des surfaces après mise en oeuvre des nouveaux procédés de nettoyage. Des techniques de détection de la pollution des métaux ont été développées. Des difficultés se présentent pour la détection de la pollution de matériaux à base de polymères hydrocarbonés (protections thermiques par exemple) par des hydrocarbures polluants et l'analyse de la nature des pollutions. Des travaux sont menés, en particulier par la NASA et THIOKOL, pour développer les techniques adéquates.

Elimination des produits énergétiques et recyclage des ingrédients

L'élimination écologique des déchets de fabrication et des chargements de propergols solides en fin de durée de vie devient obligatoire.

Trois exposés (29, 32, 33) ont montré la faisabilité et la maturité des technologies correspondantes qui ont déjà fait, ou vont faire l'objet, d'investissements importants. Il est clair cependant que ces investissements nécessitent soit le soutien de fonds publics, soit leur amortissement dans le prix de revient des produits. Quelqu'un devra payer.

De même l'équilibre économique de l'exploitation ne pourra jamais être obtenu dans le cas des produits classiques par la valorisation des ingrédients récupérés qui ne sauraient apporter qu'une contribution très modeste. Au plan technique le recyclage dans des applications à la propulsion des ingrédients de propergol, perchlorate par exemple (31, 32) parait beaucoup plus difficile, compte tenu des spécifications des propergols, que celui des explosifs qui peuvent aussi parfois trouver certaines niches dans des applications commerciales d'explosifs industriels (34, 41).

Nous retiendrons l'intervention suivante du Professeur Schubert, lors de la discussion, qui résume bien la philosophie qui se dégage, compte tenu de l'expérience allemande, même si l'évaluateur pense que quelques points particuliers pourraient être nuancés :

- "En raison des réglementations, des problèmes de reproductibilité et d'autres spécifications de besoin, il est pratiquement impossible d'utiliser des explosifs militaires pour des applications commerciales. De plus si l'on compare les quantités d'explosifs commerciaux et militaires on peut dire que ces dernières sont marginales.

- Le recyclage de l'octogène, compte tenu de son prix est pensable, l'intérêt de recycler l'hexogène ou le perchlorate dépend des quantités considérées. Les dérivés du mercure (détonateurs...) peuvent être convertis en mercure et vendus avec profit.

- Il serait surprenant de réussir à vendre pour quelques centimes du TNT récupéré. Il est difficile de vendre la nitrocellulose de récupération des vieilles poudres car sa qualité est très inférieure.

- Tous les projets de R et D visant à la conversion des ingrédients des matériaux énergétiques (excepté octogène et mercure) pour des applications commerciales ont échoué."

Nous soulignerons enfin deux exposés intéressants relatifs à des technologies un peu moins classiques. J.E. Flanagan a montré la faisabilité industrielle d'une méthode de destruction de composés organiques par des sels fondus (28), probablement efficace pour le traitement de composés particulièrement sensibles et/ou toxiques. J. Hawari (40) a présenté des techniques biologiques prometteuses de décontamination de sites pollués par des ingrédients énergétiques.

## Conclusions et recommandations

Ce Symposium a permis une excellente mise à jour des données relatives à l'impact de la propulsion sur l'environnement. Il a permis de faire le point sur les recherches de propergols améliorés et de repositionner la problématique de ces recherches :

- il n'apparaît pas, à court terme, de besoin urgent de remplacement des propergols composites actuels dans les lanceurs,

- il est raisonnable de poursuivre des travaux de recherche sur les propergols dans ce domaine avec pour objectif simultané une amélioration des performances énergétiques et un coût acceptable,

- il est judicieux que ces recherches s'appuient sur les développements en cours de propergols à signature réduite pour missiles tactiques, une partie des technologies étant communes aux deux utilisations.

- il a permis d'identifier les domaines de recherche dans lesquels des progrès sont nécessaires, tant au niveau de l'appréciation de cet impact (modélisation et mesure), qu'au niveau des propergols (performances, caractéristiques de sécurité, coût des ingrédients).

-il a montré la maturité de technologies pour l'élimination dans des conditions propres et sures des déchets de matériaux énergétiques ou des propulseurs.

- il a provoqué une interrogation sur l'économie de ces opérations d'élimination et conclu qu'il était vain d'espérer, sauf dans des cas très particuliers, une rentabilité économique du recyclage d'ingrédients récupérés. L'investissement et le coût de fonctionnement des installations correspondantes devront être supportés au moins en partie par les Etats ou les clients.

- il a illustré la réaction positive et efficace de l'industrie et, dans la plupart des pays, des agences gouvernementales responsables, aux nouvelles contraintes d'environnement. Les échanges, particulièrement au niveau du remplacement des composés ayant un effet sur la couche d'ozone ont été riches et ouverts.

Enfin, comme l'a dit C. Hawk dans la conclusion de son discours d'ouverture il est important que la communauté aérospatiale s'organise pour promouvoir des orientations ("guidelines") plutôt que de se faire imposer des réglementations.

Certains points ont été peu traités, en particulier la conception de nouveaux matériaux énergétiques susceptibles d'une élimination ou d'un recyclage plus faciles, par exemple les propergols ou poudres à base de liants élastomères thermoplastiques non réticulés dont les composants seraient récupérables par simple fusion et séparation, ou bien les technologies de production permettant de réduire les déchets (procédés continus par exemple). Ces points importants devraient être traités lors de réunions futures.

Le tronc commun qui existe entre le développement de nouveaux propergols à signature réduite pour missiles tactiques et la recherche de propergols à haute énergie à impact réduit sur l'environnement pourrait justifier un symposium consacré simultanément à ces deux sujets. Dans ce cas il faudrait veiller à ce que les caractéristiques de coût et de sécurité de ces nouveaux matériaux soient présentées et discutées. Il existe de même un tronc commun entre les recherches liées à la modélisation et la caractérisation des jets en vue des applications tactiques et les recherches sur les prévisions et mesures des espèces chimiques formées en vue d'une analyse de l'effet des jets sur l'atmosphère. Une réunion de spécialistes pourrait valablement traiter des deux sujets simultanément.

Enfin la participation de quelques spécialistes de l'atmosphère ou de la météorologie pourra être très utile si dans le futur un nouveau symposium ayant pour objet d'actualiser les connaissances dans le domaine de la propulsion et de l'environnement était organisé.

# TECHNICAL EVALUATION REPORT

**(pour version française voir pages précédentes)**

**by Alain Davenas ***

## Introduction

The 84th Symposium of the Propulsion and Energetics Panel was held in Aalesund, Norway on August 29-September 2, 1994. The Symposium theme was "Environmental Aspects of Rocket and Gun Propulsion". The announcement of the meeting emphasized the fact that "environmental issues associated with the use of missile and gun propulsion are becoming increasingly demanding. Major demilitarization initiatives have resulted in significant quantities of surplus propellant needing safe and environmentally proper disposal". This Symposium was to focus on "discussion of relevant research and engineering solutions" and to "allow this knowledge to be shared amongst the NATO research community".

The session themes were :

1. Clean propellants
2. Propellant development
3. Measurements
4. Disposal
5. Material recovery and reuse
6. Contamination

## Summary and Commentary

The initial program was very dense, with 44 papers. In fact, only 35 were presented at the meeting. The objectives of the meeting were nevertheless achieved, particularly the sharing of knowledge on this sensitive subject. The necessity of this sharing by the aerospace community was emphasized by Professor Clark Hawk in his keynote address and also the need for collaboration with the international scientific community.

Discussions were relatively numerous and open, both during and after the sessions. A particular problem, due to the language barrier, arose with the three Russian authors ; discussion at the end of their presentation was difficult and was only slightly improved by the written question and answers procedure.

The aspects specific to gun propellants were not presented, except in one useful paper on the toxicology of the liquid gun propellant XM 46. It is however clear that a great many of the issues and data presented on rocket propellants and other energetic materials were pertinent to gun propellants activities.

The program did not include specific presentations on new technologies for production of energetic materials that could minimize the impact on the environment by minimization of waste. There were no presentations on the design of new energetic materials for easy disposal and reclamation.

The Symposium was in fact divided into two main parts, quite different technically. The first part was devoted to the effect of solid rocket motor exhausts and plumes on the environment, their

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evaluation and measurement, and research and development of new propellants with a reduced impact. It was more or less a follow-up to the controversy which developed in the nineties on the impact of launchers or missiles on the stratospheric ozone layer which protects the earth from the UV radiations of the sun and the risk of acid rain and pollution around test and launch sites.

The second part was devoted to the impact of production, destruction and disposal of solid and liquid rocket motors. This is, of course, a critical problem owing to :

a)increasingly stringent regulations (open air burning of energetic ingredients being increasingly forbidden); and

b) the necessity of clean disposal of huge quantities of old or obsolete munitions.

Also the scaling down and restructuring of Defense industries implies the closure and decontamination of a great number of sites for which efficient and economical decontamination techniques and processes are needed.

This Symposium was timely. It showed that a more or less general consensus could be achieved on some important points that were the subject of much controversy in the scientific community two or three years ago, and the experience gained on environmentally safe disposal in the past few years allowed discussion of the initial lessons learned.

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* The figures in brackets refer to the number of the paper in the Symposium program.

## Evaluation *

Effects of rocket propulsion on the environment

The problem is primarily related to space launchers. As an example, one shuttle launch consumes the equivalent quantity of solid propellant burned during the firing of 30 french M4 Strategic Missiles or 30 000 air to air Magic or Sidewinder missiles. The title of Clark Hawk's keynote address was "Environmental Effects of Solid Propellants - Perceptions and Realities". The problem of perception and communication on these subjects is critical, particularly with the press, local communities, environmental groups. This is true for space events ; this is true for industry related environmental issues ; it is even more true for space environmentally related issues. A policy of open, carefully prepared communication associated with rigorous procedures for testing or launching can successfully mitigate public concern as demonstrated by the example of the policies applied at the Kennedy Space Center or at the "Centre Spatial Guyanais" in Kourou.

To communicate well, reliable, commonly agreed elements and data are an absolute necessity. An important first step was the report issued in 1991 by an AIAA working group, including A.J. Mac Donald and C. Hawk who were active participants in the Symposium, on "Atmospheric Effects of Rocket Propulsion". This excellent technical synthesis established the basis for a rational and standardized communication on these subjects for the international aerospace community. The report concluded that the impact of chemical propulsion on the environment was very limited or even negligible. A.J. Mac Donald (1) has presented an update of existing knowledge on these subjects and confirmed the analysis and

conclusions of the previous study. These conclusions are unaffected by an increase in the number of launches or the reduction of other sources of ozone-depleting compounds.

A. Tishin (2) seems to globally agree with these conclusions, even if he considers that "liquid" propulsion is less polluting than "solid" propulsion. His presentation criticized the evaluation by previous Russian authors of the level of NOx formation for the Shuttle and Energia which he estimates to be lower than calculated. Mac Donald and Tishin agree on the necessity of improving the modelling of afterburning of exhausts in the atmosphere and to develop measurements of chemical species formation along the trajectory of the launcher.

The newest element concerning these questions was provided by A.J. Mac Donald, who reported the results of experiments performed recently in the US, in the framework of preliminary studies for a new high altitude SST. The results seem to demonstrate a much more important role of "hydrogen" reactions (H, HO, $HO_2$ radicals) in ozone depletion than predicted, whereas nitrogen oxides effects are lower.

Taking all these elements into account, there is no justification, on a short term basis, for replacing the propellants used in present systems by new propellants on environmental bases. This would require considerable development and qualification investment. Only the improvement of all the functional characteristics and particularly an increase in energy would justify replacement - provided the cost increase is acceptable. The new propellant would then only be used when a new system is developed. The development of such a system should include all the requirements and all the data available at that time on the possible impact of the new launcher on the environment.

Finally E.Y. Krasilnikov in a paper titled "Rocket Engines and Ecology Problems" (23) presented some correlations he has observed between the dates of some launches and important atmospheric or seismic phenomena. He presented atmospheric models that could, in his opinion, explain this correlation. This presentation could only be evaluated by specialists in meteorology and geophysics.

Improved high energy propellants

There was a debate during the Symposium on the word "clean" as applied to propellants. This term, invented at a time when the previously mentioned analysis had not been completed, has the effect of making today's propellants based on ammonium perchlorate appear as unequivocally dirty. Mac Donald proposed to rename them "alternative propellants" which in our opinion is more appropriate if a propellant is to be changed in an existing system.

C. Beckman (6) presented the principal candidates for the replacement of present composite propellants in large motors that eliminate hydrochloric acid in the combustion gases. Propellants with chlorine scavengers in the formulation have the considerable advantage of retaining most of the basic characteristics of today's composites and the majority of the associated technologies. Volumetric specific impulse is unchanged or slightly increased but specific impulse is reduced, which would unfortunately cause a significant decrease in performance in most applications. C. Pérut (4) presented tests results and

measurements which validate the concept. This technology is available if needed. The research on the interesting concept of neutralized propellants in which hydrochloric acid is neutralized by Mg $(OH)_2$ in the plume has been discontinued. Because of the kinetic processes, results show incomplete elimination of HCl at a level which varies with ambient and operating conditions. Solution propellants, in which the oxidizer is a liquid, do not lead to a significant increase in energy. Even if the technology has been successfully demonstrated in large motors, the technology switch it implies and the related lack of experience of many aspects (reproducibility, ageing etc.) would require a massive investment in research and development difficult to justify.

Finally a significant increase in energy implies the use of new, chlorine free, energetic compounds. These compounds and their likely performances were presented and discussed by S. De May (15) and G. B. Manelis (13) (mainly CL 20, ADN and other derivatives of the dinitramide anion) and J. Mul (11) (HNF). The access to high energy, in our opinion, would also require, most of the time, the use of energetic binders.

Two important, and possibly fundamental, questions are in our opinion raised by these papers, which were not covered in the presentations and only marginally during the discussions (a) the detonability characteristics and more generally the stability and safety characteristics of these potential candidates, (b) the cost of the new ingredients (at the mass production level) and its effect on the cost of the motors. Cost is a critical factor for motors using large quantities of propellant.

Minimum visible signature propellants for tactical missiles

Secondary smoke suppression in the exhausts of tactical missile motors implies ammonium perchlorate substitution. The requirements for propellants adapted to Insensitive Munitions led to research on compounds less sensitive than RDX and HMX, traditionally used in "smokeless" propellants. This field of research involving many countries was presented in numerous papers (7, 8, 9, 14, 15, 16, 17).

Important progress in this area was reported. The development of first generations of insensitive low signature propellants seems well advanced. The formulations generally use ammonium nitrate (AN) as oxidizer and binders based on energetic polymers, mostly GAP and Poly NIMMO. GAP is now well established, Poly NIMMO is being scaled up. However we did not get the impression that the AN problem has been solved. The various solutions presented for getting rid of the phase transition problems appear to be unsatisfactory : stabilizers with toxicity problems (NiO) or smoke emission (Zn O) or ultra-dry AN, which is probably not practical outside of laboratory conditions. An important and decisive effort on this point is necessary, or all the research investment devoted to these propellants will have been in vain.

New energetic ingredients for energy increase were presented by May Chan and Susan De May ( 9, 15) particularly CL 20 and ADN. The cost of these compounds will be a critical factor, even if it is less critical for these applications than for very large motors. An important effort in this area must be made by chemists, both in searching for the most economic means of synthesis

and for estimating mass production costs.

Conclusions on the interaction between solid rocket exhausts and the environment

The presentations and discussions lead us to the following conclusions :

1. there is no technical basis justifying, in the short term, the replacement of today's composite propellants in launchers already existing or under development;

2. research work must be continued on a laboratory scale on chlorine free propellants for big boosters, as an insurance policy, in case there are new findings, or in case of political decisions caused by irrational psychological pressure;

3. research on mechanisms and modelling of ozone depletion processes caused by the interaction between the exhaust and the atmosphere and on the incorporation of heterogeneous chemistry in the models must be continued or amplified;

4. today, the only reasonable objective for the propellant should be an improvement of all characteristics and especially energy, at an acceptable cost. It should be applied only when its maturity has been demonstrated and when a new system has been developed. The criteria for the choice of the propellant will depend on the results of the research carried out on point 3;

5. after examination of the possible candidates we consider that characterization of their safety and detonation properties should be a priority, before going into their development. In the case of ADN based propellant which have apparently been developed industrially in Russia, more information exchange on their characteristics than that presented at the meeting would be useful. This information is critically needed for evaluation by the aerospace community;

6. research work on low signature propellants for tactical systems which has its own justification - besides the fact that it enables lower motor exhaust - is an excellent basis on which to evaluate new ingredients which could also be used for space boosters propellants.

Propulsion industry and environment

The increasingly stringent environmental legislation will require industry to make a considerable and expensive effort in order to adapt. This is a matter of survival. Two papers (20 and 21) presented the adaptation and investment in new testing facilities made by DASA and SNPE in order to minimize noise emission. Without these efforts the activity would have had to be terminated.

S. De May (9) and A.J. Mac Donald (37) have summarized the evolution of the legislation on effluent and waste in the USA and its impact on the propulsion industry. J.M. Tauzia has shown (32) that the evolution in Europe was the same with a few years delay : open air combustion will probably be forbidden after 1996-1997 and new European rules applying specifically to energetic materials which define precise maximum

levels of emission are in the process of elaboration.

Ozone-depleting substances

Four presentations dealt with the consequences of the Montreal Protocol: restrictions or interdiction of these substances (37, 38, 42, 43). The consequences for the production of the solid rocket motors which use chlorinated solvents for cleaning, de-greasing and bonding preparation are important. B. Goldberg (38) presented a strategy and a method for prioritizing the methodology to qualify new agents and/or new processes. Quite apart from the magnitude of the task, other difficulties are raised by the decision to extend the life of many current systems (for instance the Shuttle SRM or the Minuteman) when qualification during the development of new systems would have been easier. The data provided in the presentations will be useful to the aerospace community. It is certainly in the interest of the community to limit the request for waivers to essential phases (like bonding preparation). Also there is a common interest - as some examples in France demonstrate - for our industry to develop its own solution rather than rely on the very costly alternative proposed by the chemical industry.

An important point was underlined (37) : the adequate inspection techniques for cleaned surfaces after the change of cleaning products and/or processes. New techniques for detection of metal pollution were presented. Detection of the pollution of hydrocarbon polymer based materials (for instance thermal insulation) by hydrocarbon pollutants is difficult. In addition qualitative and quantitative analysis of pollution is needed. Work is going on at NASA and Thiokol to develop a new technique for this purpose.

Energetic materials disposal and reclamation

The ecological disposal of propellant and energetic material waste and of obsolete solid propellant motors is becoming mandatory. Three papers have demonstrated the feasibility and the maturity of solutions that are already used industrially or will be implemented in the near future.

It is however clear that these investments need either the financial support of governments or amortisation in the cost price of the product. Someone has to pay.

Neither will the economic balance of the operation be achieved for traditional energetic formulations by reclamation and reuse of basic ingredients, which process would provide only a very modest contribution. On the technical side it seems that the recycling of reclaimed ingredients - AP for instance (31, 32) - to propellant production would be much more difficult than in the case of explosives, which in some specific cases also find a niche in commercial explosives (34, 41).

On the general philosophy of this subject we will quote Professor Schubert's statement during the discussions, which, even though it might be challenged on some points, reflects quite well the general opinion of the Symposium attendee. This statement is based on the experience of demilitarization of old munitions in Germany in recent years.

1. "Because of regulations, problems of reproducibility and other requirements it is practically impossible to use military explosives for commercial

applications. If we compare the amount of commercial - and military explosives I would say : the comparative amounts of military explosives are minuscule.

2. Given its best the recycling and reuse of HMX is possible but recycling of RDX and AP depends on the quantity you have to recycle. Mercury compounds (from detonators etc) can be converted into Mercury and sold at a profit.

3. You would be lucky to sell TNT for a few cents. You can't sell NC from propellants because of low quality compared with virgin NC.

4. All the R and D projects designed to convert component substances of traditional energetic materials (except HMX and Mercury) for commercial applications have failed."

Finally we would mention two interesting papers on less traditional technologies.
J.E. Flanagan presented data on the feasibility of a method of disposal of organic compounds by molten salt oxidation (28) which is probably an efficient method for elimination of sensitive and/or toxic materials. J. Hawari (40) presented promising biodegradation methods of energetic compounds for decontamination of polluted sites.

## Conclusions and Recommendations

This Symposium provided an excellent update on the knowledge of the effects of rocket propulsion on the environment. Recent results concerning new propellants were reported. This enabled a reassessment of the rationale for research in this field :

- there is no urgent need for replacement of present propellants in launchers;

- it is reasonable to carry on research work on improved propellants with the simultaneous objectives of increasing energy at an acceptable cost;

- research in this area should take advantage of the development work being carried out in the field of low signature propulsion for tactical missiles, part of the technology being common to both subjects.

Areas in which progress is necessary were identified, either for a better knowledge of the effect of propulsion on the atmosphere (modelling and measurements) or for characterization of potential improved propellant candidates (detonation characteristics, ingredient cost).

The Symposium demonstrated the maturity of technologies for the clean disposal of energetic waste and obsolete motors. It has questioned the economics of these operations. We cannot expect, except in some very specific cases, a profit from the recycling of reclaimed ingredients from today's energetic materials. The investment and operating costs of these facilities must be supported at least partly by government or customers.

It illustrated the positive response of industry and, in most countries, of government agencies to the environmental requirements. Sharing of information, particularly in the area of ozone depleting compound replacement was open and extensive. Finally, as Clark Hawk stated in the conclusion to his Keynote Address, it is important for the community to promote guidelines over regulations in the future.

Some relevant technical points that may be of importance for the future were however ignored, for instance the design of new formulations for easier disposal and recycling of ingredient (thermoplastic elastomer binders for instance, which would allow ingredients recovery by "simple" fusion and separation) or the development of production processes that would minimize waste (continuous processes for instance). These subjects should be part of future meetings.

The development of new minimum signature propellants for missiles and the development of improved high energy propellants for launchers have an important common research base. This would justify a meeting devoted to both subjects. In this case discussion of detonation and cost characteristics of these propellants should be specified. This is also true for missile plume modelling and characterization and for rocket exhaust effects on the atmosphere. A possible meeting should deal with both aspects at the same time.

Finally, participation of specialists on the atmosphere and meteorology could be very useful if another Symposium was organized in the future to update present knowledge on the environmental impact of rocket propulsion.

# Environmental Effects of Solid Rocket Propellants, Perceptions and Realities

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## SUMMARY

The interaction between the aerospace industry and the environment is a topic of increasing interest in our world. The visibility of rocket launches to the general public has caused people to become more aware of the propulsion side of the industry and, then, to question the content of the plumes that they see as well as asking about the effects of those plumes on our environment. This represents but the tip of the iceberg. What the public sees and questions represents a small part of all that is involved in bringing a piece of aerospace hardware to the launch pad. The manufacturing processes for rocket propulsion systems entail the use of many hazardous air pollutants (HAP), ozone depleting compounds (ODC), volatile organic compounds (VOC), etc. which represent areas of concern with potentially greater impact than the emissions associated with rocket exhaust products.

The aerospace industry as a whole and the propulsion industry in particular has been working diligently in defining and addressing the issues for many years. Over 700 references dating back to 1969 deal with the impact of both solid rocket and liquid rocket propulsion on the environment and corrective actions taken

The contribution of the propulsion industry to the global problem of environmental pollution is small in contrast to other industries. The propulsion industry on-going technology programs in the areas of avoidance, monitoring and assessment, control and remediation and restoration are significant continuing steps to reduce or eliminate what it does produce.

## 1.0 INTRODUCTION

The propulsion industry has drawn attention in recent years regarding the environmental consequences of the manufacture, test and launch of chemical rocket propulsion systems. The American Institute of Aeronautics and Astronautics (AIAA), the Department of Defense (DoD), and NASA have been active in implementing programs to promote better understanding of the realities of environmental impact of such systems as contrasted to the perceptions of the general public. Additionally, the individual companies which compose the United States propulsion industry have actively pursued the sources of their contributions to the environmental problem and engaged in extensive research and information exchange to develop new approaches and share their knowledge as to possible solutions.

While there has been a recent emphasis on the issue, there are over 700 references dating back to 1969 which deal with the impact of both solid rocket and liquid rocket propulsion on the environment and corrective actions taken. At present, there is a broadly based and comprehensive program in place, not only within the U.S.A., but internationally which addresses environmental issues of the propulsion industry from manufacture to flight.

International cooperation efforts specifically identified include methyl chloroform replacement in solid rocket motor manufacturing. These include the Industry Cooperative for Ozone Layer Protection, and the Solvents Technical Options Committee of the Montreal Protocol. Within NATO there is an activity focused on ODC solvents replacement for space and missile systems which includes issues of critical bonding, LOX/GOX cleaning, and bearing cleaning.

The nature of the issues and concerns must be treated as applying to both liquid and solid rocket propulsion systems, however, this paper will focus primarily on solid rocket issues.

## 2.0 TECHNICAL APPROACHES TODAY

There are four recent U.S. initiatives to promote information exchange regarding the latest developments affecting the propulsion industry and the environment.

The American Institute of Aeronautics and Astronautics (AIAA) makes assessments that generate accurate, complete, and impartial evaluation of issues of national (and international) concern that may involve some controversy. The AIAA has made, (and is continuing to make) such assessments in the area of the interaction of the aerospace industry with the environment. Primarily, the AIAA has made such assessments

and brought an international focus upon the aerospace industry and environmental issues by conducting the workshop on "Chemical Propulsion and the Environment" and by creating the Global Environmental Change Program. Additionally, the technical committee structure facilitates a continuing level of activity which may include pursuance of environmental issues as a subset of Technical Committee (TC) interests (Liquid Propulsion TC, Solid Rocket TC, Hybrid Propulsion TC, and Support Systems TC) or as a primary focus of their interest (Atmospheric Environment TC). Two of the major AIAA initiatives in the environmental arena are summarized here.

## 2.1 Chemical Propulsion & the Environment Workshop

This workshop was accomplished in the Summer of 1991. It had a narrow focus in that it considered only the atmospheric impact of emissions associated with static test and launch of rockets. It had a broad spectrum of participants including: environmental groups such as the Sierra Club and the Federation of American Scientists, concerned governmental agencies such as the EPA, NASA, DoD, and the propulsion industry. The interaction of chemical rockets with the environment has global implications and influence, which requires global understanding and strategies. The magnitude of the global effects in the main areas of concern were determined on the basis of careful evaluation of scientific studies performed in the U.S.A., Europe, and the (former) Soviet Union. The results are summarized in Table 1.

| Area of Concern | Global Effects of Rocket Exhaust |
|---|---|
| Stratospheric Ozone Depletion | 0.0065% to 0.024% |
| Acid Rain | <0.01% |
| Global Warming ($CO_2$ Deposition) | 5 X $10^{-7}$% of total $CO_2$ Production |

Table 1. Global Environmental Effects of Nine Shuttle Launches & Six Titan Launches per Year

The recommendations summarized here included efforts to improve modeling, gain better understanding of the chemistry involved and improving the measurements of atmospheric phenomena[1]. Specifically:

- Formulate and implement heterogeneous models to improve understanding of the stratospheric effects of rocket propulsion.
- Establish accurate estimates of the $NO_x$ production by current and projected chemical rocket engines/motors.
- Quantify the atmospheric interactions, including ozone-depleting potential, for the various exhaust products as a function of altitude.
- Conduct model calculations, both local and global, which include all major exhaust species and account for photochemical and other heterogeneous atmospheric reactions.
- Further characterize effluent particulates, including their size distribution, shape, particle density, chemistry, etc. and estimates of their residence times in the atmosphere. Determine their effects on the background stratospheric aerosol content, on cloud formation, and on the stratospheric ozone. Conduct laboratory measurements of the reactions of stratospheric constituents with metal oxide particles.
- Develop analytical models for the formation of solid-particle products of combustion and for the solidification of ice particles during expansion that will enable the characterization of particulate quantity, size, shape, and number density during all launch and test phases.
- Use existing analytical models for rocket combustion, including mixing and burning with atmospheric gases (after burning), not only for performance evaluation, but also to better quantify the release of exhaust products in the atmosphere. Develop instrumentation and conduct experiments that measure the composition of rocket exhaust in real time, to generate appropriate anchoring data.
- Conduct model calculations, both local and global, which investigate influences on the mesosphere and ionosphere.
- Clarify the interactions of the effluents of the different propellant combinations to identify the environmental tradeoffs among the halogens, the different particulates, trace organic, and trace metals.

The recommended actions all had international implications and the workshop recommendations called for planning, initiation and funding of research on an international basis. AIAA initiated

action in this regard by sending the report of the workshop to the President of the International Astronautical Federation, Dr. Alvaro Azcarraga, highlighting the recommendations and encouraging the IAF to formulate a mechanism by which these actions could be implemented and funded.

## 2.2 Global Environmental Change Program

This program was initiated under the auspices of the AIAA Technical Activities Committee to improve the integration of environmental considerations into the system engineering processes of the aerospace community. This will be accomplished through the conduct of workshops, preparation of "white papers", and establishing a network for the exchange of environmental technical information both within the AIAA technical committee structure and with other institutions and societies.

A steering committee for this program has been convened. They have formulated an approach to pursue three aspects of the problem in parallel:

- Conduct workshops on how the aerospace community can help address environmental issues
- Conduct workshops on how to assess the impact of the aerospace industry on the environment
- Devise and conduct an educational program for the aerospace industry regarding environmental issues.

An example of the first would be a workshop which would focus on the issues associated with the convergence of data and programs among agencies and entities involved in environmental activities that involve aerospace capabilities. The second area could take either or both of two approaches: defining how to make use of the capabilities within the aerospace community to solve environmental problems and/or determining what is the full impact of the aerospace industry upon the environment and the efficacy of the corrective measures in place or planned. The educational program(s) might take several forms from conducting short courses on issues of the aerospace industry and the environment to preparing articles, books, and/or compilations of articles on the subject.

## 2.3 Solid Rocket Manufacturing: Investigating Environmentally ProActive Approaches

The United States Air Force has also been concerned with the impact of propulsion on the environment and has identified the Phillips Laboratory Propulsion Directorate as the lead in this area. They sponsored this conference, and designed it to promote technical information exchange among industry, Government and the U.S. regulatory agencies (federal, state and local). The focus was broad within the scope of solid rocket operations.

The U.S. rocket propulsion industry was identified as producing 12 million pounds of waste per year with propellant residue being the greatest amount followed by propellant test emissions and solvents.

The issue of ozone depleting emissions during static test and launch is put in perspective when one realizes that there are "no current ODC restrictions on launch related chlorine" either in the Montreal Protocol or in the Clean Air Act of 1990 plus its amendments[2].

The Environmental Protection Agency philosophy with respect to the management of solid rocket propellant was reported to be to affect source reduction to minimize waste. The waste might be dealt with in several possible ways including: reclamation, energy recovery or disposal. Two options for waste solid propellant disposal included use in explosives and reclamation of ammonium perchlorate.

United Technologies Chemical Systems Division has been working with both a blasting firm and an explosives development laboratory in developing means to employ solid propellant in the explosives business. This includes use directly as a product and use of energetic ingredients. They have found that class 1.3* propellant can be used directly as a blasting agent supplement and class 1.1 propellant can be used directly as a commercial booster charge. The class 1.1 and 1.3 propellant, propellant contaminated material and propellant ingredients can be used in water gel blasting agent. The experimental results show superior performance of the blasting agents with the propellant materials added. The above two options were reported as capable of consuming 97% of CSD solid propellant waste.[3]

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* This is a hazards classification system within the U.S.A. which distinguishes detonable propellant (1.1) from non-detonable propellant (1.3) based upon the card gap test.

Reclamation of ammonium perchlorate has been accomplished using waterjet extraction of the solid rocket propellant from the motor case with subsequent processing to remove the AP for future use. Assessment of the use of reclaimed AP in solid rocket motor tests indicates satisfactory performance.

Elimination of hazardous air pollutants (HAP) associated with manufacturing and other operations of the solid rocket industry is another key area of concern. The sources regulated under the National Emission Standards for hazardous Air Pollutants are:

- Clean-up solvents
- Coating application equipment
- primers/topcoats (HAP and volatile organic compound (VOC) limits)
- maskants
- inorganic paint emissions

Hand wipe cleaning was reported to represent 88% of total HAP emissions.[4] Control would be exercised by limiting the vapor pressure of a solvent in use to be less than 45 mm Hg at 20°C or limiting choices from an approved list of very low vapor pressure solvents. One approach presented[5] involved the development of blends which are specifically addressed to given operations. They draw from a list of solvents not on the HAP list, isopropyl alcohol, ethanol, acetone, and methylene n-amyl ketone. The last has proven valuable in developing blends which meet the vapor pressure standard.

## 2.4 Aerospace Environmental Technology Conference

The NASA Operational Environment Team (NOET) engaged in a major effort to examine the use of ODC and HAP in NASA programs and operations. One outcome of the effort was to sponsor a forum in which the results of NOET and other aerospace industry programs could be disseminated. The program was a well balanced and comprehensive review of the state-of-the-art. An overarching major focus of the conference was "Technology for a Sustainable Future" (the Gore Initiative). This initiative considers the environmental technologies as being divided into four categories, avoidance, monitoring and assessment, control, and remediation and restoration. Further, it defines these terms as follows:

- Avoidance represents those activities that avoid the production of environmentally hazardous substances or alters human activities in order to minimize damage to the environment.
- Monitoring and assessment defines technologies used to establish the condition of the environment and monitor its status.
- Control technologies are intended to render hazardous substances harmless before their introduction into the environment.
- Remediation and restoration encompass technologies both to render harmless, those harmful or hazardous substances after they enter the environment and methods to improve ecosystems that have declined due to naturally induced or anthropogenic effects.

The reported progress on reducing or eliminating HCl from solid rocket exhaust products appears very promising. Substituting equal amounts of sodium nitrate and ammonium perchlorate (AP) in the propellant instead of all AP resulted in an order of magnitude reduction in HCl in the exhaust (20% reduced to 2%)[6]. The resultant composite propellant was also reported as having good mechanical properties.

The research into use of aqueous solutions and super-critical carbon dioxide as degreasers in lieu of chlorinated solvents is being conducted within industry, government and academia. Aqueous degreasers with aqueous surfactants and ultrasonics provide one option which has shown promise in batch cleaning operations. Spray-in-air aqueous cleaning with either of two cleaners, Jettacin (terpene base) and Brulin 815GD (detergents, alkaline builders and inhibitors) also appear promising based upon cleaning efficiency, corrosion potential, cost and toxicity considerations. They are undergoing further test. The spray-in-air technique worked well with the Conoco HD-2 grease which is customarily used as a temporary coating for storage and shipping of solid rocket cases and metal nozzle parts.

With the revised procedures in hardware cleaning comes the need to evaluate the cleanliness of the part upon completion of the process. Many military specifications require the use of ODCs in the inspection process. Good progress was reported with non-volatile residues verification using aqueous surfactants, ultrasonics and Total Organic Carbon Analyzer (TOCA). An alternative contamination detection method reported was the use of ultraviolet imaging. It worked well with a wide variety of potential contaminants, was fast

(less than 5 seconds), sensitive (as low as 0.1 μ g/cm$^2$) and resolution (1 mm$^2$)

**3.0 ANALYSIS**

The Technology for a Sustainable Future initiative provides a framework within which we can examine the various programs and activities presently on-going in the solid rocket propulsion industry, even on a global basis.

**3.1 Avoidance**

Ozone depletion from static test or launch emissions is a topic which often gets dealt with first in discussing issues of avoidance. As previously mentioned, there are "No current ODC restrictions on launch related chlorine". Research and technology efforts continue to address means to replace the ammonium perchlorate with other reactants. This includes work on the scavenging propellants as well as chlorine free propellants. Reasonable progress is being made with scavenged propellant (2% HCl in the exhaust) with the chlorine-free options following. Additionally, hybrid rockets have grown in interest and are receiving research and development funding. They offer the potential of chlorine free exhaust.

An issue this research must address is the topic of how to determine that the new propellant formulations are not introducing some new product which may adversely affect the environment to a comparable level or worse. It is essential that any proposed changes in propellants or introduction of new propellants is accompanied with a thorough examination of the environmental implications to be assured that no new environmental issues are being introduced through their use. This includes the collective impacts associated with all processes involved from raw material to finished product to launch.

There is much yet to be learned regarding the exhaust from state-of-the-art AP containing propellants. For example, modeling the reaction of the plume with the environment requires more comprehensive knowledge than we now possess regarding[7]:

Heterogeneous chemistry and role of particulates ($Al_2O_3$ and $H_2O$ (S))

Afterburning in the plume and subsequent mixing of the products with the atmosphere. (Of special interest is $NO_x$ formation)

Reaction chemistry of alumina with ozone (This has been suggested as a concern.)

There are other aspects of the modeling which must be addressed. The global versus local effects are not amenable to specific analysis. For example, the global models must employ such a large grid that the flight of one launch vehicle or missile doesn't impact the model results.

The industry research into new cleaning procedures which will minimize or eliminate HAP and ODC is showing promise. The aqueous based and carbon-dioxide based procedures have given evidence of meeting the industry cleanliness standards and ODC free inspection methods appear viable for the needs of the industry. These areas must continue to be worked to improve the efficacy of the various methods.

New plating methods have offered the potential for eliminating cadmium and chromium from corrosion resistant applications. Chromic acid can be replaced from thin, corrosion resistant anodizing on aluminum by using a 5% sulfuric acid process. The coating is then sealed with nickel acetate rather than the sodium dichromate[8]. Cadmium plating has been replaced with zinc-nickel or tin-zinc which each provide good corrosion resistance and provide a good paint base[9].

Elimination of hand wipe solvents and other solvents (HAP) is reported to be making good progress by use of solvent blends which are tailored to meeting the vapor pressure limit of less than 45 mm Hg at, 20$^o$C, tuned to the specific cleaning application and are designed to minimize personal exposure.

**3.2 Monitoring and Assessment**

I see the monitoring and assessment aspect of the initiative in two ways, first, we must have a reliable and true measure of what we are doing now. We cannot assess our progress unless we know what we are trying to control and what levels of emissions were present when we started. Second, we must monitor the environment to determine the effects of the corrective measures we have taken.

Regarding the former, Goldberg[10] studied the amounts of ODC and HAP introduced into the atmosphere in the United States in contrast to the total production of chemicals in those categories. He found that the propulsion industry contribution of emissions was, generally, on the order of 0.001 to 0.01% of the total and, in one case, was a similar percentage of the amount of reduction of emissions anticipated from other sources.

The Earth Observing System[11] (EOS) is a system of satellites designed to produce the data necessary to assess the Earth's environmental system and the effects of man's impact upon it. The program has given balanced weight to research, data processing and space hardware. The resultant data are expected to result in improved models of the Earth's environmental system. "Model development requires understanding of processes within each component of the Earth system and of processes that involve interaction between two or more of the components ...".[12]This statement highlights a key point which is the need for multi-disciplinary approaches which cut across existing organizations. This requires an international perspective of global change and a national perspective of what we're doing which impacts the environment. The science of the EOS program is needed to guide policy. However, "...science is primarily about asking questions---answers sometimes emerge as welcome by-products." Engineering is primarily concerned with providing solutions to problems. Better communication between the engineering and science communities would help us to ask better questions and provide better answers.

Unfortunately, the measurements we make often introduce more uncertainty than certainty. Singer[13] has noted that the data provided by various sources regarding stratospheric chlorine are difficult to evaluate since "...actual observations ... have been conflicting as well." He observes that the known decrease in $SO_2$ levels (pollution controls in the USA and Europe have brought about decreases in $SO_2$ levels since 1960s.), can simulate a fictitious ozone trend since both gases absorb UV-B radiation (280-320 nanometers) in similar ways[14] and "...its magnitude is found to depend on the choice of starting date and stopping date."

As previously mentioned, the role of heterogeneous chemistry in atmospheric processes needs to be better understood. Singer notes that "...heterogeneous reactions...are more important than gas-phase reactions, at least in the lower stratosphere". The '...discovery of the (unpredicted) Antarctic ozone hole in 1985, when theorists realized that they had to include heterogeneous reactions..." supports this point. In considering the potential for rocket exhaust sources to be major role players in the issue of heterogeneous chemistry, one needs to consider that rocket produced surface area available in the stratosphere for heterogeneous chemistry is 0.004% of what El Chichon produced and 0.14% of natural background.[15]

### 3.3 Control

Open pit burning and open detonation will no longer be acceptable methods for solid propellant waste disposal. Some attractive waste disposal options have been successfully demonstrated such as use in explosives. As previously mentioned, class 1.3 propellant has been used as a blasting agent supplement and class 1.1 propellant and ingredients have been used as a commercial booster charge. It is reported that these approaches appear commercially viable.

Extraction of propellant from cases in demilitarization operations or for other purposes has been accomplished successfully for years using the waterjet operation. Reclamation of the AP has been accomplished with the resultant product of acceptable quality. The suitability of the AP for reuse in rocket motor manufacture has been demonstrated in appropriate scale.

For those means of waste control considered which employ alternative uses, they must be evaluated against such criteria as: cost competitiveness with existing commercial means, comparable performance, availability on a continuing basis, and quality of the resultant product(s).

### 3.4 Remediation and Restoration.

Experimentation is reported[16] in which bacteria capable of degrading trichloroethylene (TCE) were isolated from contaminated industrial waste water and soils. The research was of very small scale but does identify one avenue of approach to the remediation and restoration issue.

The resolution as to the efficacy of such measures must await the results of further test and analysis.

## 4.0 CONCLUSIONS

The international propulsion community is exercising good world citizenship regarding interaction of the industry with the environment.

Although the contribution of the industry to the global problem of environmental pollution is small in contrast with other industries, the propulsion industry has taken significant and aggressive measures to address its contribution to the problem and eliminate those sources.

Good progress is being made in the reduction and elimination of emissions of HAP, VOC, and ODC. The industry has also exhibited excellent

teamwork in sharing successful solutions with other members of the industry.
The setting of goals is instrumental to the successes achieved. Additionally, goals of complete elimination of HAP emissions have been shown as realistic.

## 5.0 RECOMMENDATIONS

### 5.1 Short Term

Continued dialogue among international participants in environmental issues, the aerospace industry manufacturers and users of aerospace products is essential.

Taking the initiative to working environmental issues together in a workshop format can lead to the generation of guidelines for responsible operation rather than regulations.

Continue to add to the knowledge base to aid understanding of the effects of aerospace processes on the environment. For example:

Conduct fundamental reaction chemistry research on the affect of molten $Al_2O_3$ with ozone.

Research the heterogeneous chemistry and role of particulates ($Al_2O_3$ and $H_2O$ (S)) on atmospheric processes

Afterburning in the plume and subsequent mixing of the products with the atmosphere. (Of special interest is $NO_x$ formation)

Consolidate the findings regarding new processes that have shown promise for the cleaning and inspection of aerospace hardware and implement them.

Attack the problem of eliminating solid propellant waste to minimize the disposal problem.

Continue to effect measurements to define baseline levels of emissions from the aerospace industry.

### 5.2 Long Term

The overall, long term goal is to generate good environmental policy This requires good environmental science.

The engineering and science communities must work together on technical interchange which enhances the fundamental understanding of environmental issues.

The effectiveness of the interaction of the science and engineering communities must be continually monitored and improved.

Global research must continue with a goal to reduce hazardous or ozone depleting emissions to zero. This includes:

Research to find and evaluate improved cleaning methods for aerospace hardware.

Research to find ways to minimize propellant waste at the source

Thermoplastic elastomers for propellant binders may warrant continued investigation.

Research to find more effective ways to reclaim or dispose of waste

Biological means which can process large quantities of waste.

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# ENVIRONMENTAL IMPACTS FROM LAUNCHING CHEMICAL ROCKETS

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## SUMMARY

Three independent studies have been conducted for assessing the impact of rocket launches on the earth's environment.[1,2,3] These studies have addressed issues of acid rain in the troposphere, ozone depletion in the stratosphere, toxicity of chemical rocket exhaust products, and the potential impact on global warming from carbon dioxide emissions from rocket launches. Local, regional, and global impact assessments were examined and compared with both natural sources and anthropogenic sources of known atmospheric pollutants with the following conclusions:

- Neither solid nor liquid rocket launches have a significant impact on the earth's global environment, and there is no real significant difference between the two.
- Regional and local atmospheric impacts are more significant than global impacts, but quickly return to normal background conditions within a few hours after launch.
- Vastly increased space launch activities equivalent to 50 U.S. Space Shuttles or 50 Russian Energia launches per year would not significantly impact these conclusions.

However, these assessments, for the most part, are based upon homogeneous gas phase chemistry analysis; heterogeneous chemistry from exhaust particulates, such as aluminum oxide, ice contrails, soot, etc., and the influence of plume temperature and afterburning of fuel–rich exhaust products, need to be further addressed. It was the consensus of these studies that computer modeling of interactive plume chemistry with the atmosphere needs to be improved and computer models need to be verified with experimental data. Rocket exhaust plume chemistry can be modified with propellant reformulation and changes in operating conditions, but, based upon the current state of knowledge, it does not appear that significant environmental improvements from propellant formulation changes can be made or are warranted. Flight safety, reliability, and cost improvements are paramount for any new rocket system, and these important aspects cannot be compromised. A detailed environmental cost–benefit–risk analysis must be conducted before any new chemistry or changes in rocket operating conditions should be seriously considered for any future space or defense applications.

This paper presents a summary of the results of environmental assessments contained in these independent studies.

*Vice President and Senior Staff
**Scientist

## DISCUSSION

These studies were conducted to answer a basic question: As a result of increased space launch activities, will chemical rocket propulsion have a major impact on the earth's environment? This issue was first raised by environmentalists who were particularly concerned about the deposition of hydrogen chloride (HCl) from solid rockets into the atmosphere. HCl in the presence of water can form acid rain (hydrochloric acid) in the launch area as well as deposit a chlorine–containing gas directly into the ozone layer of the stratosphere. These issues were of sufficient concern that the original U.S. Air Force–NASA joint program office for the Advanced Launch System (ALS) would not consider solid rockets for that application unless the propellants were reformulated to produce less than one percent by weight of HCl in the exhaust plume, compared to the 21 percent for current propellants. As a result, several alternative propellants that were perceived to be more environmentally acceptable were formulated in the laboratory and tested in subscale motors under U.S. Air Force–sponsored "clean propellant" programs. Initially, existing solid propellant formulations were modified to reduce the HCl content in the exhaust plume; later formulations included totally new propellants that contained non–chlorine oxidizers (these propellants were referred to as "totally clean" propellants). All of these so–called "clean" propellants have some serious drawbacks in one or more important propellant characteristics: losses in performance (specific impulse or density); difficulties in processing and/or reduced physical properties and aging characteristics; humidity sensitivity; increased safety hazards during propellant processing or use; limited ballistic tailoring; and reduced bonding capability. Moreover, many have significant increases in costs over contemporary solid propellants using ammonium perchlorate (AP) as the oxidizer. The chemistry of solid rocket propellants is the single most important factor in determining the performance, safety, reproducibility, reliability, and cost of a solid rocket propulsion system. Departing from a well–established experience base, along with the lack of understanding of the real environmental impact of chemical rocket exhaust, dictated the need to fully examine this issue before changes in solid rocket propellant chemistry were warranted.

It was decided to examine the environmental impact of all rocket propellants, both solid and liquid. Table I lists the propellant combinations that were examined and the major exhaust products from these propellants. The first propellant in the table is the standard solid rocket propellant used in all space launch vehicles incorporating solid rocket boosters (SRBs) today; all current space launch solid propellants use a rubber binder containing aluminum as the primary fuel and AP as the oxidizer. The second formulation in the table is a "clean" propellant that replaces a portion of the AP oxidizer with sodium nitrate. As this propellant burns, most of the

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

| Propellant System | Major Exhaust Products |
|---|---|
| Ammonium perchlorate . Aluminum | HCl, $Al_2O_3$, $CO_2$, CO*, $N_2$, $H_2$*, $H_2O$ |
| Ammonium perchlorate . Sodium nitrate Aluminum | NaCl, $Al_2O_3$, $CO_2$, CO*, $N_2$, $H_2$*, $H_2O$ |
| Ammonium perchlorate . Magnesium | MgO, $MgCl_2$, $CO_2$, CO*, $N_2$, $H_2$*, $H_2O$ |
| Ammonium nitrate .... Magnesium or aluminum | $Al_2O_3$ or MgO, $N_2$, $CO_2$, CO*, $H_2$*, $H_2O$ |
| Liquid oxygen ..... Liquid hydrogen | $H_2O$, $H_2$* |
| Liquid oxygen ..... Hydrocarbon | CO*, $CO_2$, hydrocarbons, $H_2O$ |
| $N_2O_4$ ..... Dimethylhydrazine | $N_2$, NOx, CO*, $CO_2$, $H_2O$ |

*Mostly consumed during afterburning

Table I.
Chemical Propulsion Components
and Exhaust Species

HCl produced is scavenged inside the combustion chamber to form sodium chloride (NaCl), common table salt, as a combustion product rather than HCl. The third propellant is also a "clean" propellant and is sometimes referred to as the "Maalox rocket." This propellant replaces the aluminum fuel with magnesium to produce the oxide of magnesium metal (MgO) rather than aluminum oxide. Magnesium oxide in the presence of water forms magnesium hydroxide, which is a strong base. Magnesium hydroxide is the primary ingredient in Maalox for neutralizing stomach acid (which is also HCl). The magnesium oxide in the rocket exhaust neutralizes the HCl in the plume as it mixes with the water in the ambient air and the water that is produced as part of the combustion process, forming a magnesium chloride ($MgCl_2$) salt in place of HCl. The fourth propellant is referred to as a "totally clean" propellant because it replaces all of the AP oxidizer with an ammonium nitrate oxidizer to prevent any chlorine–containing compounds from being formed. There are several candidate nitrate oxidizers available, and many more energetic nitrate oxidizers are in laboratory development, but the exhaust gas chemistry produced is quite similar to the one shown in the table. The last three propellants are all–liquid rocket propellants used in various space launch vehicles; the simplest chemistry is produced from liquid hydrogen and liquid oxygen that forms water as the primary combustion product with considerable free hydrogen ($H_2$) present, as the engines are generally run fuel–rich for improved reliability and performance. It should be noted that all of the propellant combinations produce large quantities of water and most produce carbon monoxide (CO); carbon dioxide ($CO_2$), and free hydrogen ($H_2$) in the exhaust plume. The storable bipropellant system using nitrogen tetroxide ($N_2O_4$) and unsymmetrical dimethylhydrazine (UDMH) also produces free nitrogen and oxides of nitrogen. The environmental impact assessment that was made assumed that all of the hydrogen and carbon monoxide produced below an altitude of 25 kilometers was converted to water and carbon dioxide as a result of afterburning with the ambient air.

## STRATOSPHERIC OZONE DEPLETION

Figure 1 depicts the various atmospheric zones surrounding the earth. The stratosphere located approximately 13 to 50 kilometers above the earth is particularly important to our environment because it contains a low concentration of ozone ($O_3$) that acts as a protective shield from damaging ultraviolet radiation from the sun.

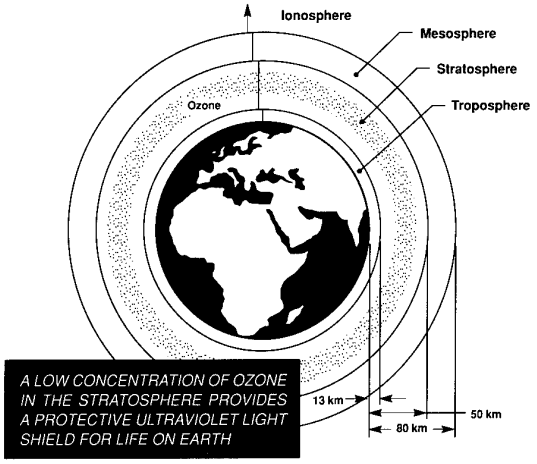



Fig. 1. Stratospheric Ozone Effects

Figure 2 presents the chemical and photochemical processes that are important in the formation of ozone from molecular oxygen in the stratosphere and the reactions associated with ozone destruction.[4] The process is very dynamic in that ozone is continuously being produced and destroyed by naturally occurring photochemical processes in the stratosphere.

**Ozone Production**

$$O_2 \xrightarrow{h\upsilon} 2O$$
$$O + O_2 + M \longrightarrow O_3 + M$$

**Ozone Destruction**

$$O_3 \xrightarrow{h\upsilon} O + O_2$$
$$O_3 + O \longrightarrow 2O_2$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$H + O_3 \longrightarrow HO + O_2$$
$$HO + O \longrightarrow H + O_2$$
$$OH + O_3 \longrightarrow HO_2 + O_2$$
$$O + HO_2 \longrightarrow OH + O_2$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$Br + O_3 \longrightarrow BrO + O_2$$
$$BrO + O \longrightarrow Br + O_2$$

Fig. 2. Natural Stratospheric Ozone Pathways

Figure 3 summarizes the naturally occurring ozone–depleting chemistries into nitrogen, hydrogen, oxygen and chlorine.[4] It is important to note that all are catalytic cycles in that the ozone–depleting species is regenerated such that it can re–enter the cycle to destroy additional ozone molecules. The asterisk on the chart reflects those ozone–depleting chemistries that are affected by rocket propulsion, i.e., nitrogen, hydrogen, and chlorine. It is interesting to note that chlorine chemistry is responsible for the least amount of ozone destruction. The reason chlorine chemistry has been of most concern is because it is the one that human activity has contributed to most.

| | 25 to 30 km Altitude (%) | Total Stratosphere (%) |
|---|---|---|
| **Nitrogen*** | | |
| $NO + O_3 \rightarrow NO_2 + O_2$<br>$NO_2 + O \rightarrow NO + O_2$ | 70 | 32 |
| **Hydrogen*** | | |
| $OH + O_3 \rightarrow HO_2 + O_2$<br>$O + HO_2 \rightarrow OH + O_2$ | 10 | 26 |
| $H + O_3 \rightarrow HO + O_2$<br>$HO + O \rightarrow H + O_2$ | | |
| **Oxygen** | | |
| $O + O_3 \rightarrow 2O_2$ | 10 | 23 |
| **Chlorine*** | | |
| $Cl + O_3 \rightarrow ClO + O_2$<br>$ClO + O \rightarrow Cl + O_2$ | 10 | 19 |

* Relevant to chemical propulsion exhaust

Fig. 3. Relative Importance of Various Catalytic Stratospheric Ozone Depletion Cycles

Analysis of more recent data obtained from aircraft flying in the lower part of the stratosphere has cast some doubt on the predominance of nitrogen oxide reactions to ozone destruction in the lower stratosphere.[5] In the spring of 1993, for the first time, atmospheric researchers were able to obtain data from an instrument–laden aircraft that observed all the important families of radicals that affect ozone, i.e., chlorine, bromine, nitrogen, and hydrogen. A new instrument measured hydroxyl (OH) and hydroperoxyl ($HO_2$) radicals as the aircraft crisscrossed the stratosphere. The data obtained indicated that the hydrogen radical family may be a more important natural loss process for ozone than the nitrogen oxide cycles. These conclusions were also supported by more recent computer models that include heterogeneous chemistry; computer models used in the past based upon homogeneous chemistry alone predicted that nitrogen oxides were the predominant ozone destruction mechanism.

Figure 4 pictorially represents the differences between an all–liquid propulsion system and the Space Shuttle, which uses both solid rocket and liquid propulsion. The exhaust products of interest—HCl, $H_2O$, and $H_2$—deposited in the troposphere by either vehicle are of little concern because $H_2$ afterburns to $H_2O$, and both HCl and $H_2O$ are quickly removed by raining out in the troposphere. Approximately two–thirds of the exhaust produced from the Space Shuttle SRBs is deposited in the troposphere, and the remainder is exhausted into the stratosphere where the boosters burn out. It is also important to note that the exhaust products produced—$H_2O$, $H_2$, and HCl—do not react directly with ozone;

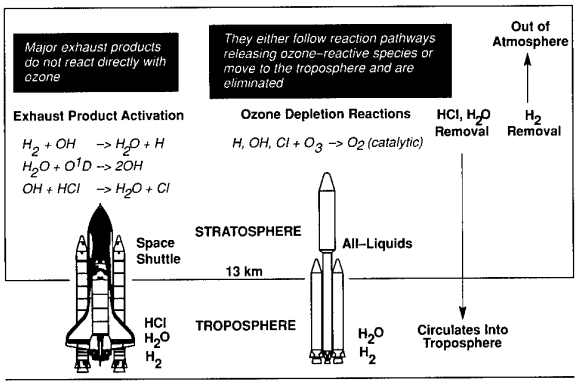



Fig. 4. Mechanisms of Potential Effect of Rocket Exhaust on Ozone

the ozone–reactive species (H, OH, Cl) must be released from the molecules in the plume before any ozone destruction can occur. Much of the HCl and water deposited into the lower portion of the stratosphere is removed by circulation into the troposphere, and considerable hydrogen deposited in the upper stratosphere is removed by escaping into the mesosphere.

Figure 5 depicts the molar concentration of important exhaust gases and where they are deposited from the Space Shuttle SRBs and the Space Shuttle main engines (SSMEs). Ozone–reaction chemistry is controlled by the molar concentration of the reacting species and the chemical reaction kinetics associated with releasing the reactive species and its subsequent reaction with ozone. It was assumed that all of the rocket exhaust produced in the stratosphere stayed there to react with ozone and none of it circulated into the troposphere or escaped into the mesosphere. It should be noted from Fig. 5 that, even though the SRBs do generate a considerable amount of HCl, from a molar basis, water and hydrogen are the major exhaust products. Even though the SSMEs produce only water and hydrogen, the SRBs, because of their much higher thrust level, deposit nearly as much water and hydrogen into the stratosphere as the SSMEs; most of the SSME exhaust is deposited above the stratosphere.

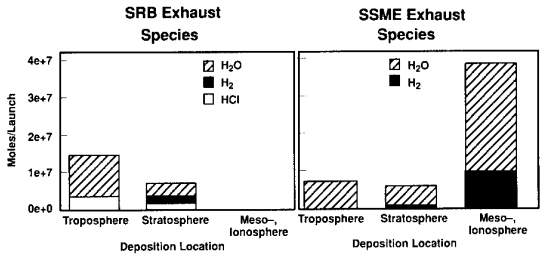



Fig. 5. Space Shuttle Exhaust Species

Much of the environmental concern with solid rocket motors was a by–product of associating solid rocket–produced HCl with chlorofluorocarbons (CFCs). Figure 6 presents a schematic representa-

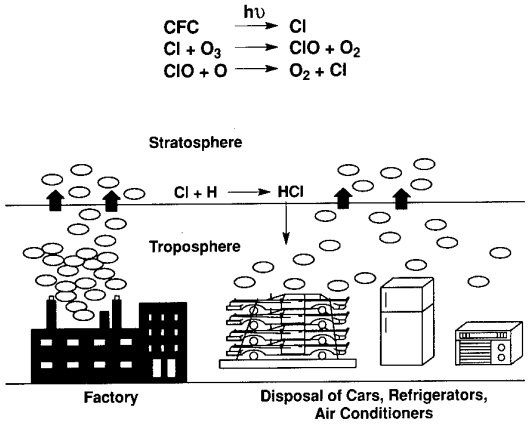



Fig. 6. Effects of CFCs on Ozone

tion of the CFC problem. CFCs are very chemically stable compounds used in refrigeration, air conditioning systems, aerosol products, and many cleaning solvents. These compounds are man-made chemicals that were designed to be chemically inert for the intended applications. As a result, there are no natural processes in the troposphere that will break down these chemicals until they reach the stratosphere, where photolysis by ultraviolet radiation releases chlorine atoms from the CFCs. The released chlorine then enters into a catalytic ozone destruction cycle. One of the major problems with CFCs is the long life and tremendous reservoir of these materials in discarded automobiles, refrigerators, air conditioners, etc., that provide a source of these chemicals to eventually enter the stratosphere for hundreds of years. Unlike HCl, which is washed out and removed as the stratospheric air circulates into the troposphere, CFCs are inert to most chemical processes in the troposphere. It is interesting to note from Fig. 6 that the chlorine released in the stratosphere from CFCs is eventually removed by the reaction of chlorine with stratospheric methane to form HCl, which can then circulate to the troposphere and be removed. As can be seen from Fig. 6, there is a significant difference between CFCs and HCl from solid rocket exhaust. In fact, the *formation of HCl* is the *primary removal process for chlorine atoms released from CFCs* in the stratosphere. Conventional wisdom indicates that all CFCs that are released to the atmosphere will eventually make it to the stratosphere, and will remain in the stratosphere until their chlorine is released by photodissociation from sunlight (a process that cannot be avoided) in the form of active chlorine (Cl) atoms; the released chlorine atoms will continue to catalytically destroy ozone until the chlorine is tied up in a reservoir specie or can be removed by forming HCl. However, most HCl deposited directly into the stratosphere from rockets must undergo a chemical reaction before the ozone–destroying chlorine atoms can be released. HCl is not readily photodissociated. As a result, some of the HCl deposited directly into the stratosphere may never release any chlorine before it has the opportunity to circulate back into the troposphere where it is readily rained out. Furthermore, HCl is a naturally occurring chemical in the earth's atmosphere, with a large natural reservoir of HCl in the troposphere and stratosphere in contrast to the unnatural molecules of CFCs that were engineered by man.

Figure 7 is a projection of the cumulative global stratospheric chlorine burden in parts per billion (ppb) over a 75–year time frame from 1979 to 2054, assuming that the Montreal Protocol ban on the production of Class I ozone depleting chemicals (ODCs) is effective by 1996 as planned.[6] Superimposed on this chart is the contribution to stratospheric chlorine in the form of hydrogen chloride from all rocket launches which represents a steady–state contribution of chlorine from HCl of approximately 0.003 ppb. This assumes a world launch rate of solid rockets equivalent to one Space Shuttle launch every month.[7] This launch rate represents a constant 40 percent increase in HCl deposited in the stratosphere from solid rocket launches over what was actually achieved in 1993.

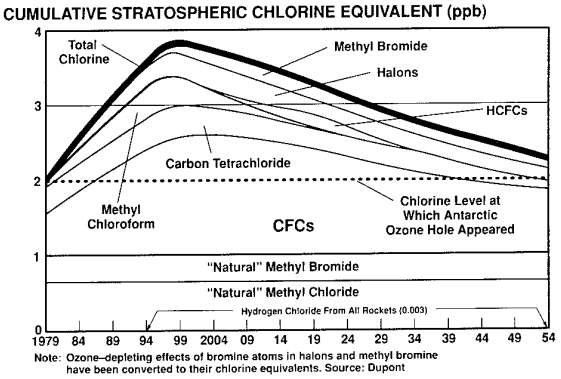



Fig. 7. Levels of Chlorine in Stratosphere Will Decrease Slowly Under Montreal Protocol

Figure 8 depicts the relative annual contributions from various sources to the stratospheric chlorine burden.[8] Industrial halocarbon–derived chemicals, primarily CFCs, producing 300 kilotons per year, are a major contributor to stratospheric chlorine and are the principle source of anthropogenic chlorine. Natural sources, primarily methyl chloride ($CH_3Cl$) from the oceans and burning vegetation, were estimated to add an additional 75 kilotons of chlorine to the stratosphere. Volcanoes can inject HCl directly into the stratosphere, and when major volcanic activity occurs, such as the 1991 Mount Pinatubo eruption in the Philippines, it tends to

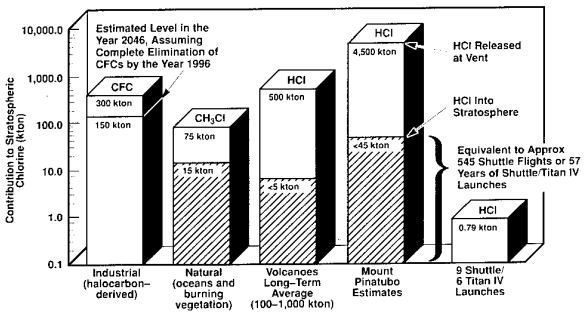



Fig. 8. Relative Annual Contributions to Stratospheric Chlorine

overshadow all other sources during the rather short period of time of volcanic activity. Volcanoes are very random and sporadic sources of chlorine, but it was estimated that on a long–term average, volcanoes could inject anywhere from 100 to 1,000 kilotons of chlorine in the form of HCl directly into the stratosphere on an annual basis.[9] The chlorine burden from SRBs producing HCl adds less than 1 kiloton of chlorine to the stratosphere per year based upon a flight rate of nine Space Shuttles and six Titan IV launches per year. It should also be noted from Fig. 8 that, if we are successful in eliminating all CFC production by 1996 as mandated by the Montreal Protocol, we will still be adding 150 kilotons of chlorine to the stratosphere some 50 years later as a result of the long life and huge reservoir of these chemicals.

It should be noted in Fig. 8 that more recent data (represented by the cross–hatched area) obtained from volcanic activity indicate that only a small fraction of the HCl emitted from a volcano ever reaches the stratosphere as hydrogen chloride gas.[10] Data obtained from Mount Pinatubo, along with detailed computer modeling studies, indicated that less than 1 percent of the HCl gas emitted from the vent of the volcano reached the stratosphere in that form; more than 99 percent of the HCl is rained out of the stratosphere by the huge quantities of steam and water contained in the volcanic cloud. The quantities of steam emitted from the volcano produce roughly 1,000 times as much water as HCl while the volcanic cloud rises and cools. Nevertheless, the Mount Pinatubo eruption in June 1991 is estimated to have released 4.5 million metric tons of HCl. Assuming only 1 percent of the HCl reached the stratosphere, it would still result in injecting 45 kilotons of chlorine into the stratosphere, which is equivalent to approximately 545 flights of the U.S. Space Shuttle.

More recent data obtained from measurements taken by stratospheric aircraft (represented by the cross–hatched area) have also indicated less methyl chloride in the stratosphere than was originally thought.[11] As shown in Fig. 8, more recent data would reduce the stratospheric loading of methyl chloride from oceans and biomass burning from 75 kilotons to approximately 15 kilotons per year. These more recent data would indicate that natural sources of chlorine are considerably lower than was originally believed. If chlorine contributions from CFCs are as high as predicted (300 kilotons per year), then these anthropogenic contributions to stratospheric chlorine would be the major source of chlorine in the stratosphere. In any event, the 0.79 kilotons per year of chlorine from rocket launches remains small compared to CFCs or natural sources of chlorine.

Figure 9 presents a Pareto chart of the stratospheric ozone–depleting chemistries and the portion that can be attributed to chemical rockets. As can be readily seen, rocket contribution to stratospheric ozone depletion is extremely small, representing approximately 0.03 percent of the ozone depletion from all other sources. Therefore, based upon the current state of knowledge, it certainly would not appear to be technically or financially responsible to spend large sums of money trying to reduce the contribution of chemical rockets to destruction of stratospheric ozone.

There have been several numbers published in the literature for the magnitude of stratospheric ozone depletion due to solid rockets over the past few years. These numbers are not inconsistent, but

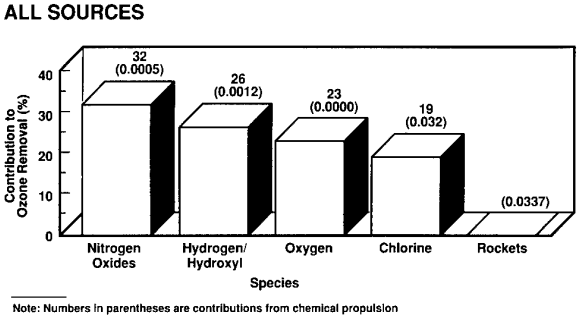



Fig. 9. Chemical Removal of Stratospheric Ozone

represent different sets of conditions as shown in Fig. 10.[12] Based on a two–dimensional (2–D) atmospheric computer model calculating local ozone depletion at a 40–kilometer altitude in the region (1,000 km by 1,000 km) above the launch site, long–term steady–state stratospheric ozone depletion approaching 0.25 percent would be calculated. This same analysis through the entire regional ozone column over the launch site reduces the ozone loss to less than 0.1 percent, which is further reduced to approximately 0.006 percent on a global scale. The global ozone depletion numbers presented in Fig. 9 are based upon first order approximations that are roughly five times more conservative than the 2–D models would predict, resulting in the 0.03 percent number shown. Since global stratospheric ozone depletion calculations based on these more sophisticated 2–D models (0.006 percent) have underpredicted ozone losses by a factor of two over the past few years, it is most probable that ozone depletion from rocket launches would not exceed a steady–state reduction of more than 0.012 percent based on the assumed yearly flight rate of nine Space Shuttles and six Titan IV vehicles.

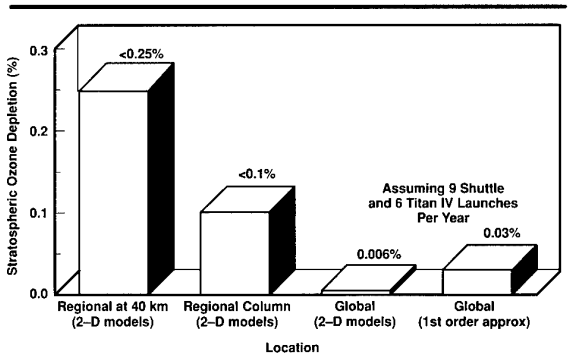
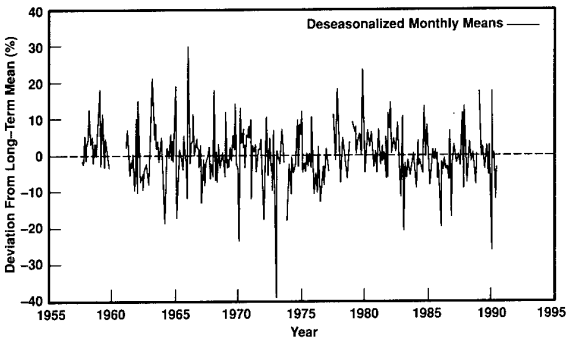



Fig. 10. Stratospheric Ozone Impact Due to Solid Rocket Motor Exhaust

There have been news media reports linking the ozone reduction in the stratosphere to rocket launches, and solid rocket motors in particular. It is clear that 0.006 to 0.012 percent reductions cannot be measured, especially when the natural annual variations in the northern hemisphere have varied over 20 percent, as shown in Fig. 11. Figure 11 covers a 33–year period from 1957 to 1991.[13]




THE LARGE NATURAL VARIATIONS WILL MAKE THE PREDICTED EFFECTS OF ROCKETS DIFFICULT, IF NOT IMPOSSIBLE, TO OBSERVE

Fig. 11. Large Natural Variations in Stratospheric Ozone

Some people have been concerned that rockets may be creating an ozone hole directly over the launch site areas. As shown in Fig. 12, a typical Space Shuttle trajectory is not even close to being vertical, and, in fact, by the time the SRBs burn out near the top of the stratosphere, the Space Shuttle has as much down–range as vertical altitude.

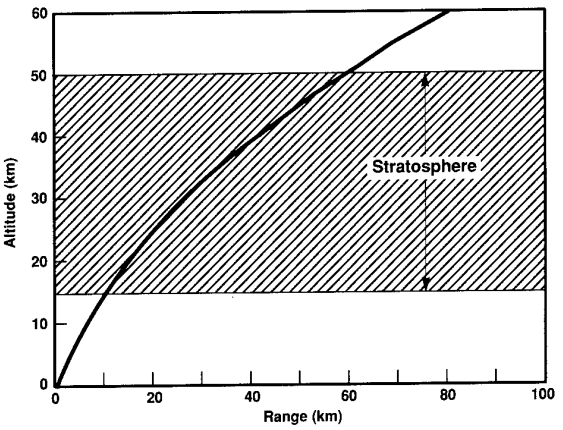



Fig. 12. Typical Space Shuttle Trajectory

Atmospheric scientists (Karol, Ozolin, and Rozanov[14]) from the Main Geophysical Observatory in Russia have examined the impact of rocket launches on local stratospheric ozone above the launch site. These Russian scientists concluded that 50 launches per year of either the U.S. Space Shuttle or Russian Energia would not significantly impact local or global ozone depletion in the stratosphere. Scaling the Russian data to an equivalent launch model consisting of nine Space Shuttles and six Titan IV launches per year results in good agreement with NASA's projection of 0.0065 percent global ozone depletion. Similar analysis conducted by the European Space Agency for the Ariane V,[3] when scaled to the same equivalent launch model, produced comparable results. The Russian scientists conducted time–dependent analytical calculations of local ozone depletion in the rocket plume as it mixes with the ambient air as the vehicle flies through the stratosphere. Calculations were conducted for both the U.S. Space Shuttle (S) and the Russian Energia (E) vehicle, as shown in Fig. 13. Figure 13 presents results at 40– and 16–kilometer altitudes for both vehicles up to one day after launch.[2] Ozone destruction in the near field of the rocket plume can be very severe (>90 percent) within just a few minutes after the launch vehicle enters the stratosphere; however, the ozone concentration is totally restored to background levels from natural mixing of the plume with surrounding air in this very localized area within a few hours after launch. It is also interesting to note that the magnitude of local ozone destruction is basically the same for the U.S. Space Shuttle with its SRBs and the all–liquid Russian Energia vehicle that does not produce any chlorine–containing compounds in the exhaust. The only difference noted between the two vehicles is that the non–chlorine Energia destroys ozone more quickly, but recovers faster, than the Space Shuttle; this recovery time difference is attributed to the HCl, as shown in Fig. 13.

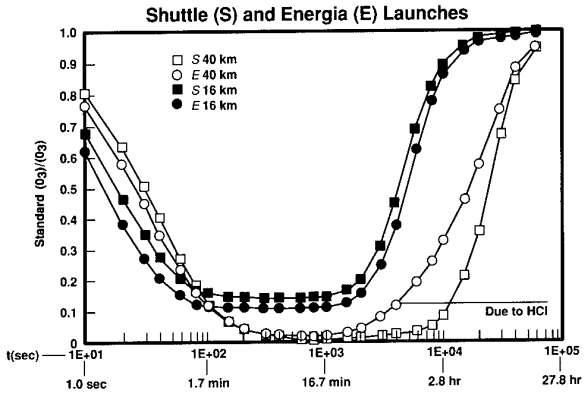



Fig. 13. Shuttle and Energia Impact on Local Ozone

The Russian atmospheric scientists Karol et al.[14] analyzed two sets of conditions to determine the local impact of $NO_x$ and chlorine production from the Space Shuttle vehicle. Figure 14 presents the impact on local column ozone changes comparing the baseline calculations shown in Fig. 13 (Scenario A) assuming HCl and $NO_x$ are the primary ozone–depleting chemistries in the plume with a second scenario (Scenario B) with decreased $NO_x$ production and all chlorine from the SRBs in the form of chlorine gas ($Cl_2$) rather than HCl. As shown in Fig. 14, total column ozone destruction at any given time is less than 8 percent and is restored to normal background levels within a few hours after launch. The production of $Cl_2$ rather than HCl results in slightly more ozone destruction, but does not significantly affect the recovery time.

Computer modeling work conducted by Denison et al. at TRW[15] suggests that HCl from solid rocket plumes may be quickly converted to $Cl_2$ at high altitudes from afterburning. The TRW paper describes model calculations examining the local effects of solid rocket exhaust on stratospheric ozone at different altitudes. The afterburning calculations suggest that a significant fraction of the

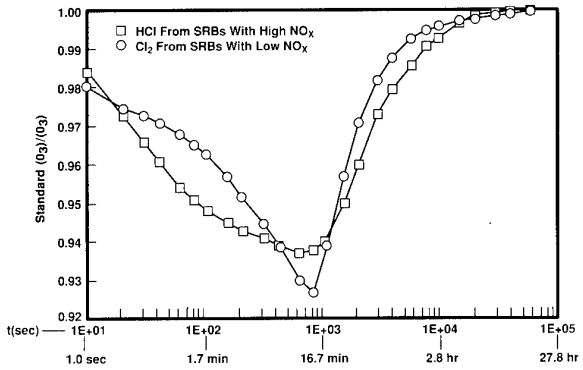



Fig. 14. Local Column Ozone Changes From Shuttle Launch

HCl is converted to $Cl_2$ in the hot plume—about 20 percent at an 18–kilometer altitude and as much as 80 percent at 30 kilometers. Ozone depletion is extensive during the first few minutes following a launch, but quickly recovers (within about one–half hour) to near background levels. It was found that the rate of plume dispersion has a very significant effect on local ozone loss. The differences in plume dispersion rates explains, at least in part, the differences between the Karol results[14] and the TRW results.[15] Both studies indicated local total column ozone depletion less than 10 percent; the major differences noted were in the time it took for recovery. The TRW results predicted much more rapid loss and recovery within seconds to minutes while the Karol results indicate somewhat similar impacts with total recovery occurring over a much longer period of time, i.e., a few hours.

Plume modeling work reported by Dr. R. B. Cohen of the Aerospace Corporation[16] has also indicated that high temperature afterburning reactions may rapidly convert the HCl to active $Cl_2$ and Cl in the plume in the stratosphere. More recent work done by German atmospheric research scientist, Dr. B. C. Kruger from the Institute for Geophysics and Meteorology at the University of Köln,[17] has examined the influence of chlorine production from solid–fuel rockets on local ozone depletion in the plume. Dr. Kruger's paper is a model study of the impact of the chlorine emissions from the Space Shuttle SRBs at various altitudes as a function of distance from the center of the plume as the plume evolves over time. Chlorine emissions were considered both in the form of HCl and $Cl_2$. The cases run were 100 percent HCl, 95 percent HCl and 5 percent $Cl_2$, and 50 percent HCl and 50 percent $Cl_2$. For the case of 100 percent HCl, Kruger predicts that ozone destruction will begin between 5 and 10 minutes after launch as the HCl reacts and begins to release its chlorine. The maximum depletion at 35 kilometers is about two percent at the center of the plume and lasts for more than 24 hours. At lower altitudes, the ozone depletion is much less—about 0.19 percent at 28.5 kilometers, and about 0.26 percent at 31.9 kilometers in altitude. Maximum column ozone depletion values given by Kruger are related to what an instrument with a given field of view (FOV) in orbit would see. In the case of 100 percent HCl, for a true vertical trajectory, the maximum column ozone decrease seen for a 1,664–$km^2$ (41 km x 41 km) FOV instrument like the NASA total ozone mapping spectrometer (TOMS) instrument would be about 0.5 percent. For the case of 50 percent chlorine and 50 percent HCl, the ozone is virtually depleted at high altitudes within 10 minutes of the launch. Maximum column ozone depletion which would be observed by an instrument with a 1,664–$km^2$ FOV is about 3 percent over the entire FOV. The predicted column values are somewhat lower than those calculated by Karol[14] and predict that the TOMS instrument would not have sufficient resolution to observe the impact on the local stratospheric ozone column from a Space Shuttle launch.

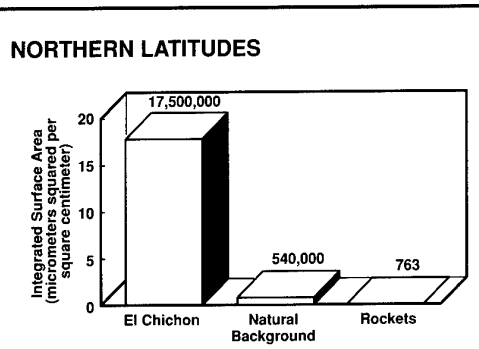
Thermochemical equilibrium calculations for Space Shuttle SRB propellant indicate HCl will be produced rather than $Cl_2$. Experimental sampling of solid rocket combustion gases at ground level has indicated that HCl is the major combustion product at a ratio of approximately 10:1 over $Cl_2$. There have not been any plume chemistry measurements made at stratospheric altitudes. There are very limited experimental data for determining the effects of rocket plumes on stratospheric ozone depletion; however, what data are available tend to support Russian scientific analysis. Ozone reductions greater than 40 percent were measured in the exhaust trail of a Titan III SRB at an altitude of 18 kilometers approximately 13 minutes after launch.[18] Considerable $NO_x$ formation was also detected in the plume and the ozone depletion was attributed to $NO_x$ at that time; chlorine measurements were not made. NASA has made several measurements of total column ozone concentration directly over Kennedy Space Center (KSC) after eight different Space Shuttle launches with the TOMS aboard the NIMBUS–7 satellite.[19] No evidence of ozone depletion was ever detected; however, the measurements that were taken were generally obtained several hours after launch. These data appear to be consistent with the Russian scientific calculations[14] and the Kruger analysis[17] which would predict that normal background levels of ozone are restored within a few hours of the launch and the ozone loss at any given time would be below the threshold of detectability within the FOV of the TOMS instrument.

Most of the local and global ozone depletion calculations to date have considered homogeneous gas phase chemical reactions only. Recent studies of the Antarctic ozone hole have identified the importance of heterogeneous chemistries on ice crystals in the polar stratospheric clouds. Decreases in mid–latitude ozone levels have also been attributed to catalytic activity on the surface of finely divided particulate matter injected directly into the stratosphere from volcanic eruptions. The question arises, "Can finely divided aluminum oxide ($Al_2O_3$) from SRBs, soot from liquid oxygen and hydrocarbon boosters, and ice contrails from all rockets also provide catalytic surfaces for ozone–destroying chemistries?"

There have been few published calculations for the potential impact of rockets in this area. The limited heterogeneous modeling of solid rocket plumes by several researchers has indicated that the effects on local plume chemistry are minor, and, therefore, the influence on local ozone depletion, if any, appears to be small.[15,17,20,21] The impact on global ozone depletion from rocket–produced aerosols is even less significant, i.e., could be responsible for about 1/1,000th of the current ozone depletion associated

with the unperturbed background heterogeneous chemistry in the absence of volcanic aerosols.[22]

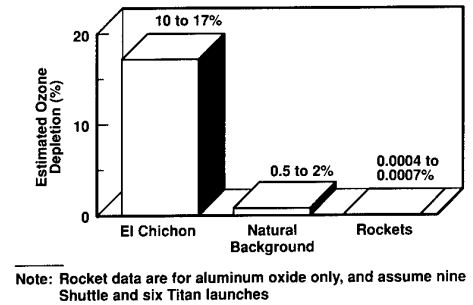
Analysis of data from volcanoes can provide good qualitative insight as to the potential magnitude of particulate matter from solid rockets. Figure 15 shows the estimated total integrated surface area of finely divided particulate matter injected into the stratosphere by the El Chichon volcanic eruption in Mexico in 1982.[23] This figure also compares the natural background levels of stratospheric aerosols to the total quantities of aluminum oxide deposited by nine Space Shuttle and six Titan IV launches if all of the $Al_2O_3$ were deposited in the same region as the El Chichon cloud. The rocket contribution does not include any ice or soot particles from the launch vehicles.




Note: Rocket data are for aluminum oxide only, and assumes nine Space Shuttle and six Titan launches

Fig. 15. Stratospheric Surface Area Available for Heterogeneous Chemistry

Figure 16 shows the maximum estimated ozone depletion in the region of the El Chichon–induced stratospheric cloud as compared to the estimated ozone depletion from natural aerosols and rockets producing $Al_2O_3$.[23,24] As can be seen from the figure, the ozone destruction within the cloud of El Chichon could be as high as 17 percent, as compared to the SRB contribution of less than 0.0007 percent on the same basis.




Note: Rocket data are for aluminum oxide only, and assume nine Shuttle and six Titan launches

Fig. 16. Estimated Effects of Heterogeneous Chemistry on Stratospheric Ozone

The 1991 eruption of Mount Pinatubo in the Philippines was far more powerful than El Chichon. Atmospheric scientists believe that the aerosols from this volcano were probably responsible for the intensification of global ozone thinning noted since the eruption of Mount Pinatubo.[5]

## ACID RAIN

Since SRBs produce hydrochloric acid in the exhaust plume, there has been considerable concern over the impact that this acid rain may have on the global environment, as well as local launch sites. All rockets produce some acid rain as a result of the formation of $NO_x$ in the near field of the plume from afterburning that forms nitric acid in the presence of water. The studies presented here only consider HCl from solid rockets as a source of acid rain.

Figure 17 depicts the annual U.S. contribution to the global acid rain problem from various anthropogenic sources, including solid rockets.[25,26,27] As can be seen from the figure, other energy conversion processes such as heating and power production (33,000 kilotons), transportation (9,100 kilotons), and industrial processes (6,100 kilotons) clearly overshadow the acid production (3 kilotons) from solid rocket launches. Most of the acid produced from these industrial activities is in the form of sulfuric acid, with significant quantities of nitric and hydrochloric acid also produced. Without considering other countries in the world, rockets are responsible for less than 0.006 percent of acid rain produced by U.S. industries alone.

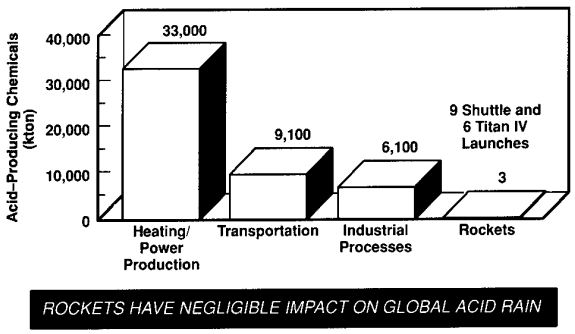



Fig. 17. Annual Contribution to Acid Rain (Continental U.S. Data)

Figure 18 reflects sources of hydrochloric acid other than rockets.[9] As can be seen in Fig. 18, natural sources of HCl from the oceans (330,000 kilotons), volcanoes (5,000 kilotons), and coal burning processes (1,980 kilotons) make solid rockets (3 kilotons) an insignificant contributor to global atmospheric HCl releases. It is estimated that launching nine Space Shuttles and six Titan IVs each year would deposit the same amount of HCl into the troposphere as is produced by the Atlantic ocean each year just east of the KSC launch site in an area of the ocean represented by a square less than 30 miles on each side. On a global scale, HCl produced by rocket launches is less than 0.001 percent of the total HCl production from the ocean alone and only 0.15 percent of anthropogenic sources, primarily coal burning power plants in the United States.

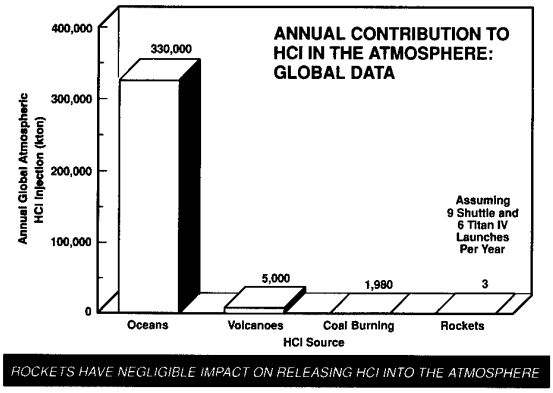



Fig. 18. Global HCl Releases

On a local scale, acid rain from SRBs is more significant and does have near–field acidification effects in the vicinity of the launch site.[28] These effects are limited to a very localized area within less than one–half mile from the launch pad directly in line with the SRB flame trenches, as shown in Fig. 19. Some plant and small fish (minnows) mortalities occur in the lagoon area just north of the launch pad, less than 0.1 square mile of area (which is much smaller than the launch pad itself). Catch basins for the sound suppression water is neutralized after each launch and the pre– and post–launch environmental conditions are documented on each Space Shuttle launch.

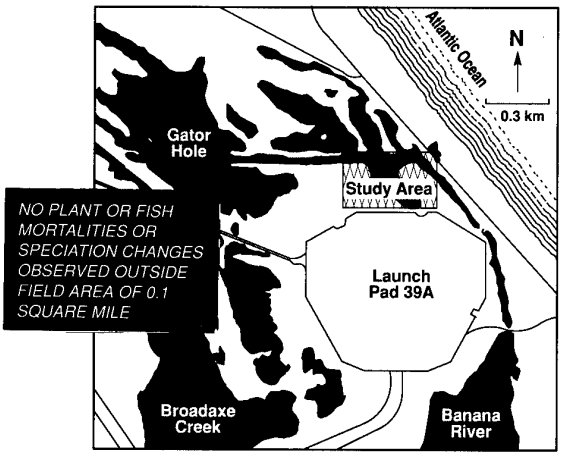



Fig. 19. Acid Rain: Near–Field Deposition Area

## TOXICITY

Hydrochloric acid is the most toxic substance associated with cured solid propellants and it is only produced by combustion. Storable liquid bipropellants consisting of nitrogen tetroxide ($N_2O_4$) and hydrazine compounds are far more toxic, but have been safely and routinely handled at various launch sites for decades. As shown in Table II, even in very minute concentrations, these liquid bipropellants can be a significant health hazard while HCl in minute quantities is only considered a corrosive or irritant.[29]

- **Liquid rocket components—nitrogen tetroxide ($N_2O_4$), dimethylhydrazine, and hydrazine—are highly toxic, and handling is a local concern**
- **HCl is the most toxic of the common solid rocket exhaust species**

| | Lethal Concentration, 50% (inhalation, rats) | Additional Concerns at Very Low Concentration Levels |
|---|---|---|
| $N_2O_4$ | 88 ppm/4 hr | Pulmonary edema |
| Dimethylhydrazine | 242 ppm/4 hr | Suspected carcinogen |
| Hydrazine | 570 ppm/4 hr | Suspected carcinogen |
| HCl | 3,124 ppm/1 hr | Corrosive/irritant |

Table II. Propellant and Exhaust Toxicity

Considerable concern has been raised relative to the toxicity and corrosiveness of the SRB ground cloud as it drifts away from the launch site. Figure 20 represents one of the rare Space Shuttle launch plume conditions that drifted inland rather than out over the ocean after the launch.[30] Bionetics Corporation has periodically monitored HCl concentrations for NASA and routinely conducts model calculations on HCl concentration in the far field of the Space Shuttle plume, as shown in Fig. 20. It should be noted that the maximum HCl concentration in the ground cloud of 0.9 parts per million is well below the American Conference of Governmental Industrial Hygienists' recommended threshold limit value (TLV) of 5 parts per million for long–term continuous exposure (8 hours per day—40 hours per week). HCl concentrations measured in the path of the Titan III SRB ground cloud as it drifted several kilometers from the launch site at Vandenberg AFB have also been well below the 5 ppm threshold limit values, i.e., 0.005 ppm to 0.5 ppm. Aircraft fly–throughs of the stabilized exhaust plumes of the Titan III and Space Shuttle at 1 to 2 kilometers above ground level have measured HCl concentrations at the TLV of 5 ppm for 10 to 60 minutes after launch.[31]

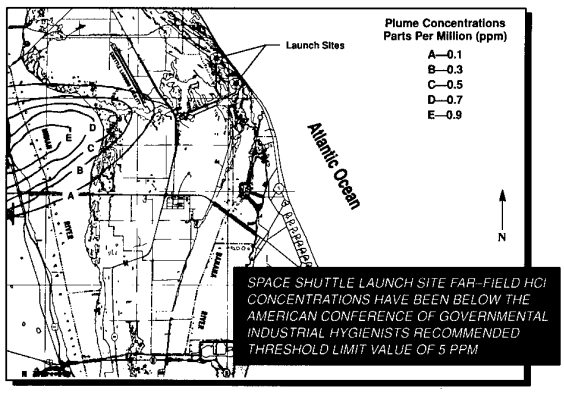


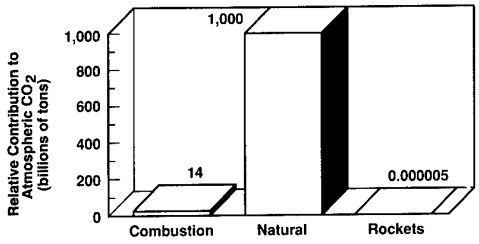

Fig. 20. Toxicity of Shuttle Exhaust Plume

There have been some published studies that have suggested an association of aluminum compounds with Alzheimer's disease. Solid rockets consume less than 0.01 percent of the 69 billion pounds of aluminum metal produced in the U.S. each year, and approximately 8 percent of the earth's crust consists of aluminum compounds, such as oxides, silicates, etc. Furthermore, many pharmaceuticals, food additives, and health care products (deodorants, for instance) contain aluminum compounds. To prevent people from throwing away their aluminum cockware and stop drinking from aluminum beverage cans, the U.S. Food and Drug Administration (FDA), the Alzheimer's Disease and Related Disorders Association, and the U.S. Environmental Protection Agency (EPA) released statements in 1989 that there was no evidence to support the hypothesis that aluminum contributed to Alzheimer's disease.

## GLOBAL WARMING

It has been postulated by several scientists that production of certain gases, such as carbon dioxide ($CO_2$), from the continued burning of fossil fuels could eventually cause more of the sun's energy to be trapped in the earth's atmosphere, resulting in global warming or a greenhouse–type effect. As shown in Fig. 21, the amount of $CO_2$ produced from chemical rockets is extremely minute, representing less than 0.00004 percent of anthropogenic sources of $CO_2$.[27,32]

**RELATIVE ANNUAL CONTRIBUTIONS TO ATMOSPHERIC $CO_2$**




*THE CONTRIBUTION OF ROCKET EXHAUST $CO_2$ TO THE GREENHOUSE EFFECT IS INSIGNIFICANT*

Fig. 21. Greenhouse Effect Gases

It has also been suggested that particles from rocket launches could also contribute to global warming conditions or possibly global cooling. As indicated earlier, aluminum oxide deposited into the stratosphere by SRBs is so small that it would take nearly 300,000 Space Shuttle launches to equal a volcano the size of El Chichon.

## CONCLUSIONS

Based upon our current state of understanding of the earth's atmosphere, the following conclusions can be drawn relative to the impact of chemical rocket launches:

1. The environmental impact of chemical rocket propulsion is extremely small, i.e., annual global stratospheric ozone depletion and tropospheric acid rain contributions are estimated to be less than 0.01 percent.
2. There is no significant difference in local stratospheric ozone depletion from the U.S. Space Shuttle with its solid rocket boosters and the all–liquid Russian Energia launch vehicle, and the impact is small even at launch rates as high as 50 flights per year of either vehicle.
3. Contrary to manmade CFCs, chemicals released from rockets are not foreign to the environment, but represent an extremely small fraction of large natural reservoirs of these materials in the atmosphere.
4. As a potential source of chlorine in the stratosphere, all rocket launches combined produce less than 0.25 percent of the chlorine introduced by CFCs on an annual basis. Enactment of the ban on the production of CFCs by 1996 will eliminate 99.75 percent of the current anthropogenic sources of new chlorine that could eventually find its way to the stratosphere.
5. The impact on the potential for global warming due to $CO_2$ from chemical rockets is minuscule (less than 0.00004 percent).
6. Local launch site area acidification is minor and manageable.
7. There is no rocket system that is totally "clean," and the environmental improvements available appear to be very limited. The amount of energy released to place objects into earth orbit will cause some minor damage to the earth's atmosphere independent of rocket chemistry.
8. The benefits of obtaining global weather and environmental data from satellites and space laboratories in earth orbit far outweigh the minor environmental impacts of placing these assets into space.

## RECOMMENDATIONS

Recommendations for further work are primarily focused on improved atmospheric computer modeling, environmental data gathering, and establishing reasonable environmental criteria for future launch systems. These following recommendations are summarized:

1. More measured data need to be obtained to verify the minimal impacts that are being projected.
2. Atmospheric computer modeling, which includes both homogeneous and heterogeneous chemistry, needs to reflect actual measured conditions for improving confidence in future projections and assessing effectiveness of potential mitigating strategies. These models need to include afterburning, equilibrium and non–equilibrium plume chemistry and combined exhaust gas chemistry from mixed propulsion launch vehicles.
3. "Clean" solid propellant work should be renamed "alternative propellants" and continued on a laboratory scale until more atmospheric experimental data are available to verify the minimal environmental impact conclusions that have been drawn to date.

4. New launch system development should include criteria for assessment of the environmental impacts along with safety, performance, reliability, and cost requirements.

5. A detailed environmental–cost–benefit–risk analysis should be conducted for any new launch system, and any potential environmental benefits that are identified should be adequately demonstrated and verified prior to incorporation into the launch vehicle.

Based upon the environmental impact studies conducted to date, there is no reason to modify any launch vehicles or change any propellant chemistry at this time.

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## Discussion

QUESTION BY R. R. WEISS : Please discuss your views on the general status of measurement techniques and what is needed for the future. Your Fig. 11, in which you show variations in stratospheric ozone, implies that improvement in the fidelity of instrumentation and/or measurement techniques may not be able to help in discerning effects of rockets and thus leads one to ask if we are good enough in this regard ?

ANSWER : Figure 11 reflects global effects which cannot be measured since annual variations are so high relative to rocket impacts on a global basis. What is needed is better instrumentation to determine the local effects above the launch sites. As indicated in my paper (p. 7) the NASA/TOMS instrument has too large a field of view (FOV) to detect such small changes in ozone destruction from Shuttle launches over KSC. A higher resolution instrument with a much smaller FOV like that being developed by the Aerospace Corporation for AFSMC should provide more accurate data relative to ozone destruction in the plume of a rocket motor.

QUESTION BY I. W. MAY : The calculations presented are based on limited numbers of Shuttle and Titan launches. How would the results change if a realistic estimate for the total world-wide rocket and missile launches is used for the calculations ?

ANSWER : The calculations were based upon an assumed annual launch rate of nine Space Shuttles and six Titan IV vehicles per year. This launch rate has never been achieved and represents far more rocket exhaust than has ever been achieved in all at the world's launches of solid rockets in a year. As indicated in Fig. 7 (p .4) of my paper, a launch rate equivalent to one Space Shuttle flight per month results in increasing global chlorine concentration in the stratosphere by 0.003 ppb. This represents more than a 40 % increase in the world launching of solid rockets in 1993. If the Ariane 5 reaches 10 launches per year as planned and the H-2 launches 2-4 times per year, the launch model used in this paper would represent approximately 75 % of the world's launches. As indicated by the paper, the effective world launch rate could increase by an order of magnitude and not significantly change these conclusions i.e. chlorine contributions from rockets would still only represent 2.5 % instead of 0.25 % of that being released by CFC's.

QUESTION BY L. CAVENY : I note your recommendation that the terminology "clean" solid propellant should be replaced by "alternate propellants". A primary reason for an improved terminology is to avoid implying that a present propellant is dirty. We need a more descriptive terminology, e.g., to characterize a propellant formulated without chlorine. How much consideration has been given to developing an improved, descriptive terminology ?

ANSWER : Not much consideration but the term "clean" should be avoided because it is untrue. There is nothing that is "clean". We should use the word "improved" propellants because there may be some other reasons for changing propellant composition rather than for environmental reasons. The magnitude of the environmental problem created by solid propellants does not warrant the huge

costs and increased risks associated with reformulation of propellants and the introduction of new ingredients. Work should be continued in the laboratory as an "insurance policy" in the event that measured data shows the problem to be more significant than conventional wisdom dictates or if regulators ignore the current scientific facts.

# THE IMPACT OF SPACE ROCKET LAUNCHES ON THE EARTH OZONE LAYER

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**Abstract.** The paper addresses the problem of assessing the composition and quantity of substances exhausted by rockets during their trajectory flights. It demonstrates the necessity of taking into account chemically non-equilibrium processes taking place during exhaust gas flow through an engine nozzle, afterburning in the atmosphere and presence of the $N_2$ technological impurity contained in the liquid oxygen oxidizer in the amount of 0.5% $N_2$. Emission magnitudes of ozone-affecting substances by Energiya, Shuttle, Zenit, Proton and MX rocket stratospheric flights are stated. It was noted that the estimated Energiya and Shuttle rocket major exhaust amounts differ from those stated in other works by one-two orders of magnitude.

The stated assessment local impact on the stratospheric ozone shows that the Energiya launch effects are by an order of magnitude lower than those of the Shuttle. This fact is determined mainly by the influence of chlorine contained in ammonium perchlorate the latter being a solid fuel oxidizer. Due to that it would be reasonable to develop chlorine-free fuels or fuels with a low chlorine content.

It is proposed to elaborate a procedure for calculating emissions of different substances by rockets, to publish atmospheric emission data on all the rockets in operation and to reach concord on this procedure with the leading organizations.

This AGARDograph was sponsored by the Propulsion and Energetic Panel.

**Keywords:** rocket, rocket fuel, chemical non-equilibrium, stratospheric ozone, ozone depletion, ozone-affecting exhausts, afterburning.

## 1. INTRODUCTION

Rocket fuel exhaust gases forming a propulsive jet are one of the main factors of the environmental effects of rocketry. When flying on a trajectory, a rocket emits into the atmosphere hundreds and thousands tons of exhaust gases. A considerable portion of them is emitted directly in to the earth ozone layer lying between the altitudes of 20 to 40 km. This layer's biological importance and its vulnerability to anthropogenic impacts are the cause of a heightened concern to all factors that may lead to the ozone depletion.

Significantly great efforts [1-9] have been undertaken to evaluate probable effects of rocket fuel exhaust gases on the stratospheric ozone. According to the latest results of research the global ozone depletion in various rocket launch scenarios constitutes a value by an order 0.01% [2,3,4,7]. As for the local impacts directly in a corridor of a heavy rocket flight the depletion is expressed in a considerable ozone concentration decrease (by 80-10%) in the corridor along the flight trajectory with a radius of 1-5 km, however the background conditions come back to normal within some hours [6,7,10].

Relying on the given values one can qualitatively assess a probable stratospheric ozone depletion caused by rocket launches as extremely low. Justification of such assessment is evidently seen when comparing it with the assessment of the similar probable deterioration caused by advanced supersonic transport aircraft flights [11]. If a probable ozone depletion constitutes 8% or less, - at best 2%, - the situation is considered as "...predictions indicate the possibility of relatively small effects of high-speed civil transport aircraft on atmosphere ozone".

However, some problems of evaluating rocket launch effects on the ozone should be verified. Though the ozone depletion is negligible it is desirable to specify the comparison of dangers caused by different fuel usage, since such comparison shown in the known works is not fully correct.

Evaluation of environmental effects of rocket launches is based on the amount of different substances emitted in the atmosphere during flights. When assessing them, one should take into account the major factor influencing the atmospheric exhaust composition more fully. These factors concern, firstly, consideration of the actual rocket fuel component composition. For instance, standard liquid oxygen contains up to 0.5% of impurities, mainly of nitrogen [12,13]. Secondly, a probable chemical non-equilibrium at exhaust gas expansion in the nozzle and, finally, rocket exhaust stream afterburning in air should be taken into consideration.

The present work contains the results of calculating emissions by different rockets with due regard for the above-stated factors. Calculations of local stratospheric ozone destruction, caused by Energiya and Shuttle launches, were made in this same way. The data obtained demonstrate that probable damage caused by a Shuttle launch is an order of magnitude higher than that caused by an Energiya launch.

## 2. ASSESSMENT OF ATMOSPHERIC EMISSION BY A ROCKET

Usually, rocket propulsion exhaust gas composition is assessed by thermodynamic analysis methods assuming chemical equilibrium availability in the combustion chamber and at exhaust gas expansion in the engine nozzle [14]. This model is in good agreement with the practical needs of engine parameter and plume calculations and, usually, composition of emitted substances is evaluated on the basis of this model.

Exhaust gas components characteristic of the main used rocket fuels are shown in Table 1.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

Table 1

**Individual Substances - Components of Main Used Rocket Fuel Combustion Products**

| Fuels | | Main combustion product components | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $CO_2$ | $H_2O$ | CO | $H_2$ | $N_2$ | NO | HCl | Cl | $Al_2O_3$ |
| Liquid | Liquid oxygen $LO_2$ + liquid hydrogen $LH_2$ | | + | | + | + | + | | | |
| | Liquid oxygen $LO_2$ + kerosene | + | + | + | + | + | + | | | |
| | Nitrogen tetroxide $N_2O_4$ + dimethyl hydrazine $C_2N_2H_8$ | + | + | + | + | + | + | | | |
| Solid | Ammonium perchlorate $NH_4ClO_4$ + aluminium + + polymer | + | + | + | + | + | + | + | + | + |

NO and Cl may be singled out as ozone-affecting substances, directly interacting with ozone resulting in ozone depletion. A number of substances omitted in the Table 1 are capable of depleting the ozone layer too. There are H and OH radicals present in combustion products in a small amount and therefore have inconsiderable effects on the ozone. Out of gaseous substances, HCl not interacting directly with $O_3$ presents the most dangerous threat for the ozone due to its tremendous exhausts as a source of free chlorine formed up as a result of HCl photochemical decomposition reactions in particular.

To quantitatively determine the composition of products emitted in to the atmosphere by a rocket one should take into consideration fuel component impurities, chemical kinetics at exhaust gas expansion in the engine nozzle and atmosphere jet afterburning. The role of these three factors is illustrated by the examples given below.

If the chemical kinetics of processes in the nozzle is not taken into account then at the nozzle exit of liquid- and solid-propellant engines the exhaust gases contain practically no nitrogen oxides. Calculations of the nozzle non-equilibrium expansion show that the NO concentration deviates from the equilibrium and freezing near the throat section [2,7,8,14]. As a result the NO rate of flow at the nozzle exit section of solid-propellant engines constitutes about 0.05% of the total rate of flow, while the figure for liquid-propellant engines working on $LO_2$ + kerosene or $LH_2$ is about 0.1% and for liquid-propellant engines working on $N_2O_4$ + dimethyl hydrazine is about 1%. In that case, if fuel containing liquid oxygen was used the presence of 0.5% of $N_2$ in the oxidizer was taken into account.

Table 2 and 3 comprise some data on rockets and engines and total emissions of main ozone-affecting substances in the stratosphere by Energiya, Shuttle, Zenit, Proton and MX rockets.

Table 2

**Data on considered rockets**

| Rockets | First stage shut-off altitude, km | Fuels | Engines | | | |
|---|---|---|---|---|---|---|
| | | | Number, models | Nominal value of pressure in chamber, $kg/cm^2$ | Stoichiometric ratio $\alpha$ | Mass rate of flow, kg/sec |
| Energiya | 50 | $LO_2$ + kerosene<br>$LO_2$ + $LH_2$ | 4,RD-520<br>4,RD-120 | 250<br>220 | 0.76<br>0.75 | 4x2,390=9,560<br>4x440=1,760 |
| Shuttle | 42 | 69,6% $NH_4ClO_4$ + + 16% Al+binder<br>$LO_2$ + $LH_2$ | 2,SRM<br>3,SSME | 40<br>210 | 0.58<br>0.75 | 2x4,150=8,300<br>3x530=1,590 |
| Zenit | 77 | $LO_2$ + kerosene | 1,RD-521 | 250 | 0.76 | 2,390 |
| Proton | 40 | $N_2O_4$ +DMH | 6,RD-253 | 150 | 0.87 | 6x530=3,180 |
| MX | 25 | 69% $NH_4ClO_4$ + +19% Al+binder | 1 | 110 | 0.6 | 830 |

Table 3

**Amount of NO, Cl and HCl emitted by different rockets in the atmosphere at the altitudes of 13 to 50 km**

| Rockets | Substance mass, kg | | | |
|---|---|---|---|---|
| | NO | | Cl | HCl |
| | 1* | 2* | 1* | 1* |
| Energiya | 780 | 890 | - | - |
| Shuttle | 240 | 635 | 800 | 75,600 |
| Proton | 1,765 | 1,823 | - | - |
| Zenit | 166 | 200 | - | - |
| MX | 14 | 21 | 36 | 4,350 |

*) 1 - Emissions of engines with due regard for chemically non-equilibrium flow through the nozzles.
2 - After jet afterburning in air. Chlorine and aluminium compound reactions were not taken into account for the calculations.

When estimating the stated values, the composition of combustion products at the nozzle entry was determined by the standard procedure of calculating chemical equilibrium [14]. The flow in the nozzle was determined taking into account the kinetics of 22 chemical reactions of main substances formed by the chemical elements O, H, N, C, Cl (O, $O_2$, H, $H_2$, OH, $H_2O$, N, $N_2$, NO, CO, $CO_2$, Cl, $Cl_2$, HCl) [7,14]. Reactions with the substances including aluminium were not taken into consideration and the concentration (molar fraction) of these substances at the nozzle exit was taken equal to the chemically-equilibrium concentration at the nozzle entry. Afterburning in air was taken into account on the basis of the differential equation system numerical solution, describing the turbulent mixing and non-equilibrium chemical processes of substances formed by the elements O, H, N, C, i.e. the reactions of substances containing Cl and Al were not taken into account.

Consideration of the materials shows that rocket engines working on fuels with liquid oxygen as an oxidizer exhaust considerable amounts of nitrogen oxides.

Jet afterburning in air was taken into account on the basis of a numerical solution of the differential equation system describing turbulent mixing and non-equilibrium chemical reactions [2,7]. The stated results show that the afterburning contributes considerably, though not decisively to the stratosphere NO emissions, since this process ceases at altitudes nearing 30 km.

Practically all components CO and $H_2$ burn-out completely during flight at heights less than 30 km. NO production in the plume is determined mainly by a temperature increase during afterburning, and in cases when the fuel component ratio is nearing the stoichiometric one, nitrogen oxide formation in the jet being afterburnt decreases considerably. For instance, the Proton rocket engines operate with the stoichiometric ratio $\alpha = 0.87$ and NO production during the afterburning is insignificant. The rest of the mentioned engines work with the $\alpha < 0.76$ and afterburning in terms of NO formation plays a more significant role. Fig. 1 gives the calculation data demonstrating that if near the earth the NO rate of flow in the jet constitutes about 1% of the rate of flow through the engine, at altitudes of 25-30 km the NO rate of flow becomes lower by two orders of magnitude. Change of rates of flow of these nitrogen

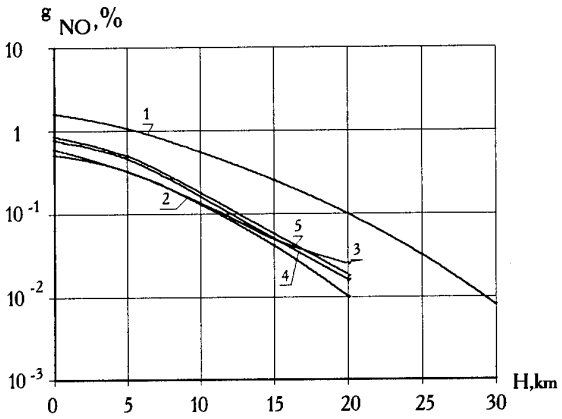



Fig. 1 Change of Additional NO rate of Flow with the Flight Altitude changing due to Jet Afterburning in Air (in Relation to Fuel Rate of Flow through the Engine):
1 - SRM, 2 - SPRE of the MX type,
3 - RD-120, 4 - RD-170, 5 - SSME.

oxides at different altitudes related to the values obtained at the earth surface level are shown in Fig. 2 and they demonstrate that a small amount of nitrogen oxides of this origin gets into the stratosphere. Comparison of our data with the results of work [1] demonstrates a rather satisfactory agreement [7,8] pointing to the models' similarity used as a basis for calculating the afterburning.

Comparing the obtained data with the data of other works one can note that work [1] did not take into account the chemical non-equilibrium at combustion product flow through the nozzles and the presence of nitrogen impurity in liquid oxygen. Work [6] concerning atmospheric emissions by Energiya and Shuttle rockets not only neglects the above-mentioned factors but the errors distorting the real values by one - two orders of magnitude were made. For example, in accordance with work [6] the Shuttle emits into the 13-50 km atmosphere layer about 30,000 kg of NO, but our figures, as is seen in Table 3, are 635 kg, i.e.

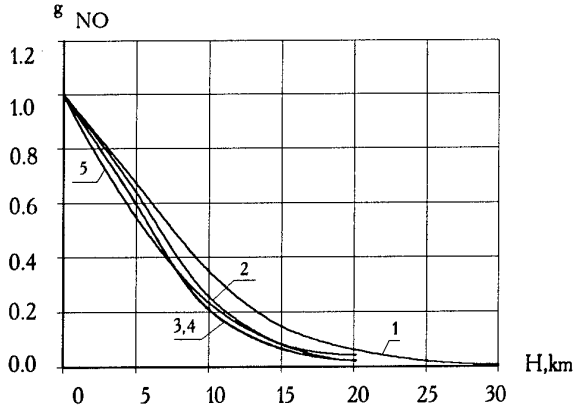



Fig. 2 Change of the NO Rate of Flow Formed During Jet Afterburning in Air in Relation to its Value at H=0 with the Altitude Change.
1 - SRM, 2 - SPRE of the MX type,
3 - RD-120, 4 - RD-170, 5 - SSME.

the difference is of two orders of magnitude. When analysing the Energiya, the authors of work [6] took the amount of nitrogen oxides exhausted into the atmosphere twice higher as compared with the Shuttle values, i.e. about 60 tonnes. The preconditions these value determinations were based on are not explained and we consider them to be erroneous. Moreover, the materials of work [6] have other errors, e.g. the mass of hydrogen $H_2$ emitted by the Energiya engines is overstated by an order of magnitude and the hydrogen, emitted by the Shuttle engines in considerable quantities, is not taken into consideration. At the same time, the chlorine exhausts of this rocket were under-stated by several times. Since these materials were used by other authors the conclusions made on their basis should be revised.

The condensed aluminum $Al_2O_3$ is one of ozone-affecting components of solid-propellant engine combustion products. The Shuttle releases about 98,000 kg of this oxide into the stratosphere layer of 13 to 50 km and the MX rocket exhausts 7,100 kg. Aerosol effects on the ozone is determined to a great extent by its dispersitivity and the properties of the surface adsorbing different components of combustion's products.

In the 60ies-80ies the $Al_2O_3$ dispersitivity was intensively studied and the research results oriented at determining specific impulse losses were generalized, for example, in work [15].

According to these data for large-sized engines the mean particle diameter

$$d_{43} = (\sum_i n_i d_i^4) / (\sum_i n_i d_i^3) \quad ,$$

determining specific impulse losses constitutes 6-10 microns. The diameter

$$d_{32} = (\sum_i n_i d_i^3) / (\sum_i n_i d_i^2) \quad ,$$

characterizing the surface is less than $d_{43}$ by 20-30%, i.e. it constitutes 4-8 microns. Investigations involving particles samplings from a cloud formed in the atmosphere after a rocket passed give considerably smaller sizes, i.e. tenth or hundredth fractions of micron. Such discrepancy is not explained but we consider the bench measurement data, to which the work [16] data are also close, to be more reliable. Therefore, we suppose that the diameter $d_{32} = 4$ μm may be taken as an average one for calculating the aerosol surface.

As a conclusion let us note that chlorine compound emissions have been taken unchanged after combustion product efflux from the nozzle. There are tentative data evidencing that during jet afterburning in air a considerable portion of HCl may be decomposed generating a great amount of chlorine of the Cl form directly threatening the ozone and of the $Cl_2$ form. The reactions with aluminium chlorine compounds (mainly $AlCl_2$) were not taken into account which in compliance with the thermodynamic analysis bind several percents of chlorine in relation to the total rate of flow in the combustion chamber.

## 3. EMISSION IMPACTS ON THE STRATOSPHERIC OZONE

As was noted above when assessing rocket flight effects on stratospheric ozone in works [4,6,10] they take into account an unreal composition of emitted products that resulted in erroneous estimations. Table 4 contains the composition and amount of the Energiya and Shuttle combustion products at the altitude of 30 km obtained in accordance with the procedure described above. These data were also used for making previous evaluations [6,10].

Applying the specified data on the combustion product composition and amount, calculations of the local ozone depletion due to Energiya and Shuttle launches were made. The calculations involved the usage of the one-level axisymmetrical diffusive-photochemical model with the isotropic horizontal diffusion, i.e. $K_x = K_y = K$.

A concentration change of each of the components in the model was described by means of the continuity equation:

$$\frac{\partial n_i}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[ rK(t)\frac{\partial n_i}{\partial r} \right] + P_i - L_i ,$$

where $K(t) = 7.88 \cdot t^{1,62}$ cm$^2$/sec, $P_i$ and $L_i$ - photochemical sources and component sinks.

The model's photochemical section includes 73 reactions of oxygen compounds ($O_3$, $O_2$, O, $O^+$), hydrogen compounds (H, $H_2$, OH, $H_2O$, $HO_2$,$H_2O_2$), nitrogen compounds (N, NO, $NO_2$, $NO_3$, $N_2O_5$, $HNO_2$, $HNO_3$, $HO_2NO_2$), chlorine compounds (Cl, ClO, HCl, HClO, $NO_2ClO$), and some reactions with methane ($CH_4$).

When assessing the Space Shuttle launch environmental effects, heterogenic decomposition of ozone molecular and oxygen free atoms on the aluminium oxide particle's surfaces were taken into account. The heterogenic decomposition rate of component A was calculated by the known formula:

$$\frac{d[A]}{dt} = \frac{1}{4}\left( \frac{8RT}{\pi\mu} \right)^{1/2} S_0 \eta [A],$$

where R - the universal gas constant, T - temperature, μ - the component A molar mass, $S_0$ - the particulate surface in an atmosphere volume unit, η - an adhesion coefficient, determining the probability of a component A molecule decomposition at collision with the surface. Since it is more convenient to use the mass of particles in the volume unit M instead of the surface, then $S_0$ may be expressed in terms of M : $S_0 = 3M/r_{32}$ for calculations.

Table 4

**Amount of different combustion product components expressed in grams per one centimeter of the altitude released into the stratosphere at the 30 km altitude**

| Components | Energiya | Shuttle | | |
|---|---|---|---|---|
| | Present work | Works [6,10] | Present work | Works [6,10] |
| $CO_2$ | 69,5 | 49,6 | 6,08 | 4,77 |
| $CO$ | 48,5 | 49,8 | 19,9 | 26,9 |
| $H_2O$ | 66,1 | 81,4 | 43,4 | 39,2 |
| $H_2$ | 2,42 | 19.6 | 2,52 | - |
| $NO$ | 0,195 | 6,33*) | 0,089 | 6,33 |
| Cl | - | - | 0,26 | 0,0663 |
| HCl | - | - | 21,2 | 23,1 |
| OH | 0,0206 | - | 0,0998 | - |
| H | $7{,}63 \cdot 10^{-3}$ | $3{,}49 \cdot 10^{-2}$ | 0,0312 | - |
| N | $0{,}215 \cdot 10^{-10}$ | - | $1{,}84 \cdot 10^{-7}$ | - |
| $Al_2O_3$ | - | - | 30,7 | 31,3 |

*) The versions with values twice higher [6] and with values twice lower and with values five times lower [10].

As was noted above $r_{32}$ = 2 μm may be taken as a mean size characterizing the surface. It was assumed in work [6] that aluminum oxide particles in combustion products are monodispersive with $r_{32}$ =0.1 μm, which results in an overestimate of heterogenic ozone depletion rate by 20 times. Making our calculations we took the adhesion coefficient equal to $10^{-3}$, this being the highest evaluation, however the calculations even with such high value of the adhesion coefficient have shown that the aerosol contribution to the ozone destruction is not great. It is confirmed also by the calculations of work [6], where the adhesion coefficient of $5 \cdot 10^{-5}$ and $r_{32}$ equal to 0.1 μm were used.

The transfer equation was solved by Thomas algorithm method on a non-uniform grid; to solve the equations describing photochemical processes the Gear method was applied.

The calculations were made for the 30 km altitude at the constant solar zenith angle of 45°. At the initial moment it was assumed that the combustion product temperature was equal to the ambient temperature and that the combustion products filled the cylindrical volume up, the radius of which was determined by the number of molecules contained in the combustion products and by the air molecule concentration at the given altitude. The Energiya cylindrical volume radius is about 20 m, and the Shuttle cylindrical volume radius is 16 m.

The main calculation data are shown in Fig. 3, demonstrating time changes of the boundaries of the zone with ozone concentration constituting 90% of its background conditions value during Energiya and Shuttle flights. As one can see, the Energiya combustion product impact area extends at 360 m from the combustion product jet axis; the Shuttle combustion product impact area expands at a distance of up to 6.5 km, i.e. by 20 times farther. Accordingly, for the Shuttle rocket the area of the zone with reduced ozone content is approximately 400 time greater than that for the Energiya launch vehicle.

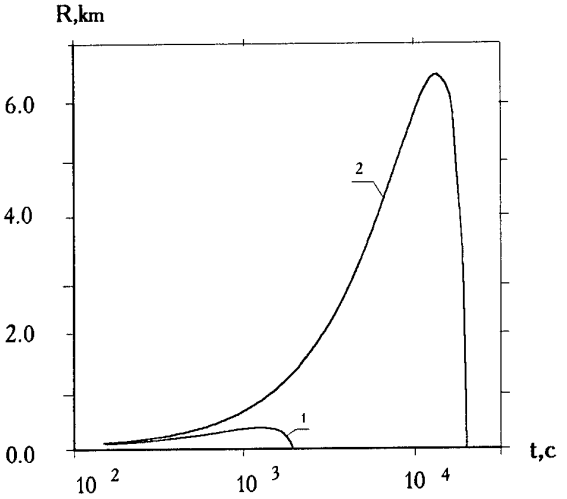



Fig. 3 The R Zone Size with the Ozone Concentration less than 90% of the Background Concentration for the Energiya (1) and Shuttle (2) Rockets as a Function of Time.

To compare these data with those of work [10] Fig. 4 shows the calculation results as a time change of the average ozone content (measured in fractions of background one) in the area of a 2 radius, where $\sigma^2 = \sigma_0^2 + 4K(L)$. $\sigma_0^2$ is a combustion product distribution dispersion at the initial moment. For the initial combustion product distribution, shaped as a cylindrical volume with the radius of $r_0$, taken for the calculations $\sigma_0^2 = r_0^2/2$. As is seen in Fig. 4, the degree of ozone content reduction in the area of Energiya launches is considerably lower than that of the Shuttle launch area, while the time of filling the area is significantly less.

Compounds of $HO_X$ and $NO_X$ families are ozone-destroying components of Energiya combustion products; as for the Shuttle compounds of the $ClO_X$ fa-

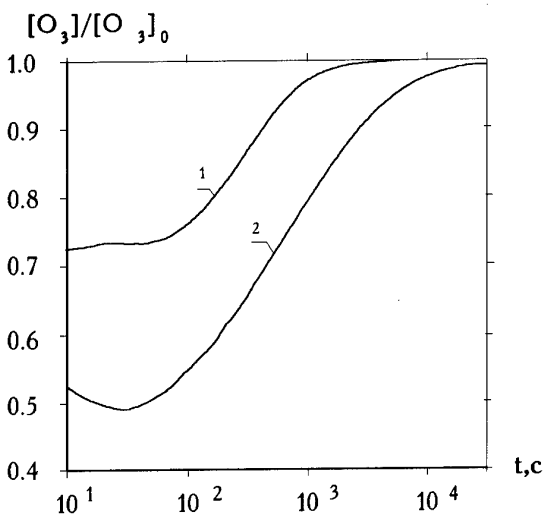



Fig. 4 Temporal Changes of the Ozone Content Relation to the Background Content in Action Area for the Energiya (1) and Shuttle (2) Rockets as a Function of Time.

mily and aerosol particulates are added to this list.

The following reactions with hydrogen compounds (H and OH) contained in rocket fuel combustion products destroy the ozone layer:

$$O_3 + H \Rightarrow OH + O_2 \qquad (R1)$$

$$O_3 + OH \Rightarrow HO_2 + O_2. \qquad (R2)$$

The ozone layer is also destroyed by $HO_2$ formed in H and OH reactions with different atmospheric gaseous components:

$$O_3 + HO_2 \Rightarrow OH + 2O_2. \qquad (R3)$$

Ozone destruction by hydrogen compounds contained in combustion products takes place only during the first 3-5 minutes after the rocket pass, then they transfer into reservoir compounds:

$$H + HO_2 \Rightarrow H_2 O_2 \qquad (R4)$$

$$OH + NO_2 + M \Rightarrow HNO_3 + M \qquad (R5)$$

$$OH + NO + M \Rightarrow HNO_2 + M \qquad (R6)$$

$$HO_2 + Cl \Rightarrow HCl + O_2. \qquad (R7)$$

The N and NO compounds contained in combustion products as well as $NO_2$ formed from them destroy the ozone layer due to the reactions:

$$O_3 + N \Rightarrow NO + O_2 \qquad (R8)$$

$$O_3 + NO \Rightarrow NO_2 + O_2 \qquad (R9)$$

$$O_3 + NO \Rightarrow NO_3 + O_2. \qquad (R10)$$

Chlorine hydrogen (HCl) contained in the Shuttle combustion products in large quantities is a reservoir compound and does not interact directly with ozone. Active chlorine is released from HCl in the reactions:

$$HCl + h\nu \Rightarrow Cl + H \qquad (R11)$$

$$HCl + O \Rightarrow Cl + OH \qquad (R12)$$

$$HCl + OH \Rightarrow Cl + H_2O. \qquad (R13)$$

The HCl dissociation rate at the 30km altitude is low ($1.79 \cdot 10^{-8}$ $sec^{-1}$), while O and OH concentrations in the combustion product impact area rapidly drop with time, therefore the rate of active chlorine release from HCl shall be low too. Besides that, active chlorine transfers into the HCl reservoir compound in reactions with minor atmospheric components:

$$Cl + HO_2 \Rightarrow HCl + O_2 \qquad (R14)$$

$$Cl + H_2O_2 \Rightarrow HCl + HO_2 \qquad (R15)$$

$$Cl + HNO_3 \Rightarrow HCl + NO_3 \qquad (R16)$$

$$Cl + CH_4 \Rightarrow HCl + CH_3 \qquad (R17)$$

and especially in reactions with molecular hydrogen ($H_2$) contained in the Shuttle combustion products in great quantities:

$$Cl + H_2 \Rightarrow HCl + H. \qquad (R18)$$

The rate of reservoir HCl transfer into active chlorine in accordance with (1) may be identified as

$$d[HCl]/dt = P^{HCl} - L^{HCl}. \qquad (3)$$

The rate of chlorine hydrogen photochemical dissociation

$$L^{HCl} = (J_{11} + k_{12}[O] + k_{13}[OH])[HCl], \qquad (4)$$

where J and K are a photodissociation and reaction rate constant coefficients, the square brackets mean the molecule concentration (usually $cm^{-3}$). The inverse process rate of forming chlorine hydrogen from active chlorine atoms

$$P^{HCl} = (k_{14}[H_2O]+k_{15}[H_2O_2]+k_{16}[HNO_3]+$$

$$+k_{17}[CH_4]+k_{18}[H_2])[Cl] \qquad (5)$$

The computed concentrations of all the components allow calculations of HCl dissociation rate in every node of the spatial grid at different moments of time applying (3), but photochemical process rates change very significantly in time and space and do not quite evidently characterize the HCl impact on the local ozone destruction. To obtain data on the destroyed chlorine hydrogen amount (W) from the process start, the concentration change rate f(r,t) in time and space was integrated:

$$W = \int_0^T dt \int_0^R 2\pi f(r,t)dr \qquad (6)$$

The computation results of temporal dependence of the decomposed chlorine hydrogen determined by the amount of the released active chlorine are shown in Fig. 5. As is seen for the first ten seconds, chlorine hydrogen is being intensively destroyed and, accordingly, active chlorine is being intensively released. Then, due to O and OH concentration decrease the HCl destruction stops and in 100 seconds after the rocket pass HCl recovery starts.

So, chlorine hydrogen being the main factor of global ozone destruction by solid rocket fuel combustion products plays an insignificant role in local environmental effects. The local ozone destruction is caused mainly by hydrogen and nitrogen compounds and by free chlorine contained in the Shuttle combustion products in considerable amounts.

The conducted calculations show that liquid-propellant rockets using liquid-oxygen-based fuels

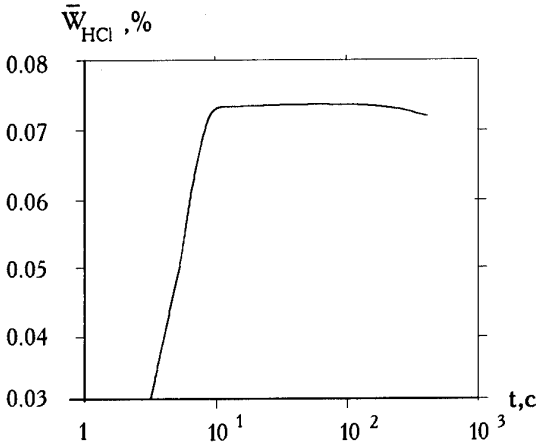



Fig. 5 Destroyed Chlorine Hydrogen Amount in Relation to its Common Initial Value from the Process Start the Time.

pose a considerably lesser threat than solid-propellant rockets the combustion products of which contain considerable quantities of chlorine hydrogen.

## 4. CONCLUSION

The discussed materials on assessing atmospheric emissions of different substances by rockets and the damage they inflict to the ozone layer demonstrate the following.

1. Cl, HCl, NO, $Al_2O_3$ are the main ozone-affecting substances exhausted by solid-propellant rockets in flight. In this case, HCl, not interacting directly with ozone but released in large quantities can impact only long after and therefore it is a global-scale threat. The remaining substances have considerable local effects lasting not more than a few hours and within 10 km around the flight trajectory. Nitrogen oxides are the main ozone-affecting substances exhausted by liquid-propellant rockets, their quantity being relatively small and, accordingly their effects on the ozone layer are of local character and relatively low.

2. Emission assessments should be performed with as high reliability as possible and for that purpose it is necessary to take into account the major factors influencing the generation of substances released into the atmosphere. For example, a small technological nitrogen impurity in liquid oxygen ($LO_2$) is the main source of nitrogen oxides (NO) released into the stratosphere by rockets using liquid fuels with $O_2$ as an oxidizer. Chemically non-equilibrium processes taking place at combustion product expansion in the engine nozzle and at atmospheric jet afterburning determine to a great extent NO emissions of liquid and solid propellant rockets.

3. The Shuttle and Energiya atmospheric emission values used in a number of works [1,4,6,10] for evaluating a probable damage to the stratospheric ozone have been found without due regard for the determining factors and besides that contain errors resulting, for example, in overstating of nitrogen oxide emissions by two orders of magnitude [6]. As a result, the conclusion as to the equal local damage to ozone inflicted by liquid-propellant and solid-propellant rockets is wrong. The local impacts of considerable chlorine exhausts by solid-propellant rockets are an order of magnitude higher than that of the liquid-propellant rockets using liquid-oxygen-based fuels.

In association with this it would be reasonable to develop and put into service solid rocket fuels not containing chlorine or fuels with a reduced chlorine content.

4. There are certain problems concerning assessment of atmospheric emissions of rockets in flight and solution of these problems would make the results more accurate. These problems relate to the non-equilibrium reactions with chlorine compounds at afterburning, and to consideration of processes involving aluminium chlorine compounds, mainly $AlCl_2$, which bind considerable amounts of chlorine, etc.

5. Due to a great difference of approaches of different authors to atmospheric emission assessment and due to the corresponding discrepancy of the results assessments of a probable damage to the ozone layer sometime turn out to be contradictory.

It seems reasonable to develop a common methodological approach to assessment of different substance emissions by rockets in flight to reach concord on the approach with specialists of the leading organizations.

It would be desirable to recommend to obtain and publish data on different substance emissions into the atmosphere by rockets in operation and by those being currently developed.

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## Discussion

QUESTION BY R. R. WEISS : Prof. Tishin concludes that A.J. Mc Donald's conclusion that there is equal local damage to the ozone layer inflicted by liquid propellant and solid propellants is wrong. His paper attributes ozone damage with LO2/LH2 systems to be the result of nitrogen impurities in LO2 which result in NO emissions due to afterburning and other non-equilibrium chemical combustion processes. He makes no note of contributions from the hydrogen radical family which Mc Donald cites as a possibly more important natural loss process for ozone than the NO cycles. Has this effect been considered in the Tishin examination, and if not, could it reconcile the difference in fundamental conclusion concerning liquid vs. solid propulsion ?

ANSWER : Our calculations for the effect of rocket motor emissions on ozone in the stratosphere took into account the hydrogen cycle, as well as the others (nitrogen, chlorine and oxygen). In Dr. Mc Donald's work, the data on the important role of the hydrogen cycle in stratospheric ozone depletion relates to the background state of the atmosphere. After the passage of the rocket, the gases close to the flight path are fundamentally changed. The role of the above-mentioned cycles in ozone depletion changes accordingly. We took all this into account. Dr.Mc Donald's mistaken conclusion that liquid and solid propellants have the same impact on ozone is based on calculations for NO emissions into the atmosphere of over 30 tons, in the case both of the Shuttle and the Energiya. According to our data, these emissions should be lower by an order of value of 2 - less than 1 ton in both cases.
Almost all the hydrogen (H2) emitted is burnt up along the flight path, up to a height of almost 40 km. Hydrogens which react with ozone (H, OH, HO2) are emitted in small amounts. According to the calculations, these substances are incorporated into reservoir compounds which do not interact with ozone, within 3 to 5 minutes.
As a result, it becomes apparent that damage to stratospheric ozone by LO2-based fuels is determined by NO emissions. These are relatively small for both types of fuel, and the chief source of serious local ozone depletion is chlorine.
This explains our conclusion, that ozone damage is much greater when modern solid fuels are used, than is the case with LO2-based liquid fuels.

# PROPERGOLS SOLIDES POUR LANCEURS SPATIAUX GENERANT PAS OU PEU DE GAZ CHLORHYDRIQUE

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## RESUME

Les propergols classiques pour accélérateurs de lanceurs spatiaux contiennent en tant qu'oxydant du perchlorate d'ammonium et génèrent de ce fait du gaz chlorhydrique. Bien que les répercussions sur l'environnement soient extrêmement faibles, des études sont réalisées pour en réduire encore l'impact.

La SNPE a engagé des travaux suivant deux axes, les propergols contenant des taux élevés de perchlorate d'ammonium et un capteur de chlore et les formulations ne contenant pas d'espèce chlorée. Le présent article décrit les résultats obtenus sur le premier type de composition.

Les propergols avec capteur de chlore présentent une impulsion spécifique volumique d'un niveau identique à celui des compositions actuelles, mais une impulsion spécifique plus faible, et de bonnes propriétés rhéologiques, mécaniques et balistiques. Des expérimentations réalisées sur les effluents de moteur de 1 kg ou de 40 kg ont permis de valider le concept et le choix des formulations.Le taux d'acide chlorhydrique, mesuré par une méthode électro-chimique et par spectrométrie infrarouge, est très fortement réduit, d'environ un facteur 100. Les taux d'oxyde d'azote, déterminés par chimiluminescence, restent faibles. La morphologie et la granulométrie des particules captées ont été déterminées.

## ABSTRACT

Conventional solid boosters which utilize ammonium perchlorate as the propellant oxidizer generate hydrogene chloride. Although the environmental effects are very small, studies are performed in order to reduce its impact still further.

In this aim, SNPE studies two kinds of propellant compositions, scavenged and chlorine free propellants. This article describes the results concerning the first kind of propellant.

Scavenged propellants have lower specific impulse but the same volumetric specific impulse level than current booster propellants. Their processing characteristics and their mechanical and ballistic properties are suitable. The range of ballistic tailorability is sufficiently broad to realize any typical booster grain design. Measurements of hydrogen chloride and nitrogen oxides and particle collections were made in the plume during static test firing of 1 kg and 40 kg motors. Infrared spectrometry and electrochemical measurements have shown a very high reduction of the amont of hydrochloric acid exhausted, in ratio of one hundred. Chemiluminescence measurements revealed that the nitrogen oxides rates remain very low. Morphology and particle size distribution were determined for the exhaust particles.

## 1 - INTRODUCTION

Les propergols solides pour les accélérateurs des lanceurs spatiaux contiennent, en tant qu'oxydant, un fort taux de perchlorate d'ammonium et génèrent de ce fait des proportions importantes de gaz chlorhydrique. De par sa nature, celui-ci est susceptible de contribuer aux pluies acides. Le chlore issu de ce gaz peut d'autre part interagir avec l'ozone. Les études réalisées, notamment aux Etats-Unis, montrent que l'impact de ces émissions sur l'environnement est très faible pour les cadences de lancement envisagées aujourd'hui pour jusqu'à l'an 2000-2010 en raison des très faibles quantités émises par rapport à celles provenant des autres sources, naturelles ou industrielles [1 à 6].

Néanmoins, des études ont été engagées, dans de nombreux pays, pour mettre au point des propergols solides à impact réduit sur l'environnement, par

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diminution importante ou suppression du gaz chlorhydrique dans les gaz de combustion.

Trois types de solutions techniques sont étudiées par différentes équipes ; elles reposent soit sur la neutralisation de l'acide chlorhydrique présent dans les effluents du moteur, soit sur la captation du chlore dans la chambre de combustion, par réaction avec un alcalin, soit sur la suppression du chlore de la formulation du propergol.

Le concept de neutralisation de l'acide chlorhydrique consiste à remplacer l'aluminium par du magnésium [7] et repose sur le schéma réactionnel suivant :

$$Mg + O \rightarrow MgO$$
$$MgO + H_2O \rightarrow Mg(OH)_2$$
$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + H_20$$

Le magnésium est oxydé pour former de l'oxyde de magnésium. Après éjection dans l'atmosphère, celui-ci se transforme, en présence d'eau, en hydroxyde de magnésium qui réagit avec l'acide chlorhydrique pour donner du chlorure de magnésium. La neutralisation de l'acide chlorhydrique est donc subordonnée à la présence d'eau dans l'atmosphère. Celle-ci peut être fournie par le propergol, soit directement soit par la postcombustion de l'hydrogène, par le moteur principal et par l'humidité de l'air.

Dans le cas des compositions avec capteur de chlore, le chlore issu du perchlorate d'ammonium est capté lors de la combustion du propergol par du potassium ou plus généralement du sodium qui est le plus souvent introduit sous la forme de nitrate [5, 8].

Les deux types de propergols précités conduisent à la génération d'un chlorure ; une autre voie consiste à employer un oxydant ne contenant pas de chlore. Le nitrate d'ammonium est considéré depuis de très nombreuses années comme un produit très intéressant en raison de son faible coût et de sa faible sensibilité. Toutefois, il nécessite d'une part des précautions particulières pour éviter les problèmes liés aux variations de volume consécutives aux changements de phase cristalline intervenant à certaines températures. Il est d'autre part peu énergétique et conduit à des performances faibles en liant polybutadiène. Cet handicap peut être compensé par l'utilisation d'un liant à base d'un polymère énergétique tel que le polyazoture de glycidyle (PAG). Ce produit, qui est commercialisé, permet d'atteindre un niveau de performance équivalant à celui de la composition à base de perchlorate d'ammonium utilisée actuellement. L' intérêt de ce polymère se retrouve pour de nombreux types de propergols [9, 10].

D'autres oxydants, qui sont le plus souvent étudiés pour des applications militaires, permettent d'accéder à des niveaux énergétiques très supérieurs à ceux relatifs aux propergols précités [5, 11 à 13] (*figure 1*).

La SNPE a engagé depuis de nombreuses années des travaux suivant ces différents axes, propergols au perchlorate d'ammonium contenant un capteur de chlore, compositions à liant PAG chargées au nitrate d'ammonium et formulations à base de nouveaux oxydants.

Le présent article s'attache uniquement à la description des résultats acquis dans le domaine des propergols au perchlorate d'ammonium contenant un capteur de chlore.

## 2. PROPRIETES DES PROPERGOLS CONTENANT UN CAPTEUR DE CHLORE

### 2.1. Généralites

Le capteur de chlore est très généralement introduit dans le propergol sous la forme de nitrate. Les performances énergétiques sont plus élevées avec le nitrate de sodium qu'avec le nitrate de potassium ; c'est donc ce premier produit qui a été retenu pour les expérimentations. Environ 40 % du perchlorate d'ammonium est remplacé par du nitrate de sodium pour assurer la captation du chlore.

Les calculs thermodynamiques, réalisés pour une composition de ce type, mettent en évidence les points suivants (*tableau 1*) :

- la majorité du chlore est captée dans la chambre de combustion,

| | Chambre | Plan de sortie tuyère |
|---|---|---|
| *Pression (atm)* | 70 | 1 |
| *Température (K)* | 3310 | 2157 |
| *Produits de combustion (1) (% en masse)* | | |
| HCl | 3,43 | 1,40 |
| NaCl | 13,6 | 17,3 |
| Na | 1,82 | 0,80 |
| NaH | 0,10 | $4.10^{-5}$ |
| NaOH | 0,69 | 0,10 |

*(1) limités aux produits chlorés et à ceux contenant du sodium.*

**Tableau 1 : Calcul thermodynamique des produits de combustion d'un propergol contenant un capteur de chlore (PBU/PA/NNa/Al)**

- lors de la détente dans la tuyère, la réaction de captation du chlore par le sodium se poursuit, le taux d'acide chlorhydrique s'établit à environ 1,4 % alors qu'il est de 21% pour la composition nominale ;

- dans le plan de sortie de la tuyère, il subsiste une faible quantité d'acide chlorhydrique et de sodium. La réactivité de ces produits étant très importante, les réactions devraient se poursuivre rapidement dans l'atmosphère. Les mesures réalisées dans les effluents d'un moteur, qui sont décrites dans le paragraphe suivant, ont permis de le vérifier. Le taux de NaCl formé est de l'ordre de 17 %.

Les calculs thermodynamiques mettent également en évidence que le NaCl est à l'état gazeux dans le plan de sortie de la tuyère. Il n'y a donc pas à craindre que ce produit participe aux pertes d'impulsion spécifique liées au caractère diphasique de l'écoulement. La température de liquéfaction étant de 1959 K, la condensation du NaCl intervient rapidement dans l'atmosphère.

Les ions $Na^+$ et $Cl^-$ sont naturellement très abondants dans l'atmosphère. Le NaCl ne présente aucun caractère toxique.

Les études réalisées sur les particules présentes dans la troposphère ont montré que le chlorure de sodium est susceptible de dégager du chlore, après réaction chimique avec certains polluants présents dans l'atmosphère, suivant les mécanismes suivants :

$NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g)$
$NaCl(s) + 2NO_2(g) \rightarrow NaNO_3(s) + NOCl(g)$
$NaCl(s) + N_2O_5(g) \rightarrow NaNO_3(s) + ClNO_2(g)$
$NaCl(s) + ClONO_2(g) \rightarrow NaNO_3(s) + Cl_2(g)$

Ces réactions hétérogènes ont été étudiées au laboratoire, à la température ambiante, pour des concentrations de polluant très supérieures à celles mesurées dans la troposphère [14 à 19 ]. Dans ces conditions opératoires, elles sont rapides mais limitées par la formation d'une couche de nitrate de sodium solide sur la surface des particules de chlorure de sodium. Les chlorures de potassium et de magnésium sont très certainement susceptibles de présenter le même comportement. Ces réactions ne sont pas documentées pour les conditions d'ambiance et de concentration prévalant dans la stratosphère. Elles ne sont toutefois pas à exclure.

Un autre facteur très important est la granulométrie des particules de chlorure de sodium qui va influer sur leur temps de séjour dans la stratosphère, et sur l'avancement des réactions précitées.

Ces différents éléments indiquent que la solution capteur de chlore permet d'éviter les retombées acides éventuelles au voisinage immédiat du point de tir et la possibilité de la destruction de l'ozone à proximité du panache d'effluents juste après le lancement (5) et de limiter considérablement la quantité de chlore émise dans la stratosphère.

Les oxydes d'azote prennent part à certaines réactions chimiques faisant intervenir l'ozone [20]. Ces produits sont générés en très faibles quantités par les propergols solides. Ils peuvent se former lors de la postcombustion des effluents des moteurs, liquides ou solides, avec l'air extérieur, ce phénomène peut intervenir jusqu'à une altitude d'environ 25 000 m.

Les calculs de jet, qui ont été réalisés en axisymétrique, stationnaire, isobare, turbulent et réactif, montrent que le seul produit formé en quantité notable est le monoxyde d'azote et que les taux sont faibles (*tableau 2*).

Des mesures ont toutefois été réalisées pour évaluer l'influence de la nature de la composition du propergol sur la formation des oxydes d'azote.

| Composition / Oxydes d'azote formés | PBU PA/Al | PBU PA/NNa/Al |
|---|---|---|
| *Plan de sortie de la tuyère* | | |
| NO | $0,19.10^{-3}$ | $0,45.10^{-3}$ |
| *Après post combustion* | | |
| NO | $0,57.10^{-2}$ | $0,62.10^{-2}$ |
| $NO_2$ | $0,10.10^{-4}$ | $0,26.10^{-4}$ |
| $N_2O$ | $0,16.10^{-5}$ | $0,17.10^{-5}$ |

**Tableau 2 : Calcul des taux d'oxyde d'azote dans le plan de sortie de la tuyère et après la postcombustion du jet avec l'air**

### 2.2. Propriétés des propergols contenant un capteur de chlore

Les travaux ont porté sur des compositions à liant polybutadiène chargées au perchlorate d'ammonium (PA), au nitrate de sodium (N Na) et à l'aluminium (Al) et sur des formulations contenant, en plus des constituants précités, du nitrate d'ammonium (NA).

L'incorporation du NA., dans une composition PBU/PA/NNa/Al, présente l'intérêt de permettre une réduction du taux de chlorure émis. Son taux doit être limité pour éviter les difficultés inhérentes aux compositions PBU/NA/Al concernant l'obtention d'une vitesse de combustion suffisamment élevée et le rendement de combustion de l'aluminium. Ces études ont été réalisées pour un taux d'aluminium de 20 %

***Performances théoriques***

Dans une composition aluminisée, le remplacement du PA par du NNa, au taux nécessaire pour assurer la neutralisation du chlore, conduit à une diminution de l'impulsion spécifique comprise entre 15 et 20 s suivant les formulations. Le NNa étant beaucoup plus dense que le PA, l'écart est beaucoup plus faible pour l'impulsion spécifique volumique. L'utilisation d'un oxydant plus dense est également favorable pour augmenter le taux de charge massique. Une composition PBU/68NNa-PA/2OAl présente par rapport à une composition PBU/68PA/18Al (taux de charge de la composition Ariane V) une perte d'impulsion spécifique de l'ordre de 7,3 % mais une baisse d'impulsion spécifique volumique limitée à 1 % (*tableau 3*).

Le passage à un taux de charge de 90 % permet d'atteindre une impulsion spécifique volumique supérieure de 0,5 % à celle de la composition PBU/PA/Al.

Une autre possibilité d'augmenter les performances énergétiques, qui est cumulable avec la précédente, consiste à incorporer un faible taux d'hexogène ou d'octogène dans la composition. L'introduction de 10% de RDX dans une composition à 10 % de liant conduit à un gain de 2,1 % sur l'impulsion spécifique et de 0,8 % sur l'impulsion spécifique volumique. L'introduction d'un tel taux n'est pas de nature à modifier la réponse de la composition au test d'aptitude à la détonation derrière barrière qui est inférieur à une carte.

Le niveau d'impulsion spécifique volumique de la composition d'Ariane V peut donc être atteint avec les compositions avec capteur de chlore. Ces compositions sont donc énergétiquement intéressantes dans tous les cas où c'est le terme impulsion spécifique volumique qui prévaut pour les performances.

L'incorporation de NA dans une composition avec capteur de chlore conduit à une augmentation de l'impulsion spécifique mais à une diminution de l'impulsion spécifique volumique (*tableau 3*).

| *Composition* | | | | | | |
|---|---|---|---|---|---|---|
| PBU | 14 | 14 | 14 | 12 | 10 | 10 |
| PA | 68 | | | | | |
| PA - NNa | | 44 | 66 | 68 | 70 | 60 |
| NA | | 22 | | | | |
| RDX | | | | | | 10 |
| Al | 18 | 20 | 20 | 20 | 20 | 20 |
| *Performances théoriques* | | | | | | |
| Is 70/1(s) | 264,5 | 251,1 | 246,6 | 245,2 | 244 | 249,1 |
| $\rho$(g.cm$^{-3}$) | 1,759 | 1,761 | 1,834 | 1,876 | 1,917 | 1,893 |
| Is$\rho$(s.g.cm$^{-3}$) | 465,2 | 442,3 | 452,4 | 460,1 | 467,7 | 471,6 |

**Tableau 3 : Performances théoriques des propergols avec capteur de chlore**

***Faisabilité et propriétés mécaniques***

Les expérimentations ont porté sur des compositions à 12 % ou à 14 % de liant à base de PBHT R45 HT contenant une proportion de PA et de NNa correspondant à la neutralisation du chlore. L'influence de l'incorporation de NA a été évaluée pour un taux de 22 %. Elles ont été conduites jusqu'à l'échelle du malaxeur de 100 litres. Les niveaux de viscosité en fin de malaxage et leur évolution dans le temps sont compatibles avec la réalisation de chargement de grande taille. Les propriétés mécaniques sont tout à fait satisfaisantes (*tableau 4*).

***Propriétés balistiques***

Les catalyseurs de combustion contenant du chrome ayant été exclus en raison des propriétés toxicologiques de cet élément et de l'application envisagée, la vitesse de combustion a été réglée en utilisant de l'oxyde de fer.
Les propriétés cinétiques ont été déterminées par des tirs de blocs à canal central de 1 kg.

La vitesse de combustion des compositions PBU/PA/NNa/Al est très facilement réglable entre 5 et 13 mm/s à 7 MPa ce qui permet de couvrir très largement la plage d'intérêt pour l'application envisagée. Les possibilités de réglage sont beaucoup plus limitées pour la formulation contenant 22 % de NA.

L'obtention d'un exposant de pression satisfaisant nécessite une optimisation de la formulation. La valeur de 0,4 a été obtenue pour la composition PBU/PA/NNa/Al à 88 % de taux de charge.

| *Composition* | PBU 14 % PA/NNa/ NA/Al | PBU 14 % PA/NNa/ Al | PBU 12 % PA/NNa/ Al |
|---|---|---|---|
| *Performances théoriques* | | | |
| Tc (K) | 3121 | 3350 | 3503 |
| Is 70/1 (s) | 251,1 | 246,6 | 245,2 |
| Is ρ (s.g.cm$^{-3}$) | 442,3 | 452,4 | 460,1 |
| *Faisabilité* | | | |
| - viscosité (kpoise) | 9 | 6 | 6,4 |
| - vie de pot (heure) | 6 | > 6 | > 6 |
| *Propriétés mécaniques* | | | |
| Sm (MPa) | 0,66 | 1,06 | 0,80 |
| ε (%) | 17 | 21 | 18 |
| em (%) | 22 | 28 | 28 |
| er (%) | 28 | 30 | 30 |
| *Propriétés balistiques* | | | |
| Vc (7MPa) (mm/s) | 5,7 | 10 | 8,3 |
| n | 0,44 | 0,69 | 0,40 |

**Tableau 4 : Propriétés des compositions avec capteur de chlore**

*Comportement aux épreuves de sécurité*
Ces propergols présentent un excellent comportement aux épreuves de sécurité standard. Ils sont peu sensibles aux sollicitations thermiques ou mécaniques. Ils ne sont pas sensibles à l'électricité statique et présentent un indice d'aptitude de détonation derrière barrière inférieur à 1 carte.

| Composition / Epreuve | PBU 14 % PA/NA/NNa/ Al | PBU 14 % PA/NNa/Al |
|---|---|---|
| Sensibilité au frottement (Julius Peters) (N) | 240 | 200 |
| Sensibilité au choc (mouton de 30 kg) hauteur de non réaction (m) | 2,25 | 1,75 |
| Température d'autoinflammation (°C) | 248 | 291 |
| Vitesse de combustion à Patm (mm/s) | Non combustion en échantillon | 0,4 |
| Sensibilité à l'électricité statique | Non sensible | Non sensible |
| Indice d'aptitude à la détonation derrière barrière Nombre de cartes | <1 | <1 |

**Tableau 5 : Comportement des propergols avec capteur de chlore aux épreuves de sécurité**

*Coût*
Les compositions avec capteur de chlore se distinguent des propergols composites classiques uniquement par le remplacement d'une partie du perchlorate d'ammonium par du nitrate de sodium. Cette matière première est d'un faible coût et son emploi ne nécessite pas l'utilisation d'installation spécifique. Le procédé de mise en oeuvre reste inchangé par rapport à celui en vigueur pour les propergols composites. Les propergols avec capteur de chlore sont donc d'un coût équivalant à celui des propergols composites classiques.

## 3 - MESURES SUR LES EFFLUENTS

Des expérimentations ont été réalisées sur les effluents de moteur de 1 kg ou de 40 kg pour valider le concept capteur de chlore et le choix des compositions. Elles ont consisté à comparer les taux d'acide chlorhydrique et d'oxyde d'azote mesurés dans le panache de compositions contenant un capteur de chlore, avec ceux évalués, dans les mêmes conditions opératoires, sur la composition PBU/PA/Al.

Des prélèvements de particules ont également été réalisés pour évaluer la granulométrie du chlorure de sodium émis.

L'allumage des blocs était assuré par une microroquette chargée avec un propergol homogène pour éviter qu'il influe sur les résultats. Le débit massique est de 0,5 kg/s pour les blocs de 1 kg et de 5 kg/s pour ceux de 40 kg.

### 3.1. Description de l'instrumentation et des conditions expérimentales

La concentration en chlore et en acide chlorhydrique présents dans le panache a été mesurée par des capteurs électrochimiques dont le principe est le suivant : les gaz diffusent à travers une membrane poreuse et réagissent ensuite avec un électrolyte spécifique qui baigne une électrode. Le capteur délivre une tension directement proportionnelle à la concentration en chlore et en acide chlorhydrique. La précision de la mesure est d'environ 10 %. Le temps de réponse du capteur est inférieur à 2 s et dépend de la concentration mesurée.

La concentration en acide chlorhydrique gazeux a de plus été évaluée par spectrométrie infrarouge sur les tirs de blocs de 40 kg. Les mesures ont été réalisées sur un parcours de 20 m situé perpendiculairement à l'axe du jet et à une distance de 50 m du plan de sortie de la tuyère (*figures 2 et 3*). Cet appareil détermine le spectre d'absorption infrarouge des gaz situés sur le chemin optique. La concentration du gaz recherché est déterminée par comparaison avec des spectres en bibliothèque qui correspondent à des

milieux de nature et de concentration déterminées. La fréquence d'acquisition est de 0,5 Hertz.

Le dispositif expérimental destiné à mesurer les taux d'acide chlorhydrique a été complété par un système de barbotage constitué de 5 barboteurs remplis d'eau. L'aspiration est assurée par une pompe à palette en aval des barboteurs. Le débit (~5l/min) d'aspiration dans chaque récipient est contrôlé par un débitmètre numérique. Le temps d'aspiration dans chaque barboteur est piloté par des électrovannes. Ce système permet d'effectuer des prélèvements de durées déterminées à différents instants. L'appareil est positionné loin du propulseur afin de s'affranchir des distorsions susceptibles d'être induites par la vitesse des effluents.

Les concentrations en NO et $NO_2$ ont été mesurées par chimiluminescence , en un point du jet.

Des récupérations de particules ont été effectuées à l'aide d'un collecteur de particules. Cet appareil est constitué d'une buse d'aspiration et d'une série de filtres métalliques. Les particules aspirées s'impactent sur les différents filtres en fonction de leur granulométrie. La morphologie et les dimensions des particules prélevées sont évaluées par microscopie électronique. Les éléments de numéro atomique supérieur à 8 sont identifiés par spectrométrie X.

Le positionnement de l'instrumentation a été défini en tenant compte de la gamme des capteurs, de la température et des concentrations locales attendues . L'implantation des capteurs correspondant aux essais sur les blocs de 40 kg est représentée sur la *figure 3.*

### 3.2. Résultats des mesures

L'évolution au cours du temps, de la concentration en acide chlorhydrique et en chlore, mesurée par un capteur électrochimique situé à 16 m du plan de sortie de la tuyère, est représentée sur la *figure 4* pour un tir d'un bloc de 1 kg de la composition PBU/68PA/20Al. La concentration augmente rapidement dès que les gaz issus du propulseur atteignent le capteur. Elle décroît ensuite progressivement en raison de la dilution des effluents avec l'air. Elle atteint la valeur maximale de 200 ppm. Celle-ci n'est que de 1,9 ppm pour la composition PBU/PA/NA/NNa/Al et de 0,8 ppm pour la formulation PBU/PA/NNa/Al, pour une distance au plan de sortie de la tuyère de 14 m. Pour une distance de 16 m, elle s'établit à 0,6 ppm pour ces deux compositions ; ce niveau correspond à la limite de détection des capteurs et ne permet donc pas de différencier les deux formulations. Les résultats obtenus sur les tirs de blocs de 40 kg sont similaires ; les valeurs mesurées sur les compositions contenant un capteur de chlore sont en effet environ 100 fois inférieures à celles relatives à la composition de référence.

Ces résultats sont confirmés par les mesures par spectrométrie infrarouge qui mettent également en évidence un taux d'acide chlorhydrique environ 100 fois inférieur pour la formulation avec capteur de chlore (*tableau 6*).

| Composition | Concentration en HCl (ppm) |
|---|---|
| PBU/PA/Al | 291±10 |
| PBU/PA/NNa/Al | 2,1±1,1 |
| PBU/PA/NA/NNa/Al | 4,3±2,5 |

**Tableau 6 : Mesure de la concentration en HCl par IFRT Valeurs maximales à 50 m du PST d'un bloc de 40 kg**

Le système de barbotage n'a permis d'obtenir que des résultats qualitatifs. Les effluents de la composition PBU/PA/Al sont acides, alors que ceux des formulations contenant un capteur de chlore sont très proches de la neutralité.
Les concentrations en oxyde d'azote mesurées par chimiluminescence sont présentées dans le tableau 7. Les taux d'oxyde d'azote sont faibles pour les trois compositions testées, le produit majoritaire est le monoxyde d'azote. Les mesures réalisées à 14 m du plan de sortie de la tuyère sur la composition de référence mettent en évidence que les oxydes d'azote sont 150 fois moins abondants que l'acide chlorhydrique. La formulation au nitrate d'ammonium présente un taux d'oxyde d'azote inférieur à ceux des deux autres formulations.

| Composition | Taux d'oxyde d'azote | | |
|---|---|---|---|
| | NO ppm | $NO_2$ ppm | NO +$NO_2$ ppm |
| PBU/PA/Al | 2 | 0,75 | 2,75 |
| PBU/PA/NNa/Al | 3,1 | 0,1 | 3,2 |
| PBU/PA/NA/NNa/Al | 1,6 | 0 | 1,6 |

**Tableau 7 : Mesure de la concentration en oxyde d'azote mesurée par chimiluminescence Valeurs maximales à 14 m du PST d'un bloc de 1 kg**

L'observation par microscopie électronique des particules captées dans les effluents d'une composition PBU/PA/NNa/Al met en évidence la présence de particules cubiques parmi les particules sphériques d'alumine. La spectroscopie X a permis

de vérifier qu'elles sont constituées de NaCl. Leur dimension est en général comprise entre 0,5 µm et 5 µm avec une prédominance des grosses particules. Les particules fines sont fréquemment accolées aux sphères d'alumine.

## CONCLUSION

Les propergols avec capteur de chlore constituent une solution technique pour réduire l'impact des moteurs à propergol solide sur l'environnement qui consiste à remplacer une partie du perchlorate d'ammonium par un produit contenant un élément, tel que le sodium ou le potassium, qui réagit dans la chambre de combustion avec le chlore, pour former un chlorure

Ces compositions présentent une impulsion spécifique volumique d'un niveau équivalent à celui de la composition actuelle, mais une impulsion spécifique plus faible, et de bonnes propriétés rhéologiques, mécaniques et balistiques.

La validité du concept a été vérifiée par des mesures, réalisées dans les effluents de blocs de 1 ou de 40 kg, qui ont mis en évidence la très faible émission en acide chlorhydrique et en chlore, environ 100 fois inférieure à celle de la composition nominale, uniquement chargée en perchlorate d'ammonium et en aluminium.

Ces propergols possèdent une faible sensibilité aux sollicitations thermiques et mécaniques et ont un indice d'aptitude à la détonation derrière barrière inférieur à une carte. Ils n'utilisent qu'une matière première nouvelle, le nitrate de sodium, qui est d'un faible coût. La mise en oeuvre de cet oxydant et de ces formualtions ne nécessite pas l'utilisation de technologie ou de procédé particulier.

Les propergols au perchlorate d'ammonium et contenant un capteur de chlore constituent donc une solution technique applicable à court terme, pour réduire la répercussion des moteurs à propergol solide sur l'environnement.

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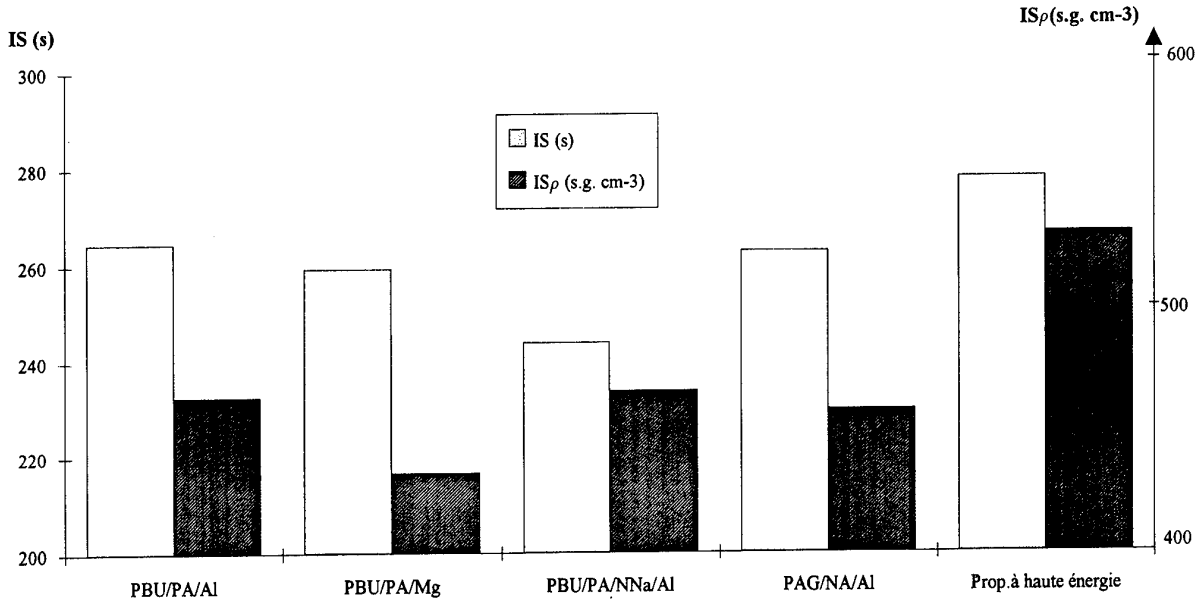



**Figure 1: Propergols n'émettant pas ou peu d'acide chlorhydrique**
*Performances théoriques (70/1)*

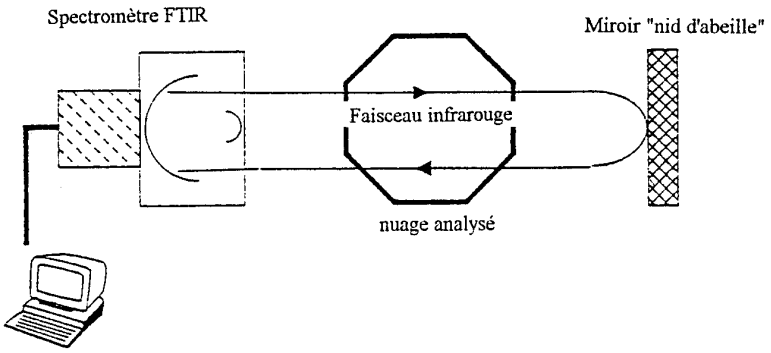



**Figure 2 : Principe de fonctionnement du spectromètre FTIR**

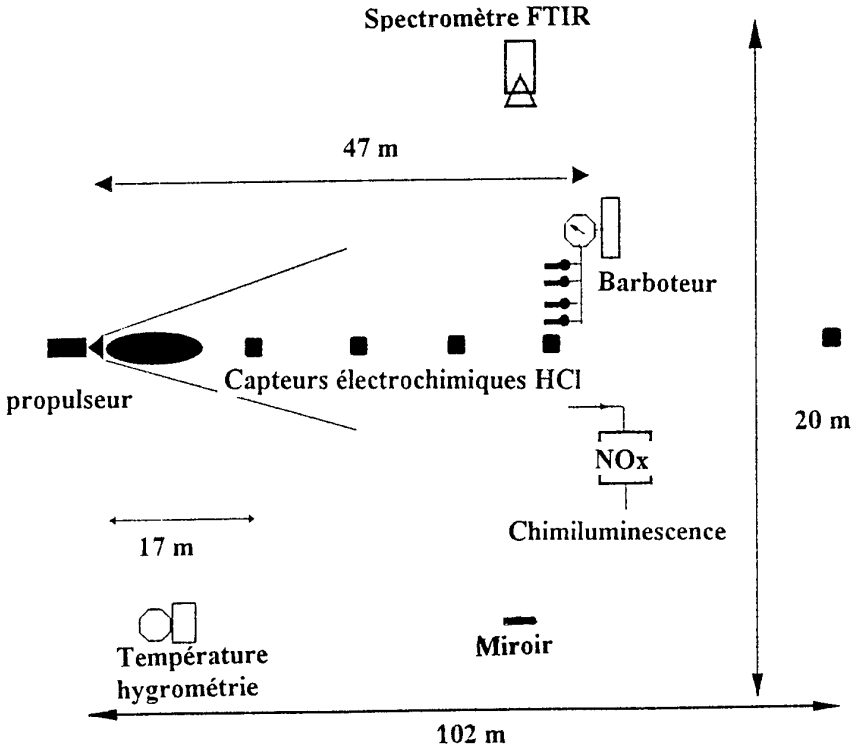



**Figure 3 : Implantation de l'instrumentation placée dans les effluents d'un moteur de 40 kg**

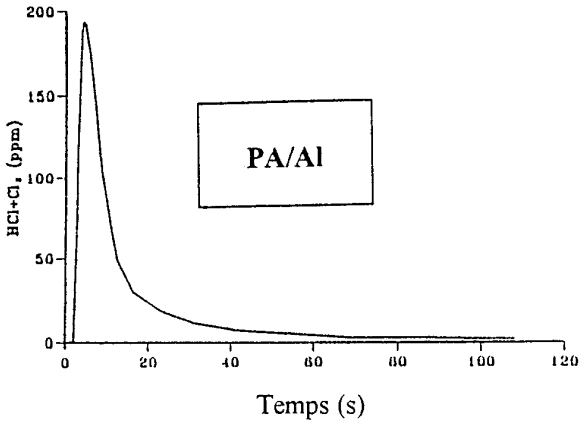



**Figure 4 : Mesure par capteur électrochimique du taux de HCl + $Cl_2$ à 16 m du PST d'un moteur de 1 kg Composition : PBU/PA/Al**

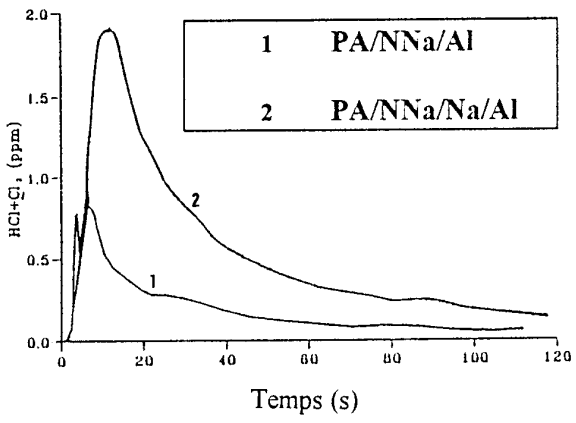



**Figure 5 : Mesure par capteur électrochimique du taux de HCl + $Cl_2$ à 14 m du PST d'un moteur de 1 kg**

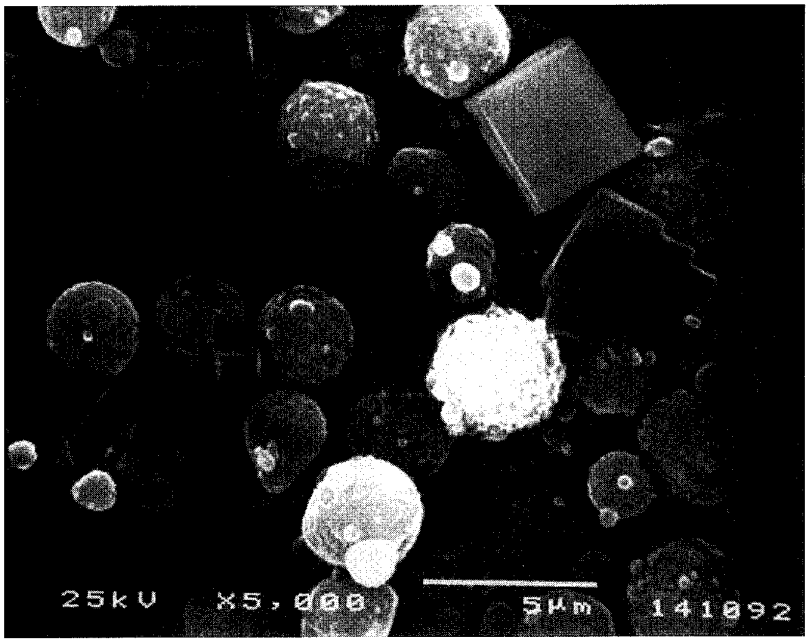



**Figure 6: Particules récupérées dans les effluents de la composition PBU/PA/NNa/Al**

## Discussion

QUESTION BY K. MENKE : How does the efficiency of neutralization and the stability of the propellants look like, if Mg neutralized and NaNO3 neutralized AP composite propellants are compared to each other ?

ANSWER : Nous avons choisi de travailler sur les compositions au NaNO3 plutôt que sur celles au Mg parce que les réactions chimiques conduisant à la captation du chlore dans la chambre de combustion nous paraissaient plus susceptibles de conduire à une bonne efficacité que la neutralisation du chlore par le Mg(OH)2 formé dans les effluents, par la réaction du MgO et de l'eau.

QUESTION BY R. STRECKER : Do you have any explanation for the rather high pressure exponent of O.69 with an AP/NAN/Al propellant ?

ANSWER : Les exposants de pression élevés ont été obtenus pour certaines qualités de perchlorate d'ammonium et de nitrate de sodium.

QUESTION BY R. STRECKER : Have you looked for sodium aluminate combustion products ?
ANSWER : Ce produit n'a pas été recherché. Les mesures par spectrométrie X ont montré que la très grande majorité du chlore et du sodium se trouve sous la forme de particules cubiques de chlorure de sodium.

QUESTION BY B. GOLDBERG : Comment on the overall effect to the ozone layer with the reduction of HCl but increases of NOx ?

ANSWER : Les écarts entre les taux de NOx pour la composition de référence (68 % PA, 18 % Al) et pour la composition contenant un capteur de chlore ne sont pas significatifs.

QUESTION BY B. GOLDBERG : How does NaCl product affect ozone layer and how much of it is there ?

ANSWER : L'incorporation du capteur de chlore conduit déjà à une réduction du taux de chlore d'environ 40 %. La captation du Cl par du Na et la formation de particules de NaCl est de nature à limiter d'une façon importante les effets locaux résultant de l'action du chlore.

Pour les effets globaux deux aspects sont à considérer :
- l'émission du Cl par les particules de NaCl. Les réactions chimiques hétérogènes susceptibles de conduire au dégagement de Cl (N2O5, ClONO2...) sont décrites pour les conditions régnant dans la troposphère. Elles sont limitées par la formation d'un produit solide. Il n'est pas exclu qu'elles interviennent pour les conditions prévalant dans la stratosphère, mais les réactions étant limitées, elles ne devraient conduire au dégagement que d'une fraction du chlore.
- l'influence des particules. L'influence des particules de NaCl sur les réactions hétérogènes conduisant à la destruction de l'ozone n'est pas documentée. Il faut toutefois noter que le taux de NaCl égaré est deux fois moins important que le taux d'alumine.
Il parait donc légitime de penser que les effets globaux sont également fortement réduits. Des études seraient probablement nécessaires pour évaluer l'influence précise du NaCl.

# CLEAN PROPELLANTS FOR SPACE LAUNCH BOOSTERS

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## Abstract

The Phillips Laboratory Propulsion Directorate has been developing propulsion systems for space launch application which address environmental concerns (the clean propellant programs) since the late 1970s. The Applications Division (RKA) developed an environmental approach to eliminate hydrochloric acid as an exhaust product. This approach is in line with the Air Force space launch propulsion strategy. Application of environmentally acceptable propellant technology is evident in each step in the manufacturing process through conservation/disposal. Future propulsion systems will be required to comply with environmental regulations and laws. The Environmental Protection Agency has raised concern about acid rain and is calling for significant reduction of hydrochloric acid in the atmosphere. They have developed models to predict the environmental impact of hydrochloric acid from space launches in the atmosphere and its role in ozone depletion. The space launch strategy team stressed that these predictions of environmental impact need to be substantiated with hard data.

It is essential that the space launch propulsion community develop alternative environmentally acceptable space launch propulsion systems. Development of space launch scavenger propellants has significantly reduced the amount of hydrochloric acid released into the atmosphere from greater than 20% to less than 2%. Solution propellant technology has potential as a chlorine-free propellant for space launch application. Advanced Environmental Propellant Development will evaluate high energy ingredients to replace current low density or low performance ingredients in propellant formulations to achieve equal or better performance of current solid systems. These steps are essential to ensure the future of space launches.

## Introduction

Environmental concern about acid rain and the acid content of the space launch cloud led to development of alternatives to current space launch propulsion technologies and modifications to current propellant manufacturing methodologies. The Jet Propulsion Laboratory (JPL) investigated replacing ammonium perchlorate with ammonium nitrate as the oxidizer in propellant formulations. They hoped this technology would eliminate hydrochloric acid from the launch cloud without adversely affecting motor performance. The Air Force approach to reducing or eliminating hydrochloric acid was two fold. The first approach, to eliminate hydrochloric acid in the motor by reacting the acid in the motor chamber to form a alkaline metal chloride salt (table salt), is known as the scavenger technology. The second approach, to eliminate chlorine from the propellant, is known as the chlorine-free technology. Before the rise of ozone depletion impact concerns, the scavenger technology was the preferred approach. Although the chlorine-free approach is now preferred, the technology lacks maturity and cost effectiveness (affordability) at this time. The trend toward increased environmental regulation and law, particularly as it relates to ozone depletion, will affect propulsion technologies across the entire propulsion spectrum. Environmental impact needs to be accurately measured and verified before appropriate corrective measures can be implemented. Meaningful atmospheric modeling and assessment of environmental impact for each propellant technology and data verification of the atmospheric prediction models is essential. For each propellant manufacturing and disposal procedures need to to be environmentally acceptable. The propellant needs to have reasonable life cycle costs, reduce cost per pound of payload, and have high reliability.

The Environmental Protection Agency has established a conservation and disposal philosophy for the management of solid propellant and solid propellant waste disposal. Source reduction is the primary approach and disposal is the least desirable approach with reclamation and energy recovery in between these approaches. Waste reduction is addressed during the manufacturing process. Disposal is the focus of efforts after manufacture. The standard operating procedures used for solid propellant and solid propellant waste disposal are open burning/open detonation/static firing (OB/OD/SF). Under the Resource Conservation and Recovery Act (RCRA), these operations are being discontinued. The fact that OB/OD/SF operations are being curtailed and are banned in some localities requires development of

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alternative environmentally acceptable disposal technologies.

Today's changing political environment challenges the propulsion community to meet space launch mission requirements within new restraints. The Phillips Laboratory, Propulsion Directorate is advocating alternatives to current space launch systems and modernization of current system which address both environmental compatibility and life cycle costs. This paper documents their strategy for space launch propulsion development, demonstration, and qualification.

## Space Launch Atmospheric Characterization

Solid space launch motors release large quantities of hydrogen chloride, water, and aluminum oxide into the atmosphere, but exactly what effect this release has on the stratospheric ozone layer is uncertain. A large percentage of these exhaust products from Titan IV and Space Shuttle launches is deposited in the troposphere. Although short term and/or long term effects have been predicted from numerous modeling efforts, actual atmospheric measurements have not been taken to verify the validity of the model predictions.

To establish confidence in the atmospheric predictions, the unknown chemistry involving the aluminum oxide particles and chlorine compounds needs to be established. Current chlorine models postulate that OH radicals are created which convert HCl back into Cl atoms, which directly attack ozone. Other possible chlorine effects could be due to an increased concentration of the chlorine oxide dimer, $(ClO)_2$ that initiates an ozone destruction cycle, or the elevated local chlorine may neutralize the local nitrogen oxides and chlorine above this level can destroy ozone. It has been postulated that aluminum oxide particles could destroy ozone directly or that catalysis chemistry, such as that found in polar stratospheric clouds, could reactivate chlorine reservoir species. This chemistry is not presently established and programs are either planned or underway to determine the chemical kinetics. Models should be developed to better predict launch plume and troposphere interaction. Modeling efforts and atmospheric chemistry verification are being coordinated, but the space launch community alone lacks the capability to establish the necessary technology base. However, if they do not provide an acceptable propulsion strategy, they may be in conflict with projected regulations and laws which will increasingly restrict or prohibit space launch operations. These regulations and laws include international protocols, federal regulations, and state and local ordinances.

The Propulsion Directorate's propellant strategy focuses on hydrochloric acid minimization or elimination. Propellant development efforts have successfully modified propellant formulations to achieve a ten-fold decrease in hydrochloric acid level. During this scavenger technology demonstration, each solid propellant supplier provided a small (70-lb BATES) and large (Super BATES/800-lb) test motors for test firings. The performance of all motors was excellent and the ballistics met space launch system requirements. Hydrochloric acid reduction was verified. Geomet samplers and Drager tubes were used to characterize the acid content of the exhaust cloud. The Geomet samplers were used for the open-air tests and the Drager tubes were used for exhaust cloud containment tests. The sodium nitrate propellants had a nominal acid level of 2% as compared with the theoretical level of 1%. Propellants containing magnesium instead of aluminum did not exhibit the same level of acid reduction as measured by the Geomet samplers; however, acid reduction as measured by the Drager tube was comparable with sodium nitrate results. The kinetics of the magnesium containing propellant limits its desirability.

## Environmental Space Launch Propulsion

Space launch activities have changed. Early concern with acid rain led to Phillips Laboratory Propulsion Directorate's present charter as environmental steward for "cradle to grave" propellants used for all space launch efforts. Environmental trends, regulations, and laws influence future technology thrusts. The Air Force Materiel Command (AFMC) and particularly the Phillips Laboratory Propulsion Directorate has incorporated environmental pollution prevention and compliance in all of their space launch and propulsion technology thrusts. Propulsion technology includes manufacture, resource minimization, handling, performance, and disposal. Increasing environmental compliance costs have created a priority for development of environmentally acceptable methods to manufacture, operate, and dispose of space launch systems. Current motors which contain ammonium perchlorate are manufactured using procedures that will be environmentally regulated. The concern that environmental regulations may interrupt current production schedules is real, and necessitates creation of procedures for alternate manufacture that would meet environmental regulations. The Solid Propulsion Environmental Issues Program is directed towards establishing environmentally acceptable manufacturing procedures for scavenger propellants.

The program approach is to establish an *anticipated* environmental strategy based on current trends, regulations, and laws. The program will demonstrate implementation of environmentally acceptable procedures in manufacturing large motors using scavenger propellant. The process technologies shall focus on waste and hazardous material reduction, ingredient substitution, prevention of toxic releases during manufacture, and maintenance of current performance levels. The reduction of hazardous material use and reduction of propellant/process waste during motor manufacture is a significant environmental achievement. Maintainability/reliability costs and the cost benefit/payback period for using environmentally acceptable methods of manufacturing are unknown, but are anticipated to be large. Regulators, government, and the solid propulsion community held a manufacturing workshop to address environmentally acceptable propellant development and manufacturing processes. Procedure evaluation/development in conjunction with an industry survey is underway. The Air Force is developing environmental technologies for manufacturing space launch components. These manufacturing techniques parallel the solid propellant manufacturing effort with motor components. Several of the changes might be applicable to other programs. Impact on overall system performance must be examined to minimize system incompatibilities.

The program will assess the performance of individual components incorporating environmentally acceptable manufacturing changes. Methods to minimize system impact will be evaluated, including incorporating new processes and/or materials such as 3-D carbon-carbon throats, etc. The analysis will include costs and performance. The analysis of candidate materials and components will serve as the baseline for further study. Components will be evaluated in subscale tests. Their impact on performance, cost, and system reliability will be used to screen these components. Subscale test results will be used to evaluate impact on current missile design. The component performance assessment will include aging effects and maintenance requirements. The program is in its initial stages and no significant progress has been made to date.

As stated earlier past and current space launch propellants contain significant amounts of ammonium perchlorate and aluminum. Their combustion products include hydrochloric acid and aluminum oxide. There were environmental concerns with acid rain since these propellants released a nominal 20% level of hydrochloric acid in the launch cloud. JPL's 1974 investigation was the first to minimize or eliminate hydrochloric acid from the launch cloud. JPL's candidate propellants are listed in Table I.

**Table I. JPL Propellant Candidates**

| Propellant | TP-H1148 | A | B | C | D | X |
|---|---|---|---|---|---|---|
| Density, $lb/in^3$ | 0.0641 | 0.0625 | 0.0629 | 0.0622 | 0.0623 | 0.0616 |
| Ammonium nitrate, % | 0 | 36 | 31 | 41 | 41 | 41.5 |
| Ammonium perchlorate, % | 69.7 | 10 | 15 | 10 | 15 | 10 |
| HMX*, % | 0 | 0 | 0 | 0 | 0 | 17.5 |
| Aluminum, % | 16 | 18 | 18 | 18 | 18 | 10 |
| Hydrochloric Acid, % | 20.9 | 2.8 | 4/2 | 2.8 | 4.2 | 3.0 |

* Cyclotetramethylene tetranitramine

There is a performance penalty for each of these propellants of lower specific impulse or lower propellant density. Additionally, the JPL investigation was limited by the poor combustion characteristics of ammonium nitrate and the lack of ballistic tailorability indicated by the inclusion of ammonium perchlorate in the formulations.

There are two approaches to remove hydrochloric acid as an exhaust product. The most obvious way is to formulate a chlorine-free propellant. The chlorine-free propulsion system replaces ammonium perchlorate with a chlorine-free oxidizer thus preventing chlorine compound formation during combustion. Another approach, the "scavenger motor" concept, uses an additive to react with the chlorine, resulting in reduced acid. Sodium nitrate can be used as the additive to "scavenge" chlorine, resulting in sodium chloride (salt) formation in the motor chamber or magnesium to react with hydrochloride in the chamber and the exhaust cloud to form magnesium chloride (neutralization technology). The magnesium propellant system technology has been discontinued since the required hydrochloric

acid elimination did not occur. The gross reactions are shown below.

Chlorine Reactions

Current Space Launch Propellants

$$AP(NH_4ClO_4) + Al + CH_x\ (BINDER) \rightarrow N_2 + H_2O + HCl + Al_2O_3 + H_2 + CO_x$$

Scavenger Propellants

$$AP + NaNO_3 + Al + CH_x\ (BINDER) \rightarrow N_2 + H_2O + NaCl + HCl + Al_2O_3 + H_2 + CO_x$$

Chlorine-Free Propellants

$$XNO_3 + Al + CH_x\ (BINDER) \rightarrow N_2 + O_2 + H_2O + Al_2O_3 + H_2 + CO_x$$

Table II lists the properties for the environmental propellant candidates. Not all of the environmental candidates are being developed. The Air Force program is developing the Scavenged, chlorine-free Ammonium Nitrate, and Chlorine-free Solution propellants. Although the Air Force is not currently developing advanced environmentally acceptable propellants, there are efforts to address next generation ingredients.

The scavenged propellant approach balances the moles of chlorine in the propellant with the moles of the scavenging element which is sodium. This hypothetically eliminates all of the hydrochloric acid in the exhaust products while experimentally there is approximately 1 - 2% of hydrochloric acid remaining. The limitation of using sodium nitrate is low specific impulse. The propellant does have numerous advantages as compared with other propellants. In addition to its high density, it possesses many of the attributes of Titan and large motor hydroxy-terminated polybutadiene (HTPB) binder propellants.

Table II. Environmental Propellant Candidates

| Propellant | Shuttle | Scavenged | AN - Cl-Free | SLN-Cl-Free | Adv Cl-Free |
|---|---|---|---|---|---|
| $\varrho$ (density), lb/in$^3$ | 0.0641 | 0.0689 | 0.0605 | 0.0617 | 0.06 |
| ISP (specific impulse), sec | 261.4 | 244.3 | 259.2 | 260.4 | 274 |
| $\varrho$ISP/$\varrho$ISP-TP-H1148 | 1.000 | 1.017 | 0.947 | 0.970 | 1.01 |
| $R_b$ (burn rate), ips | 0.42 | 0.42 | 0.43 | 0.39 | 0.53 |
| $\eta$ ($R_b$ exponent) | 0.35 | 0.40 | 0.43 | 0.39 | 0.56 |
| Binder | PBAN | HTPB | HTPE | PVA | HTPB |
| Fuel/Al | 16 | 19 | 28* | 20 | 17 |
| Physical Properties | | | | | |
| Modulus, psi | 475 | 550 | 572 | 230 | - |
| Stress, psi | 105 | 145 | 155 | 250 | - |
| Strain, % | 38 | 42 | 43 | 260 | - |

*55% aluminum/45% magnesium

All of the solid propulsion contractors have formulated a scavenged formulation using large-scale processing, 600-gallon mixers and procedures. CSD and Thiokol successfully demonstrated alternate processing technology, continuous mixing. CSD manufactured scavenger propellant was sucessfully fired in 70-lb BATES test motors and in a Super BATES test motor. Thiokol successfully manufactured 70-lb BATES test motors containing their neutralized scavenger propellant produced using their continuous processing approach.

Table III lists the scavenged propellant results for scavenged propellants which the solid propulsion contractors delivered to the Phillips Laboratory for ballistic evaluation. Both 70-lb BATES test motors and 800-lb Super BATES test motors were fired and their performance characterized. The solid propulsion

contractors successfully demonstrated scavenger propellants that match the ballistic and physical properties of the Titan and Shuttle propellants.

Table III. Scavenged Propellant Results

| Propellant | TP-H1148 | TC | ASPC | CSD | ARC | HAC |
|---|---|---|---|---|---|---|
| ϱ (density), lb/in$^3$ | 0.0641 | 0.0689 | 0.0677 | 0.0682 | 0.0660 | 0.0688 |
| ISP (specific impulse), sec | 261.4 | 244.5 | 244.3 | 143.3 | 251.6 | 245.8 |
| ϱISP | 16.557 | 16.846 | 16.659 | 16.478 | 16.582 | 16.931 |
| $R_b$ (burn rate), ips | 0.42 | 0.40 | 0.42 | 0.40 | 0.34 | 0.43 |
| $\eta$ ($R_b$ exponent) | 0.35 | 0.59 | 0.41 | 0.37 | 0.37 | 0.27 |
| Binder | PBAN | HTPB | HTPB | HTPB | HTPB | HTPE |
| Fuel/Al | 16 | 19 | 21 | 19 | 19 | 22.5 |
| Oxidizer/AP | 69.7 | 39.5 | 38.6 | 38.8 | 32.5 | 35.1 |
| Oxidizer/$NaNO_3$ | 0 | 29 | 27.9 | 29.0 | 23.5 | 25.4 |
| Oxidizer/Other | 0 | 0 | 0 | 1/PP* | 12/ RDX** | 0 |
| $\eta^0$ (70−lb BATES) | 93.9 | 93.6 | 92.5 | 93.7[1]/93.5[2] | 93.0 | 92.9 |
| $\eta^0$ (Super BATES) | 94.5*** | 94.4 | 95.9 | 94.1[2] | 94.6 | 94.2*** |

[1] - Propellant manufactured using batch mix process
[2] - Propellant manufactured using continuous mix process
* - Potassium perchlorate
** - Cyclotrimethylene trinitramine
*** - Estimated value

The solution propellant differs significantly from conventional propellants. Solution propellants are relatively simple using solid polymers rather than the viscous polymers such as hydroxy-terminated polybutadiene. The unique oxidizer is a low viscosity liquid rather than the conventional granular solid. These properties allows the manufacturer to limit processing steps and the fact that they undergo a physical cure rather than a chemical cure facilitates lower cost, low shear manufacturing operations. Solution propellant has been manufactured in a larger mixer. A Super BATES motor cast with solution propellant was successfully tested at Phillips Laboratory Propulsion Directorate. Although this propellant has attractive physical properties, its low modulus is a concern for space launch applications. Significant work is required to establish the safety and aging baseline for this family of propellants.

Current environmentally acceptable chlorine-free solid propellants have not matched the total impulse of current solid rocket motors. The removal of environmentally questionable materials reduces motor performance by lowering specific impulse or propellant density. The Advanced Environmental Propellant Development (AEDP) program will evaluate the high energy ingredients identified by environmental research findings as substitutes for current low density or low energy ingredients. A limited number of materials available in small quantities and several promising oxidizers hold promise as being both environmentally and energetically acceptable. A test program is being accomplished to determine compatibility, hazard, ballistic and property data for identified acceptable substitute fuels necessary for propellant formulation scaleup.

This effort will screen energetic materials for environmental acceptability. Screened ingredients will be acquired and/or scaled-up for evaluation. Formulations will be tested to determine compatibility of ingredients with each other. Selected formulations will be cast into test motors and fired to demonstrate their environmental acceptability as well as their ballistic and physical properties. Limited formulation characterization has been accomplished for the advanced formulations being studied. Replacing ammonium perchlorate with ammonium dinitramide (ADN) is the advocated approach because increased performance offsets density loss. Other

approaches may be required to address elimination of exhaust particulates.

Table IV. Solution Propellant Properties

| | |
|---|---|
| Propellant | 0.0617 |
| ISP (specific impulse), sec | 260.4 |
| ϱISP | 16.067 |
| $R_b$ (burn rate), ips | 0.385 |
| $\eta$ ($R_b$ exponent) | 0.55 |
| Fuel/Al | 18 |
| Oxidizer - liquid | 68 |
| Physical Properties | |
| Modulus, psi | 230 |
| Stress, psi | 250 |
| Strain, % | 260 |

Utilization of large motors in space launch systems places increased operational safety requirements as compared with current space launch systems. The effort to eliminate hydrochloric acid requires insensitive alternatives to existing propellants. Current environmentally acceptable propellants deviate significantly from solid propellant historical databases. Their utilization raises safety concerns since there is an insufficient hazards database. Our safety work addressed the hazard properties of Titan IV type propellant and chlorine-free propellants to determine their suitability for space launch applications. The environmentally acceptable propellants could be expected to perform over a wide range of applications (from use as a drop in replacement to use in a new system).

Large scale detonability and impact testing was conducted on the baseline propellant, an analog Titan IV propellant. The Space Shuttle propellant with a polybutadiene acrylonitrile (PBAN) binder, ammonium perchlorate, and aluminum propellant has similar characteristics. The generic propellant composition was hydroxy-terminated polybutadiene (HTPB) binder, ammonium perchlorate, and aluminum. The critical diameter test was conducted on a 22-inch by 72-inch cylinder with a C4 charge. The sample did not detonate and there was little evidence of burning propellant. Safety data should be comparable for the scavenger propellants since scavenger propellants are comparable to the Titan IV analog propellant and Shuttle propellant. A critical diameter test was conducted with a 6-inch by 18-inch sample of chlorine-free generic ammonium nitrate, aluminum, and hydrocarbon binder system. Results were also negative. The 22-inch critical diameter test is the largest critical diameter test conducted on a hydroxy-terminated polybutadiene propellant to date.

## Space Launch Conservation/Disposal

The initial space launch propellant disposal technology applies an advanced chemical reactor technology to destroy/convert energetic materials. Operating disposal processes for energetic materials which involve high-temperature and high-pressure are costly with inherent health and safety risks. In order to dispose of or transform highly energetic materials to environmentally benign compounds reaction chemistry involving catalysis and nonground state pathways (advanced chemical reactor technology) will be investigated. The chemical reactor systems will operate at low temperature and low pressure minimizing the possibility of uncontrolled environmental emissions and reducing health and safety risks. Experiments will be conducted to identify effective homogeneous and heterogeneous catalysts to destroy or convert selected energetic materials. An effort will be undertaken to establish the effectiveness of nonground state chemistry in destroying energetic materials and chemical wastes and to establish the reaction rates and mechanisms, operating parameters, and process limitations in processing propellants. Data will be collected into a database for use in process demonstration and validation.

The next step to be taken in space launch solid propellant systems disposal includes recovery of propellant components. Incorporating process developments that do not require significant quantities of hazardous of unacceptable organic solvents, application of chemical reactor technology is investigated as a means of destroying or converting selected space launch propellants. Since OB/OD/SF/incineration is being discontinued, other removal, separation, and destruction processes need to be developed. Development of environmentally acceptable propellant must include validated processes to dispose of or transform space launch propellants into environmentally benign compounds in a bench scale reactor process. Bench-scale tests will be conducted to demonstrate propellant removal and chemical/biological destruction of the selected space launch propellant prior to full-scale qualification. Bench-scale chemical reactor systems will be designed and constructed to determine the cost/benefit of full-scale facility development.

## Space Launch Propulsion Status

A space launch team composed of members representing AFMC laboratories and Space and Missiles Center has been formed to address environmental alternatives to current space launch propulsion. The team's position is that the environmental atmospheric impact of space launch systems has not been verified and that atmospheric predictions need to be substantiated with hard data. There are several environmental approaches to propellant development and demonstration that may be pursued. Various approaches are necessary because the environmental impact of different technologies has not been determined.

Scavenger propellant development is an established technology which has been demonstrated in large motors. This manufacturing technology addresses immediate environmental propulsion needs. The propellant system of choice is the sodium nitrate and ammonium perchlorate system. The magnesium and ammonium perchlorate system has been eliminated from consideration. An effort has been initiated to establish the required motor component technology to support a scavenger propulsion system.

Several approaches to Chlorine-free propellant technologies are being developed. In the near-term, ammonium nitrate propellant formulation is being addressed under an advanced development program. Far-term approaches are being studied under research and development programs. The primary far-term approach, solution propellant technology, although very promising requires a large investment to establish its viability as a space launch propulsion system technology. The other far-term approach, advanced propellant development, encompasses many potential paths. One such approach was suggested by Z. Pak in his AIAA paper, AIAA-93- 1755, involves replacing ammonium perchlorate with ADN. Improved performance makes ADN inclusion attractive although the propellant's density may restrict drop-in application. There are indications that Russian technologists have successfully used ADN, but not in space launch efforts. Use of ADN as well as use of other promising ingredients require extensive characterization and synthesis investments. The life cycle cost efforts and safety characterization studies are extremely limited for this group of propellants, and waste minimization and disposal should be addressed early in this development efforts.

## Space Launch Propulsion Summary

Environmentally acceptable solid propellant used in space launch applications is crucial to future space launch systems. The vulnerability of these systems to the whims of environmental activists is unacceptable. Development of environmentally acceptable propellants to meet mission needs and development of a space launch strategy to direct research and development efforts are a serious concern. System users and providers need to increase their participation in developing systems to meet near and far-term space launch mission requirements.

There are several technologies being developed to meet near-term and far-term space launch system mission requirements. It appears feasible to produce a constant volume (drop-in scenario) environmentally acceptable scavenger propellant to replace current propellant without significantly modifying the current space launch envelope. The scavenger propellants have demonstrated the same ballistic and physical properties. The grain design and hardware changes would not require significant changes.

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## Discussion

QUESTION BY A. DAVENAS : Could you give us an order of the typical batch to batch variations of burning rate with a solution propellant.

ANSWER : We do not have batch to batch reproductibility on burning rate with large mixes (30 gallons or larger) because we have done a small number or these mixes. No large mixes have duplicated identical propellant formulations. Small mixes (normally two gallon or less) have exhibited acceptable reproductibility. The variation in burning rate has been less than + 0.05 ips (inches per second) in small motor tests.

QUESTION BY A. DAVENAS : Do you think this could be a problem, or not, for practical applications ?

ANSWER : Although numerous propellant questions require resolution before a practical application is possible, burning rate should not be a problem from a processing operation. Quality control by propellant compounds will be the source for the largest burning rate variation because propellant ingredient manufacture and control has not been adequately addressed.

QUESTION BY A. DAVENAS : Are there possibilities to modify the burning rate of a solution propellant without modification of the composition main properties (i.e. ballistic additive or modifiers which do not change significantly the basic formulation).

ANSWER : The modification of the propellant burning rate is accomplished with additives in the liquid oxidizer. Conventional additives do not influence or are not compatible on the propellant ballistics. Normally an additive is necessary to adjust the burning rate. The additives have little or no effect on the propellant physical properties, however, aging effects have not been determined. No attempt has been made to modify burning rate by modifying the solid polymer. Modification of the solid polymer would have a significant effect on the physical properties. This effect would be negative.

QUESTION BY A.J. Mc DONALD : You considered performance comparison of propellants to be represented by the product of Isp and density ($\rho$). For space booster applications the relationship is not linear i.e. for Shuttle it is Isp . $\rho$ 0,6. What is the value of the exponent on density for the Titan IV ?

ANSWER : The density impulse ( $\rho$ . ISP) was not a criteria for the clean propellant development program. Propellant performance was secondary to propellant sensitivity and propellant cost.
We acknowledge there is a density exponent effect, but we have not done a system study to determine a density exponent. We have done approximation with density exponents of 0.5, 0,6 and 0,9. The accuracy of these estimates is unknown and they indicated a performance penalty from two to ten percent.

# Improved Environmental Properties of a Solid Composite Propellant

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## SUMMARY

Due to the environmental aspects of solid propulsion, the possibility to reduce or eliminate the concentration of HCl in rocket exhausts without compromising performance is of interest. This can be achieved in various ways. In an AP based propellant AP may be partially or fully replaced by another oxidizer. The influence on the amount of HCl in a rocket exhaust by partial replacement of AP with HMX in a specified AP/HTPB based propellant is presented together with effects on various other propellant properties. This include computer simulations and experiments on the energy content and the rocket exhaust signature as well as tests on mechanical and hazard properties of the propellant.

## LIST OF SYMBOLS

| | |
|---|---|
| AN | ammonium nitrate |
| AP | ammonium perchlorate |
| GAP | glycidyl azide polymer |
| HMX | cyclotetramethylene tetranitramine |
| HNF | hydrazinium nitroformate |
| RDX | cyclotrimethylene trinitramine |
| HTPB | hydroxy terminated polybutadiene |
| polyNIMMO | polynitratomethyl–methyloxetane |
| $A_e$ | nozzle exit area, $m^2$ |
| $A_t$ | nozzle throat area, $m^2$ |
| $c^*$ | characteristic exhaust velocity, m/s |
| F | thrust, N |
| $I_{sp}$ | specific impulse, m/s |
| $\dot{m}$ | mass flow, kg/s |
| $m_{tot}$ | propellant mass, kg |
| $P_c$ | chamber pressure, Pa |
| $P_e$ | nozzle exit pressure, Pa |
| $t_b$ | burning time, s |
| $\varrho$ | density, $kg/dm^3$ |

## 1 INTRODUCTION

When a propellant is to be developed, several requirements have to be fulfilled. It is, however, not always possible to obtain all the desired properties. Some of them can be achieved, but it may be at the expense of others.

An overall requirement for most propellants is a high energy content. Increasing the number and concentration of certain additives will yield a high specific impulse. The mechanical properties will, however, deteriorate as the content of solids increases. Aluminized propellants are highly energetic, but the smoke evolution is relatively high. A high specific impulse is often the result of a high flame temperature. This is a problem for the nozzle throat material, which may not withstand the high temperature. Melting or cracking of the material may affect the performance of the rocket motor. A coolant can be added in order to achieve a colder propellant. This may, however, result in a decrease of the energy level.

Our work has been concerned with finding a composition with reduced secondary smoke and a lowered flame temperature without these modifications resulting in a reduction of energy. In an AP/HTPB based propellant AP was partially replaced by HMX. During this development the effect of the replacement on various propellant properties as a function of HMX content were studied. Part of the work has been done using simulations. This is true for specific impulse, flame temperature and rocket exhaust signature. Results from firings for measurements of thrust and production of secondary smoke will be given. We will also present some results from the testing of mechanical and hazard properties. A hazard classification had to be performed as the amount of HMX is quite high and the propellant had to be a class 1.3 material.

## 2 ENERGY CONTENT

### 2.1 Simulations

Thermodynamic simulations have been performed to calculate the specific impulse and the flame temperature of different propellant compositions [1]. The input to the program are the composition of the propellant, chamber and nozzle exit pressure and the expansion ratio of the nozzle. Chemical equilibrium and fast reactions are assumed. The propellant deflagrates under constant pressure, and the product gases expand through a nozzle to the ambient pressure.

In these simulations the chamber and nozzle exit pressure are 6.9 MPa and 0.1 MPa respectively, and the content of HMX in the propellant is varied between 0% and 30% (by weight).

#### 2.1.1 *Flame Temperature*

Figure 2.1 shows the temperatures in the chamber and the nozzle throat as a function of increasing amount of HMX. By increasing the HMX content in the propellant from 0% to 30%, the chamber temperature is reduced by 7.7% and the nozzle throat temperature by 10.3%.

#### 2.1.2 *Specific Impulse*

The reduction of the flame temperature by increasing amounts of HMX results in a reduction of the specific impulse, as seen in Figure 2.2. This reduction is, however, less than the reduction of the flame temperature for the same amount of HMX. By increasing the HMX content from 0% to 30%, the specific impulse is reduced by 1.9%.

### 2.2 Verifications

In order to verify the calculations of specific impulse, firings of propellants with 0% and 25% HMX have been conducted. The characteristic exhaust velocity, $c^*$, was also determined. It is usually a figure of merit of the propellant combination and combustion chamber design, and is essentially independent of the nozzle characteristics [2]. $c^*$ is an important parameter in the design of propellant loads. $I_{sp}$ is a function of pressure and nozzle design as well as the composition of the propellant.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

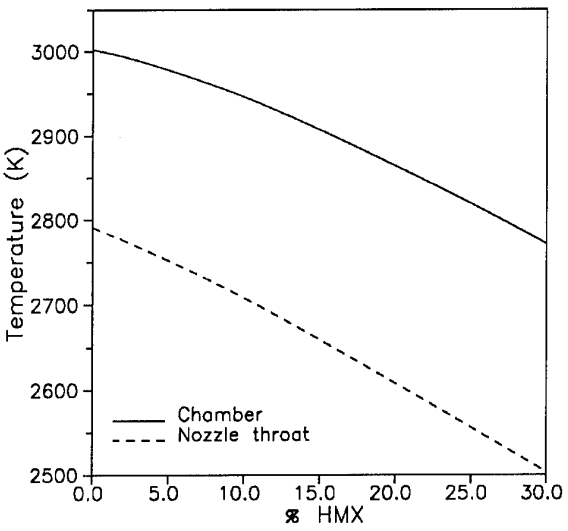



Figure 2.1 Flame temperature as a function of HMX content.

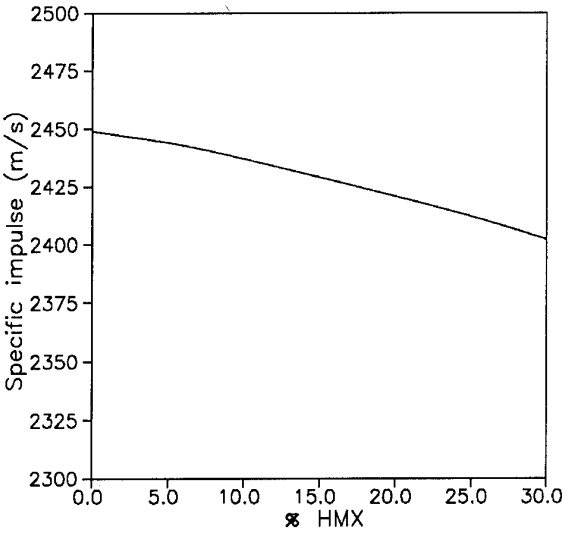



Figure 2.2 Specific impulse as a function of HMX content.

Propellant grains with a cylindrical centre hole were casted in steel cylinders. The grain was inhibited at the front end and burned from the inside and from the aft end. The mass of propellant was approximately two kilos. This specific shape of the load results in a nearly constant burning surface area throughout the firing, which is necessary in order to keep the chamber pressure constant. This is important as specific impulse is a function of the chamber pressure. When the $I_{sp}$ of two propellants are to be compared, the pressure in the two firings must be the same. The propellants have different burning rates, and the nozzle throat must therefore be modified to yield the same chamber pressure. The nozzles must have the same expansion ratio, $A_e/A_t$, which was set to 5.0. The chamber pressure during the firings was approximately 5 MPa.

The specific impulse can be defined as

$$I_{sp} = \frac{F}{\dot{m}} \qquad [m/s]$$

where F is the thrust [N] and
$\dot{m}$ is the mass flow [kg/s].

The characteristic exhaust velocity is defined as

$$c^* = \frac{P_c A_t}{\dot{m}} \qquad [m/s]$$

where $P_c$ is the chamber pressure [Pa] and
$A_t$ is the nozzle throat area [$m^2$].

The specific impulse is found using measurements of the thrust

$$I_{sp} = \frac{\int_0^{t_b} F dt}{m_{tot}}$$

where $m_{tot}$ is the propellant mass [kg] and
$t_b$ is the burning time [s].

The burning time is defined as the time interval from where the chamber pressure is 1 MPa until it again reaches 1 MPa after the motor has burned out.

| Firing no. | HMX % | $P_c$ MPa | Measured $c^*$ m/s | Measured $I_{sp}$ m/s | Calculated $c^*$ m/s | Calculated $I_{sp}$ m/s |
|---|---|---|---|---|---|---|
| 1 | 0 | 5.14 | 1524 | 2249 | 1518 | 2298 |
| 2 | 0 | 5.05 | 1528 | 2254 | 1517 | 2295 |
| 3 | 25 | 4.77 | 1500 | 2211 | 1518 | 2272 |
| 4 | 25 | 4.78 | 1500 | 2214 | 1518 | 2273 |

Table 2.1 Measured and computed values from thrust measurements.

Table 2.1 shows computed and measured values for the $I_{sp}$ and $c^*$. The calculated value is obtained when the chamber pressure from a firing is used in the program.

There is good agreement between the measured and theoretical values. For the composition without HMX, the $I_{sp}$ deviates by 2% from the calculated one. With HMX the difference is 2.7%. A certain discrepancy is to be expected due to the assumptions of chemical equilibrium and ideal gases in the program. The parallels from the tests are reproducible and differ only by 0.2% without HMX and 0.1% with HMX. The decrease in specific impulse by adding 25% HMX is measured to 1.8%. The difference was calculated to be 1.1%. The experiment supports well our calculations on energy content in the two propellant compositions.

## 3 BALLISTIC AND MECHANICAL PROPERTIES

The total amount of solids in the propellant is 87%. Addition and removal of HMX is done at the expense of the amount of AP. The content of AP consists of three particle sizes, 400 μm, 90 μm and 10–13 μm in the ratio 2.96:1.93:1. The replacement of AP with HMX is done in such a way that this ratio is maintained. The particle size of HMX used is 4.3 μm. In the tests of ballistic and mechanical properties presented, the amount of HMX varies between 10% and 30% (by weight).

### 3.1 Burning Rate and Pressure Exponent

The burning rate and the pressure exponent are calculated from the pressure/time history of static firings of 2 inch test-motors.

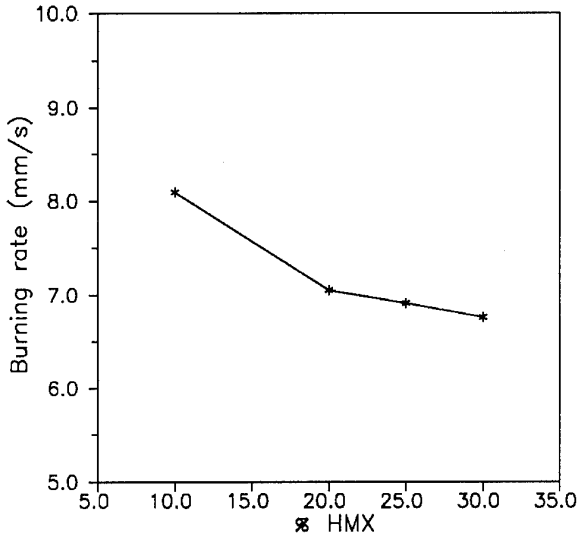



Figure 3.1 Burning rate, at 6.9 MPa, as a function of HMX content.

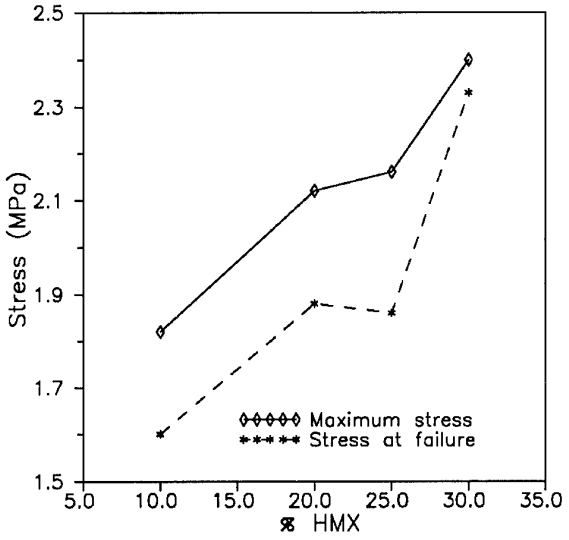



Figure 3.3 Stress as a function of HMX content.

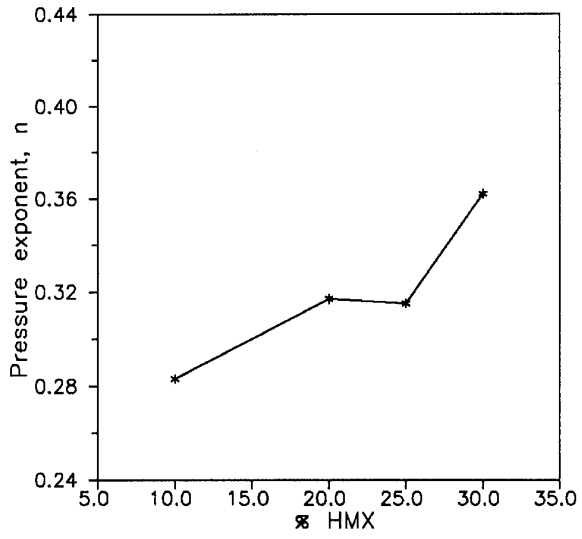



Figure 3.2 Pressure exponent as a function of HMX content.

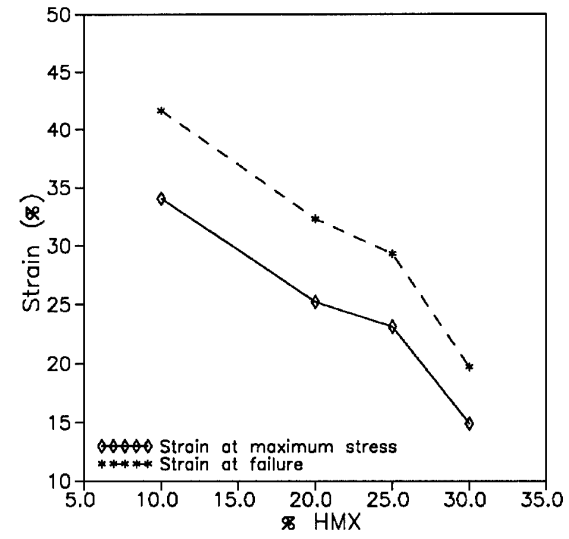



Figure 3.4 Strain as a function of HMX content.

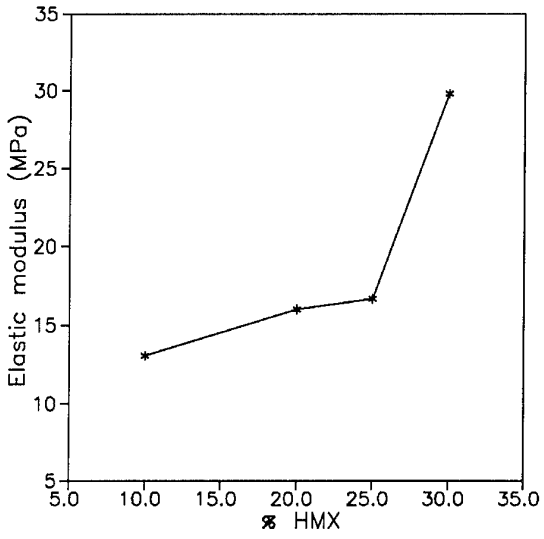



Figure 3.5 E–modulus as a function of HMX content.

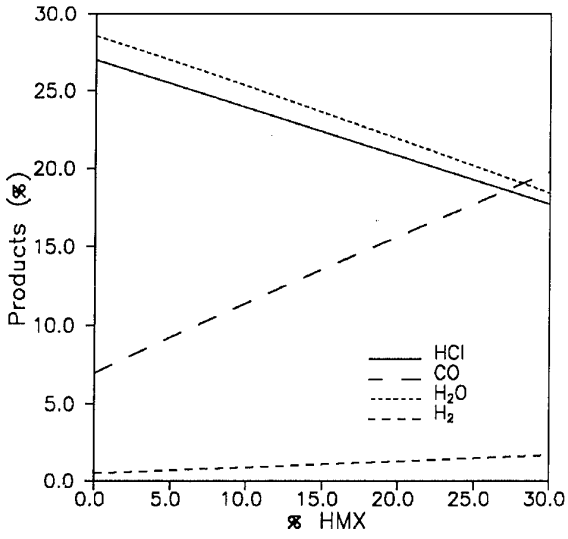



Figure 4.1 Product gases at the nozzle exit, given in weight %, as a function of HMX content. $P_c$ = 5 MPa and $P_e$ = 0.1 MPa.

Figure 3.1 shows that the burning rate of the propellant decreases as the content of HMX increases.

The pressure exponent, however, increases with increasing amounts of HMX, as shown in Figure 3.2.

### 3.2 Mechanical Properties

The mechanical properties are determined using a MTS Tensile Testing Machine. The material behaviour (stress, strain and stiffness), measured at –35°C, are shown in Figures 3.3, 3.4 and 3.5. The curves show some irregularities. This is due to the limited number of test specimens, but the results clearly indicates the mechanical behaviour.

The tensile tests indicate that by increasing the amount of HMX, the propellant becomes stiffer.

## 4 SIGNATURE

The signature of the exhaust gases of a rocket motor is a set of properties which may enable an observer to detect, identify and locate the rocket. One of these properties is the possibility of secondary smoke formation. Another property of hot gases is the emittance of radiation over a wide range of the electromagnetic spectrum.

Secondary smoke is produced when certain gases condense and create droplets in an amount large enough to spread or absorb visible light [3]. The formation takes place in the boundary layer between exhaust and air some distance behind the nozzle. Secondary smoke consists of $H_2O$, HCl, HF or other condensed gases. In a propellant with AP these gases are $H_2O$ and HCl. The amount of secondary smoke depends on the concentrations of these gases and on the temperature and relative humidity of air.

Secondary combustion, which will take place if there are large amounts of CO and $H_2$ in the exhaust, will increase the smoke formation. These gases react with $O_2$ in the air to produce $CO_2$ and $H_2O$.

The properties of the exhaust gases can be predicted by a set of computer programs. The first program [1] computes the composition of the exhaust gases at the nozzle exit, and is the same program which calculates specific impulse and flame temperatures. Figure 4.1 shows product gases at the nozzle exit for propellants with various amounts of HMX. The amounts of HCl and $H_2O$ are reduced by replacing AP with HMX. The formation of secondary smoke will therefore probably be reduced. There is, however, an increase in the amounts of both CO and $H_2$, which will cause increased secondary combustion.

From an environmental point of view a large reduction of HCl would be preferred, which means adding large amounts of HMX. However, our work was carried out under the restriction that the propellant had to be a 1.3 class material. This limits the amount to approximately 25%–30%, as will be seen in chapter 5. By increasing the HMX content from 0% to 30%, the decrease in the formation of HCl is 34%.

The gas composition at the nozzle exit is used as input to a program [4] which predicts the detailed structure of a highly turbulent, chemically reacting rocket exhaust plume. The output from this program is input to other programs which compute properties such as secondary smoke formation and IR radiation.

### 4.1 Secondary Smoke

Static firings at sea level of a rocket motor with different propellants with different amounts of HMX are simulated. The secondary smoke formation is studied as a function of the amount of HMX, the temperature and the relative humidity of the air. The results are plotted in an Oliver diagram in Figure 4.2. As can be seen, the possibility of smoke formation increases with lower temperature and higher relative humidity. The region for smoke formation increases with decreasing amount of HMX.

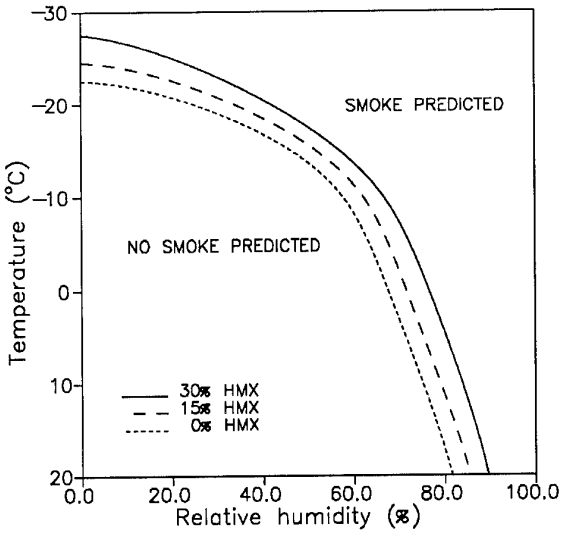



Figure 4.2 Predicted secondary smoke formation at sea level for propellants with 0%, 15% and 30% HMX.

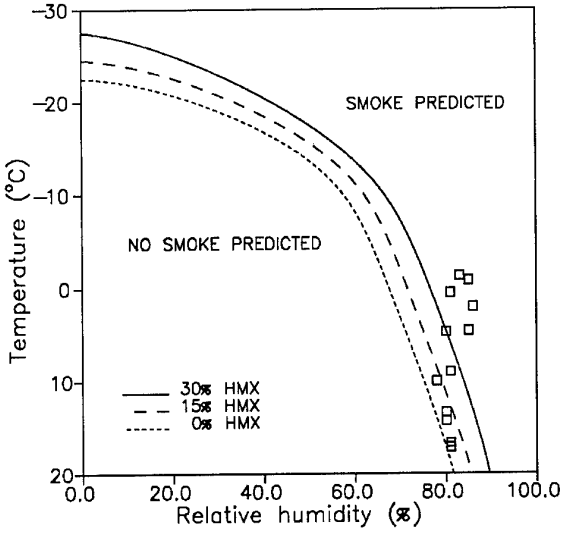



Figure 4.3 Oliver diagram with monthly mean values of temperature and humidity at Ferder Fyr.

In order to evaluate the importance of the results, plots of the monthly mean values of temperature and relative humidity at different places along the Norwegian coast [5,6] were drawn into the Oliver diagram. As an example we have used the data from Ferder Fyr shown in Figure 4.3. During the wintertime there are possibilities of smoke formation for all the propellants. During the summer, no smoke formation is predicted for the propellants with 15% and 30% HMX. At other locations where the temperature and humidity differ from those at Ferder Fyr, the smoke formation will be different.

### 4.2 IR Radiation

Hot gases emit radiation over a wide range of the electromagnetic spectrum. Exhaust gases from rockets contain relatively large amounts of water vapor and carbon dioxide. The main part of the emission will therefore take place in certain parts of the spectrum, where the emission from these gases is large.

IR radiation from rocket exhausts are calculated at different distances from the missile as a function of the amount of HMX in the propellant. The temperature was set to 0°C and the view angle was 90°.

Figure 4.4 shows total radiant intensity in the 1.5–5.6 μm IR band, as a function of path length, for propellants with different amounts of HMX. The relative humidity was 80%. Higher amounts of HMX yield larger values for the IR radiation. This was unexpected as the flame temperature is lowered as the amount of HMX increases. The explanation is that HMX lacks oxygen, compared to AP. Complete oxidation of the ingredients is not obtained. Instead the gases will undergo a strong reaction when they mix with air after they have left the nozzle exit. The temperature in this region will increase and result in increased IR radiation. The intensity decreases with increasing distance due to atmospheric absorption.

### 4.3 Verifications

In order to verify the simulations of secondary smoke formation, small scale test motors have been fired statically under different climatic conditions. Two different propellants were used, one without HMX and one with 25% HMX. The smoke evolved was recorded using a video camera.

The motor contains approximately 330 grams of propellant casted in a steel cylinder. The grain has a cylindric hole in the center. The propellant thickness is 12.5 mm. It burns radially from the inside and from both ends. The shape of the grain makes the burning surface constant during the firing. Hence the pressures in the chamber and the nozzle exit remain constant.

The firings were scheduled such that they occured under climatic conditions which would yield different results for the two propellants. The temperature and the relative humidity were measured daily with a combined thermometer/hygrometer. When suitable values of temperature and humidity were obtained, two motors, one of each kind of propellant, were fired within 5 minutes of each other. The firings took place during the summer at relatively high temperature and humidity. Figure 4.5 shows a diagram of temperature and humidity with the points from the firings plotted in.

Table 4.1 contains data on the firings and information on simulated smoke formation. Firing no. 1 was expected to evolve smoke whereas no. 2 was not. The video recordings show smoke evolution in firing no. 1. Only a little smoke was evolved in no. 2. The difference in smoke formation was obvious. It was reduced by the presence of HMX. No smoke evolution was predicted for firings no. 3 and 4, although no. 4 was close to the limit. In no. 3, which contained HMX, hardly any smoke was observed. No. 4, without HMX, produced only a small amount of smoke.

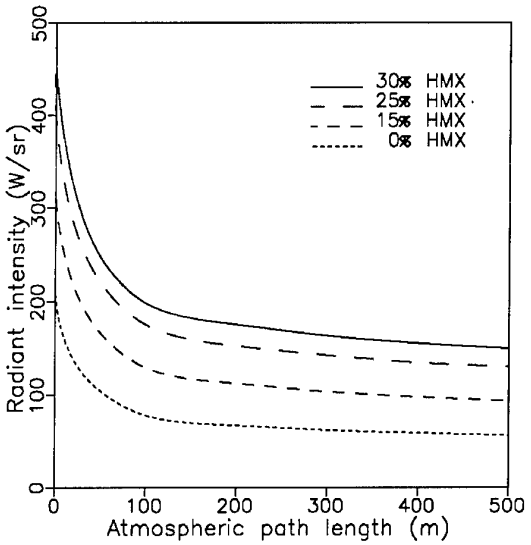



Figure 4.4 Radiant intensity as a function of atmospheric path length (for the 1.5–5.6 μm IR band).

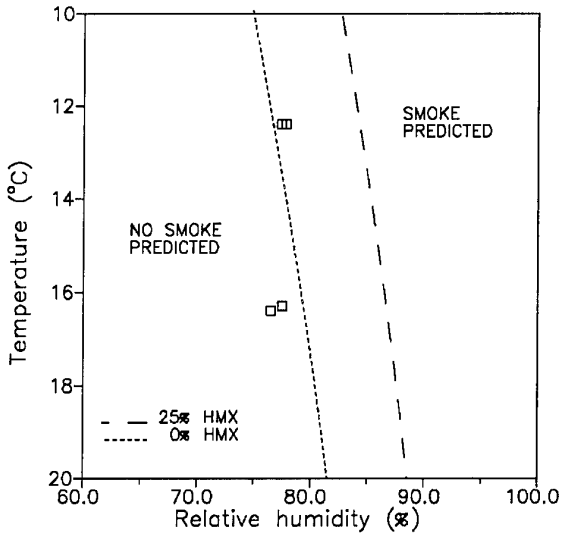



Figure 4.5 Test conditions plotted in an Oliver diagram for propellants with 0% and 25% HMX.

| Firing number | % HMX | Temperature, °C | Relative humidity, % | Smoke predicted, yes/no |
|---|---|---|---|---|
| 1 | 0 | 12.4 | 77.8 | yes |
| 2 | 25 | 12.4 | 77.4 | no |
| 3 | 25 | 16.4 | 76.5 | no |
| 4 | 0 | 16.3 | 77.5 | no |

Table 4.1 Climatic conditions during the firings and predicted results on smoke formation.

According to the simulations, firings no. 2, 3 and 4 should not have produced any visible secondary smoke. The tests show, however, that some smoke has been evolved. One explanation may be that the lines representing the limits for smoke/no smoke occur abruptly, and give no room for transition regions.

The results from the firings correlate reasonably well with the simulated predictions of smoke formation from the two kinds of propellants. Under certain climatic conditions there will be a large difference in secondary smoke formation. The firings partially confirm the calculations done on IR radiation. A strong visible flame was observed for the propellant that contains HMX. A weaker flame was obtained when no HMX was present.

## 5 HAZARD CLASSIFICATION

Solid propellants are required to burn in a controlled manner. An accident may result in fire and heat radiation. A composition such as this is classified as a class 1.3 material. A composite propellant that contains only AP and HTPB has this classification. Compositions that contain large amounts of explosives such as RDX or HMX belong to class 1.1 materials. An accident involving these materials may result in high pressure and scattering of fragments. The damage is dependent on the amount of explosives involved.

The initial propellant composition in this program contains only AP as an oxidizer and is a 1.3 material. As more and more HMX is introduced in the composition, it will become more sensitive, and the classification can change. To fulfill our needs it is desirable to add as much HMX as possible, but the propellant must remain a 1.3 material. Results from the card gap test clearly defines which class of material the composition belongs to. A number of 70 cards represents the limit between the two classes of materials. At the limit, the probability of obtaining a detonation is 0.5.

The card gap test has been performed on compositions of 30% and 25% HMX. The limits were obtained at 66 and 57 cards, respectively. Another parameter affecting the results is the particle size of the HMX particles. The detonation sensitivity will increase with the particle size. In these tests small HMX particles (< 5 μm) were used.

The hazard classification can, however, not only be based on the results from the card gap test. There are a number of tests that must be conducted before the propellant can be classified as a 1.3 material [7]. The 30% HMX composition is close to the limit denoting high explosives. Small variations in the particle sizes may result in another limit for the detonation probability. A complete hazard classification was therefore conducted on a composition with 25% HMX with a particle size less than 5 μm. This hazard classification included the following tests: card gap test, detonation test, ignition and unconfined burning test, thermal stability test, impact sensitivity test and the friction test. The results of these tests lead to a 1.3 material classification.

## 6 FUTURE WORK

We plan to replace the HTPB binder by an energetic binder. Energetic binders have mostly been used in explosives in order to obtain low vulnerability compositions. Due to the high energy of the binder the content of solids can be lowered, and the sensitivity is thereby decreased without loosing energy. The addition in our propellant is mainly to increase the energy content, but there are also other positive effects.

| AP % | HTPB % | GAP % | $I_{sp}$ m/s | $\varrho I_{sp}$ Ns/dm$^3$ |
|---|---|---|---|---|
| 65 | 10 | – | 2488 | 4338 |
| 62 | 13 | – | 2422 | 4099 |
| 60 | 15 | – | 2369 | 3934 |
| 55 | 20 | – | 2217 | 3514 |
| 65 | – | 10 | 2468 | 4539 |
| 62 | – | 13 | 2527 | 4579 |
| 60 | – | 15 | 2526 | 4531 |
| 55 | – | 20 | 2489 | 4359 |

Table 6.1 Computed $I_{sp}$ and $\varrho I_{sp}$ for propellant compositions with various amounts of HTPB and GAP binders. The amount of HMX is 25% in all compositions. $P_c$ = 6.9 MPa and $P_e$ = 0.1 MPa.

We have considered one type of energetic material, the glycidyl azide polymer (GAP). Simulations on the energy content of propellant formulations with a GAP binder have been done. The results are compared with those of an HTPB binder. The values are shown in Table 6.1. The GAP binder yields the highest values, except for the $I_{sp}$ at 10% binder matrix. The difference increases with increasing binder content. A polymer content of only 10% is not realistic due to bad processability and poor mechanical properties. We have observed that an HTPB binder content of 13% yields good properties. Due to the higher density of GAP compared to HTPB, it is necessary to have a higher binder content to obtain a processable composition. It seems that 15–20% will be a reasonable level. Energetically, the GAP binder is favorable over the HTPB binder.

Computations of the composition of the product gases at the nozzle exit for the GAP propellant shows that the amount of HCl will be approximately the same as when using the HTPB binder. However, GAP used in combination with the oxidizer hydrazinium nitroformate (HNF) will produce gases free of HCl. Simulations have shown that a further increase in energy content is to be expected [8]. The HNF is a powerful solid oxidizer, which cannot be used in combination with HTPB, due to attack of the double bonds in HTPB. GAP, however, is compatible with HNF.

HNF is produced at a laboratory scale by Aerospace Propulsion Products bv (APP) in the Netherlands. The Norwegian companies Raufoss A/S and the Norwegian Defence Research Establishment (NDRE) are seriously considering a cooperation with APP/TNO on HNF, and discussions are going on concerning test methods and worksharing.

Another explosive ingredient that has been developed recently is the energetic binder polyNIMMO, produced by ICI. This polymer together with GAP are the two binders that Norway (Raufoss, Dyno and NDRE) is investigating in the WEAG TA–25 CTP–3 "Energetic binders" program. Results from the study show that polyNIMMO is an interesting compund which we will consider in propellant compositions.

## 7 CONCLUSIONS

The effect on various properties of an AP/HTPB propellant by partially replacing AP by HMX has been studied. The effects of this modification are a lowered flame temperature and decreased secondary smoke formation. The energy content is reduced only minimally. The addition of HMX will, however, result in increased IR radiation and increased detonation sensitivity. The simulations on specific impulse, secondary smoke and IR radiation have to a certain extent been verified by static firings.

Partial replacement of AP by HMX improves the environmental properties of an AP/HTPB propellant by reducing the formation of HCl. However, when the propellant is restricted to be a 1.3 class material, the potential improvement is limited due to increased sensitivity. According to safety tests the maximum amount of HMX, with particle size less than 5 μm, is approximately 25% (by weight). This reduce the amount of HCl by 29%.

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## Discussion

QUESTION BY A.J. Mc Donald : Is the increased IR signature of the HMX propellants a result of afterburning in the outer portion of the plume from the increased CO and H2 of HMX propellants which offsets the cooler flame temperatures ?

ANSWER : Yes, that is our interpretation of the results on infrared radiation.

# Development of Less Polluting Propellants

## Characteristic Features of AN/GAP-Propellants

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## 1. ABSTRACT

Propellants based on ammonium nitrate and GAP are candidates not only for less polluting but high energetic, minimum smoke propellants with reduced sensitivity. They may act as suitable candidates for the substitution of double base propellants so far used in rocket motors for tactical defense. The difficulties for the development of such a propellant system depend on the chemical nature and problems connected to the ingredients. Drawbacks are caused by the numerous phase changes of AN, its hygroscopicity, lower energy and low reactivity. The key problems for the development are the unfavorable combustion behaviour and sometimes bad stability of AN/GAP formulations.

Some of the main features of these propellants have been developed and illustrated in this paper. These are performance, chemical stability combustion behaviour and detonation sensitivity. Four different kinds of pure and phase stabilized ammonium nitrates are compared regarding stability and combustion behaviour in propellant formulations with GAP and nitrate ester plasticizers. In consideration of stability, performance and detonation sensitivity the system of pure AN (SCAN), GAP, TMETN, BTTN without nitramines has been chosen for further development.

## 2. LIST OF SYMBOLS

| | |
|---|---|
| $I_s.\rho$ | volumetric specific impulse |
| $I_s$ | specific impulse |
| $\rho$ | density |
| GAP | Glycidyl azido polymer |
| AN | Ammonium nitrate |
| SCAN | Spray crystalized AN |
| TMETN | Trimethylolethane trinitrate |
| BTTN | 1,2,4-Butanetriol trinitrate |
| PSAN | Phase stabilized AN |
| Ni-,Cu-,Zn-PSAN | with NiO, CuO, ZnO phase stabilized AN |
| BDNPF/A | Bisdinitropropylformale-acetale |
| RDX | Cyclo-1,3,5-trimethylene-2,4,6-trinitramine (Hexogen) |
| PMMA | Polymethacrylmethacrylate |
| DPA | Diphenyl amine |
| NDPA | Nitrodiphenyl amine |
| MNA | Methylnitroaniline |

## 3. INTRODUCTION

As it is known from literature a lot of work has been done on the development of AN propellants on metallized[1)] as well as on smokeless formulations.[2)] The smokeless variants of propellant systems consisting of AN and energetic binders have been provided for high energy less sensitive

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substitutes for doublebase propellants to be used for tactical missile applications. They should have higher energy, better elasticity, lower freezing point and lower sensitivity to sympathetic detonation as well as to other hazards like bullet impact, fast and slow cook off.

Formulation work has been published on Ni-PSAN/GAP-propellants with BDNPF/A[3], nitric acid esters and acido plasticizers[4], which mostly demonstrated for the propellants to have either low performance, problematical stability or a bad combustion behaviour. The same handicaps, but a slightly higher performance have been observed for PSAN-propellants with nitramine binders.[5]

Nevertheless the AN/GAP-system incorporates the potential for high energetic non polluting propellants, which are really less sensitive and exhibit smokeless burning.

## 4. OBJECTIVES

The objective of this work was to study the main features and influences on the properties of AN/GAP propellants. The goals for propellant development are:

* high performance: $I_S \geq 240$ s at 7 MPa
* low sensitivity to sympathetic detonation and other potential hazards
* smokeless combustion, together with non polluting solid combustion products
* acceptable, for tactical missile (TM)-application profitable burning properties
* good processibility, mechanical properties and stability

## 5. CONCEPT FOR DEVELOPMENT

Development concept includes the examination, variation and adjustment of propellant and ingredient properties concerning the non metallized propellant system based on ammonium nitrate, GAP and energetic plasticizers. The parameters which have to be adjusted are:

- solids loading, kinds and properties of solid ingredients:
  - AN- or PSAN-type and specification, application of pure or phase stabilized AN (PSAN) by reaction with
    nickel oxide - Ni-PSAN
    copper oxide - Cu-PSAN
    zinc oxide - Zn-PSAN
    and concentration of phase stabilizing oxide
  - particle size distribution of AN or PSAN
  - addition of nitramines, types, specification and particle size distribution
- GAP-specification
  - its functionality and molecular weight
  - type of curing agent, NCO/OH-value
- energetic plasticizers
  - types, energy and percentage incorporated in the propellant
  - GAP/plasticizer ratio
- further additives
  - like contents and specification of burn rate modifiers, adhesion promoters and stabilizers.

ICT has the advantage to have developed a process for the manufacturing of AN and different types of phase stabilized

ammonium nitrate by spray atomization from the melt, which are tailored for propellant application. The AN and PSAN products are manufactured with small particle sizes, spherical shape and low water content. Types and properties are listed in fig. 1. If pure AN has been sprayed from the melt, its particles have a water content of 0,02 to 0,04 %. The absence of water prevents the AN from undertaking the deteriorating crystal transition to phase III between 30 °C and 40 °C.[6)]

For this reason the pure ammonium nitrate derived from the spray atomization process was involved in the development process, too. It is further named as SCAN = spray crystallized ammonium nitrate.

The density of SCAN and PSAN types are outlined in fig. 2. Due to a higher density of Ni- and Cu-PSAN, propellants with these PSAN types can be processed to higher solid loadings. With an appropriate particle size distribution solid loadings up to 75 % are possible for the Ni-PSAN/GAP/TMETN system. For SCAN-propellants only 70-72 % are possible including 5-10 % RDX with small medium particle size (5 µm).

The 3 % level of metal oxide phase stabilizer seems to be the optimum between phase stabilizing effect[6)] and performance loss, connected to the partial replacement of AN by metal complex. SCAN, Ni-PSAN with 3 % $Ni_2O_3$, Cu-PSAN with 3 % CuO and Zn-PSAN with 3 % ZnO have been involved in the development of propellants, mostly with the two mean particle sizes of 160 µm and 55 µm.

Main emphasis was taken on finding solutions for the key problems of AN-propellants:

* performance
* stability and
* combustion behaviour.

## 6. THERMOCHEMICAL PERFORMANCE CALCULATIONS

Thermochemical calculations were performed with a largely realistic high energetic propellant system based on:

| | |
|---|---|
| AN: | 40 - 80 % |
| GAP/N100: (9:1) | 10 - 60 % |
| BTTN/TMETN: (4:1) | 0 - 50 % |

From literature data and comparative calculations it was known, that high values for the specific impulse of AN/GAP propellants are only achievable with nitrate ester plasticizers, and BTTN/TMETN to be those with the highest energy and compatibility with GAP.[4)] The values calculated for the specific impulse and volumetric specific impulse with a 70 : 1 expansion ratio are outlined in fig. 3 and fig. 4. The corners of the triangle represent compositions of:

* 60 % GAP/N100, 40 % AN, 0 % plasticizer
* 100 % AN, 0 % GAP, 0 % plasticizer
* 60 % plasticizer, 40 % AN, 0 % GAP

The lines mark 5 % concentration steps in each direction.

It is clearly to be seen that the demanded high values of specific impulse $I_{sp}$ = 240 - 245 s (70:1) are only fulfilled for compositions with a high plasticizer content. Due to the higher density of AN the maximum value for the volumetric specific impulse is located at 70 % AN, 10 % GAP and 20 % BTTN/TMETN with 3810 Ns/dm³. The weight related specific impulse, however, is calculated to be 239,9 s for that composition. Including stabilizers and burn rate modifiers the maximum value of the specific impulse for the

AN/GAP propellant system without nitramines will not exceed 235 s with a 70:1 expansion ratio.

## 7. CHEMICAL STABILITY

Stability of the AN/GAP-propellant system is expected to be a crucial property because all the main components may originate gas evolution and decomposition effects.[3,7,8] For this reason a lot of stabilizing agents have been tested in SCAN- and Ni-PSAN/GAP/TMETN-formulations. The most important results are pointed out in fig. 5 and fig. 6.

For the Dutch Test the percent weight loss from 8 - 72 h storage at 105 °C should not exceed the 3 % level, for vacuum stability the gas evolution from a 2,5 g sample for 40 h at 100 °C should not exceed 5 ml or 0,5 - 1 ml at 80 °C respectively.

Looking at the results in fig. 5 and fig. 6 it is clearly to be seen that pure AN = SCAN exhibits the best stability with GAP and TMETN. It is the only one to fulfill vacuum stability requirements at 100 °C.

Maybe due to a starting decomposition reaction of the phase stabilizing metal complexes, stability of the Ni- and Zn-PSAN/GAP/TMETN formulations is within the limit at 80 °C but not at 100 °C. Cu-PSAN, however, originates more instability, this maybe caused by incompatibility with the azido groups of GAP.

DPA, MNA and NDPA have been found to be suitable stabilizers for the AN/GAP/TMETN system. DPA seems to have the highest stabilizing efficiency regarding to these short running preliminary tests.

## 8. COMBUSTION BEHAVIOUR

Regarding literature desirable combustion properties like high burning rates and low pressure exponents never have been developed for smokeless burning AN-propellants with energetic binders. In fact the first burn rate, pressure curves of SCAN, Cu- and Zn-PSAN propellants exhibited low burn rates and high pressure exponents $n > 0,6$. These curves are shown in fig. 7. They are connected to 73 % solids loading, an AN or PSAN ratio 160/55 µm = 6:4 and a GAP/plasticizer ratio of 2:1. Due to this low amount of plasticizer and the absence of nitramines the specific impulse of these formulations is calculated to be as little as 210 - 214 s (70:1). The phase stabilizing copper complex in Cu-PSAN originates a strong burn rate enhancing effect compared to Zn-PSAN and pure AN.

Addition of small particle size RDX (5 µm) increases the burn rates for AN and PSAN propellant systems by 10 to 20 %. This is illustrated in fig. 8. Also 3 % of a lead salt, carbon black burn rate modifier are incorporated in the propellants. The Ni-PSAN propellant developed a more promising burning behaviour under these conditions due to the burn rate enhancing effect of the nickel complex in Ni-PSAN. The calculated specific impuls, however, due to the low amount of plasticizer is as low as 218 s (70:1).

Significant improvement resulted with change of the AN particle size distribution and a new burn rate modifier for all AN and PSAN propellants. This is illustrated in fig. 9 and fig. 10. All propellants exhibit pressure exponents below 0,6. The most remarkable effect is seen with Cu-PSAN ($n = 0,49$).

The burn rates of the Ni- and Cu-PSAN propellants exceed 8 mm/s at 7 MPa, those of Zn-PSAN and SCAN propellants are between 7 and 8 mm/s at 7 MPa. The burn rate enhancing effects of the Ni- and Cu-PSAN oxidants are clearly to be seen in these formulations.

Due to a GAP/plasticizer ratio of 1:1 the specific impulse of these propellants is

between 226 - 229 s at 70:1 expansion ratio.

As it has been pointed out in chapter 6 further improvements in performance are only possible, if a high plasticizer content is applied. With RDX and a high plasticizer content the efficiency of the new burn rate modifier, however, diminishes. But this has not been found for propellants without RDX.

Because it also has been shown (see below) that incorporation of RDX diminishes sensitivity to detonation pressure further propellant development concentrated on systems without RDX and with optimized burn rate modification. For stability reasons (see above) work focused on propellants with SCAN = pure ammonium nitrate. Some of the results of these formulations are outlined in fig. 11. The propellants exhibit specific impulses up to 235 s (70:1) burn rates between 7 - 8 mm/s at 7 MPa and pressure exponents from n = 0,52 - 0,58. They achieve reasonable stability, which may be good enough for practical purpose.

## 9. SENSITIVITY TO DETONATION

The AN/GAP propellant system in most cases was proposed as a candidate to meet insensitive ammunition requirements. According to MIL St. 2105 the detonation sensitivity should be below 70 cards in the 40 mm Gap tst to US and UN standards. Because this also was an objective of our work, Gap tests were performed at an early stage of development. The results of 50 mm Gap test with PMMA-Gap material are illustrated in fig. 12. The detonation pressure belonging to 70 cards in the 40 mm Gap test roughly corresponds to a 28 mm Gap thickness in the 50 mm test. As it can be seen in fig. 13 propellant formulations with 10 and even 5 % RDX are clearly above this limit. Only AN/GAP formulations without RDX fulfill the insensitive ammunition requirements.

## 10. CONCLUSION

In this work the main features of AN/GAP propellants have been developed to meet the objectives of low sensitivity, smokeless combustion, non polluting combustion products and high performance.

For stability reasons pure AN in the form of spray crystallized ammonium nitrate (SCAN) has been preferred for other phase stabilized AN products. To meet sensitivity requirements nitramines have not been incorporated in the final formulation. A high performance is connected to a high plasticizer content in these propellants. The limit for the specific impulse of nitramine free formulations is roughly 235 s, because stabilizer and burn rate modifier are necessary to achieve reasonable stability and combustion behaviour. The latter is influenced by the AN particle size distribution, the GAP/plasticizer ratio, RDX content, Cu- or Ni-PSAN oxidants and suitable burn rate modifiers.

In consideration of stability, performance and detonation sensitivity the following system has been chosen for further development:

| | | |
|---|---|---|
| AN (SCAN) | : | 65 % |
| GAP | : | 10 % |
| TMETN/BTTN | : | 21,5 % |
| DPA | : | 0,5 % |
| Burn rate modifier | : | 3 % |

* The theoretical performance of this system amounts to:

$I_s$ = 234 s

$I_{sp} \cdot \rho$ = 3680 Ns/dm$^3$

for a 70 : 1 expansion ratio.

* The chemical stability is within the limiting values up to 100 °C.

* With a new burn rate modifier burn rates r = 7-8 mm/s at 7 MPa and pressure exponents
  n = 0,52 - 0,58 (2-25 MPa)
  are achievable.

* The processibility is good for 66 - 68 % solids loading with a higher percentage of 55 µm AN and without RDX.

* Without RDX the propellant has a low detonation sensitivity with 4 mm PMMA-Gap corresponding to 236 kbar detonation pressure and meets the requirements for a class 1.3 propellant.

* According to thermochemical calculations the propellant has an AGARD PEP coefficient = 0,35 for primary signature, which corresponds to an AA classification.

## 11. ACKNOWLEDGEMENTS

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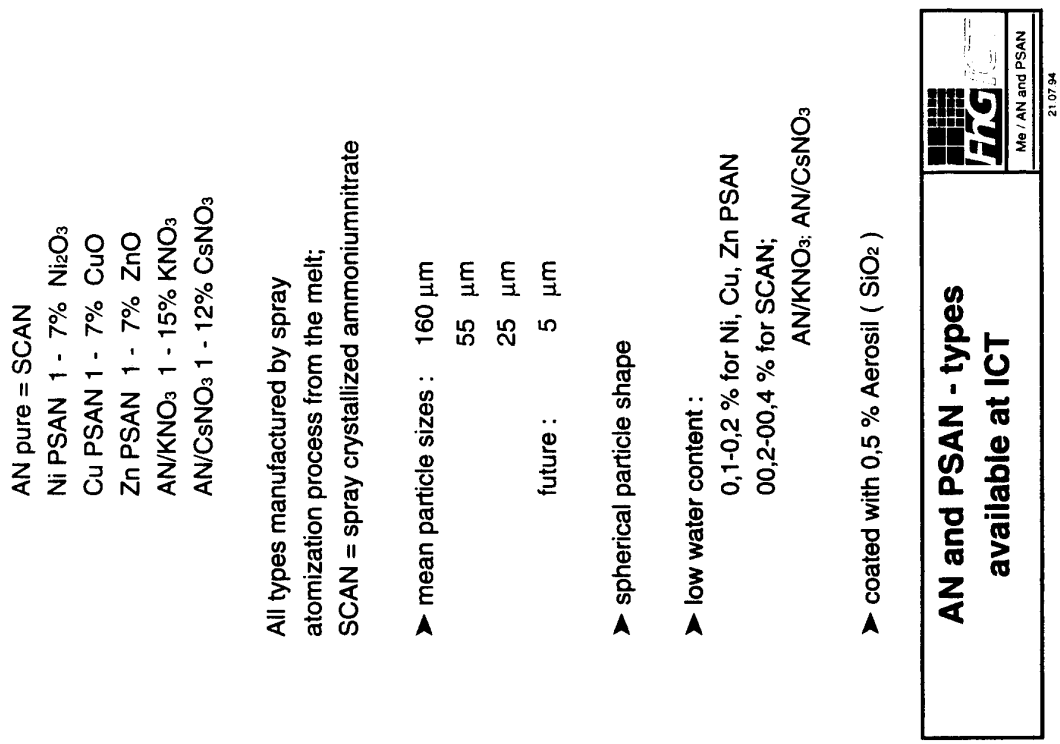



Fig. 1: AN and PSAN-types available at ICT

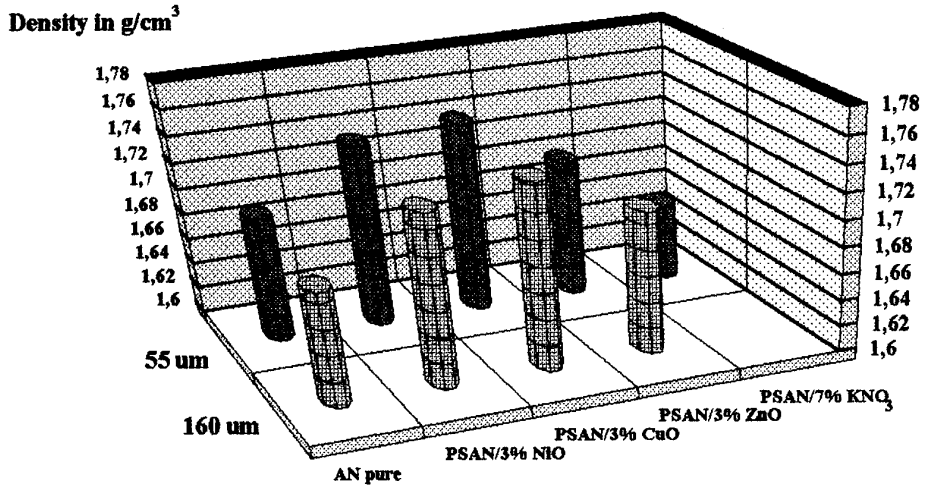



Fig. 2: Density of AN and PSAN types with 160 µm and 55 µm mean particle size

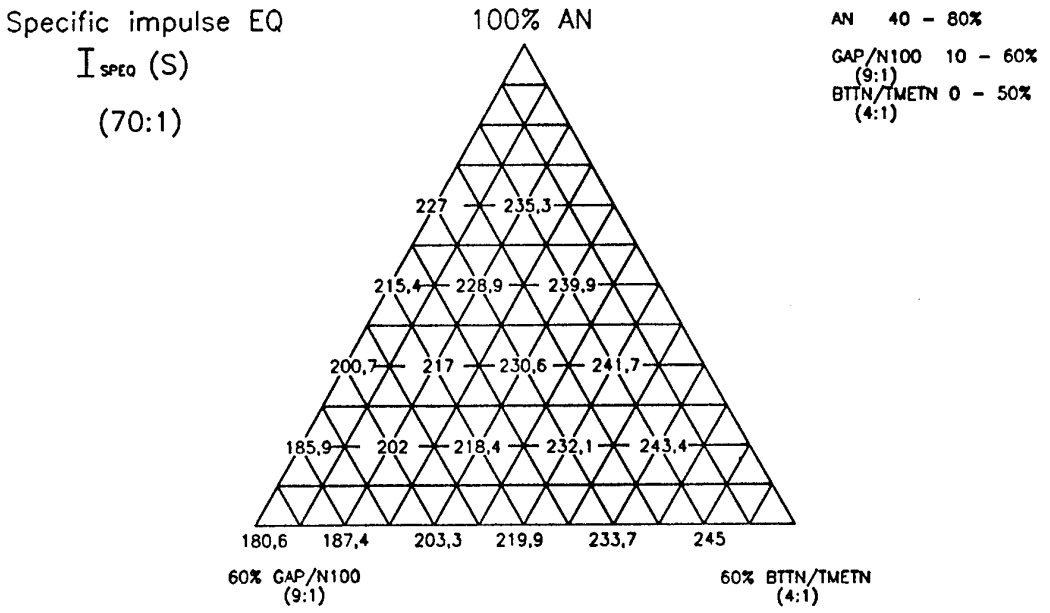



Fig.3: Calculated specific impulse of AN/GAP/BTTN/TMETN-formulations (70:1)

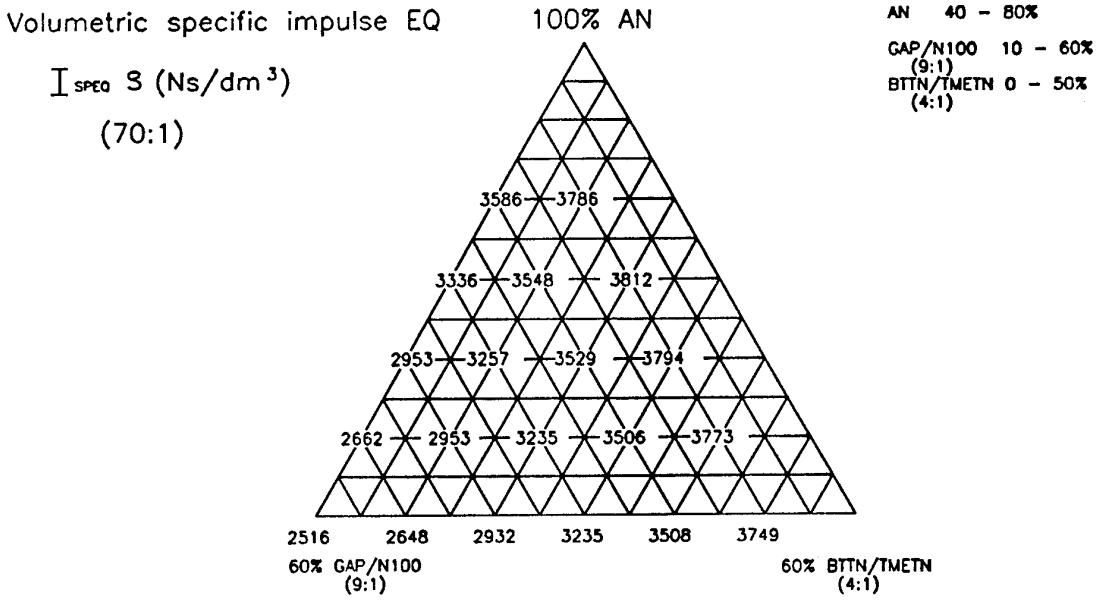
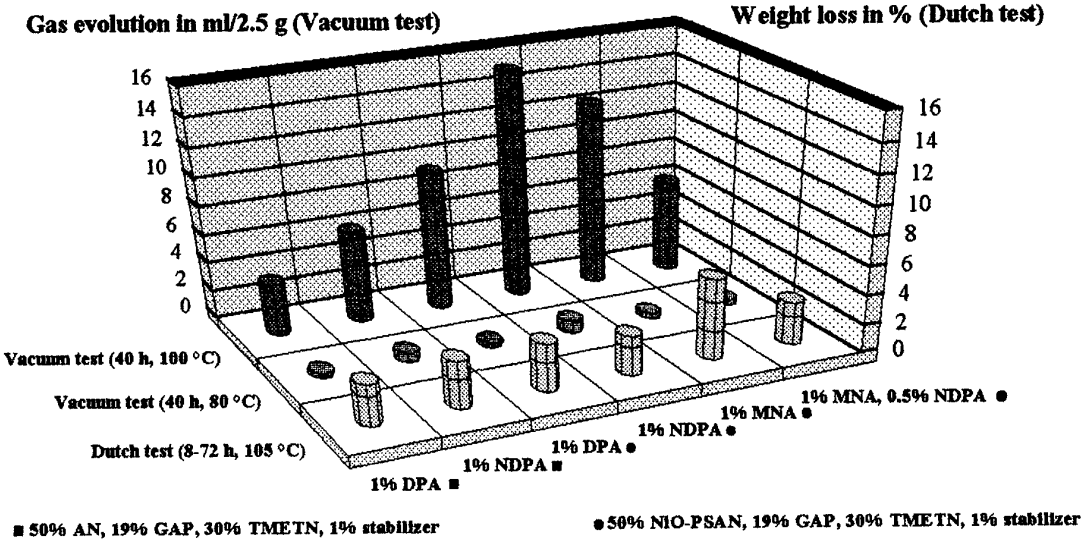
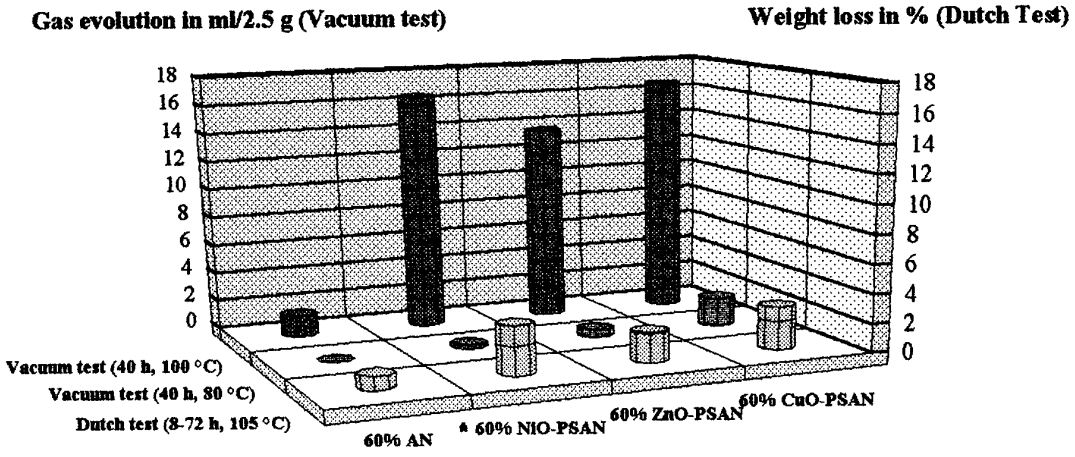



Fig.4: Calculated volumetric specific impulse of AN/GAP/BTTN/TMETN-formulations (70:1)




*AN- or NiO-PSAN/TMETN formulations with different stabilizers*

Fig. 5: Results of Dutch test and vacuum stability of AN/GAP- and Ni-PSAN/GAP-formulations with different stabilizers




* *NDPA as stabilizer*

*AN- or PSAN/TMETN/RDX formulations with 0.5% DPA as stabilizer*

Fig. 6: Results of Dutch test and vacuum stability of AN/GAP- and PSAN/GAP-formulations

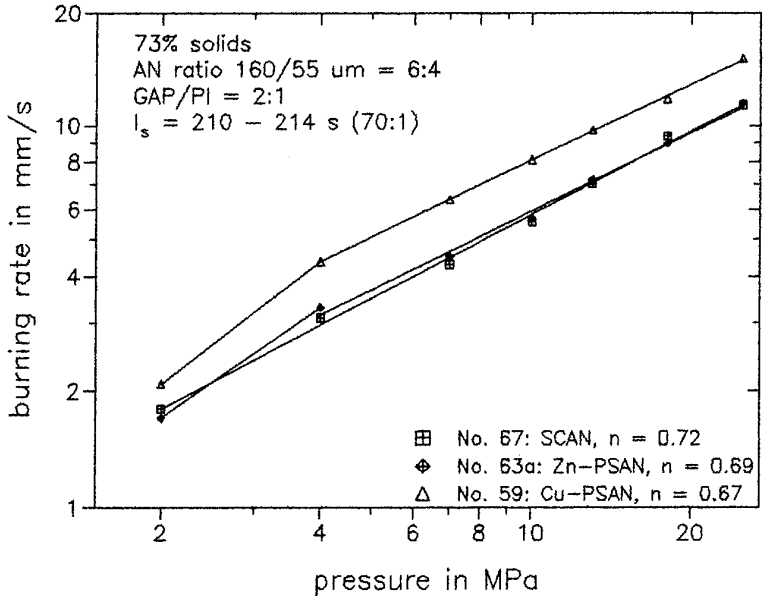



Fig. 7: Burning behaviour of Cu–PSAN, Zn–PSAN and SCAN/GAP propellants without RDX and low contents of plasticizer (TMETN)

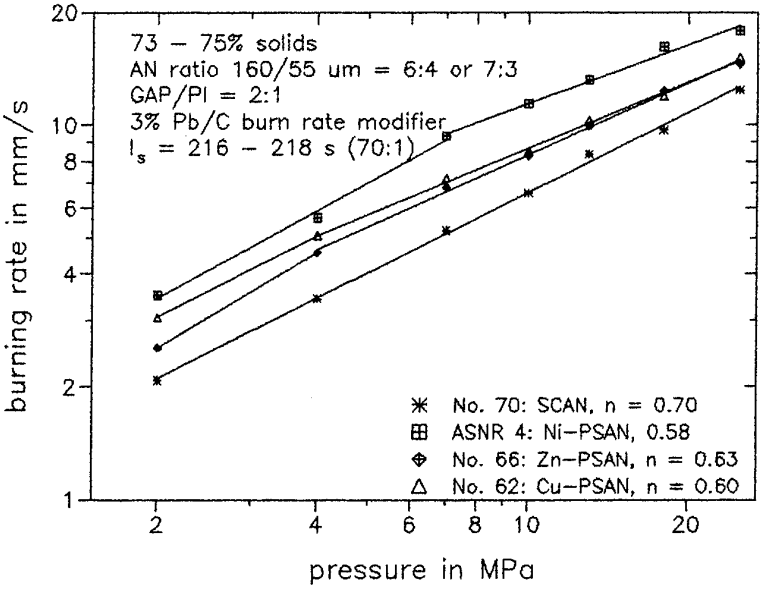



Fig. 8: Burning behaviour of Cu–PSAN, Zn–PSAN Ni–PSAN and SCAN/GAP propellants with 10% RDX and Pb/C burn rate modifier

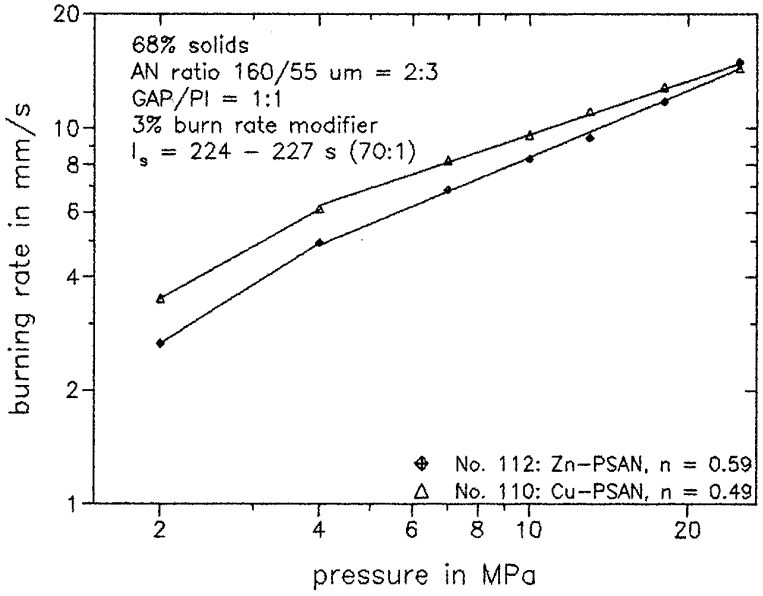



Fig. 9: Burning behaviour of Cu–PSAN and Zn–PSAN/GAP propellants with 10% RDX

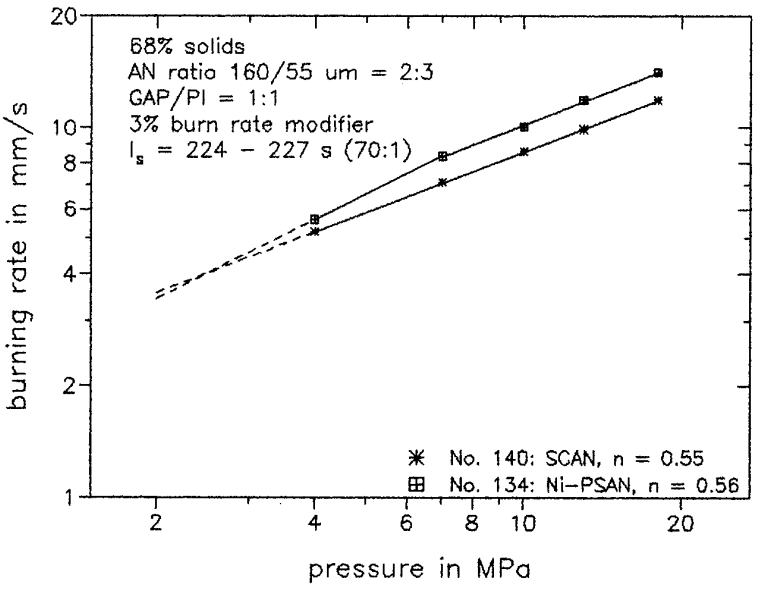



Fig. 10: Burning behaviour of Ni–PSAN and SCAN/GAP propellants with 10% RDX

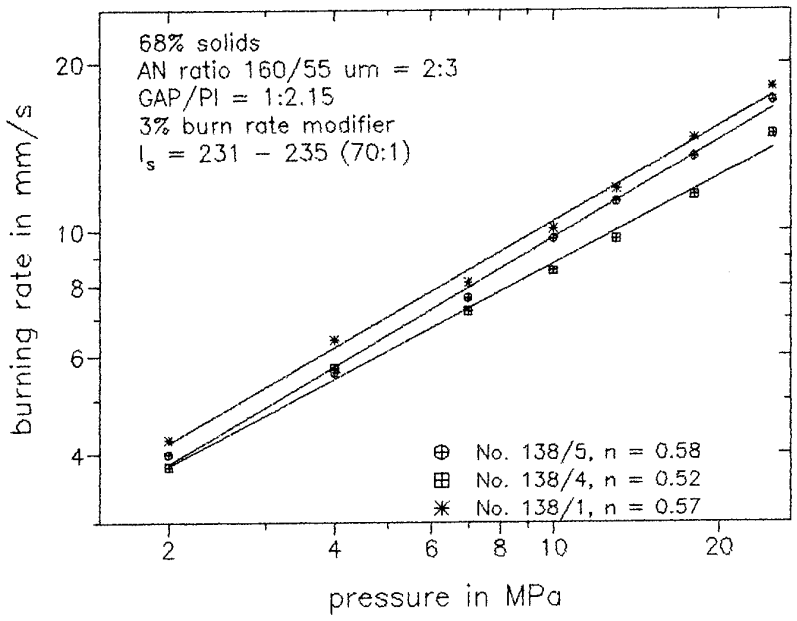
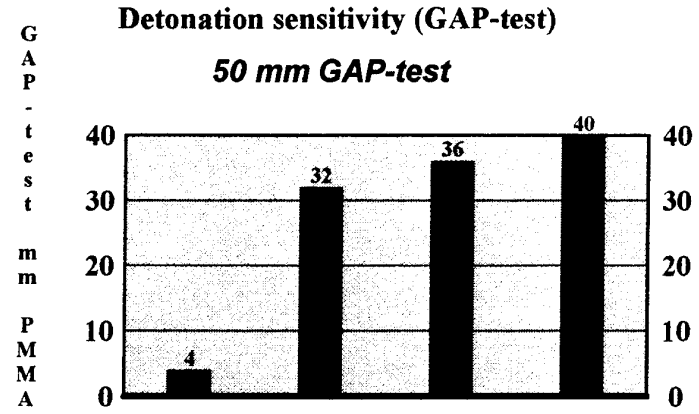



Fig. 11: Burning behaviour of SCAN/GAP propellants without RDX and high plasticizer content (GAP/Pl. = 1: 2.15)




| RDX (%) | 0 | 5 | 10 | 10 |
|---|---|---|---|---|
| TMETN (%) | 21.5 | 21.5 | 15.5 | 7.5 |
| BTTN (%) | - | - | - | 14 |
| initiation pressure (kbar) | 236 | 65 | 55 | 43 |

**AN/GAP formulations with 68% solids**

Fig. 12: Results of 50 mm Gap-tests from AN/GAP propellants with varying amounts of RDX and TMETN/BTTN plasticizer

## Discussion

QUESTION BY C. PERUT : Pourriez-vous donner une indication concernant les propriétés mécaniques ? Sont-elles de nature à influer sur les résultats Card Gap Test ?

ANSWER : The AN/GAP propellants we have examined in Gap Test exhibited viscoelastic mechanical properties at high, low and normal temperatures with roughly 0,2-0,3 N/mm2 tensile strength, 20 % elongation and 2-3 N/mm2 modulus. Up to now we haven't looked at any influence on the detonation sensitivity, but probably are going to do this in the next future.

QUESTION BY C. CARRIER : Are you not concerned by the reported toxicity of NiO-PSAN ?

ANSWER : We have taken into account the toxicity of NiO-PSAN, but have included it in our work because NiO is one of the best phase stabilizing agents for AN. Also a lot of work has been done on NiO-PSAN propellants in the past. As it has been pointed out NiO-PSAN also has a favorable influence on combustion behaviour. Due to stability and toxicity however we chose a formulation based on pure AN.

# Development of Environmentally Acceptable Propellants

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## 1. SUMMARY

The propellant formulators at the Naval Air Warfare Center Weapons Division, China Lake, CA, following the guidelines of Insensitive Munitions and the global emphasis on a clean environment, have been developing environmentally responsible and insensitive propellant formulations for future weapon use. In this paper, a family of minimum-signature propellants composed of GAP and AN will be described. These propellants have shown excellent processing, mechanical, and combustion properties. In addition, they are considerably less sensitive to shock, heat, and mechanical impact than the conventional propellant material.

This paper also summarizes the results of studies conducted on ADN to establish its properties when used in propellant applications. The research work primarily involved determining the safety characteristics of neat ADN and ADN propellant compositions, evaluating the thermocompatibility of ADN with a number of energetic binder ingredients, and examining the processing and aging properties of potential energetic binder/ADN propellants.

## 2. NOMENCLATURE

| | |
|---|---|
| ABL | Allegany Ballistics Laboratory |
| ADN | ammonium dinitramide |
| AN | ammonium nitrate |
| AP | ammonium perchlorate |
| BIC | ballistic impact chamber [test] |
| BTTN | 1,2,4-butanetriol trinitrate |
| BVR | burn-to-violent reaction [test] |
| DSC | differential scanning calorimetry |
| DTA | differential thermal analysis |
| $Fe_2O_3$ | iron (III) oxide |
| GAP | glycidyl azide polymer |
| HCl | hydrochloric acid |
| HMX | cyclotetramethylenetetranitramine |
| HTPB | hydroxyl-terminated polybutadiene |
| kP | kilopoise |
| MNA | N-methyl-p-nitro aniline |
| NAWCWPNS | Naval Air Warfare Center Weapons Division |
| NF | no fire |
| NOL | Naval Ordnance Laboratory |
| PGN | polyglycidyl nitrate |
| RDX | cyclotrimethylenetrinitramine |
| SCB | slow cookoff bomb [test] |
| TEGDN | triethyleneglycol dinitrate |
| TGA | thermogravimetric analysis |
| TMETN | trimethylolethane trinitrate |
| VTS | vacuum thermal stability |
| E | modulus, psi |
| $\varepsilon_b$ | elongation at break, % |
| $\varepsilon_m$ | strain at maximum tensile stress, % |
| $\sigma_m$ | maximum stress, psi |

## 3. INTRODUCTION

High-performance energetic materials continue to be critical for future weapons development. However, toxicity to humans, environmental concerns in production, demilitarization, and other life-cycle phases of energetic materials have also become critically important issues. Solid rocket propellants that have been developed in the past do not permit easy disposal in an environmentally responsible manner, nor do they have the low observability characteristics desired in many applications today. In addition, energetic materials developed in the past do not take hazard susceptibility into consideration.

The use of AN as an oxidizer for insensitive minimum-signature propellants is of great interest to researchers in the propellant formulation community. This ingredient is characterized by minimal pollution, low-signature combustion products, and relatively low sensitivity to shock and impact initiation. Using both AN as the oxidizer and GAP as the binder, minimum-signature propellant materials were produced. These formulations are compatible with the clean environment concept from both the clean exhaust and ease of disposal aspects.

ADN and ADN propellant materials have been also characterized and seem to hold great promise.

## 4. GAP/AN PROPELLANTS PREPARATION AND COMPOSITION

GAP/AN propellants are composed of energetic binders and low levels of fine solid oxidizers. The solid material consists of superfine HMX or RDX and anhydrous AN. The energetic binder is composed of GAP and a nitrate ester mixture of BTTN and TMETN.

Processing of the propellant consisted of adding the solids mixture to the binder ingredients in a conventional vertical shear mixer. After solids addition, a 2- to 3-hour vacuum mixing cycle occurred before curative addition. The end-of-

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mix viscosity was 2 to 3 kP at 110°F, and the mix remained castable for more than 5 hours. Multiple gallon mixes have been made.

## 5. GAP/AN PROPELLANTS EXPERIMENTAL RESULTS

### 5.1 Mechanical Properties

The mechanical properties of GAP/AN propellant were extensively characterized at 75, 145, -40, -50, and -65°F. The strain rates used were 0.2, 2.0, and 20.0 in/min. The results are listed in Table 1. GAP/AN propellant exhibited extremely good mechanical properties at all the temperatures tested. The exceptionally good strain capability (over 50%) at low temperatures (-50 and -65°F) has been known to be one of the most difficult properties to achieve in propellants containing GAP and AN. This is because GAP is not as good as inert polymers in terms of load bearing, and AN provides rather limited capability as a solid reinforcement compared to HMX or RDX.

### 5.2 Hazard Sensitivity

Table 2 provides the results of hazard testing conducted with GAP/AN propellant and compares them with the results obtained with a conventional Class 1.1 minimum-signature propellant. These data clearly indicate that GAP/AN propellants are much less sensitive than the conventional propellant. Burning reactions were observed in GAP/AN propellant when it was subjected to slow cookoff bomb (Ref. 1) and small-scale bullet impact and sensitivity tests (Ref. 2 and 3), while high order detonation reactions resulted with the conventional propellant. In addition, GAP/AN propellant is much less prone to shock initiation, as indicated by the NOL card gap test results (Ref. 4); it requires more than 76 kbar of pressure to initiate the shock-to-detonation reaction in this new propellant, while a pressure of less than 30 kbar will cause the conventional Class 1.1 propellant to detonate in the same test.

### 5.3 Aging Experiments

The propellant was cast into 6- x 6-inch cylinders for aging stability tests. The following conditions were set: 140°F isothermal, and temperature cycling from 150°F to -50°F. The mechanical properties of aged material were assessed at various time intervals and the results, as shown in Tables 3, 4, and 5, indicated that the mechanical properties of the propellant remained good throughout the aging period. No detectable weight loss, dimensional change, or burn rate change were found when the aged material was compared with the virgin propellant.

The effect of humidity on this propellant was assessed by conditioning the propellant samples in chambers with different relative humidities at ambient temperature. The results showed that the propellant retained good mechanical properties even after two weeks conditioning at 50% relative humidity. However, the propellant has not been tested at temperatures higher than ambient or relative humidities higher than 50%.

## 6. ADN EVALUATION

ADN is also being evaluated as a solid material for additional performance enhancement. ADN is a very powerful oxidizer which, according to calculations, can replace AP in propellant compositions to give equal or greater performance than conventional HTPB/AP propellants. The development of ADN propellants would eliminate toxic HCl from solid rocket motor exhaust thereby greatly minimizing the secondary smoke signature that is caused by the nucleation/condensation of water vapor and HCl mixtures. However, ADN has only recently been synthesized in the United States. Mr. Z. Pak, a scientist from the Russian Academy of Natural Science, has published, early in 1993, a paper (Ref. 5) that reveals the development of ADN propellants in his country (Ref. 6 and 7). This paper has stimulated a lot of interest in ADN propellant research work.

### 6.1 Safety Properties of ADN and ADN Propellants

As a neat solid, ADN melts at 92-94°C, has a density of 1.8 g/cm$^3$, and a measured heat of formation of -289 cal/g. It does not show any phase change between -100 and +100°C at ambient pressure.

The ADN used in this work was made by Dr. Bill Norris and recrystallized to remove AN and other contaminants.

The safety properties of ADN are summarized in Table 6. ADN, as a neat solid material, has shown to be slightly more impact and friction sensitive than HMX or RDX.

Hand mixes of propellant were made with ADN and GAP/BTTN or PGN/BTTN binders. Samples were mixed and cured with no problems at 120°F. These samples were submitted for safety testing. The results, as illustrated in Table 7, showed that the propellant samples have impact and friction sensitivity characteristics similar to the neat ADN solid. This means that, when ADN was combined with nitrate-ester-containing binder, the nitrate esters did not sensitize the ADN in the propellant mixture. On the other hand, when AP was introduced into the nitrate ester plasticized binders, the mixtures became very sensitive to impact (50% point, <5 cm) and friction (<100 lbs in ABL friction test).

### 6.2 Thermochemical Compatibility of ADN and Various Energetic Binders

TGA and DSC analyses were conducted on samples of ADN (>99.5% purity). The results showed it to be less thermally stable than HMX or AP. When neat ADN was heated, it began to lose weight around 120°C, and exhibited a 1% weight loss at 128°C; on the contrary, HMX and AP do not begin to lose weight until temperatures exceed 200°C.

The VTS and DTA data of ADN with GAP/BTTN and GAP/GAP azide binders are listed in Table 8. All the samples showed that ADN had good compatibility with the other ingredients when tested at 80°C. The onset of weight loss, as indicated by DTA data, did not occur until the temperature reached over 139°C.

It has been observed in the laboratory that ADN degrades to form ammonium nitrate when exposed to ultraviolet light. Its half life can be as short as 5 days, depending on the amount of sunlight or fluorescent light the samples are exposed to. Hygroscopicity may be another problem associated with ADN. Extra precautions were taken to store ADN and ADN propellant samples in a dark and dry environment.

### 6.3 Aging and Stability of ADN Propellants

Propellant samples (five-gram hand mixes) containing ADN and various binders were prepared. The binders included GAP/BTTN, GAP/TMETN/TEGDN, and GAP/GAP azide.

A preliminary aging study of these samples was conducted. The specimens were placed in an oven and aged at 160°F for 8 weeks. The samples were removed every two weeks for ADN analyses. Dr. Mel Nadler of NAWCWPNS has developed a simple and effective method to measure the amount of ADN in situ by using Fourier transform Raman spectroscopic techniques. Raman spectroscopy (Ref. 8) is a technique that consists of measuring the laser light scattering of a molecule when it is going through symmetrical vibrations that give rise to the largest change in polarization. A Nicolet Fourier transform Raman spectrometer equipped with a near infrared device (Nd:YAg laser, 1.064 μm) was used, and the light scattering data were processed with an interferometer.

ADN propellant samples aged for 0, 2, 4, 6, and 8 weeks were analyzed; the results indicated that the ADN present in the three binders showed little or no decomposition. All of the 8-week-old samples had similar amounts of ADN; they also exhibited good physical properties and negligible amounts of AN, which is considered to be the decomposition product of ADN. A nitrate ester stabilizer, MNA, was incorporated (0.7%) in the ADN propellants. The residual amounts of MNA in the propellant samples are being analyzed.

## 7. CONCLUSIONS

Both AN and ADN are attractive ingredients for developing insensitive, less polluting propellants, since AN is a natural fertilizer and ADN will decompose to AN when exposed to sunlight. AP-containing propellants have raised concerns such as toxicity to humans and animals and future disposal. Replacing AP with AN or ADN would eliminate HCl pollution, reduce toxicity levels, achieve insensitivity, and simplify the waste disposal problem.

Preliminary work indicates that GAP/AN propellants hold promise as replacements for state-of-the-art minimum-signature propellants and provide some improvements in environmentally friendly qualities.

The preliminary evaluation work on ADN and ADN propellants gave also very encouraging results. The safety data indicated that ADN has safety properties similar to those of RDX and HMX. ADN appears to be compatible with many energetic binders, and, most importantly, it showed good long-term aging stability (i.e., 160°F for 8 weeks) when it was used with GAP/BTTN and GAP/GAP azide binders.

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**TABLE 1. Mechanical Properties of GAP/AN Propellant (25-Gallon Mix).***

| Temperature (°F) | Strain Rate (in/min) | E (psi) | $\sigma_m$ (psi) | $\varepsilon_m$ (%) | $\varepsilon_b$ (%) |
|---|---|---|---|---|---|
| 145 | 0.2 | 189 | 62 | 42 | 42 |
| | 2.0 | 222 | 62 | 34 | 34 |
| | 20.0 | 272 | 81 | 39 | 39 |
| 75 | 0.2 | 219 | 81 | 47 | 48 |
| | 2.0 | 270 | 87 | 43 | 44 |
| | 20.0 | 330 | 96 | 41 | 41 |
| -40 | 0.2 | 914 | 284 | 48 | 52 |
| | 2.0 | 1300 | 374 | 57 | 64 |
| | 20.0 | 1724 | 505 | 69 | 75 |
| -50 | 0.2 | 1264 | 392 | 56 | 60 |
| | 2.0 | 2068 | 514 | 61 | 67 |
| | 20.0 | 3800 | 669 | 59 | 70 |
| -65 | 0.2 | 3314 | 704 | 52 | 57 |
| | 2.0 | 12578 | 937 | 22 | 50 |
| | 20.0 | 76931 | 1717 | 8 | 18 |

* Standard JANNAF tensile specimen.
Engineering data based on original area.

**TABLE 2. Summary of Subscale Hazard Test Results.**

| Test | Class 1.1 Propellant | GAP/AN Propellant |
|---|---|---|
| SCB | Detonation | Burning |
| NOL card gap, # of cards (kbar) | 170 (30) | 58 (76) |
| BIC, psi/s | 954 | 18 |
| BVR | Detonation | Burning |

**TABLE 3. Aging/Mechanical Properties of GAP/AN Propellant.* (Aging accomplished at 140°F isothermal in 6- X 6-inch cylinders.)**

| Time | E (psi) | $\sigma_m$ (psi) | $\varepsilon_m$ (%) | $\varepsilon_b$ (%) |
|---|---|---|---|---|
| 0 | 270 | 87 | 43 | 44 |
| 1 week | 230 | 82 | 44 | 45 |
| 2 weeks | 230 | 79 | 40 | 42 |
| 4 weeks | 258 | 84 | 43 | 43 |
| 6 weeks | 253 | 81 | 42 | 42 |
| 8 weeks | 255 | 83 | 40 | 42 |
| 10 weeks | 252 | 83 | 45 | 45 |

* Standard JANNAF tensile specimen, 2 in/min (uniaxial), 77°F.
Engineering data based on the original area.

**TABLE 4. Aging/Mechanical Properties of GAP/AN Propellant.* (Aging-humidity effect.)**

| Relative Humidity (%) | Time | E (psi) | $\sigma_m$ (psi) | $\varepsilon_m$ (%) | $\varepsilon_b$ (%) |
|---|---|---|---|---|---|
| 5 | 0 | 270 | 87 | 43 | 44 |
| 33 | 1 week | 219 | 80 | 47 | 48 |
| 50 | 2 weeks | 219 | 78 | 54 | 56 |

* Standard JANNAF tensile specimen, 2 in/min (uniaxial).
Engineering data based on the original area.
GAP/AN propellant survived well at 50% relative humidity for two weeks.

**TABLE 5. Aging/Mechanical Properties of GAP/AN Propellant.* (Temperature cycling = +150 to -50°F for 9 weeks in 6- X 6-inch cylinders.)**

| Temperature (°F) | E (psi) | $\sigma_m$ (psi) | $\varepsilon_m$ (%) | $\varepsilon_b$ (%) |
|---|---|---|---|---|
| 77 | 90 | 59 | 150 | 150 |
| 145 | 100 | 45 | 75 | 75 |
| -46 | 727 | 213 | 125 | 130 |

* Standard JANNAF tensile specimen, 2 in/min (uniaxial), 77°F.
Engineering data based on the original area.

**TABLE 6. Safety Properties of ADN Compared to RDX.**

| Sample (neat solid) | Impact Sensitivity (50%, 2.5 kg, cm) | ABL Friction Sensitivity (50%, lbs) | Electrostatic Sensitivity (0.25 J) |
|---|---|---|---|
| ADN (SRI-12) | 12 | 400 | 10/10 NF |
| ADN #142121-2 | 8 | 355 | 10/10 NF |
| ADN #142119-1 | 11 | 324 | 10/10 NF |
| RDX #77L550 (class II) | 15-17 | 501 | 10/10 NF |

The conditions during testing were as follows: relative humidity = 10-20%, ambient temperature.

**TABLE 7. Safety Properties of ADN Formulations.**

| Sample (3-gram hand mixes) | Impact Sensitivity (50%, 2.5 kg, cm) | ABL Friction Sensitivity (50%, lbs) | Electrostatic Sensitivity (0.25 J) |
|---|---|---|---|
| GAP/BTTN/ADN (60%)* | 9 | 501 | 10/10 NF |
| GAP/BTTN/ADN (60%)* | 9 | 339 | 10/10 NF |
| GAP/BTTN/ADN (60%)* | 13 | 363 | 10/10 NF |
| GAP/BTTN/ADN (60%)* | 9 | 282 | 10/10 NF |
| GAP/BTTN/ADN (60%)* | 10 | 339 | 10/10 NF |
| PGN/BTTN/ADN (65%) | 9 | 200 | 10/10 NF |

* These represent five different laboratory lots of ADN prepared by Dr. Norris at China Lake.

The conditions during testing were as follows: relative humidity = 10-20%, ambient temperature.

**TABLE 8. Vacuum Thermal Stability Test Results.**

| ADN Propellant Sample | VTS at 80°C | DTA (°C) | |
|---|---|---|---|
| | | Onset | Peak |
| GAP/BTTN/ADN<br>GAP/BTTN/ADN/$Fe_2O_3$<br>GAP/BTTN/ADN/Lead citrate | 0.24, 0.15<br>0.04, 0.06<br>0.08, 0.13 | 139 | 152, 164 |
| GAP/BTTN/ADN/CL-20/$Fe_2O_3$<br>GAP/BTTN/ADN/CL-20<br>GAP/BTTN/ADN/CL-20/lead citrate | 0.07, 0.25<br>0.19<br>0.21, 0.25 | 140 | 163 |
| GAP/GAP Azide/ADN | 0.07, 0.09<br>0.09, 0.11 | 143 | 160 |

# ESTABLISHING A SCIENCE-BASED ENVIRONMENTAL CLEANUP LEVEL FOR LIQUID PROPELLANT XM46

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## SUMMARY

Liquid propellant XM46 is a developmental propellant that will be used with the regenerative injection gun in the Advanced Field Artillery System. Individuals may be accidentally exposured to XM46 during operational or maintenance procedures, and there may be residual contamination of soil or water after spills are cleaned up. XM46 is moderately toxic; the primary systemic effects are the production of methemoglobin, altered liver function, and enlargement of the spleen and liver. XM46 also produces skin irritation and is a strong eye irritant. Genotoxicity evaluations of XM46 were negative.

XM46 was further evaluated to determine its potential to produce reproductive toxicity, such as alterations in paternal fertility, maternal pregnancy and lactation, dominant lethal effects, and growth and development of offspring. A teratology study was also undertaken to determine if XM46 causes birth defects in the developing fetus. No evidence of fetal toxicity related to XM46 exposure was noted in any of the dose groups; it was concluded that XM46 is not a reproductive toxicant or teratogen in the rat. Based on the results of these studies, a Reference Dose (RfD) was established on which to base safe maximum contaminant levels for environmental exposures.

Negotiations with the U.S. Environmental Protection Agency to adopt alternative risk assessment practices are underway in an attempt to establish a scientifically defensible cleanup level.

## 1.0 INTRODUCTION

Liquid propellant XM46 is a developmental propellant for the next generation Advanced Field Artillery System. XM46 will be used as part of the regenerative injection gun system, which will replace the M109 series of 155mm howitzers. This gun will have an increased range and rate of fire compared to existing artillery systems using conventional propellants. Liquid propellant is expected to offer additional advantages over solid propellants due to significant reductions in production and transportation costs, higher storage quantities in combat vehicles and reduced vulnerability to accidents or enemy fire.

The XM46 formulation (formerly identified as LP1846) is composed of hydroxylammonium nitrate (HAN), Chemical Abstracts Service (CAS) Number 134 65 082, triethanolammonium nitrate (TEAN), CAS Number 27096 29 3, and

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water in the ratio 60.8:19.2:20.0 (v/v) HAN:TEAN:water. Both HAN and TEAN are strongly reducing and oxidizing agents and can react with many organic and inorganic materials. Impurities are generated by reaction of XM46 with components of the gun systems (e.g. metals), manufacturing intermediates, or materials introduced by improper handling after production. Decomposition leads to the formation of nitric acid and ammonium nitrate with subsequent destabilization of the propellant mixture (Klein et al., 1991).

## 2.0 SUMMARY OF PREVIOUS STUDIES

Army regulations require: a) evaluation of the potential health hazards and preparation of an initial health hazard assessment (IHHA), and b) development of an environmental assessment before a weapon system can be fielded. The IHHA report (US Army, 1991) which assessed the health hazards associated with XM46 development and future use identified dermal/ocular exposure to XM46 and inhalation of XM46 aerosol as the major hazards. The primary known systemic effect of XM46 is the production of methemoglobin (metHb) which appears in the blood soon after oral, inhalation, or dermal exposure. Increased metHb is a non-specific indicator of exposure to a chemical, and may not be the most serious consequence of exposure. Use of metHb values alone only partially measure systemic effects associated with XM46 exposure. Recently, the U.S. Army Medical Research Detachment was tasked to update toxicity information for the IHHA report for the advance field artillery system and future armored resupply vehicle. Results from toxicity studies not completed at the time of IHHA report are presented here, and this information was used to calculate an RfD upon which to base the cleanup.

XM46 produces systemic toxicity by combining with hemoglobin in the blood to form metHb, which reduces the ability of the blood to supply oxygen to body tissues. Varying degrees of anoxia (i.e., lack of oxygen to tissue) may result depending on the amount of metHb formed. Normal metHb levels are less than 2%, and a metHb value of 1.5 percent has been recommended as a biological exposure index of overexposure, without judging the degree of adverse effects. At 15% metHb cyanosis and headache, symptoms which are indicative of anoxia, occur. At 25% metHb individuals will seek medical treatment. Conversations with Poison Control Centers confirmed that methylene blue is an effective treatment for methemoglobinemia; however, it is not routinely administered unless metHb levels exceed 20%.

The systemic toxicity of XM46 is due primarily to HAN, which readily dissociates into hydroxylamine and free nitrate at neutral pH. The major health effects of XM46 (methemoglobin formation and severe skin injury are similar to those of hydroxylamine (Gross, 1985).

## 3.0 RECENTLY COMPLETED STUDIES

In a range-finding phase of a dominant lethal assay in CD-1 mice, the $LD_{50}$ of XM46 was found to be 720 mg/kg of body weight (Cooper and Caldwell, 1994a).

### 3.1 Dominant Lethal Assay

There is the potential for accidental exposure of both male and female personnel to XM46 during propellant transfer and gun loading procedures. Animal data relevant to the ability of XM46 to induce genetic damage in exposed personnel is necessary in order to assess the health risk associated with this compound. The purpose of this investigation was to assess the ability of XM46 to induce dominant lethal changes in the male gametes of the mouse. A dominant lethal alteration is one occurring in a germ cell which does not cause dysfunction of the gamete, but which is lethal to the fertilized egg or developing embryo. Induction of the dominant lethal event after exposure to a chemical substance indicates that the substance has affected germinal tissue in the test species. Dominant lethal effects are generally accepted to be the result of chromosomal damage (structural and numerical anomalies) but gene mutation and toxic effects cannot be excluded.

Previous assessments of XM46 have shown the compound not to be genotoxic. XM46 was negative in a rat hepatocyte DNA repair assay (unscheduled DNA synthesis) (Bakke, 1990) and the Chinese Hamster Ovary cell/HGPRT assay (Rudd and Lee, 1990). Inconclusive results were obtained when XM46 was tested for clastogenic effects using Chinese hamster ovary cells because only the highest dose tested induced chromosomal aberrations. The results were further confounded by the low pH of the final cell suspension since pH extremes can cause chromosome breaks (Blachman, 1990).

This study was conducted using male and female CD-1 mice and was divided into two phases. Phase I was a range finding study designed to determine the dose of XM46 to be employed in the definitive study (Phase II). In Phase I, male mice were divided into eight groups of six mice each (control and seven treatment groups). Treatment groups received a single dose of XM46 at concentrations of 914, 762, 635, 529, 500, 400, and 300 mg/kg, respectively. The control animals received sterile water. Food and water was withheld for four hours prior to treatment. Animals were weighed and observed daily for 14 days following dosing. The results of the Phase I study indicated that 400 mg/kg was the lowest dose level at which no deaths occurred. This dose was, therefore, selected as the highest dose administered in Phase II of the study.

Phase II of the study was conducted in three replicates. In each replicate 100 male mice were randomly divided into five groups of 20 animals each consisting of a negative control (sterile water), positive control (cyclophosphamide 60 mg/kg administered intra peritoneally), and three treatment groups. The treatment groups were dosed for five days with XM46 daily at the rate of 100, 200, and 400 mg/kg/day. All males were weighed daily during the five-day dosing period and for two days following dosing. Seven days following the initiation of dosing each male was caged (cohabited) with two unexposed virgin females for a period of seven days. At the end of the

seven day mating period these females were replaced with two new virgin females. This weekly mating sequence was continued for seven weeks.

Following the seven day cohabitation period, the female mice were transferred to holding cages. Fourteen days following the midweek of the cohabitation period, these females were euthanized with $CO_2$. At necropsy their uteri were examined for the presence of live fetuses, dead fetuses, and resorption sites.

Male body weight data together with the average number of implants per female were analyzed using Kruskal-Wallis nonparametric ANOVA procedures followed by Dunn's Multiple Comparison Test. The following proportional data were analyzed using a Chi-Squared Test for Independence - animals pregnant:animals mated (fertility index); number of females in each group with two or more dead implants:total number of pregnant females; number of live implants per female in each dose group: number of live implants per control female (frequency of dominant-lethal mutations). Differences were considered statistically significant at $P < 0.05$.

There were no statistically significant differences noted in fertility of any of the dose groups over the seven-week period. The results of this investigation revealed that there was no difference in overall fertility in any of the animals tested. Likewise, the number of implants per female was not affected in treated animals, suggesting that male exposure to XM46 does not effect the implantation process. In summary, there is no indication that XM46 possesses dominant lethal effects in the mouse.

### 3.2 Reproduction/Fertility Effects

A study to evaluate the potential of XM46 to produce alterations in paternal fertility, maternal pregnancy and lactation, and growth and development of offspring of Sprague-Dawley rats was performed by the use of a modified Screening Information Data Set (Kinkead et al, 1994). Findings are discussed below.

Sprague-Dawley derived outbred albino rats were assigned to groups of 12 per sex such that the mean body weights of all groups were homogeneous by statistical analysis at study initiation. Rats were observed twice daily for signs of toxic stress. Male rat body weights were measured weekly. The test compound was administered orally in drinking water throughout the study at concentrations of 200, 1000 and 2000 mg XM46 per L of water. One-half of the male rats were dosed from 14 days prior to mating and throughout the mating period for a total of 28 days. The remaining males and all female rats were dosed from 14 days prior to mating, during mating and gestation, postpartum (21 days), and for four weeks postweaning for a total of 90 days. Pups were maintained on treated water through four weeks postweaning. Opto-Varimex activity tests were performed on the parental rats: on male rats at initiation of treatment, postmating, prior to sacrifice and on dams at initiation of treatment, during the postpartum period and again prior to sacrifice.

One-half of the male rats (six per group) were necropsied following 28 treatment days. The other six male rats per group were necropsied following 90 days of treatment. Sperm count and morphology for males were evaluated. Female rats were necropsied following 90 treatment days. The spleen, liver, and kidneys were removed from representative animals and fixed in 10% buffered formalin solution. After routine processing the tissues were embedded in paraffin and stained with hematoxylin and eosin for microscopical examination. Pups were examined for gross lesions at necropsy. Blood samples were taken from fasted parental animals at sacrifice. Methemoglobin levels were measured within one hour of blood collection.

No mortality occurred in parental rats during the course of the study. No treatment-related differences were noted in mean body weights of treated rats when compared to the control groups. Water consumption significantly decreased in both sexes of treated rats when the test compound was introduced. The water consumption of the treated rats continued to be significantly less than controls throughout the 90-day study. For the duration of the study male rats consumed approximately 30, 30, and 35 mL/day resulting in a dose of 136, 67, and 17 mg XM46/kg/day for the high-, mid-, and low-dose groups, respectively. The female rats consumed approximately 18, 22, and 25 mL/day during the premating and postweaning periods resulting in a dose of 140, 80, and 20 mg XM46/kg/day for the high-, mid-, and low-dose groups, respectively. During gestation the dose increased to 230, 120, and 30, and during lactation the dose was 375, 220, and 50 mg XM46/kg/day for each group, respectively.

In males necropsied after 28 days, a treatment-related splenomegaly was evident. Relative spleen weights were increased by 400%, 290%, and 140% at the high-, mid-, and low-dose levels, respectively. Following 90 days of treatment the remaining male rats were sacrificed. Relative spleen weights measured at sacrifice were increased by 550%, 290%, and 130% at the high-, mid-, and low-dose levels, respectively.

Splenomegaly was also evident in the female rats sacrificed after 90 days of treatment. Relative spleen weights were increased by 645%, 375%, and 128% in the high-, mid-, and low-dose groups, respectively. Relative kidney weights of the high-dose female rats were also significantly increased over control values.

A treatment-related decrease in red blood cells, hemoglobin, mean corpuscular volume, mean corpuscular hemoglobin, and mean corpuscular hemoglobin concentration occurred in both sexes of rats at the conclusion of the study. These same parameters also showed a significant decrease in male rats following 28 days of treatment. Methemoglobin levels measured at the conclusion of the study were increased in both male and female rats. The metHb levels in male rat groups were increased by approximately 475%, 425%, and 200% over control values in the high-, mid-, and low-dose treatment groups,

respectively. One half the female rat groups (six/group) received untreated water for 24 hours prior to sacrifice while the remaining rats continued on treated water until sacrifice. The female rats receiving untreated water for 24 hours had metHb values approximately 275%, 280%, and 125% above control values, while those receiving treated water through sacrifice were increased approximately 580%, 450%, and 175% over controls. This finding indicates a reversibility of the metHb effect.

The treatment showed no adverse effects on mating as 100% of the animals mated. The fertility index was 90% in groups given the control and high-dose treatment, but was 100% in the mid- and low-dose groups. No significant treatment-related differences were noted in length of gestation, sex ratio, gestation index, of mean number of offspring per litter. During the 21-day lactation phase, mean pup weights showed no statistically significant difference between treated and control groups. Sperm concentration and motility did not differ significantly from those of male control animals.

No clinical signs of motor skills loss were noted during the study. This was confirmed by Opto-Varimex tests during the course of the study, where no differences in locomotor skills were found in treated or control animals.

Observed histopathologic lesions of statistical, clinical, and pathologic significance were limited to the liver, spleen, kidney, and bone marrow.

### 3.3 Teratology Study

Cooper and Caldwell (1994b) undertook a study to determine the potential threat to the unborn fetus should female Army personnel become exposed to this compound during pregnancy. Timed pregnant rats were purchased on day four of pregnancy and divided into four dose groups of 25 animals each. Animals were dosed with XM46 on days 5 through 14 of pregnancy at the rate of 0.0, 162.5, 325, and 650 mg/kg body wt/day. Cesarean section was performed on gestation day 20. Maternal body weight was significantly reduced in the 650 mg/kg/day dose group on day 15 of pregnancy. There was no exposure related differences in fetal weight, number, sex, or frequency of malformations observed in fetuses from control vs treated dams.

Pregnant female rats were weighed and received a physical examination on days 5, 10, 15, and 20 of pregnancy. On day 20 of pregnancy the animals were euthanized and a complete gross necropsy examination was performed. The number of corpora lutea was recorded. Following weighing of the gravid uterus, the fetuses were removed, sexed, weighed, and examined for gross abnormalities. The number of dead fetuses and the number of resorption sites (early deaths) was also recorded. Following gross examination, half of the fetuses were immersed in Bouin's solution for later detailed examination of soft tissues using Wilson's technique. The remaining fetuses were placed in alcohol following their removal from the uterus then later processed using

a double-staining procedure designed to stain cartilage and calcified bone prior to skeletal examination. Uteri which appeared to be nonpregnant were immersed in a solution of 10% sodium sulfide and later examined for the presence of implantation sites.

Maternal body weights, fetal body weights, litter size, and feed weights were analyzed using one-way analysis of variance (ANOVA) followed by Dunnet's post hoc test, when appropriate. Pre-implantation loss and post implantation loss were analyzed using a Chi-square test. Fisher's exact test (one tailed) was used for pairwise comparisons when Chi-square procedures found significance at $P \leq 0.05$.

The body weight of dams receiving XM46 at 400 mg/kg/day differed from the body weight of control animals on days 15 and 20 of pregnancy. No other indications of maternal toxicity were noted during the course of the study. There was no statistical difference in the weight of the fetuses between dose groups. Likewise, there was no significant difference in the number of fetuses per litter between control dams and those receiving XM46. Pre- and post-implantation loss did not differ significantly between groups. A detailed examination of the fetuses from treatment and control groups revealed several malformations and variations, however, the incidence of these abnormalities was not treatment related.

This study revealed minimal maternal toxicity as evidenced by weight loss in the high-dose animals. No evidence of fetal toxicity related to XM46 exposure was noted in any of the dose groups. Based on these data it is concluded that XM46 is not a teratogen in the rat.

As noted above, the pregnant rats assigned to this study were dosed on day 5 through 14 of pregnancy rather than on days 6 through 15 as normally recommended. Based on the incidence of fetal defects noted in the study, it is not likely that beginning the dosing period one day early had a significant effect on the number or type of developmental variations and malformations observed. However, given the fact that rat embryos normally implant on day five of pregnancy, a day five dosing paradigm increases the possibility that the implantation process may be disrupted. The results from this study indicate that implantation was not affected.

**3.4 Skin Sensitization Studies**

XM46 was tested in standard skin sensitization studies in Hartley guinea pigs (Weller, et al, 1989). Negative results were obtained when 0.1% HAN was administered by intradermal injection. However, when applied to guinea pig skin, XM46 proved to be a strong skin sensitizer. The sensitization response to XM46 in guinea pigs may be associated with hydroxylamine, a potent skin sensitizer (Gross, 1985).

Individuals working with XM46 have reported burning sensations and lesions within 24 hours following dermal exposure, and sensitization was reported in one worker that handled HAN (Parmer et al., 1992). If the material is not flushed,

erythema will be produced in contaminated areas within several hours, followed by severe dermatitis within 24 hours (Weller et al., 1989).

A number of mechanisms for skin injury and/or dermal penetration have been proposed. Classical dermal penetration models for many substances are based upon affinity with lipid materials in the stratum corneum. Most models of dermal penetration use the octanol/water partition coefficient as an index of lipid solubility. XM46 however cannot depend upon lipid solubility as a route of entry because HAN and TEAN, which are ionized at the pH of the skin surface (pH 5), reside almost exclusively in the aqueous phase.

The predominant ions in solution are hydroxylammonium, triethanolammonium, and nitrate. In considering the effects of XM46 on various surfaces and scenarios, its acidic nature may change. At pH of 2 or less nearly all of the HAN is the $(NH_3OH)^+$ form. As the pH is raised some HAN is converted to free base, $NH_2OH$, and at pH 6 nearly half is in this form. Further addition of strong base increases the amine concentration and at a pH greater than 9, only the free amine exists. Decomposition leads to the formation of nitric acid and ammonium nitrate (Klein et al, 1991). Nitrate is expected to be capable of denaturing protein. Skin damage may also be caused by hydroxylamine or other breakdown products of HAN, which is unstable at physiological pH. One such product, ammonia, is known to produce skin blisters.

The following studies in human volunteers were performed: Contact Urticaria Assay (non-immunologic), 21 Day Cumulative Irritancy Assay, and a Modified Draize Skin Sensitization Study. XM46 was not found to have any skin sensitization potential in human volunteers. (Caldwell, unpublished data).

## 4.0 DERIVATION OF EXPOSURE LEVELS

The Reference Dose (RfD) is the toxicity value used most often to evaluate the noncarcinogenic effects of exposure to chemicals.

### 4.1 Reference Dose

According to the U.S. Environmental Protection Agency (EPA), an RfD is "an estimate (with uncertainty spanning perhaps an order of magnitude or greater) of a exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime" (EPA, 1989). For many noncarcinogenic effects, there are protective mechanisms that must be overcome before an adverse effect will be manifested in the human body. A typical example would be liver cells, where redundant numbers and function permit some level of exposure to a chemical to be tolerated by an organism below which no adverse effect is manifested.

In the development of an RfD, all the available studies on the toxicity of a chemical by a specific route of exposure are examined and judged for scientific merit. The U.S. EPA has indicated a

willingness to revise its policy to apply standard default uncertainty factors in determining the proposed RfD for XM46. Default uncertainty factors include:

- a factor of 10 for a less than chronic (e.g., lifetime) study
- a factor of 10 to account for variation in the general population and protect sensitive individuals
- a factor of 10 for extrapolation from animal data to humans to account for interspecies variability
- a factor of 10 if "lowest observable adverse effect level" is used instead of "no observable adverse effect level"
- a factor of 10 for database deficiencies based on professional judgment

### 4.2 Maximum Contaminant Level

The RfD is determined by dividing the "no observable adverse effect level", obtained from toxicity studies, by the product of the safety factors. Using the default uncertainty factors, the RfD is 0.002 mg/kg/day, which results in a 0.07 mg/L maximum contaminant level (MCL).

We are developing alternative risk assessment methodologies employing these research data to convince the EPA to abandon its default policy for XM46. We propose a science-based MCL, on which to base environmental clean-up actions, of 7 mg/L in water, which although 100 times higher than that determined using default uncertainty factors, is consistent with the MCL of 10 mg/L for nitrates.

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# HYDRAZINIUM NITROFORMATE AND ITS USE AS OXIDIZER IN HIGH PERFORMANCE SOLID PROPELLANTS

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## 1. SUMMARY

Hydrazinium nitroformate (HNF) is viewed as a promising new oxidizer. It has a high energy content and does not contain chlorine. When combined with an energetic binder like glycidyl azide polymer (GAP), high performance tactical propellants with low signatures are obtained. When adding aluminum fuel to the formulation, improved propellant performance is obtained for propellants suitable for space applications. In this paper, environmental, plume signature and theoretical performance aspects of HNF/GAP based solid propellants are considered, and the ballistic and material properties of HNF are summarized.

## 2. INTRODUCTION

Considerable concern has been expressed world wide on the effects of solid propellant combustion products on stratospheric ozone, acid rain, air quality, global warming and the toxicity of combustion products.

Modern commercial space launch vehicles employ liquid oxygen/hydrogen engines combined with solid propellant boosters. For example, the Space Shuttle boosters contain 502 tons of solid propellant each. Similarly, the boosters of the Ariane V launcher that will make its maiden flight in 1995, contain 196 tons of solid propellant each. Conventional propellants employ ammonium perchlorate (AP) as solid oxidizer and hydroxy-terminated polybutadiene (HTPB) as fuel and binder for the oxidizer, enhanced in performance through the addition of aluminum as a fuel. After combustion, reaction products like hydrochloric acid (HCl) are formed on a ±20 % by weight basis as well as carbon monoxide (CO), carbon dioxide ($CO_2$), hydrogen ($H_2$), water ($H_2O$), and aluminum oxide ($Al_2O_3$). The $Al_2O_3$ is released as particulate matter.

During ascent into space, the vehicle passes through the various layers of the atmosphere where the combustion products are deposited. The HCl-acid is considered as the most troublesome combustion product as it is partially responsible for atmospheric effects like acid rain and depletion of the ozone layer in the stratosphere. The burden on the earths atmosphere may be reduced by the replacement of AP with chlorine-free oxidizers, that result in propellants with similar but preferably better performance figures.

Possible oxidizers are given in Table 2.1. From the Table it is particularly clear why AP is such a good oxidizer. Typical explosive ingredients like e.g. HMX and CL-20 do not show a positive oxygen balance even though they contain a lot of oxygen. These oxidizers may be employed to increase the energy content of a typical propellant. New promising oxidizers like hydrazinium nitroformate (HNF) and ammonium dinitramine (ADN) have a lower oxygen balance than AP. However, when combining them with energetic binders like glycidyl azide polymer (GAP), this is compensated for through the more positive oxygen balance of GAP as compared to the conventional binder HTPB.

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| Compound Oxidizer | Oxygen balance [%] |
|---|---|
| AP | 27.24 |
| AN | 19.99 |
| HNF | 13.11 |
| ADN | 25.79 |
| RDX | -21.61 |
| HMX | -21.61 |
| NQ | -30.75 |
| CL-20 | -10.95 |
| HTPB | -322.96 |
| GAP | -121.09 |
| PGN | -60.46 |
| PLN | -114.18 |
| BAMO | -122.88 |
| NC 12.6 | -34.51 |

*Table 2.1: Oxygen balance of oxidizers and binders*

This will result in propellant formulations with maximum performance at higher binder fractions then is conventionally attainable.
Thermodynamic calculations carried out with the NASA-Lewis code show a 6-7 % higher theoretical specific impulse for an optimal HNF/Al/GAP propellant as compared to a conventional AP/Al/HTPB propellant when looking at formulations suitable for space applications, and an 11-12 % higher theoretical specific impulse for an HNF/GAP propellant as compared to a conventional AP/HTPB propellant with 4 % by weight Al, when looking at formulations suitable for tactical applications.

In Section 3, environmental aspects of solid propulsion will de discussed, followed by theoretical propellant properties in Section 4. Plume aspects are covered in Section 5, and Section 6 gives some general properties of HNF. Section 7 presents initial ballistic properties determined with HNF/Al/GAP based propellants.

## 3. ENVIRONMENTAL ASPECTS

When a conventional AP/Al/HTPB propellant is burning, HCl acid, CO, $CO_2$, $H_2$, $H_2O$ and $Al_2O_3$ are produced. Table 3.1 shows the reaction products for a typical conventional propellant formulation and an advanced propellant formulation based on HNF/Al/GAP. The propellant with high aluminum content has maximum performance in terms of specific impulse and is suitable for space applications. The propellant with a minimum or zero content of aluminium is suitable for tactical applications as it has good qualities with respect to plume signature.
Due to the presence of CO and $H_2$ in the plume of the rocket motor and the mixing of the gases in the plume with the entrained surrounding air, afterburning may occur. Afterburning results in the oxidation of CO and $H_2$ to $CO_2$ and $H_2O$. Due to the presence of nitrogen in the plume (in combustion products and entrained air), NO and $NO_2$ (generally in combination referred to as $NO_x$) are formed because of the presence of sufficient oxygen. The temperature sensitive mechanism by which $NO_x$ is formed was first given by Zeldovich. The amount of $NO_x$ formed in the rocket plume depends on the amount of combustable gases, the efficiency of mixing of the rocket plume and the surrounding atmosphere, the temperature at which the afterburning takes place and the time frame available for the reaction. The $NO_x$ production rate ranges from 6 - 7 % of the propellant mass at low altitude to 1 % of the propellant mass at high altitude (lower half stratosphere) [1].
Space launches contribute worldwide for a fraction of 5.5E-5 in HCl acid to the global deposition of acid producing chemicals (mainly sulphur oxides and nitrogen oxides).
When a rocket is launched into space it passes through a number of layers of the earth's atmosphere, viz.: the troposphere (0 - 13 km), the stratosphere (13 - 50 km) which contains the ozone-layer, the mesosphere (50 - 80 km), and the ionosphere (above 80 km).
Ozone itself is produced via the photolysis of molecular oxygen in the stratosphere. The ozone layer absorbs ultraviolet radiation. Mainly UV-C radiation (200 - 290 nm) but

| Property | Conventional Space | Advanced Space | Conventional Tactical | Advanced Tactical |
|---|---|---|---|---|
| AP [% by W] | 68 | -- | 82 | -- |
| HNF [% by W] | -- | 59 | -- | 85 |
| Al [% by W] | 18 | 21 | 4 | -- |
| HTPB [% by W ] | 14 | -- | 14 | -- |
| GAP [% by W] | -- | 20 | -- | 15 |
| $p_c$ [MPa] | 10 | 10 | 10 | 10 |
| $A_e/A_t$ | 100 | 100 | 10 | 10 |
| $T_c$ [K] | 3378.09 | 3818.68 | 3016.02 | 3365.54 |
| $I_{sp}$ [m/s] | 3096.6 | 3287.8 | 2498.2 | 2710.0 |
| $I_{vac}$ [m/s] | 3217.0 | 3436.0 | 2686.5 | 2926.7 |
| CO [% molar] | 2.4179-1 | 2.4651-1 | 1.5246-1 | 7.3546-2 |
| $CO_2$ [% molar] | 2.2069-2 | 1.7944-3 | 1.0490-1 | 1.6527-1 |
| HCl [% molar] | 1.4918-1 | -- | 1.7546-1 | -- |
| $H_2$ [% molar] | 3.7160-1 | 3.4149-1 | 1.7525-1 | 4.0573-2 |
| $H_2O$ [% molar] | 5.4792-2 | 8.9596-3 | 2.8556-1 | 3.5959-1 |
| $N_2$ [% molar] | 7.4590-2 | 2.9665-1 | 8.7729-2 | 3.6087-1 |
| $Al_2O_3$(A) [% molar] | 8.5976-2 | 1.0415-1 | 1.8635-2 | -- |

*Table 3.1 : Performance and reaction products of space and tactical propellants*

also part of the UV-B radiation (290 - 320 nm) is absorbed. This kind of UV radiation induces skin cancer in humans through modification of the DNA in skin cells, but also reduces the photosynthesis process in plants.

A number of reaction cycles have been identified that destroy ozone. In relation to solid propellant combustion most important are: the photochemical oxygen cycle, the nitrogen cycle, the chlorine cycle and the hydrogen cycle. The latter three cycles are catalytic, meaning that the ozone depleting species are regenerated. Table 3.2 shows these reactions. Many more reaction paths may be given, however, in order to keep things simple, only the major reactions are given. Clearly the above cycles may interact. Of the above reactions the chlorine cycle is most important as chlorine compounds have been identified as most damaging to the ozone layer in the stratosphere. It is interesting to note that even water contributes to the ozone depletion in the stratosphere. This holds for water in a gaseous state, but also ice crystals may catalytically destroy ozone.

Ozone is unaffected by HCl acid, however, the HCl yields free chlorine through a reaction with an hydroxyl radical. Moreover, due to afterburning in the rocket plume, the HCl is transformed directly to $Cl_2$. The latter transfers through photo dissociation (sunlight) to Cl atoms, which then may enter the chlorine cycle. A number of options is available for propellants manufacturers of high performance propellants for space applications to arrive at reduced emission levels of HCl acid as well as produce little or no $NO_x$ through the suppression of afterburning. These options are neutralized, scavenged and reduced chlorine or non-chlorine propellants.

| |
|---|
| Chlorine cycle<br><br>$Cl + O_3 \rightarrow ClO + O_2$<br>$ClO + O \rightarrow Cl + O_2$ |
| Oxygen cycle<br><br>$O_3 + hv \rightarrow O + O_2$<br>$O_3 + O \rightarrow 2O_2$ |
| Nitrogen cycle<br><br>$NO + O_3 \rightarrow NO_2 + O_2$<br>$NO_2 + O \rightarrow NO + O_2$<br>$NO_2 + hv \rightarrow NO + O$ |
| Hydrogen cycle<br><br>$H + O_3 \rightarrow OH + O_2$<br>$OH + O \rightarrow H + O_2$<br>$OH + O_3 \rightarrow HO_2 + O_2$<br>$HO_2 + O \rightarrow OH + O_2$ |

*Table 3.2: Ozone reducing cycles*

Combustion products may be neutralized through the replacement of aluminum by magnesium (e.g. 70 % AP, 16 % Mg, 14 % HTPB). The MgO produced in the rocket motor reacts outside of the combustion chamber with water to form magnesium hydroxide. The latter reacts with HCl to produce $MgCl_2$. This salt is not of any environmental concern as its two ions are very common in nature. There is a small loss (-3 % as compared to the conventional propellant) in specific impulse by the use of magnesium instead of aluminum. Propellant ingredient cost and processing are similar to the conventional propellant, however, propellant aging properties are expected to be less good than for conventional propellant formulations due to the poor aging properties of magnesium. If sodium nitrate ($NaNO_3$) is combined with AP (equal fractions on a molar basis), the sodium ions scavenge the chloride ions and NaCl is formed. This results in a substantial reduction of the HCl emission. Performance is slightly lower than for the conventional propellant. Propellant ingredient and production cost will be similar. Sodium nitrate has a higher density as compared to AP which is advantageous as it leads to a higher volumetric impulse.

The solution presented above for the removal of HCl from the rocket plume emitted into the stratosphere by either neutralizing or scavenging may only partially solve the problem, as products like NaCl, $MgCl_2$ may release their chlorine through various chemical paths. The time-scale in which this takes place will however be longer than when HCl was released directly into the stratosphere. Moreover, these condensed products (particle size is expected to be a few microns) may easily fall out of the stratosphere, before they become active, diminishing their effect on the ozone layer.

Chlorine-free propellants are based on other non-chlorine oxidizers like ammonium nitrate (AN), ammonium dinitramine (ADN) or hydrazinium nitroformate (HNF).

AN has been extensively studied. It has low performance, requires phase stabilization to prevent phase transition at 32 °C, and is very hygroscopic relative to AP. Moreover, the propellant shows a relatively high pressure exponent (0.5 - 0.6) and high temperature sensitivity. However, in combination with new energetic binders like glycidyl azide polymer (GAP) it approaches conventional formulations in terms of specific impulse. GAP is a new energetic binder that is commercially available.

ADN is a promising new energetic oxidizer which is under investigation at present in the United States, France and in FIS countries. It is at present not commercially available.

HNF is like GAP commercially available. In performance, it is better than ADN, and combined with GAP and aluminum it raises the specific impulse by 6-7 % as compared to the reference propellant.

When considering new solid propellant ingredients like HNF as a replacement for the conventional oxidizer AP, not only environmental impact should be considered but also aspects like cost, operability, long term system stability (i.e. life-cycle cost), material availability, reliability, system performance, production hazards and so one and so forth. A number of these aspects is at present being studied.

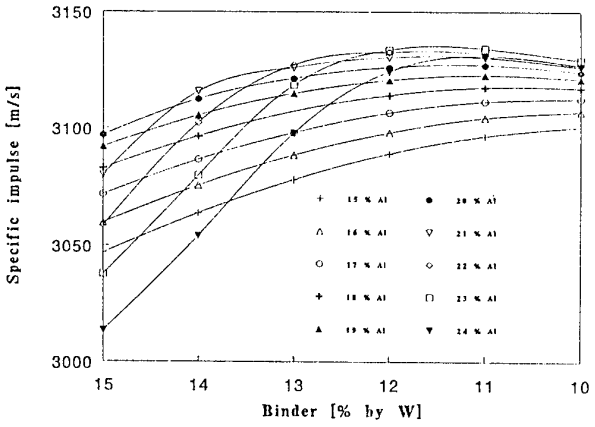



*Fig. 4.1: AP/Al/HTPB propellant performance*

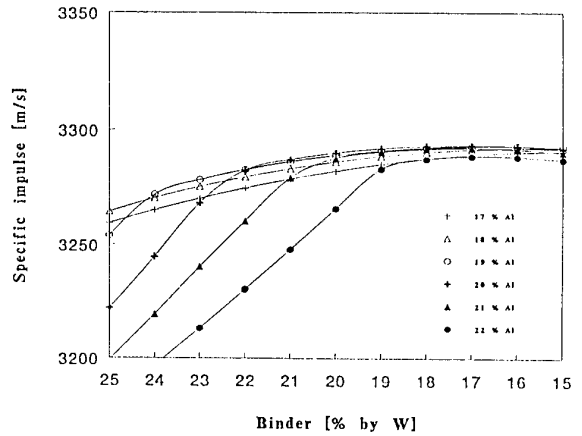



*Fig. 4.2: HNF/Al/GAP propellant performance*

## 4. PROPELLANT PERFORMANCE

Theoretical performance calculations were carried out with the NASA-Lewis thermodynamic code [2-4]. Two situations were considered, being optimal performance and low signature.

First there is the application of an HNF/Al/GAP based propellant as compared to the conventional AP/Al/HTPB propellant for space applications. These propellants will incorporate relatively large fractions of aluminum for maximum performance. Figures 4-1 and 4-2 show the specific impulse figures for such propellants, determined at a combustion pressure of 10 MPa and an area ratio of 100, as a function of the binder fraction.

For a conventional AP/Al/HTPB based propellant, the theoretical specific impulse increases with aluminum content up to about 23 % by weight of aluminum. The optimum shifts to a lower binder percentage when the aluminum fraction increases. Typical space booster propellants employ 18 % of aluminum by weight. Although Fig. 4-1 suggest higher performance at a higher aluminum percentage, the availability of oxygen (e.g. from CO, $CO_2$, OH, and other O containing species) for the oxidation of aluminum, will be less for higher aluminum fractions [5]. Unburned aluminum leads to a loss in specific impulse and should be prevented. For an AP/HTPB based propellant, an amount of 18 % of aluminum yields a practical optimum.

For an HNF/Al/GAP propellant, differences obtained through the addition of aluminum are less pronounced (see Fig. 4-2). A theoretical optimum (read maximum) is obtained at a binder fraction of 18 % GAP for an aluminum fraction of 20 %. However, as for the conventional propellant, this optimum may not be realised in practice, hence, the real optimum will probably occur at an aluminum fraction of 18 % or less. Moreover, the effect of increasing the binder fraction on the specific impulse is fairly small, hence, a binder fraction of 20 % or higher will be acceptable. This is advantageous from a production point of view as the GAP binder is more viscous as a raw material than HTPB.

Second, there is the requirement for a low signature of the plume of a solid propellant tactical rocket motor. For conventional propellants, depending on their application, up to 4 % by weight of aluminum may be added to the propellant formulation. For an advanced propellant based on HNF and GAP, no additional aluminum must be tolerated and is not really required. The calculations carried out are for a combustion pressure of 10 MPa and an area ratio of 10, as compared to the 100 used for the previous calculation. Calculation results in the form of specific impulse versus binder fraction are given in Figs. 4-3 and 4-4. For a tactical AP/HTPB propellant a binder fraction of at least 14 % seems realistic. Up to 4 % of aluminum may be used to obtain a 2 % increase in performance as compared to the non-aluminized propellant.

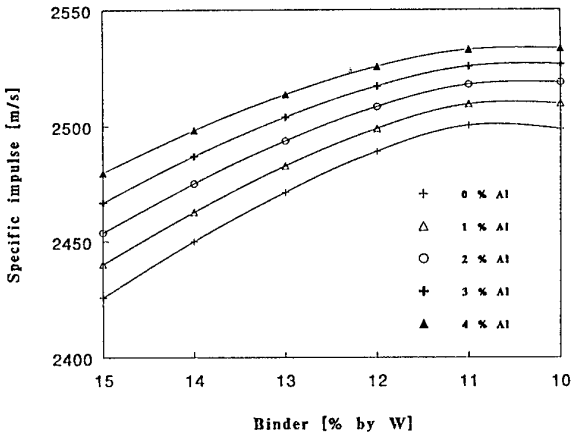



*Fig. 4.3: AP/Al/HTPB propellant performance*

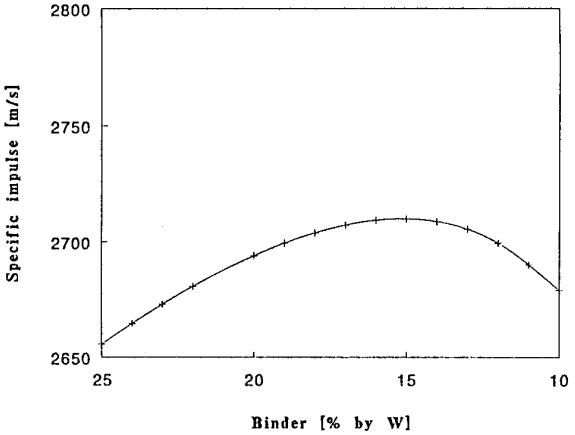



*Fig. 4.4: HNF/GAP propellant performance*

The HNF/GAP propellant attains its optimum at a 15 % binder fraction, however, a larger binder fraction (e.g. 20%) seems more suitable from a production point of view. The specific impulse obtained is 8 % and 10 % higher than respectively the non-aluminized and the 4 % Al conventional propellants.

## 5. PLUME SIGNATURE ASPECTS

The propellant that is combusted in a solid propellant rocket motor produces high temperature gas at high pressure. These gases are accelerated through a nozzle. The resulting reaction force (third law of Newton) is the thrust generated on the missile body. These gases are generally underexpanded, hence, the plume that these gases generate will show a pattern of expansion and compression waves. The resulting flow field is very complex as is shown in Fig. 5-1.

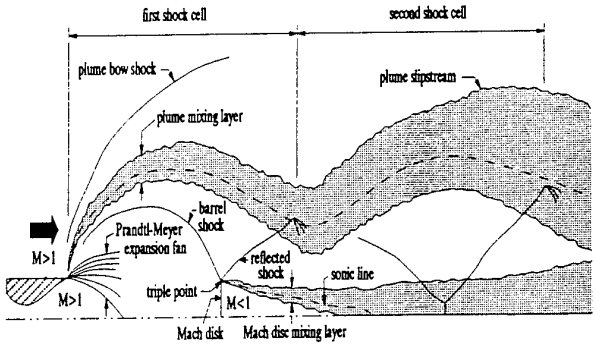



*Fig. 5.1: Rocket plume near flowfield*

Rocket plumes may be observed in the infrared (IR, 0.1 - 0.4 μm), the visible (0.4 - 0.8 μm), the ultraviolet (UV, 0.8 - 100 μm) and the microwave (100 - 150000 μm or 2 - 300 GHz) wavelength bands.

UV radiation in plumes is the result of continuum particulate matter radiation and from chemiluminescence, e.g. the CO + O reaction, and from excited OH generated by various reactions. Visible radiation is generally dominated by particulate matter continuum radiation. IR radiation is caused by rotational-vibrational transitions in molecules of gases present in the plume and the accompanying emission of photons. Species responsible for the IR radiation are mainly $CO_2$ and $H_2O$ (both band radiators), but also CO, HCl and $N_2O$. Again particle continuum radiation contributes to IR radiation from plumes. Microwave emissions is due to free-free emission which results from the collision of free electrons with molecules in the plume. If conventional propellants are optimized the combustion products contain substantial amounts of carbon monoxide (CO) and hydrogen ($H_2$). These species lead to a low molecular weight of the combustion products and hence to a high specific impulse ($I_{sp} \approx \sqrt{(M/T_c)}$). In the plume these gases mix with the entrained air and may further react with the oxygen to produce $CO_2$ and $H_2O$ thereby releasing heat that raises the temperature of the plume. These higher

temperatures increase the emission of radiation from the plume in the IR, visible, UV and microwave frequency bands and hence enhance the detectability of the missile. Moreover, if a microwave up-link is used for missile trajectory updating, the signal transfer may be severely disturbed.

The smoke generated by a missile is generally divided into primary and secondary smoke.

Primary smoke is mainly caused by solid and also liquid particulate matter in the plume that absorbs and scatters background radiation to the extent that the plume is in contrast with the clear sky background. Particulate matter is normally aluminum oxide for aluminized propellants, but also stems from igniter ingredients (e.g. $B/KNO_3$), burning rate catalysts (e.g. $Fe_2O_3$), combustion stabilizing agents (e.g. ZrC), afterburning suppressants (e.g. potassium salts), ablated and eroded liner materials (e.g. carbon), or water crystals at great height.

It may be clear that for propellant formulations that do not contain aluminum, the extent of the primary smoke strongly diminishes.

Secondary smoke forms as a result of the interaction of the combustion products in the plume with the ambient atmosphere. Secondary smoke usually consists of water, water-hydrogen chloride solutions and water-salt solutions. Secondary smoke is formed if the local vapour pressure exceeds the saturation value at the local temperature and pressure, causing condensation to occur on nucleation sources (e.g. primary smoke particles). If HCl is present in the plume, condensation will occur more rapidly as the HCl decreases the effective saturation pressure.

New propellants combine energetic oxidizers like HNF and ADN with energetic binders like GAP, yielding propellants that have in terms of specific impulse a higher performance as compared to a non-aluminized and 4 % Al conventional propellant (reduced smoke). These propellants do not contain solid matter except for minimal fractions for burning rate control and combustion stabilization. They produce no or little primary smoke. In addition they do not contain chlorine and secondary smoke is minimized.

To get a rough estimate of the difference in plume signature, calculations with the REP3-87 were carried out. This computer code was developed by the Defense Research Agency (DRA) in Fort Halstead (UK). It neglects recirculation at the missile base and solves for the axisymmetric parabolized Navier-Stokes equations. It calculates chemical reactions in the plume, and determines pressures, temperatures, densities, velocities and species concentrations.

A typical REP3-87 calculation result is given in Fig. 5.2 for a conventional AP/Al/HTPB propellant. Figure 5.2a shows the temperature, velocity, Mach number, pressure and density on the plume centerline. The afterburning occurring in the plume is visible from an increase in temperature. Figures 5.2b and 5.2c present the species on the centerline. The occurrence of afterburning corresponds with an increase of intermediate reaction species like e.g. OH and O.

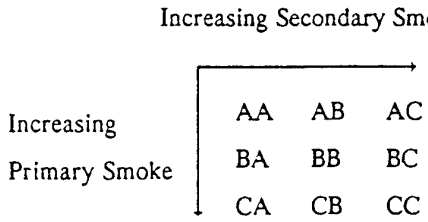



*Fig. 5.3: AGARD smoke classification*

AGARD has defined a smoke classification based on the amount of primary and secondary smoke (Fig. 5.3). AA may be termed "minimum smoke", AC corresponds to "reduced smoke" and CC stands for "smoky". The amount of primary smoke is measured from the transmittance of the plume cloud, defined as [6]:

$$AGARDP = 1 - \exp\{ -\Sigma_i(\%M_{pi}.N_i/SG_i)\}$$

If AGARDP $\leq$ 0.35 $\rightarrow$ 'A -' Classification
If 0.35 < AGARDP $\leq$ 0.9 $\rightarrow$ 'B -' Classification
If AGARDP > 0.9 $\rightarrow$ 'C -' Classification

Secondary smoke is slightly more complicated as it depends on the presence of HCl and $H_2O$ in the rocket plume. It is based on the relative humidity threshold for condensation due to saturation. Secondary smoke is hence defined through [6]:

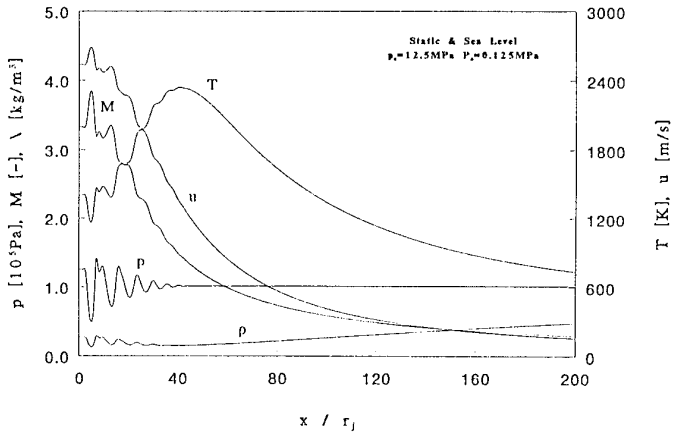



*Fig. 5.2a: REP 3 results for AP/Al/HTPB (p, T, ρ, M, u at centerline)*

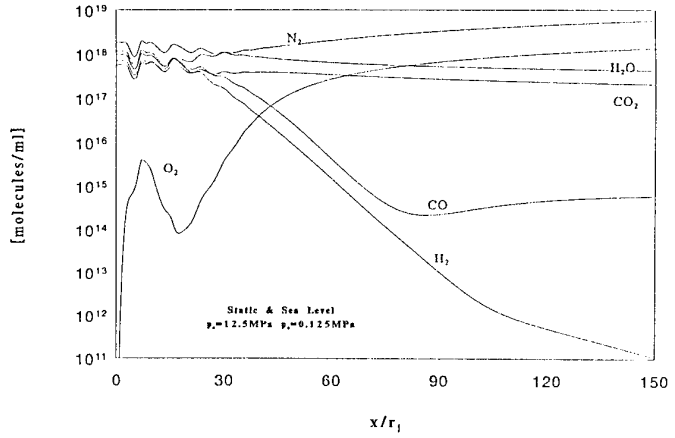



*Fig. 5.2b: REP 3 results for AP/Al/HTPB (species part I)*

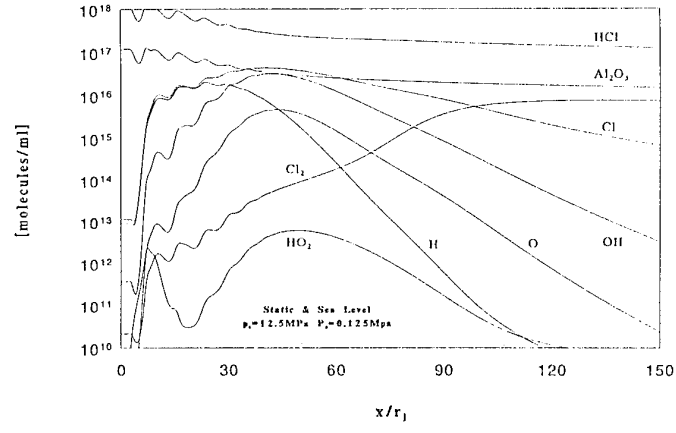



*Fig. 5.2c: REP 3 results for AP/Al/HTPB (species part II)*

$$RH_{amb} = 100 \cdot (K - f_{total} \cdot 0.16589)$$

$$f_{total} = f_{H2O} + f_{HCl} + f_{HF}$$

If $90\ \% < RH_{amb} \leq 100\ \%$ → '- A' Classification
If $55\ \% < RH_{amb} \leq 90\ \%$ → '- B' Classification
If $RH_{amb} < 55\ \%$ → '- C' Classification

Table 5.1 shows a conventional and two new propellant formulations. The conventional propellant has a poor plume signature (classification BC). The two new formulations do not employ aluminum and do not produce hydrogen chloride so that they have a relatively stealthy plume, both classified as AA.
Another feature worth noting is the fact that these new propellant formulations still produce CO and $H_2$ in sufficient quantities to cause afterburning. When allowing for a small decrease in propellant performance through a reduced binder fraction, these afterburning species may be reduced to an extent that afterburning no longer takes place (bottom Table 5.1). This is termed "natural" afterburning suppression which is in contrast to artificial afterburning suppression [7] (addition of potassium salts to the propellant formulation). The latter absorbs the free OH radicals present in the plume that are intermediate products of the afterburning reaction, hence, suppressing the afterburning. A negative side effect of the potassium salts is their contribution to the solid matter fraction in the plume, i.e. to the primary smoke.

## 6. PROPERTIES OF HNF

HNF was first discovered in 1951. Initially, a substantial effort was directed towards HNF synthesis and stabilisation as well as towards methods for HNF crystal particle size control. However, due to both the hazardous synthesis method of nitroform, which resulted in accidents, and the incompatibility of HNF with at that time suitable binders like HTPB, as a result of the attack on the double bonds, the research and development was stopped.
HNF was rediscovered in 1987 by TNO under a programme funded by the European Space Agency and the Netherlands Agency for Aerospace Programs (NIVR). The programme

| Propellant | AP/Al/HTPB | HNF/GAP (opt) | HNF/GAP (no afterb.) | ADN/GAP (opt) | ADN/GAP (no afterb.) |
|---|---|---|---|---|---|
| GAP [% by W] | -- | 12 | 10 | 20 | 18 |
| $T_f$ [K] | 3016.02 | 3365.54 | 3341.28 | 3130.21 | 3111.66 |
| $T_e$ [K] | 1449.92 | 1837.37 | 2095.89 | 1584.95 | 1687.96 |
| $I_{sp}$ [m/s] | 2498.2 | 2710.0 | 2679.0 | 2624.5 | 2618.6 |
| Tr | 0.85 | 1.00 | 1.00 | 1.00 | 1.00 |
| $RH_{amb}$ [%] | 40 | 92 | 91 | 91 | 91 |
| AGARD classif. | BC | AA | AA | AA | AA |
| CO [mole fract] | 1.5246-1 | 7.3546-2 | 9.1266-3 | 2.6198-2 | 5.1726-3 |
| $H_2$ [mole fract] | 1.7525-1 | 4.0573-2 | 3.5923-3 | 2.9909-2 | 5.1652-3 |

*Table 5.1 : Smoke classification for conventional vs. new propellants*

| Property | AN | AP | RDX | HNF | GAP |
|---|---|---|---|---|---|
| Molecular weight, [kg/kmol] | 80.04 | 117.5 | 222.1 | 193.9 | 2200 |
| Density, [kg/m$^3$] | 1720 | 1950 | 1820 | 1860 | 1270 |
| Heat of formation, [kJ/mol] | -365 | -296 | +70.7 | -72 | +117.2 |
| Melting point, [°C] | 170 | 130 (decomp.) | 204 | 115-124 | -- |
| Friction sensitivity, [N] | 353 | > 100 | 120 | 25 | > 360 |
| Impact sensitivity, [Nm] | 49 | 15 | 7.5 | 3-15 | > 30 |
| Toxicity-$LD_{50}$, [mg/kg] | non-toxic | non-toxic | 100 | 128 | non-toxic |

*Table 6.1 : Comparison of properties of HNF with AP, RDX and AN*

has among other the objective to prove the theoretical performance improvement of 6 - 7 % of an optimal HNF/Al/GAP formulations over a conventional AP/Al/HTPB formulation employed for space applications.

Nitroform, necessary for the production of HNF can now be manufactured safely (by e.g. the Rockwell method). The properties of HNF are in Table 6.1 compared to those of AP and RDX. In particular a comparison with AP must be made, as it is still the most important conventional oxidizer.

The Table shows that the density of HNF is slightly lower than for AP, whereas the density of GAP is higher than for HTPB.

The impact sensitivity is a measure for the susceptibility to decomposition for a momentum transfer to the propellant by a drop weight. The higher the value for impact sensitivity, the less sensitive the substance. This property is relevant for propellant manufacture and should be as large as possible

but certainly larger than 5 - 10 Nm.
The friction sensitivity is a measure of a friction force leading to a reaction. This property is also of relevance to propellant production and should be higher than 10 - 20 N. One should realise that the value for the friction sensitivity and the impact sensitivity depends on the rheological properties of the sample, e.g. particle size and particle shape.
The toxicity of a substance is given by the $LD_{50}$ value which is the lethal doses in 50 % of the cases, given in mg per kg bodyweight of a mammal.
The stability of HNF depends among others on its purity. The purity is measured through the hydrazine ($N_2H_4$) content. Table 6.2 shows the relation of the stability vs. hydrazine percentage.

| Purity [% $N_2H_4$] | Vac. stability test 48 hrs, 60°C [ml/g] |
|---|---|
| 97.35 | 0.31 |
| 98.01 | 0.64 |
| 98.16 | 0.90 |
| 99.84 | 0.61 |
| 99.99 | 0.79 |

*Table 6.2 : Effect of hydrazine on stability*

A standard vacuum thermal stability test (VTS) is carried out by keeping a small sample for 48 hours at a temperature of 100 °C. The melting point of HNF is about 125 °C, hence it was decided to carry out VTS tests for HNF or for an HNF containing composition at 60 °C and for 48 hours. For HNF, the activation energy for decomposition is 79 kJ/mol. This results in a decrease of the reaction rate to 5 % from the value for 100 °C. Hence, when the limit of 5 ml/g is retained this corresponds with a storage life of the composition of 5 % of the original 5 year period (60 months), being 3 months.
It is however specified that HNF or an HNF containing composition is stable when the gas production remains below 1.0 ml/g. Moreover, the melting temperature of HNF should be higher than 120 °C. This corresponds with an HNF content of 97 % by weight. The remaining 3.0 % are due to nitroform (NF) content and solvents remaining from the production process.

## 7. BALLISTIC PROPERTIES

Ballistic properties have been determined for HNF/Al/GAP (59/21/20) propellant samples within the framework towards a proof of concept. Initial samples were pressed instead of cast for two reasons. First, a suitable curing system for the propellant was not available, and second the solid loading required could not be met with the available HNF crystals. Ballistic tests were carried in a laboratory scale burner. At very low pressures (0.1-1 MPa), the combustion of the aluminium was found to be poor resulting in relatively low $c^*$ values (about 1200 m/s as compared to the predicted value of 1631 m/s at a pressure of 0.5 MPa). Substantial amounts of unburned aluminium were found in the combustion chamber after each low pressure test. Combustion experiments show smooth, steady state pressure-time curves. For the indicated low pressure region the burning rate pressure relation $r = 5.96 \cdot p_c^{0.66}$, where $p_c$ is in MPa and r is in mm/s, fits the data. At higher pressures, combustion pressures were transient. A value for the characteristic velocity determined from the pressure time trace is close to the predicted one (about 1590 m/s as compared to the theoretical one of 1667 m/s at 5.1 MPa). Using all data, the burning rate pressure relation is fitted best by: $r = 8.29 \cdot p_c^{1.11}$. A high pressure exponent leads to a high sensitivity of the chamber pressure to changes in burning surface and nozzle throat area. For practical applications an exponent below 0.7 is preferred.
High pressure exponents are not unusual. For example, AP based composite propellants may exhibit pressure exponents ranging from 0.3 to 0.9 with an exponent generally less sensitive to pressure change. On the contrary, for cyclotetramethylenetetranitramine (HMX)

based propellants with an inert binder, the exponent is within the range 0.6 - 0.7 below 20 MPa. The value may exceed 1.5 between 20 and 70 MPa after which it decreases to a value of approximately 1.0 at pressures above 70 MPa [8].

## 8. CONCLUSIONS

For space applications, thermodynamic calculations carried out with the NASA-Lewis code show a 6-7 % higher theoretical specific impulse for an optimal HNF/Al/GAP propellant formulation as compared to a conventional AP/Al/HTPB propellant formulation. For tactical applications, a 11-12 % higher theoretical specific impulse may be obtained for an HNF/GAP propellant as compared to a conventional AP/HTPB based propellant with a maximum of 4 % by weight Al.

The plume afterburns if the concentration of CO and $H_2$ in the plume of the rocket motor is sufficient. Due to the occurrance of afterburning in the plume, $NO_x$ (NO and $NO_2$) is formed. $NO_x$ production rate ranges from 6 - 7 % of the propellant mass at low altitude to 1 % of the propellant mass at high altitude (lower half stratosphere).

A number of options are available for propellants for both space and tactical applications with reduced emission levels of HCl acid that produce little or no $NO_x$ due to the suppression of afterburning. These options are neutralized (e.g. Mg containing), scavenged (e.g. $NaNO_3$ containing) and reduced chlorine or nonchlorine propellants (e.g. HNF or ADN containing). The former two propellants have a reduced theoretical impulse whereas the HNF based formulations are environmentally much safer to use and show increased performance in terms of specific impulse.

## 9. NOMENCLATURE

| | |
|---|---|
| $A_e$ | - nozzle exit surface area |
| $A_t$ | - nozzle throat area |
| f | - molar fraction |
| $I_{vac}$ | - specific impulse in vacuum |
| $I_{sp}$ | - specific impulse |
| K | - saturation depression factor |
| M | - molar mass, Mach number |
| $M_{pi}$ | - mass fraction condensible i-th species |
| $N_i$ | - optical properties i-th species |
| p | - pressure |
| $p_c$ | - chamber pressure |
| r | - burning rate |
| $r_i$ | - nozzle exit radius |
| $RH_{amb}$ | - saturation relative humidity |
| $SG_i$ | - specific gravity i-th species |
| T | - temperature |
| $T_c$ | - flame temperature |
| $T_{glass}$ | - glass transition temperature |
| $T_{mp}$ | - melting point temperature |
| Tr | - transmittance |
| u | - velocity |
| x | - axial distance |
| $\Delta H_f^\circ$ | - standard heat of formation at 298 K |
| $\rho$ | - density |

## 10. ACRONYMS

| | |
|---|---|
| ADN | = ammonium dinitramide ( $N_4H_4O_4$ ) |
| Al | = aluminum |
| AN | = ammonium nitrate ( $NH_4NO_3$ ) |
| AP | = ammonium perchlorate ( $NH_4ClO_4$ ) |
| GAP | = Glycidyl azide polymer ( $[C_3H_5N_3O_1]_n$ ) |
| HNF | = Hydrazinium nitroformate ( $N_2H_5C(NO_2)_3$ ) |
| HMX | = Octogen ( $C_4H_8N_8O_8$ ) |
| HTPB | = Hydroxy-terminated polybutadiene |
| PGN | = Polyglycidyl nitrate ( $[C_3H_5N_1O_4]_n$ ) |
| PLN | = Poly nitromethyl oxetane ($[C_3H_9N_1O_4]_n$ ) |
| RDX | = Hexogen ( $C_3H_6N_6O_6$ ) |

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# Discussion

QUESTION BY C. CARRIER : Did you say that HNF is a commercially available material ?

ANSWER : Yes HNF is now a commercially available material and may be obtained from Aerospace Propulsion Products in Netherlands.

# Shock Sensitivity of Ammonium Nitrate Based Propellants

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## SUMMARY

Ammonium nitrate (AN) is the base component of a recent family of gas generators and rocket composite propellants with lower pollutants. They have the same polyurethane (PU) binder based in hydroxyl terminated polybutadiene (HTPB), a plasticizer (DOA) and a curing agent (IPDI), of the classic ammonium perchlorate (AP) based composite propellants. The impossibility of burn a pure AN - PU propellant at atmospheric pressure, with AN concentration standard of 80 weight percent (%), leads to find an inert additive component in order to increase insulation and decrease global initial density. The glass micro balloons (GMB) have these properties. AN-PU-GMB compositions varying the AN concentration from 80 to 90%, keeping constant the 4% of GMB, are our tested compositions.

The existence of detonation regime in a propellant shows the security level at non stationary regimes and at fragment impact initiation. An experimental technique to measure initiation of propellant, with a shock induced from a plastic explosive, is presented. A double resistive wire was placed coaxially inside acceptor, in order to allow the continuous measurement of detonation velocity and the position of extinction section, when it occurs. An aluminium crush bar, under detonation probe, shows clearly the extinction section zone. Experimental results show any initiation of detonation on mixtures AN-PU-GMB with concentration of AN lower than 83%. It is observed the initiation of AN-PU-GMB propellant with concentrations of AN of 83%, followed by extinction, near 110 mm, also verified by the observation of shocked propellant sample and crushed bar profiles. It was measured the initiation of AN-PU-GMB of concentrations of AN of 90%, followed by a non stable detonation, with a detonation velocity of ≅3200 m/s, and a periodicity of interruptions of period distance of ≅5 mm.

The obtained results prove the validity of tested procedures and show the possibility of using 4% of GMB as additives, in AN-PU base propellants with concentrations of AN up to 83%.

## 1. INTRODUCTION

The existence of detonation regime in an energetic material corresponds to a thermodynamic reacting regime different from the deflagration (vd. Campos [1]. It shows the security level at fragment impact initiation (vd. Workshop on Prop. Ignition Mic. [2]). Traditional methods used to measure detonation velocity (ionization probes with time counters) allow to determine its mean value but do not allow a continuous measurement. However ionization probes prove the strong conductivity of detonation shock front.

Shock initiation of an explosive refers to the process in which a shock wave, passing through an energetic material, grows into a detonation wave. It has been studied extensively and described in general "sensitivity tests", consisting of placing one of the wedges of explosive test sample against a large planar shock-wave generator and observing when and where, the rapid change of shock velocity occurs, in the explosive sample. A sequence of such shots, varying initial shock pressure in the explosive, allows to define a graph of run distance $L_D$ to detonation, and of its initiation delay $\tau$, as a function of induced shock pressure P. This graph is known, in logarithmic scale, as the Pop-plot (after Alphonse Popolato [3]). The Pop-plot and Hugoniot data have been used to describe and compare shock sensitivity of many explosives (vd. [4], [5]). Nevertheless the detonation velocity D can be stable for values less than its maximum value $D_\infty$ , obtained plotting measured D as a function of inverse charge diameter (vd. Presles et al. [6], Gois et al. [7]). Consequently, it is very difficult to define the transient value of D, above which the detonation can be considered self-sustained. This fact leads to simplify this procedure, performing for security tests, successive shock experiments only with the maximum possible intensity of the induced shock, verifying the existence or failure of detonation.

Ammonium nitrate (AN) is the base component of a recent family of gas generators and rocket composite low pollutants propellants. Those propellants have the same polyurethane (PU) binder, based in hydroxyl terminated polybutadiene (HTPB) with a plasticizer (DOA) and a curing agent (IPDI), of the classic ammonium perchlorate (AP) based composite propellants. The disadvantages of this kind of propellant come from of its low flame temperature and specific impulse. The impossibility of burning at atmospheric pressure a pure AN-PU propellant, with AN concentration standard of 80 weight percent (%), leads to find an inert additive component in order to increase insulation and decrease global initial density. The glass microballoons (GMB) have these properties and are used in many energetic materials, namely emulsion explosives (vd. [8], [9], [10]). GMB material can be assumed as inert in combustion process. Nevertheless GMB can also sensitise the propellant in a detonation regime - it is very known its sensitization properties in nitromethane, reducing its critical diameter and allowing stable detonation with lower detonation velocities (vd. [7], [11]). In our study it was selected a AP/AN-PU propellant as reference, with concentrations respectively of 40, 40 and 20%, because it is the composition with the minimum AP concentration possible to have a sure ignition at atmospheric pressure (vd.Araújo e Frota [12]). In the other AN-PU-GMB tested compositions the AN concentrations are varying from 80 to 90%, keeping constant 4% of GMB.

The following text presents:
- the summary of characteristics of components and compositions,
- theoretical detonation characteristics of selected propellants, using THOR code, an evaluation of collapse of one shocked GMB, inside detonation products of a homogeneous explosive,
- the experimental conditions followed to evaluate the existence or failure of detonation in the shock induced propellant, in order to conclude the validity of selected compositions and experimental conditions.

## 2. COMPONENTS CHARACTERISTICS AND COMPOSITIONS

### 2.1. Selected components

Curing agents, plasticizers, crosslinkers, stabilizers and antioxidants are very important to achieve optimal mechanical and energetic properties (vd. [13]). Our propellant binder is a more simplified composition because the aim of the present study is to evaluate and measure the shock sensitivity of AN based propellants with GMB as additive.

The perfect insertion of filler particles in the organic polymeric binder matrix needs an adequate viscosity during the preparation phase in order to avoid air bubbles, to coat filler particles with a binder film and to disperse them inside the heterogeneous system (vd. Quinchon et al.[14]). It is composed by HTBP with dyoctil adipate (DOA), as plasticizer, and isophorone diisocyante (IPDI) as curing agent.

#### 2.1.1. Filler particles

Three kind of filler particles, are used assumed as chemical pure materials (vd. Table 1). Its particle size distribution, shown in Fig. 1, were established by Laser Diffraction Spectrometry. They were used completed dry and are stored in an electric heated oven at 60°C.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

| Reference and name (suplier) | Density |
|---|---|
| AP - Ammonium perchlorate - NH4ClO4 - (SNPE) | 1950 kg/m3 (TMD) |
| AN - Ammonium nitrate - NH4NO3 - (Nitroazote) | 1720 kg/m3 (TMD 1725 kg/m3) |
| GMB - Glass microballoons - Silicate glass shell (SiO2) with air inside - (Q-Cel 520 FPS - AKZO-PQ) | Effective - 200 kg/m3 Bulk - 110 kg/m3 |

Table 1 - Selected filler particles.

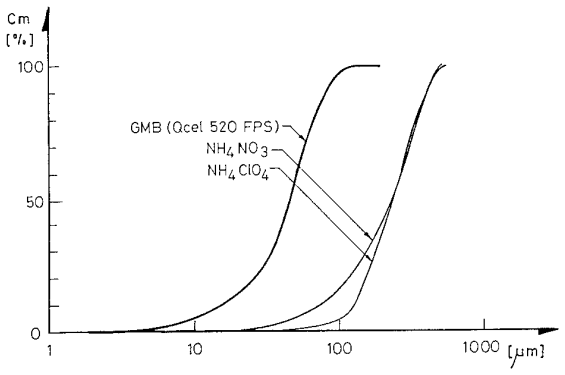



Fig. 1 - Particle size diameter of AP, AN and GMB.

**2.1.2. Binder components**

The binder components were used as received and assumed as pure chemical products (vd. Table 2). The rheological properties of these binders were recently studied by Frota and Araújo [15]. On binder system was composed by 82.57% of HTPB, 9.17% of DOA and 8.26% of IPDI.

| Reference and name (suplier) | Function |
|---|---|
| HTPB - Hydroxyl- terminated polybutadyene - (HTPB R45HT - Elf Atochem) | Pre-polymer |
| IPDI - Isophorone diisocyanate (Merck) | Curing agent |
| DOA - Dyoctil adipate (Fluka) | Plasticizer |

Table 2 - Binder components

**2.1.3. Propellant compositions and preparation**

Three kinds of propellants were prepared, changing successively the filler nature and concentration.

The AP/AN based propellant is designed by D1 (donor) and the AN based propellants were designed by A1 to A4 (acceptors), being A2, A3 and A4 compositions with GMB. Table 3 shows their molar and mass compositions, equivalence ratio related to the stoicheiometry and measured density. Air concentration was calculated as a function of measured density.

Experimental propellant mixtures were prepared under vacuum conditions in a double "z" blades contra rotating mixer of capacity 800 $cm^3$(Werner, Inc.). The pre-polymer HTPB was previous mixed with the plasticizer DOA and a solvent (methyl ethyl ketone - MEK) in order to decrease viscosity and allow the fine coating of particles. Then, the particles were added to the binder. During mixing, the vacuum and constant temperature of 60°C allow to extract all the MEK (confirmed by its final mass). After many hours of mixing process, when the viscosity of the mixture becomes constant, the curing agent was added and mixed to the mixture. The sample tubes were then filled and cured in a oven at 60°C during more than 1 day.

| Mixture (AP/AN-PU-GMB) | Molar composition | Mass composition (%) | Equiv. ratio | Density |
|---|---|---|---|---|
| **D1 (≈40/40-20-0)** | 33.455 AP + 49.116 AN + 12.951 HTPB + .523 DOA + .797 IPDI + .020 AIR | 39.29 AP + 39.30 AN + 17.70 HTPB + 1.94 DOA + 1.77 IPDI + .01 AIR | 2.043 | 1411 kg/m3 |
| **A1 (≈80-20-0)** | 98.232 AN + 12.965 HTPB + .523 DOA + .797 IPDI + .030 AIR | 78.57 AN + 17.72 HTPB + 1.94 DOA + 1.77 IPDI + .01 AIR | 2.056 | 1321 Kg/m3 |
| **A2 (≈76-20-4)** | 94.454 AN + 12.453 HTPB + .502 DOA + .766 IPDI + .075 AIR + 6.410 GMB | 75.55 AN + 17.02 HTPB + 1.86 DOA + 1.70 IPDI + .02 AIR + 3.85 GMB | 1.967 | 1180 kg/m3 |
| **A3 (≈83-13-4)** | 103.405 AN + 8.147 HTPB + .329 DOA + .501 IPDI + .130 AIR + 6.340 GMB | 82.69 AN + 11.13 HTPB + 1.22 DOA + 1.11 IPDI + .04 AIR + 3.81 GMB | 1.443 | 1071 kg/m3 |
| **A4 (≈90-6-4)** | 112.398 AN + 3.783 HTPB + .153 DOA + .233 IPDI + .270 AIR + 6.377 GMB | 89.95 AN + 5.17 HTPB + .57 DOA + .52 IPDI + .08 AIR + 3.83 GMB | .988 | 827 kg/m3 |

Table 5 - Compositions, equivalence ratio and density of tested mixtures.

## 3. THEORETICAL PREDICTIONS

**3.1. Detonation characteristics of selected propellants**

THOR code is based on theoretical work of Heuze et al.[16] [17], and later modified (vd. IEPG Reports [18], [1]) in order to calculate composition and thermodynamic properties of explosive compositions, for Chapman-Jouguet detonation conditions. Several equations of state are used, namely BKW, Boltzmann, H9, H12 and JCZ3. The results have been compared within themselves and with results of different codes in open literature (Quatuor Code from Heuze et al.[16], [17], using BKW EoS, TIGER Code (vd. [19]) and Mader Code [4]], and using the KHT EoS of Tanaka Code, [20]). The selected EoS to perform our calculations have been BKW and H9, because the first is the most common EoS in bibliography and the second is the natural development of a Boltzmann EoS type, presenting very similar results of KHT and JCZ3 EoS. (vd. Campos [1]).

The chemical equilibria conditions, allow to determine the chemical concentration of the components products of reaction, for imposed P and T conditions, in order to find the minimum value of global Gibbs free energy $G = \Sigma x_i \mu_i$, being the Gibbs free energy of each component $\mu_i = G_{oi}(T) + R\,T \ln P + R\,T \ln (x_i)$. The values of $G_{oi}(T)$ are the Gibbs free energy expressed as a function of temperature. They can be obtained from JANAF Thermochemical Tables [21], and from polynomial expressions of Gordon and McBride [22].

The solution of the composition problem involves simultaneously:

- the thermodynamic equilibrium, obtained with mass and species balance, and the equilibrium condition $G=G_{min}$ $(P,T,x_i)$, previously described, generally applying to the condensed phase in the model proposed by Tanaka [20],
- the thermal equation of state (EoS),
- the energetic equation of state, related to the internal energy $E = \Sigma x_i e_i(T) + \Delta e$, $e_i(T)$ calculated from JANAF [21], and from polynomial expressions of Gordon and McBride [22],
- the Chapman-Jouguet conditions (mass, momentum and energy balances and $dp/dV\,]_S = (P-P_o) / (V-V_o)$ ) for the detonation regime,

- the selection of components, depending of atomic initial composition ($CO_2$, CO, $H_2O$, $N_2$, $O_2$, $H_2$, OH, NO, H, N, O, HCN, $NH_3$, $NO_2$, $N_2O$, $CH_4$, HCl, $Cl_2$ gases and two kinds of solid carbon - graphite and diamond), being the glass shell of GMB composed by $SiO_2$ in two phases, solid and gas, but assumed always as inert in reaction.

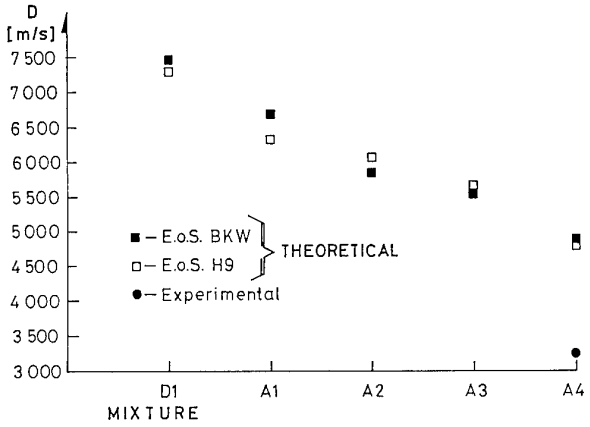



Fig. 2 - Detonation velocity for selected propellants.

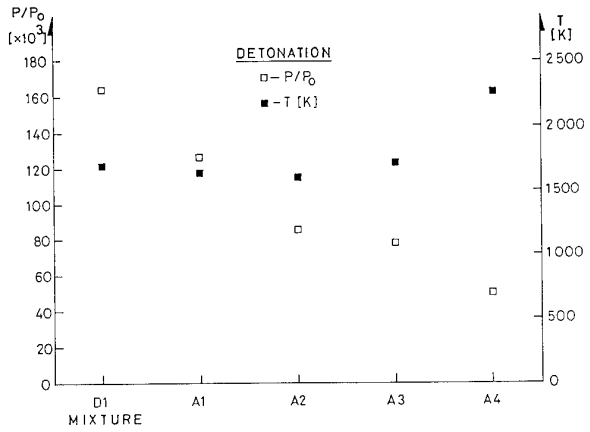



Fig. 3 - Calculated CJ pressure and temperature of selected propellants.

Theoretical results of detonation velocity D, pressure P and detonation temperature T, for Chapman Jouguet conditions, assuming the thermodynamic equilibrium of detonation products, are presented in Figs. 2 and 3. The analysis of these results reveals a very good agreement with theoretical calculations of Tanaka code [20], predicting D=5395 m/s, P=9.65 GPa and T=1069 K for pure AP and D=5265 m/s, P=6.46 GPa and T=2212 K for AN/FO (ammonium nitrate/fuel oil) of 90/10%, but suggesting immediately the impossibility of detonating any of these mixtures, on exception of A4, because it is known (vd. [23]) the impossibility of detonating small charges of ANFO explosives (its critical diameter is ≅35 mm for a steel confinement and stoicheiometry mixture (94/6%) and its detonation velocity is ≅3300 m/s).

### 3.2. Evaluation of collapse of GMB under detonation conditions

It is important to evaluate the deformation of one GMB, under detonation conditions. This complex phenomena is related to the hot spot formation in explosive detonation. Many different mechanisms have being proposed to characterise hot spots formation: gas compression [24], plastic work of collapsing cavities [25], rapid shear [26] and high-speed jets impact against the downstream wall [5]. However, it is not known the contribution of each one on the hot spot formation.

The evaluation of the deformation and collapse of one GMB is performed using DYNA3D code (vd. Hallquist [27], [28]), assuming the explosive material as nitromethane, because it is a very known, liquid, homogeneous, pure chemical explosive [29], with known detonation characteristics (D=6230 m/s at 18ºC).

The GMB shell was assumed as $SiO_2$ material (vd. LASL Shock Hugoniot Data [30]). This shell was modeled as a brick structure and as a shell (vd. Zukas [31]). Numerical results show clearly the deformation of GMB shell like a "sombrero hat", as a function of time, generated by the detonation products of NM (vd. Fig. 4). The influence of particle size of GMB is very important. Numerical simulations have been performed changing the diameter of GMB. The evolution of $\delta t/\tau$, as a function of inverse particle diameter 1/d, is shown in Fig. 4 (being $\delta t$ the time duration, between the initial instant when the detonation front touch the GMB shell and the instant when the deformed GMB shell arrives to the center of particle, and being $\tau$ the time takes by the detonation front to cover the same distance - obtained by particle radius divided by detonation velocity). These results show not only the limit value of $\delta t/\tau$=1.50 for large particles, with existence of a shell jet for large particles, in a good agreement with open literature (vd. Walter and Zukas [32]), but also clearly show the collapse of very small particles. For very small particles, the formation of GMB shell jet takes so long that we can consider the deformation of GMB like a pure collapse (implosion) situation.

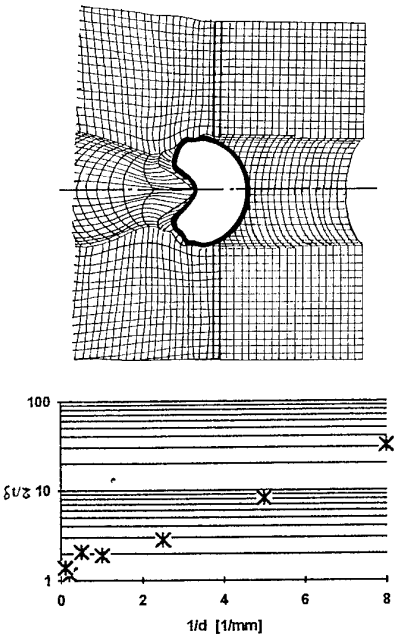



Fig. 4 - Typical deformation of GMB and evolution of $\delta t/\tau$ as a function of 1/d.

## 4. EXPERIMENTAL PROCEDURES AND RESULTS

### 4.1 Experimental assembly

The experimental assembly used to measure initiation delay and run distance to detonation is composed by a donor, a gap, an acceptor having inside a double resistive wire and an witness aluminium plate (vd. Fig. 5). The donor was plastic explosive PE4A (delivered by SPEL, S.A.), composed by 90% of RDX and 10% by a plastic binder, having D=7850 m/s and P=26 GPa (similar composition of PBX 9007 of LLNL [29]). Gap is formed by PMMA plates of constant thickness of 2 mm. The acceptor charge has an internal diameter of 25.5 mm, the confinement was brass tube 1.5 mm of thickness.

In order to verify the existence of detonation on the acceptor, a parallel double thin resistive wire (resistivity of 177 Ω/m and diameter of 100 μm) was fixed in the axis of the acceptor charge, connected as a tension divisor circuit for a stabilised source (with a variable resistance $R_V$ formed by the double resistive wire and a constant resistance $R_C$). This double resistive wire, for heterogeneous explosives, was placed inside an aluminium tube of 1.2 mm diameter. The detonation wave, inducing a short-circuit between wires, generates a variation of tension that shows its position along the wires (vd. Mendes et al.[23]) . The existence of a signal transition shows, by the changing of resistivity or interruption between two wires, the extinction or even the interruption of reaction front.

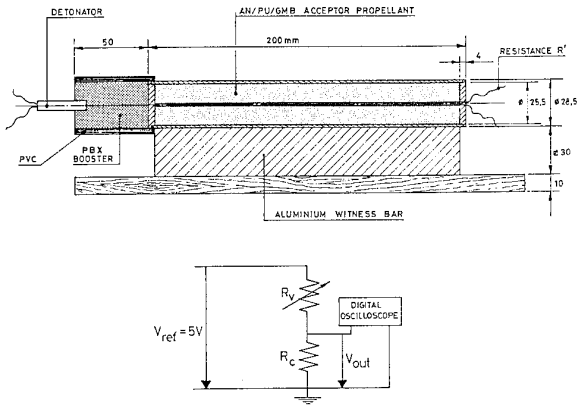



Fig. 5 - Detonation assembly and tension divisor.

When shock wave runs in detonation tube, the variable resistance $R_V$ decreases. The voltage at terminals of the constant resistance $R_C$ increases. The conductivity of shock wave increases strongly when the detonation regime is obtained. So, on detonation regime, it is assumed the detonation front with a negligible resistance. The output voltage, $V_{out}$, can be obtained by $V_{out} = V_{ref} \cdot R_C / ( R_C+R_V+R_i)$ , where $R_i$ represents the assembly internal resistance of current source and cables. Its value can be obtained by $R_i = R_C.( V_{ref} - V_f )/V_f$ , where $V_f$ represents the final of output voltage, when $R_V$ become zero.

Considering now the resistance $R_V$ given by $2\rho(Lo-x)$, where $\rho$ is the resistivity of the wire, Lo is the length of detonation tube and x is the run distance of the detonation front (corresponding to detonation velocity D multiplied by time t), the output voltage can be given by $V_{out}=Rc \cdot V_{ref} / (Rc+2\rho(Lo-x)+Ri)$, allowing the correlation between output voltage and detonation front position (vd. Mendes et al. [23]).

An aluminium bar, with a cross section of 30x30 mm, placed under the acceptor, shows clearly the extinction section. The induced crush deepness allows the correlation between the measured real time and location of extinction zone.

In order to evaluate the critical thickness of detonation it is also verified the transmission and the extinction of detonation inside the experimental assembly shown in Fig. 6, built with the same aluminium bars described above.

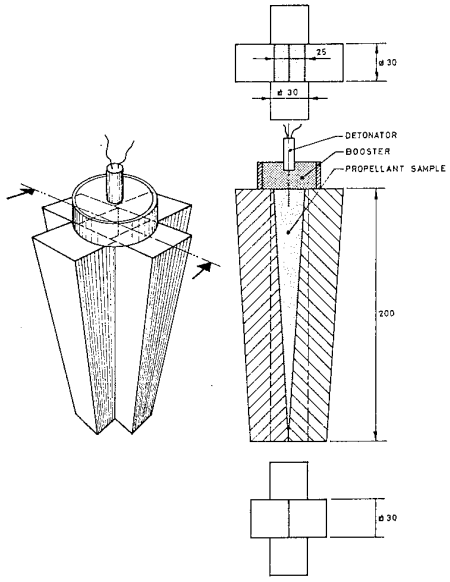



Fig. 6 - Critical thickness detonation assembly.

### 4.2. Experimental results and discussion

The shock induced by the plastic explosive, with a CJ pressure of 26 GPa, generates the compression of the energetic material and it even possible to find the shocked propellant inside broken brass tube (vd. Figs. 7). Generally it is observed the broken brass tube without propellant - this suggests the possible combustion after the shock transmission (vd. Fig. 8).

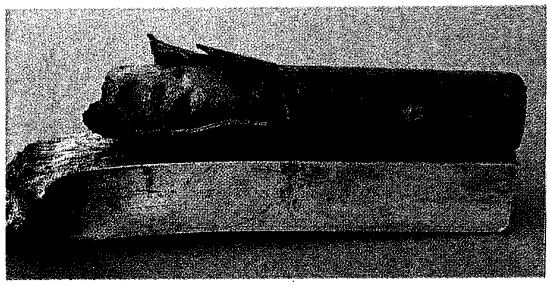


Fig. 7 - Shocked sample of propellant D1.

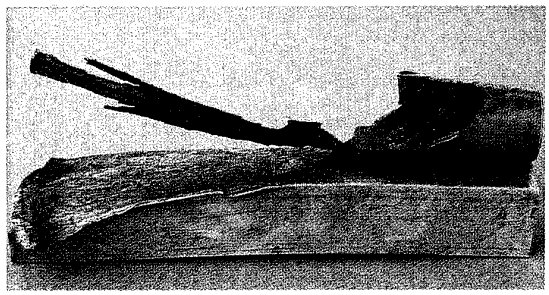


Fig. 8 - Typical shocked sample of propellant A2.

The obtained crushed profiles are shown in Fig. 9. The AN-PU-GMB propellants are more sensible than AP/AN-PU without any GMB, which proves the sensitisation effect of GMB in detonation regime.

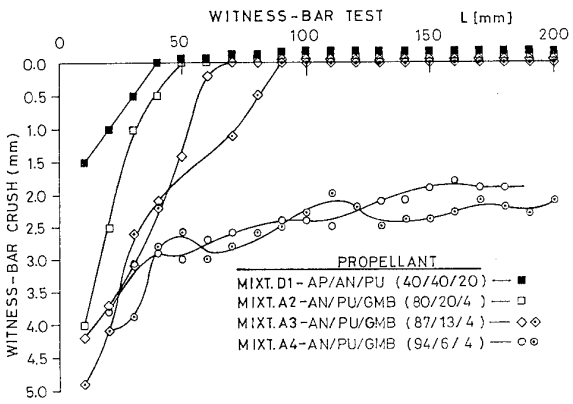



Fig. 9 - Aluminium crushed deepness profiles.

The electronic records of reaction front progression of propellants A3 and A4 show respectively:

- the initiation of a shock front reaction in A3 sample followed by its extinction near 110 mm (vd. Fig. 10), verified by the observation of shocked propellant sample (vd. Fig. 11) and crushed bar profiles (vd. Fig. 9),
- the initiation of A4, followed by a non-stable detonation with a detonation velocity of ≅3200 m/s (vd. Fig. 12), with a shown periodicity of interruptions of period distance of ≅5 mm (vd. fig. 13).

This last result leads to us to evaluate the critical thickness of this mixture with the assembly shown previously in Fig. 6. The obtained result show a critical thickness between 4 and 5 mm (vd. Fig. 14).

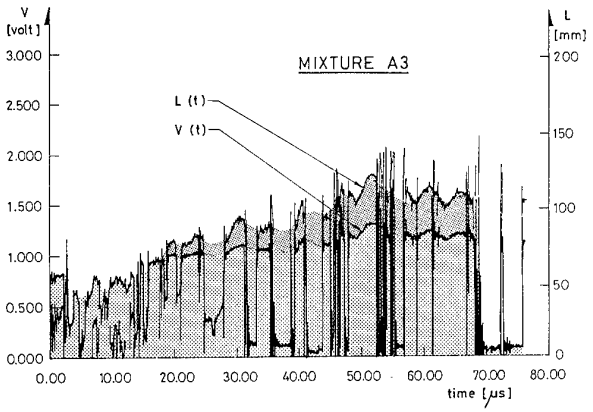



Fig. 10 - Records of reaction front progression of sample of A3 propellant.

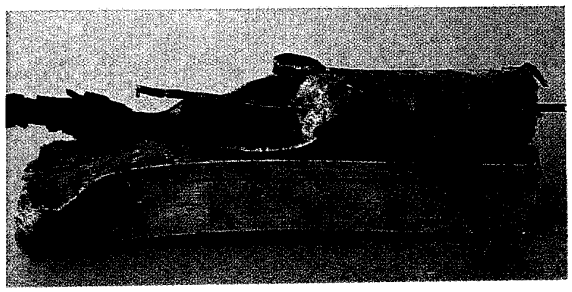


Fig. 11 - Shocked sample of propellant A3.

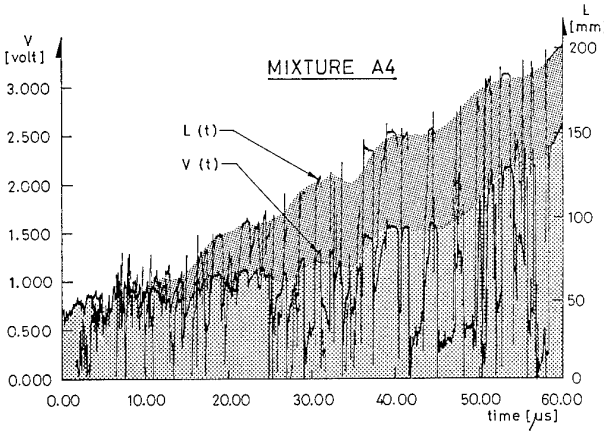



Fig. 12 - Record of reaction front progression of sample of A4 propellant.

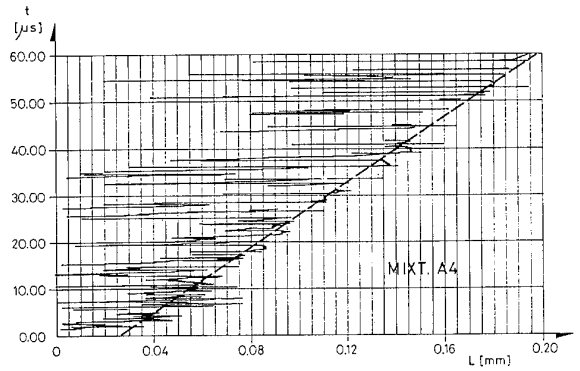



Fig. 13 - Record of spatial progression of non stable detonation of A4 propellant.

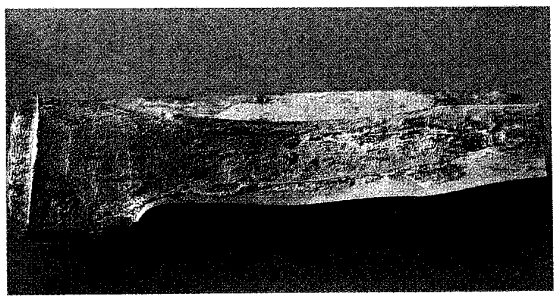


Fig. 14 - Observation of critical thickness assembly tested with A4 propellant.

This last result suggests the large influence of GMB in reducing critical diameter related to the base propellant. Consequently, in future experiences it will be tested less concentrations of GMB with this AN-PU based propellant.

The obtained results prove the validity of tested procedures and show the insensivity of reference propellant D1. The utilization of 4% of GMB as additives, in order to allow combustion of an AN-PU propellant is possible until concentrations up to 83% of AN.

## 5. CONCLUSIONS

The predicted detonation characterisitics of selected propellants, using THOR code, show a good agreement with other codes, but they are quite different from experimental known results. Evaluation of collapse of one GMB, under detonation of a homogeneous explosive shows the influence of its particle size diameter.

An experimental technique to measure initiation of propellant, with a shock induced from a plastic explosive, is presented. A double resistive wire was placed coaxially inside acceptor, in order to allow the continuous measurement of detonation velocity and the position of its initiation or extinction section. An aluminium crush bar, under detonation probe, shows clearly the extinction section zone.

Experimental results show any initiation of detonation on mixtures AP/AN-PU and on AN-PU-GMB with concentration of AN lower than 83%. The obtained crushed profiles show AN-PU-GMB propellants are more sensible than AP/AN-PU without any GMB, which proves the sensitisation effect of GMB in detonation regime. It is observed the initiation of AN-PU-GMB propellant with AN concentrations of 83 %, followed by its extinction near 110 mm, also verified by the observation of shocked propellant sample and crushed bar profiles. It was measured the initiation of AN-PU-GMB of AN concentrations of 90 %, followed by a non-stable detonation with a detonation velocity of ≅3200 m/s and a periodicity of interruptions of period distance of ≅5 mm.

These results suggest the large influence of GMB in reducing critical diameter, related to the base propellant. The obtained results proves the validity of tested procedures and show the possibility of using 4 % of GMB as additive, in AN-PU base propellants with concentrations of AN less than 83 %.

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## Discussion

QUESTION BY A.J.McDonald : Does the detonation sensitivity of AN based propellants by incorporating GMB imply that very porous propellant may also transition to detonation ?

ANSWER : A very porous propellant has also a lot of possible hot spots. Consequently the deflagration-detonation transition can easily to occur or it occurs earlier than in a compact propellant. The detonation sensitivity is also increased in a porous propellant.

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The combustion products of conventional solid rocket propellants are known to comprise substantial quantities of pollutants, primarily hydrogen chloride and other chlorine-containing compounds, carbon monoxide, and fine particulate alumina. Some propellants yield, additionally to abovementioned, highly toxic beryllium and fluorine compounds. The concentration of the pollutants at the nozzle outlet can be essentially evaluated by thermodynamic calculation on the basis of the chemical composition of the propellant and conditions of stationary work of the engine. The evolution of the pollutants in the environment after they leave the nozzle is investigated but poorly. One can assume, however, that formation of the products of incomplete oxidation - dioxines and other carcinogens, in particular - is highly likely, especially on the stages of ignition and extinguishing of the engine. The main source of the pollutants in the combustion products is the ammonium perchlorate ($NH_4CLO_4$), which is main oxidizer in conventional solid propellants.

Any substantial decrease in environmental damage from solid rocket propellants can be achieved if only formulations that do not contain neither chlorine, nor fluorine, nor beryllium are employed. An additional improvement of environmental safety can be achieved if metals (e.g. aluminum) are totally eliminated from the formulation.

Presently, two types of propellants free of chlorine and fluorine are widely used and studied. Those are propellants based on cellulose nitrate (two-base powders) and octogen-based ones. They are extensively used and their advantages and disadvantages are well known.

However, there exist certain additional directions for development of fluorine- and chlorine-free propellants. Those are related to employing oxidizers that to date are not extensively used in aerospace engineering.

Major problems that should be discussed when one decides whether it is possible to develop a propellant based on a new compound are the energetics of the propellant, chemical stability, and regularities of its combustion. The problems of cost, technology, composition of particular formulations, mechanical characteristics, etc. are also very important. However, without first three being positively solved, the solution of further questions makes no sense. In this work we consider the following components intended to substitute ammonium perchlorate and octogen (HMX): ammonium nitrate ($NH_4NO_3$), hydrazine nitrate($N_2H_5NO_3$), ammonium dinitramide ($NH_4N(NO_2)_2$,ADN), and hydrazine nitroform ($N_2H_5C(NO_2)_3$). Additionally, the data on boranhydrazine ($BH_3N_2H_4$) and sodium perchlorate ($NaClO_4$) are presented. The sodium perchlorate is a metal perchlorate that in combustion yields ecologically safe chlorine compounds (NaCl). Here we do not consider the following known high-energy chlorine-free compounds, hydrazine azide ($N_2H_5N_3$), hydroxyammonium nitrate ($NH_4ONO_3$), and hexanitroethane ($C_2(NO_2)_6$), because studies of their thermal stability showed that these compounds are highly unstable.

Table 1.

| compound | k=f(T),sek$^{-1}$ | $\tau_{0.1\%}$ |
|---|---|---|
| $N_2H_5N_3$ | $10^{8.0}\exp(-24000/RT)$ | 2 years |
| $C_2(NO_2)_6$ | $10^{16.5}\exp(-35800/RT)$ | 6.85 month |
| $NH_4ONO_3$ | $10^{4.6}\exp(-16500/RT)$ | 1 day |

k is the rate constant of decomposition according to initial rate.
$\tau_{0.1\%}$ is the time of 0.1% decomposition at 20°C (impurities disregarded)

The energetics of the compounds was calculated on the basis of the following experimentally measured characteristics.

For comparative thermodynamic calculations we used a model hydrocarbon matrix(HM) of the composition $CH_{1.65}$ having $\Delta H$ =-90 kcal/kg, and $\rho$ = 0.92 g/cm$^3$ and a high-energy matrix (cellulose nitrate + trinitroglycerol) (AM) of the composition $C_{20.833}H_{27.87}O_{36.792}N_{9.495}$, $\Delta H$ = -625 kcal/kg, and $\rho$ = 1.62 g/cm$^3$.

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Surely, those are not most advantageous matrices but they , nevertheless, allow to comparatively analyze the different oxidizers.

Table 2.

| compound | heat of formation ΔH, kcal/kg | density ρ, g/cm |
|---|---|---|
| $NH_4ClO_4$ | -597 | 1.95 |
| HMX (octogen) | 77 | 1.92 |
| $NH_4N(NO_2)_2$ | -270 | 1.82 |
| $N_2H_5NO_3$ | -661 | 1.68 |
| $NH_4NO_3$ | -1091 | 1.725 |
| $N_2H_5C(NO_2)_3$ | -98 | 1.9 |
| $NaClO_4$ | -740 | 2.53 |
| $B_2H_6N_2H_4$ | -336.6 | 0.94 |
| $BH_3N_2H_4$ | -233 | 0.95 |

The model fuel formulations had the following thermodynamic characteristics calculated for pressure of 40 bar within combustion chamber and that of 1 bar at the nozzle outlet (Table 3).

The results of thermodynamic calculations show that energetics of the formulations based on $NH_4N(NO_2)_2$ and $N_2H_5C(NO_2)_3$ are superior not only with respect to $NH_4ClO_4$-based propellants but exceed those based on HMX. Additionally, the temperatures within combustion chamber and at the nozzle outlet are lower, compared to those for the conventional propellants. The energetics of $N_2H_5NO_3$ is intermediate between those of $NH_4ClO_4$ and HMX. The formulations based on $NH_4NO_3$ and $NaClO_4$ expectedly have low energetics. Nevertheless, one should not discard them outright, because in some cases low cost and availability of these components, accompanied with certain other advantages may make them reasonable to be employed.

TABLE 3.

| Formulation | | | specific momentum I, s | density ρ, g/cm$^3$ | The temperature within chamber $T_{ch}$,K | The temperature at the nozzle outlet $T_{out}$,K |
|---|---|---|---|---|---|---|
| oxidizer | matrix, wt% | fuel, wt% | | | | |
| $NH_4ClO_4$ | HM-10% | Al-20% | 250.8 | 1.844 | 3616 | 2520 |
| //-// | HM-10% | - | 240.3 | 1.758 | 2998 | 1902 |
| HMX | AM-22% | Al-20% | 257.4 | 1.95 | 3702 | 2548 |
| $NH_4N(NO_2)_2$ | HM-10% | Al-20% | 262.0 | 1.76 | 3583 | 2331 |
| //-// | HM-11% | - | 249.0 | 1.64 | 2967 | 1580 |
| $N_2H_5NO_3$ | HM-11% | Al-20% | 254.0 | 1.65 | 2913 | 1766 |
| //-// | HM-12% | - | 215.6 | 1.53 | 1955 | 932 |
| $NH_4NO_3$ | HM-11% | Al-20% | 244.6 | 1.68 | 2884 | 1799 |
| //-// | HM-12% | - | 204.6 | 1.56 | 1876 | 921 |
| $N_2H_5C(NO_2)_3$ | HM-10% | Al-20% | 265.0 | 1.81 | 3578 | 2360 |
| //-// | HM-11% | - | 253.6 | 1.70 | 3073 | 1604 |
| $NaClO_4$ | HM-15% | Al-20% | 224.9 | 2.05 | 3650 | 2608 |
| //-// | HM-15% | - | 211.2 | 2.00 | 3080 | 2031 |
| - | - | $BH_3N_2H_4$ | 249.6 | 0.95 | 1562 | 758 |
| | | $B_2H_6$ $N_2H_4$ | 278 | 0.94 | 2114 | 1176 |

The unicomponent propellants $BH_3N_2H_4$ and $BH_3N_2H_4BH_3$ are exceptional. The reaction of chemical combustion proceeds predominantly according to the scheme $B_2H_6N_2H_4 \longrightarrow 2BN + 5H_2$. This results in high energetics at very low temperatures within the chamber and at the nozzle outlet. The disadvantages of these propellants are their low density and lack of a binder. They can be used in the form of hard pressed blocks. Possibly, they can find specific applications where energetics is of primary importance, e.g., in a spacecraft.

Naturally, the composition of the combustion products substantially differs from that of $NH_4ClO_4$-based propellants. Table 4 presents the calculated concentrations of main components of combustion products at the nozzle outlet (mol/kg).

Table 4.

| Formulation | | | Combustion products | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| oxidizer | matrix, wt% | fuel, wt% | $Al_2O_3$ | $Cl_2$ | HCl | CO | $CO_2$ | $N_2$ | NO | $H_2$ | $H_2O$ | BN | NaCl |
| | | | mol/kg | | | | | | | | | | |
| $NH_4ClO_4$ | HM-10% | Al-20 | 3.70 | 0.2 | 5.73 | 6.69 | 0.54 | 2.98 | $2\cdot10^{-3}$ | 9.78 | 4.98 | - | - |
| -//- | HM-10% | - | - | 0.04 | 7.62 | 0.77 | 6.46 | 3.83 | $8\cdot10^{-4}$ | 0.48 | 17.0 | - | - |
| HMX(octogen) | AM-22% | Al-20 | 3.70 | - | - | 12.4 | 0.04 | 8.87 | $2\cdot10^{-4}$ | 10.4 | 0.22 | - | - |
| $NH_4N(NO_2)_2$ | HM-10% | Al-20 | 3.70 | - | - | 6.88 | 0.36 | 11.3 | $6\cdot10^{-4}$ | 13.2 | 3.92 | - | - |
| -//- | HM-11% | - | - | - | - | 3.55 | 4.40 | 14.3 | $2\cdot10^{-6}$ | 4.5 | 16.4 | - | - |
| $N_2H_5NO_3$ | HM-11% | Al-20 | 3.70 | - | - | 7.71 | 0.24 | 10.9 | $8\cdot10^{-7}$ | 22.2 | 2.53 | - | - |
| //- | HM-12% | - | - | - | - | 3.21 | 5.37 | 13.9 | - | 16.2 | 13.9 | - | - |
| $NH_4NO_3$ | HM-11% | Al-20 | 3.70 | - | - | 7.28 | 0.67 | 8.62 | $3\cdot10^{-4}$ | 17.6 | 6.2 | - | - |
| //- | HM-12% | - | - | - | - | 2.03 | 6.61 | 11.0 | - | 11.3 | 17.8 | - | - |
| $N_2H_5C(NO_2)_3$ | HM-10% | Al-20 | 3.70 | - | - | 11.0 | 0.1 | 9.56 | $1\cdot10^{-4}$ | 14.6 | 0.73 | - | - |
| //- | HM-10% | - | - | - | - | 8.2 | 4.61 | 12.2 | $1\cdot10^{-6}$ | 6.91 | 11.8 | - | - |
| $NaClO_4$ | HM-15% | Al-20 | 3.65 | $5\cdot10^{-2}$ | 1.07 | - | - | - | - | 7.1 | 0.45 | - | 4.15 |
| //- | HM-15% | - | - | $3\cdot10^{-3}$ | 0.25 | - | - | - | - | 0.46 | 5.33 | - | 6.55 |
| | - | $BH_3N_2H_4$ | - | - | - | - | - | 10.8 | - | 76.1 | - | 33.5 | - |
| | - | $B_2H_6N_2H_4$ | - | - | - | - | - | - | - | 87.7 | - | 21.8 | - |

Obviously, employment of chlorine-free oxidizers results in chlorine- and hydrogen-chloride-free combustion products. This also excludes possible formation of chlorinated dioxines. The change of $NH_4ClO_4$ for $NaClO_4$ results in a substantial decrease in content of chlorine and HCl in the combustion products.

Noteworthy is a substantial decrease in the concentration of nitrogen oxides in combustion products. High concentrations of hydrogen and carbon monoxide do not comprise an environmental threat, since combustion products are mixed with atmospheric air and burn out. Any quantitative data on what fraction of carbon monoxide and hydrogen of the rocket exhaust survive and how atmospheric pressure and particular design of the rocket engine affect the process are not known to the author.

The stability of propellants.

In majority of the cases, when the formulation is correctly composed and components do not mutually react, the stability of the fuel is controlled by the stability of the major component, the oxidizer. This is confirmed by a numerous studies on kinetics performed in Chernogolovka Institute of Chemical Physics, and in a number of laboratories throughout the world. The rate of thermal decomposition of the propellant usually equals the decomposition rate of the least stable component. The heat effect of decomposition may enhance due to secondary reactions of active species of decomposition products and other constituents of a propellant.

The kinetic studies performed in Chernogolovka Institute of Chemical Physics showed that the ammonium and

hydrazonium cations in ionic salts are highly stable. Nevertheless, the ammonium and hydrazonium cations in ionic salts are capable of fast proton exchange. For this reason, the stability of ammonium and hydrazonium salts is always much lower with respect to the analogous salts of alkali metals. The mechanism of thermal decomposition of the ammonium and hydrazonium salts is in many respects similar and can be elucidated on the example of the simplest representative of the class, ammonium nitrate.

A common feature of ammonium and hydrazonium salts is their capability of fast proton transfer according to the scheme

$$(BH^+A^-)_s \overset{K_{ps}}{<\!\!\longrightarrow} B_s + HA_s, \qquad (1)$$

where B is ammonia or hydrazine, HA is acid (nitric, perchloric, etc.), $BH^+$ is (ammonium or hydrazonium) cation, $A^-$ is the cation of respective acid, and $K_p$ is the equilibrium constant in solid (liquid) phase.

Since both employed acids and bases are relatively strong, the equilibrium in reaction (1) is substantially shifted to the left and equilibrium concentrations of B and HA are low. The equilibrium concentration of vapors of acid and base over the surface of solid (liquid) salt corresponds to the equilibrium concentrations $B_s$ and $HA_s$

$$p_B = k_{gB}(B)_s \quad p_{HA} = k_{gHA}(HA)_s \qquad (2).$$

The presence of the vapor and, hence, vaporization (sublimation) of the salts possible, plays an important role in the combustion.

Hydrazine and respective acids are unstable compounds and decompose. In the simplest case the net rate of decomposition is determined by the concentration of reactants

$$w = k_1 C_{Bs}^n + k_2 C_{HAs}^m,$$

where $k_1$ and $k_2$ are the rate constants of decomposition of $B_s$ and $HA_s$, respectively, and n and m are the reaction orders. Additional reactions can also occur, namely, interaction of the primary products of decomposition with the fresh ions or acid and base formed according to reaction (1) and also reactions between the primary products.

For example, in decomposition of ammonium nitrate, the following principal reactions proceed

1. $(NH_4NO_3)_s <\!\!\longrightarrow NH_{3s} + HNO_{3s}$
2. $3HNO_{3s} <\!\!\longrightarrow N_2O_5 + H_3O^+ + NO_3^-$
3. $N_2O_5 \longrightarrow NO_2 + NO_3 \longrightarrow 2NO_2 + 0.5O_2$
4. $NH_4^+ + N_2O_5 \longrightarrow$ final products
5. $NH_4^+ + HNO_3 \longrightarrow$ final products

The reactions 1 and 2 are fast and the rate of decomposition W can be expressed as follows

$$W = k_1 C_{N_2O_5} + k_2 C_{NH_4^+} C_{N_2O_5} + k_3 C_{NH_4^+} C_{HNO_3}$$

At temperature T > 220 °C, the third term prevails, at lower temperatures, the second and, to less extent, the first.

Thus, the stability of ammonium and hydrazine salts is governed primarily by the acid—base equilibrium (1), stability of the acid and base formed by (1), and also by the presence of additional reaction paths, as for example, present in ammonium nitrate.

The common feature of all the ammonium and hydrazonium salts considered is their high sensitivity to the acidity of the salt (stoichiometry), high susceptibility to admixtures capable of shifting the acid—base equilibrium (in particular, water content). Since the reaction is a complex one, its temperature dependence is determined by a combination of the equilibrium and rate constants. All these constants have different activation energies or (equilibrium constants) heats of reaction. In effect, the limiting reactions can change in different temperature ranges, the apparent activation energy experiencing corresponding changes. Therefore, the estimates of low-temperature stability require a special analysis.

The stability of $NaClO_4$ is determined by the stability of $ClO_4^-$ anion. Decomposition of boranehydrazine, hexanitroethane and HMX proceed via different mechanisms. The time of 0.1% decomposition at 20 °C and parameters of apparent rate constants are summarized in Table 5.

The data are given without account of possible effect of admixtures on the initial decomposition rates. In certain occasions, given is the estimate of stability obtained using the measurements on molten salts, when very low decomposition rates in solid did not allow direct measurements. One should keep in mind that upon transition from liquid to solid, the rate constant may decrease by the factor of $10 - 10^4$ due to stabilizing effect of the crystalline lattice. In this respect, the data presented in Table 5 are the pessimistic estimate.

Table 5.

| Compound | lgA, $sec^{-1}$ | E, kcal/mol | $\tau_{0.1\%}$, yr |
|---|---|---|---|
| $NH_4ClO_4$ | 8.0 | 30000 | $7 \cdot 10^3$ |
| β-HMX (octogen) | 11.2 | 37900 | $3.8 \cdot 10^7$ |
| $NH_4N(NO_2)_2$ | 13.7 | 36200 | $6.65 \cdot 10^2$ |
| $N_2H_5NO_3$ | 12.2 | 38000 | $4 \cdot 10^5$ |
| $NH_4NO_3$ | 14.4 | 47200 | $1.5 \cdot 10^{10}$ |
| $N_2H_5C(NO_2)_3$ | 18.0 | 43000 | $3.8 \cdot 10^3$ |
| $NaClO_4$ | 13.0 | 60000 | $10^{21}$ |
| $BH_3N_2H_4$ | 11.6 | 30500 | 15 |
| $B_2H_6N_2H_4$ | | 2400 | 2 |

From the viewpoint of stability, all the compounds presented in Table 5 can be used in solid propellants. Making of a particular working formulation will require additional studies and search for components that will not deteriorate stability of these oxidizers.

Combustion.

Extensive experimental and theoretical studies of combustion of the solid propellants performed in Chernogolovka Institute of Chemical Physics, and in other laboratories in different countries allowed to establish the following common regularities of combustion.

1. The chemical reactions controlling the combustion rate and regularities of the process are localized within the near-surface layer of solid phase. (The combustion of HMX and formulations based on it is the matter of special discussion).
2. The controlling stage in kinetics of chemical reactions is the decomposition of oxidizer in solid phase.
3. Additionally to decomposition of oxidizer, the sublimation and dispersion of oxidizer, thermal decomposition and oxidation of the matrix occur in condensed phase.
4. The rate of oxidizer decomposition is controlled by the surface temperature.
5. The temperature of the surface is governed by the heat effect of decomposition, dispersion, the fraction of sublimated matter, the heat of evaporation, the degree of matrix oxidation in solid, and the heat capacity of the fuel, the heat effect and degree of decomposition and evaporation of the fuel. The heat flux from gas usually is not a governing factor.

Since some of the aforementioned processes (sublimation, degree of fuel oxidation, etc.) depend on pressure, the surface temperature and, hence, combustion rate depend on pressure.

Therefore, the data on combustion of main oxidizer are the primary one for decision on whether particular formulation can be used. The combustion of $NH_4ClO_4$-based systems can be realized on a simpler system without sublimation of oxidizer and heat effect being primarily related to oxidation of matrix. The boranehydrazine complexes are unicomponent systems and do not require analysis of the effect of other components.

The table 6 presents experimental data on combustion of the studied compounds compared to theoretical calculation. The calculation was performed on the basis of independently measured kinetic and thermophysical characteristics.

Table 6.

| Compound | Pressure experiment/ calculated | | | |
|---|---|---|---|---|
| | P, bar | r, cm/s | n | $\sigma \cdot 10^3$, $K^{-1}$ |
| $NH_4ClO_4$ | 40 | 0.5/0.3 | 0.7/0.47 | 2/2.9 |
| $NH_4NO_3$ | 70 | 0.4/0.34 | 0.85/1.03 | -/- |
| $N_2H_5NO_3$ | 50 | 0.8/0.70 | 0.82/0.90 | 3.1/2.5 |
| $NH_4N(NO_2)_2$ | 20 | 1.8/1.5 | 0.7/82 | -/- |
| HMX(octogen) | 40 | 0.9/2.7 | 0.9/0.8 | -/- |
| $BH_3N_2H_4$ | 40 | 0.5/0.56 | 0.5/0.5 | -/- |

Here r is combustion rate, n is pressure index, and $\sigma$ the temperature coefficient.

One can see that experimental values well correlate with the calculated ones (but for octogen) and regularities of the combustion of ammonium perchlorate do not substantially differ from those of other compounds considered. The data presented shows that these compounds with respect to their combustion characteristics can constitute a basis for propellants that meet the requirements of aerospace industry.

Naturally, the combustion rate, its dependence on pressure and initial temperature can experience changes upon transition from pure oxidizer to mixed solid propellants.

It was already mentioned afore that the presence of a fuel is revealed via changing heat effect and temperature of the oxidizer decomposition. Main effect, as is envisaged by experiment, is produced by

(a) composition and reactivity of products of oxidizer decomposition,
(b) reactivity of the fuel in oxidation and thermal decomposition,
(c) characteristic dimensions of the particles in the system, which affect the ratio of the rates of oxidation and decomposition and heat transfer in solid.

Figure 1 presents as an illustration the calculated dependence of the combustion rate versus the ratio of the rates of oxidation and decomposition.

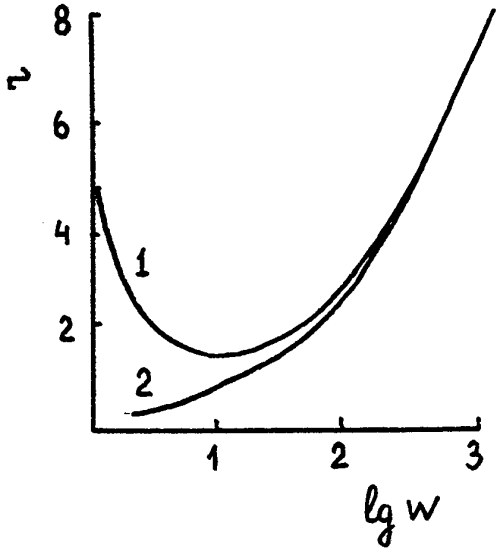



Fig.1. The dependence of combustion rate on the ratio of the rates of oxidizer decomposition and oxidation of fuel. (1) is mixed fuel and (2) pure oxidizer.

The figure also presents the dependence of the combustion rate on the reactivity of the products of oxidizer decomposition with respect to fuel. One can see that for highly reactive fuel, the combustion rate of propellant can substantially increase, as compared to pure oxidizer, or be equal to the latter.

The particle size can have a strong and diverse effect on combustion.

When reactivities of the products of oxidizer decomposition and the fuel in oxidation reaction are high, then, upon diminishing particles, the surface of interphase contact and, hence, the degree of oxidation of binder increases. This results in an enhanced heat effect of solid phase combustion, higher surface temperature and combustion rate (Fig. 2, curve 1). When the reactivity is low and fuel strips the oxidizer of heat, thus decreasing temperature of oxidizer decomposition, the combustion rate of propellant decreases with diminishing particle size (Fig. 2, curve 2). In the general cases both branches of size—rate dependence should be observed (the dashed line presents resulting dependence). In experiment, however, because reactivity changes dramatically from one reaction system to another, for a particular oxidizer—fuel pair one can usually obtain only one branch, either decrease or increase of the combustion rate with particles' sizes.

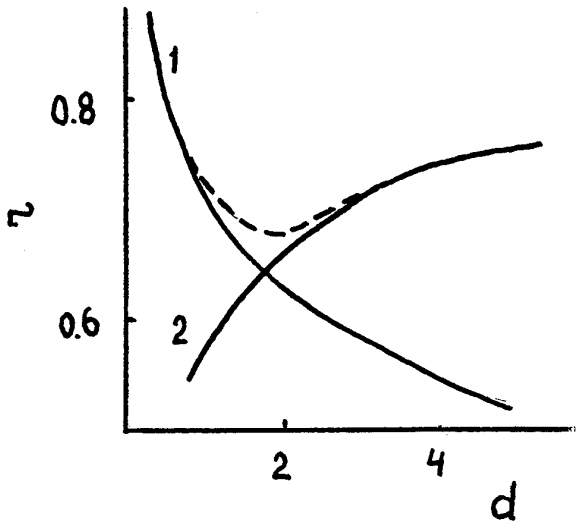



Fig. 2. The dependence of combustion rate on the dimensions of the particles of oxidizer;(1) is chemically reacting oxidizer and fuel and (2), heat exchanging only.

The diversity of possible systems does not allow to analyze development of the practical propellant formulations in this work. Nevertheless, the general conclusion that the compounds considered may constitute a basis for mixed solid rocket propellants is obvious.

And finally some general conclusive remarks. The propellants that can be developed on the basis of the afore considered compounds are inherently more environmentally safe than those based on ammonium perchlorate. The energetics of possible formulations are substantially diverse. They provide possibility to develop a propellant with energetics higher than that of HMX and ammonium perchlorate. The stability and principal characteristics of combustion of the systems considered meet the requirements of aerospace industry.

Depending on a specific aim this or that formulation will be used for, the propellant should be specially optimized with its characteristics adjusted to the aim. The scope of applications of possible propellants developed on these systems is determined not only by performance of the propellant per se but also by economic and technological considerations and specific requirements to characteristics affecting particular use. Those problems need a specific consideration.

This work was performed in cooperation with G.N.Nechiporenko, D.B.Lempert, G.M.Nazin, Yu.I.Rubtsov, and V.A.Strunin in Chernogolovka Institute of Chemical Physics of the Russian Academy of Sciences.

## Discussion

QUESTION BY A.J.Mc DONALD : Have you determined how much ADN or hydrazine nitroform can be included in propellant and still maintain class 1.3 designation i.e. less than 70 cards to attenuate donor shock wave to prevent detonation ?

ANSWER : ADN and hydrazine nitroform are explosives. However, they have worse performances than HMX. The problem of propellant including to a definite class depends not only on the nature and oxidizer amount in it. The concrete propellant requires special discussion about its nature, contents, other components, particles sizes, and other problems.

# DEVELOPMENT OF INSENSITIVE ROCKET PROPELLANTS BASED ON AMMONIUM NITRATE AND POLYNIMMO

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## 1. SUMMARY

Current composite propellant compositions for rocket motors make use of ammonium perchlorate (AP) and aluminium in a polyurethane binder based on a hydroxy terminated polybutadiene (HTPB). Increasing concern for the environment has resulted in a great deal of effort being devoted to finding replacements for AP which has a tendency to produce large amounts of HCl during combustion.

Ammonium nitrate (AN) has been considered in the past as a replacement for AP but its use has been limited due both to a reduction in ballistic performance associated with its use, and to problems connected with phase changes in AN which can occur during the storage of AN or AN based propellants. Recent developments in the field of energetic binders have however resulted in the availability of several polymers such as polyNIMMO (PN), polyGLYN (PG), and glycidyl azide polymer (GAP), which when used in conjunction with AN, compensate for any reduction in performance caused by the replacement of AP. Similarly the use of phase stabilised grades of AN have minimised the problems associated with phase changes in AN on storage.

The present paper details the work that was carried out at ICI Explosives in Scotland and the Defence Research Agency at Fort Halstead in England which led to the development of an insensitive low visible signature propellant formulation based on the use of ammonium nitrate with plasticised polyNIMMO as the binder. Theoretical calculations on a range of candidate compositions along with the ballistic, sensitiveness and rheological properties of the propellant formulation are described. In addition various options for its further development are considered.

## 2. THEORETICAL CALCULATIONS OF PROPELLANT PROPERTIES

Computer calculations were carried out using a NASA type code on a wide range of propellant formulations to determine the effect of various changes such as the use of different binders, the addition of aluminium, energetic plasticisers and/or RDX had on the theoretical performance of the propellant. The empirical formulae and the heats of formation assumed for the various ingredients are given in Table 1 while the results obtained for Specific Impulse (SI) are shown in Figures 1 to 7. A target SI was set for the proposed propellant of 2300 to 2350m/s - this was to be achieved with a minimum smoke signature.

It should be noted that the compositions used were all idealised/simplified in that the effect of additives such as catalysts, instability suppressants, etc were ignored in the calculations.

The effect of various binders (HTPB, PN and PG) on the specific impulse of propellants is illustrated in Figures 1 to 4. It is apparent that the use of energetic binders such as polyNIMMO and polyGLYN does not in itself increase the maximum energy available from a given weight of propellant. Instead it appears that the binder/filler ratio at which the maximum energy is achieved is shifted, higher binder levels being required when using more energetic (higher oxygen content) polymer systems. This effect is of particular relevance when developing low vulnerability compositions where any increase in the level of binder in a propellant at the expense of sensitive fillers would be expected to improve the low vulnerability properties of the material.

It is also apparent from figures 1 to 4 that the use of energetic binders in themselves is not sufficient to compensate for the loss in energy in shifting from AP to

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

**Table 1**
**Empirical Formulae and Heats of Formation used in Computer Code**

| Ingredient | Empirical formulae | | | | cal/mole | Density |
|---|---|---|---|---|---|---|
| Aluminium | Al 1.0 | | | | 0 | 2.7g/cm3 |
| Ammonium nitrate | N 2.0 | H 4.0 | O 3.0 | | -87,280 | 1.73 |
| Amm. perchlorate | N 1.0 | H 4.0 | O 4.0 | Cl 1.0 | -69,700 | 1.95 |
| BDNPA/F | N 4.0 | H 13.0 | O 10.0 | C 7.5 | -121,000 | 1.39 |
| BTTN | N 3.0 | H 7.0 | O 9.0 | C 4.0 | -97,300 | 1.52 |
| RDX | N 6.0 | H 6.0 | O 6.0 | C 3.0 | 15,900 | 1.82 |
| HTPB | N 0.009 | H 1.45 | O 0.019 | C 1.0 | -3,810 | 0.94 |
| polyNIMMO | N 0.2 | H 1.8 | O 0.8 | C 1.0 | -14,700 | 1.26 |
| polyGLYN | N 0.333 | H 1.667 | O 1.333 | C 1.0 | -21,380 | 1.42 |

AN as the main filler. The addition of low levels, around 10%, of aluminium can boost the energy of the AN systems to around that of AP compositions but this would also result in a propellant with an unacceptably high level of smoke.

The use of energetic plasticisers such as BDNPA/F or BTTN (see figure 5) increases the energy slightly. The addition of these plasticisers would also be expected to improve the processability of compositions based on PN and PG which are comparatively high viscosity materials which limits the level of filler that can be added while still retaining processability. Further increases in SI can be achieved by the partial replacement of AN with RDX (see figures 6 and 7) which boosts the impulse to the target level set for the propellant.

## 3. DEVELOPMENT OF COMPOSITION

Although from the theoretical work it was known that compositions using BTTN as plasticiser would be of a higher energy that those containing BDNPA/F it was realised from preliminary sensitiveness work that BTTN compositions tended to be comparatively sensitive. It was therefore decided to concentrate initial laboratory formulation work on systems using BDNPA/F plasticised PN as binder. From theoretical work this required the addition of approximately 30% RDX to the composition to achieve the SI target of 2300 to 2350m/s, assuming the rest of the filler was composed of AN.

AN prills phase stabilised with ZnO and with an average particle diameter of 165um from ICT in Germany were used along with Grade 1 RDX (Specific Surface approximately 5000cm-1, average particle size 20um) from Royal Ordnance in the UK as fillers. The plasticiser BDNPA/F was sourced from Aerojet while the polyNIMMO (difunctional) was available from the pilot plant within ICI Explosives at Ardeer. A multifunctional isocyanate, Desmodur N100 (ex Bayer) which reacts with PN to form a polyurethane was used in all the compositions.

Initially it was hoped to develop a castable composition based on a 1/1 PN/(BDNPA/F) binder. However laboratory trials indicated that even with a filler level of only 75% the mix obtained was too viscous to cast satisfactorily. Filler levels lower than this would result in compositions with SI's below the target level. Further formulation work was therefore concentrated on developing an extrudable composition. Overall filler level was increased to 80% while the PN/plasticiser ratio was increased to approximately 3/1 to give a composition which could be easily extruded. This resulted in the final propellant formulation (AN8) as shown below:

| | |
|---|---|
| Ammonium Nitrate (phase stabilised) | 45% |
| RDX | 35% |
| polyNIMMO | 14% |
| BDNPA/F | 4.67% |
| Desmodur N100 | 1.33% |

Catalyst (Dibutyl tin dilaurate) level was adjusted to give a pot life of approximately 3 hours at 60C. Full cure was achieved after approximately 3 days at 60C.

Theoretical calculations indicate that this composition should have an SI of approximately 2330m/s at 6.9MPa taking into account the level of phase stabilisers present in the AN.

## 4. PROPELLANT PROPERTIES

Several batches of the propellant were produced on the small scale plant at Ardeer in Scotland. Following cure, test pieces were machined from the propellant for evaluation both at Ardeer and at the DRA. All samples were stored at a relative humidity of 10% or less prior to testing to prevent any problems due to moisture absorption by the AN. Various safety, rheological and ballistic/performance tests were carried out on the propellant. The results obtained are shown in Figures 8 and 9 and in Tables 2 to 4.

## 5. FURTHER DEVELOPMENTS

The glass transition temperature of the above composition is approximately -25C (from DSC measurements). This is high for many propellant applications where a Tg of -40 to -50C or lower would be preferred. This can be achieved by increasing the level of BDNPA/F in the formulation but this would be at the expense of processability and final propellant strength/hardness.

Recent work however on NENA's, a new range of energetic plasticisers available from ICI Explosives USA, has however indicated that these materials can

**Table 2**
**Safety Characteristics of Composition AN8**

| | |
|---|---|
| Ignition Temperature | > 200C |
| Vacuum Stability | 0.52ml/g after 72 hours at 60C |
| Friction Sensitivity (BAM) | limiting load 360N |
| Critical Diameter | 10 to 15mm |
| Card Gap Test (50% point) | 31.8mm (4.7 GPa) |

**Table 3**
**Physical Properties of Composition AN8**

| | Temperature | Stress (MPa) | Strain (%) | Stress Modulus (MPa) |
|---|---|---|---|---|
| Initial | -40C | 0.47 | 1.1 | 52 |
| | 20C | 0.12 | 18.7 | 0.86 |
| | 60C | 0.08 | 21.7 | 0.5 |
| After 3 months at 60C | 20C | 0.1 | 19.6 | 0.66 |

| | |
|---|---|
| Density | 1.60g/ml |
| Glass Transition Temp (from DSC) | -25C |
| Shore Hardness (A Scale) | 85 |

**Table 4**
**Performance and Ballistics of Composition AN8**
**(see also Figures 8 and 9)**

| | |
|---|---|
| Burning rate at 7 MPa and 20C | 4.7mm/s |
| Pressure exponent | 0.65 |
| Temperature coefficient (-40 to 60C) | 0.5% |
| Specific Impulse (theoretical) | 2330m/s at 6.9MPa |
| Flame Temperature (Chamber) | 2566K |
| (Exit) | 1137K |
| Visible Signature Classification (AGARD)* | AA i.e. minimum smoke) |

* Note: AGARD classification is determined from the products of combustion for a propellant as calculated using a chemical equilibrium adiabatic combustion code.

**Table 5**
**Effect of Plasticisers on polyNIMMO**

| Mix No | PN (g) | MeEt NENA (g) | Et NENA (g) | Butyl NENA (g) | BDNPA (g) | Des N100 (g) | Gel Time (min) | Tg (C) | Exotherm | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Onset(C) | Peak (C) |
| 289 | 37.44 | | | | | 2.56 | 98 | -15 | 147 | 200 |
| 332 | 37.44 | 12.48 | | | | 2.56 | 105 | -41 | 147 | 195 |
| | 37.44 | 37.44 | | | | 2.56 | | -63 | | |
| 333 | 37.44 | | 12.48 | | | 2.56 | 111 | -41 | 150 | 195 |
| 334 | 37.44 | | | 12.48 | | 2.56 | 124 | -42 | 150 | 195 |
| 290 | 37.44 | | | | 12.48 | 2.56 | 109 | -25 | 155 | 195 |
| 291 | 37.44 | | | | 37.44 | 2.56 | 169 | -36 | 165 | 197 |

also be used to plasticise energetic polymers such as polyNIMMO. Laboratory tests on the viscosity and glass transition temperatures of various mixes of NENA's with polyNIMMO have been compared with similar data from BDNPA/F mixes (see figures 10 and 11 and Table 5). These tests indicate that the NENA's are much more effective at reducing both the viscosity of polyNIMMO and the Tg of cured binders i.e. NENA's are better plasticisers for PN than BDNPA/F .

It should also be noted that methyl-ethyl NENA in addition to being a very effective plasticiser for energetic binder systems also contributes more to the final energy of the composition than BDNPA/F. Substituting NENA into the current propellant composition would thus allow for a reduction in the overall filler level while maintaining the energy of the system. This combined with the reduction in viscosity of the polyNIMMO during processing may permit the development of a castable composition.

Recent work (ref. 1) on molecular modelling of polymer/plasticiser interactions has agreed well with the above observations on NENA's and BDNPA/F. Initial results from the modelling work suggest that the NENA's act in an almost ideal fashion, increasing the polymer free volume (and thus decreasing Tg) as much as would be theoretically expected. The same is not true for BDNPA/F which performs well below theoretically ideal levels. This is apparently due to some form of temporary crosslinking occurring as a result of interactions between BDNPA/F and polyNIMMO - this type of interaction is known to inhibit plasticisation. (Note: This work will be reported in full at the Life Cycles of Energetic Materials meeting in December 1994.)

Further work is also planned on alternative grades of AN with the effect of both particle size and phase stabilisers on ballistics being studied. Recent work at Ardeer on the production of PROGRAN a propellant grade of ammonium nitrate (ref. 2) has resulted in the development of a free flowing grade of ammonium nitrate with a tightly controlled particle size distribution. The effect of this material on processability and ballistics will also be studied.

## 6. CONCLUSION

An insensitive rocket propellant composition has been developed based on the use of a plasticised polyNIMMO as the binder and ammonium nitrate as the principal energetic filler. The propellant has acceptable ballistics and performance. However further work using alternative energetic plasticisers is required to improve the glass transition temperature of the final propellant and to allow the development of a castable composition. The effect of alternative grades of ammonium nitrate on propellant properties also requires study.

## 7. REFERENCES

1. E Robson, G A Leiper and A S Cumming, Private communication.

2. W B H Leeming, R Oliver, F Pourmahnaei and M Rodgers, ADPA Conference
Orlando, March 1994, pages 197 to 203.

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Figure 1

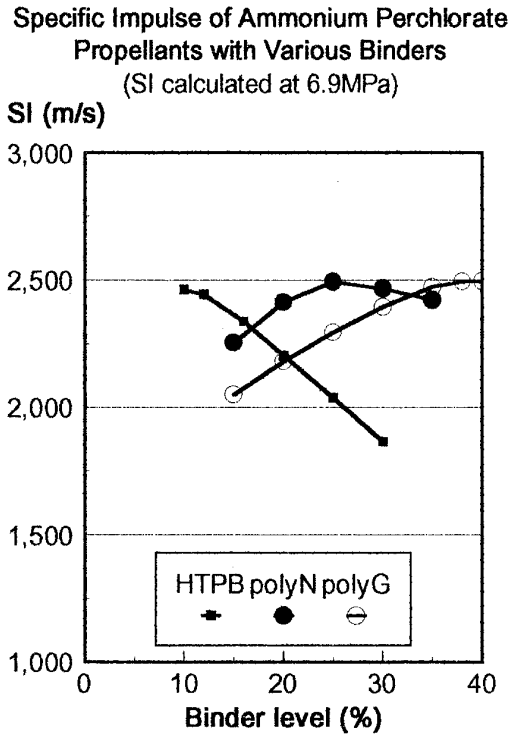



Figure 2

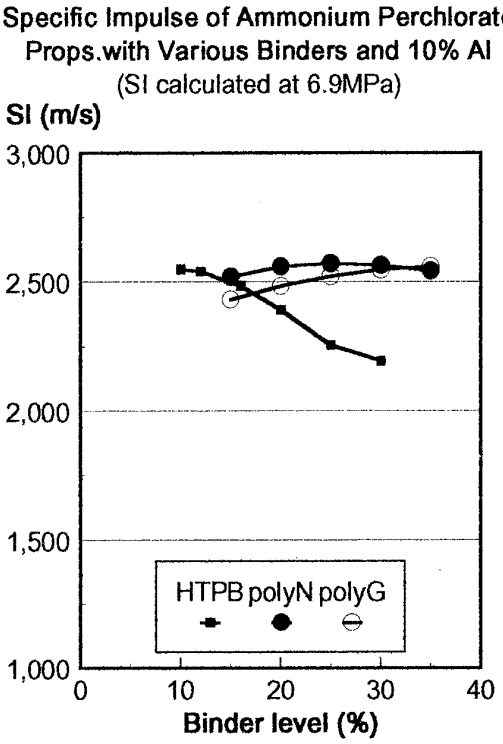



Figure 3

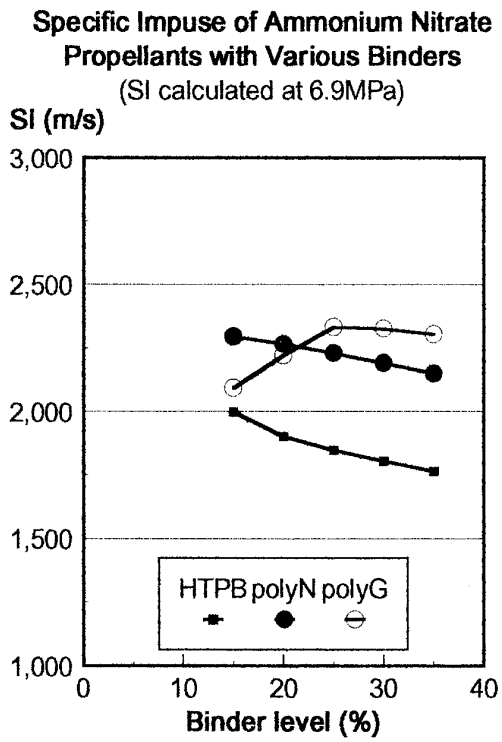



Figure 4

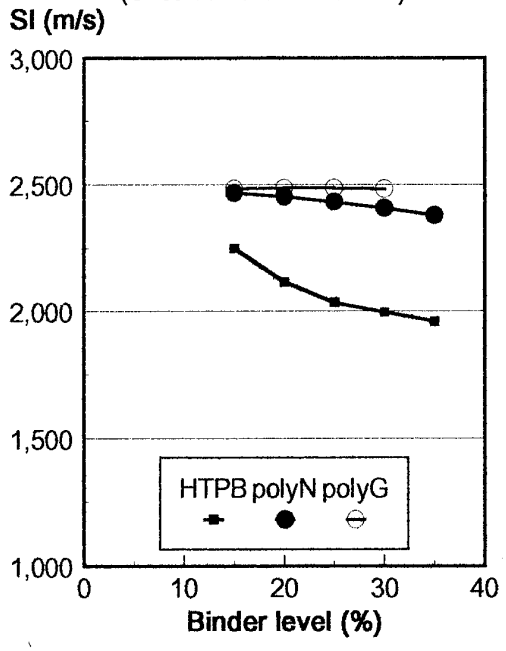


Figure 5

**Effect of Energetic Plasticisers on SI of AN based Composite Propellants**
(SI calculated at 6.9MPa)

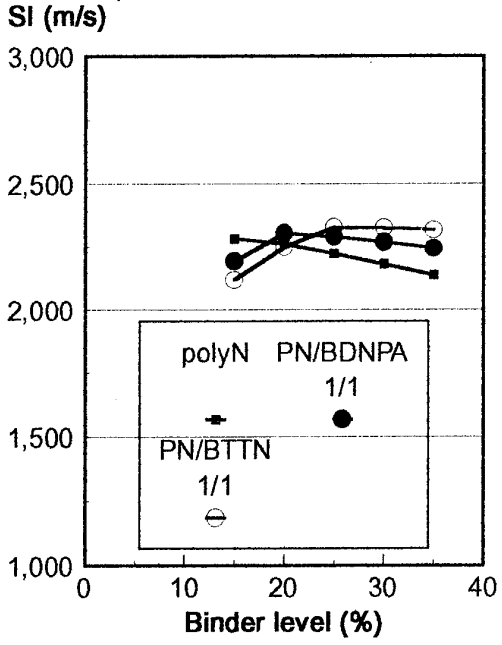
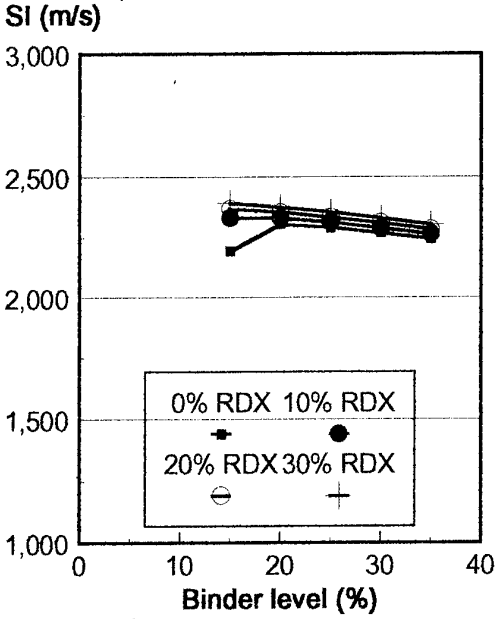



Figure 6

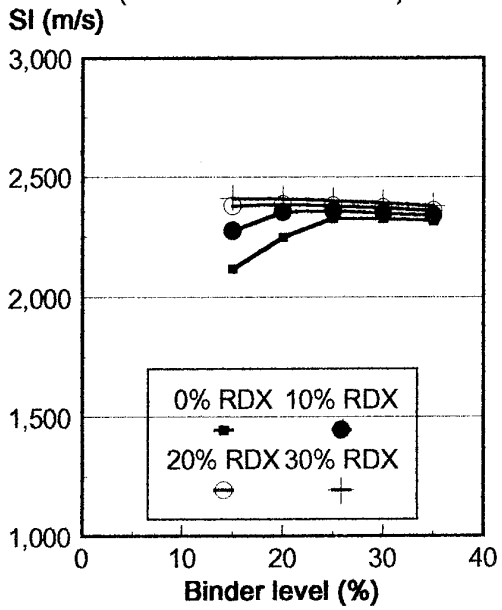
**Effect of RDX level on SI of AN based Composites with PN/BDNPA-F Binder**
(SI calculated at 6.9MPa)




1/1 Ratio of PN/plasticiser

Figure 7

**Effect of RDX level on SI of AN based Composites with a PN/BTTN Binder**
(SI calculated at 6.9MPa)




1/1 Ratio of PN/Plasticiser

Figure 8

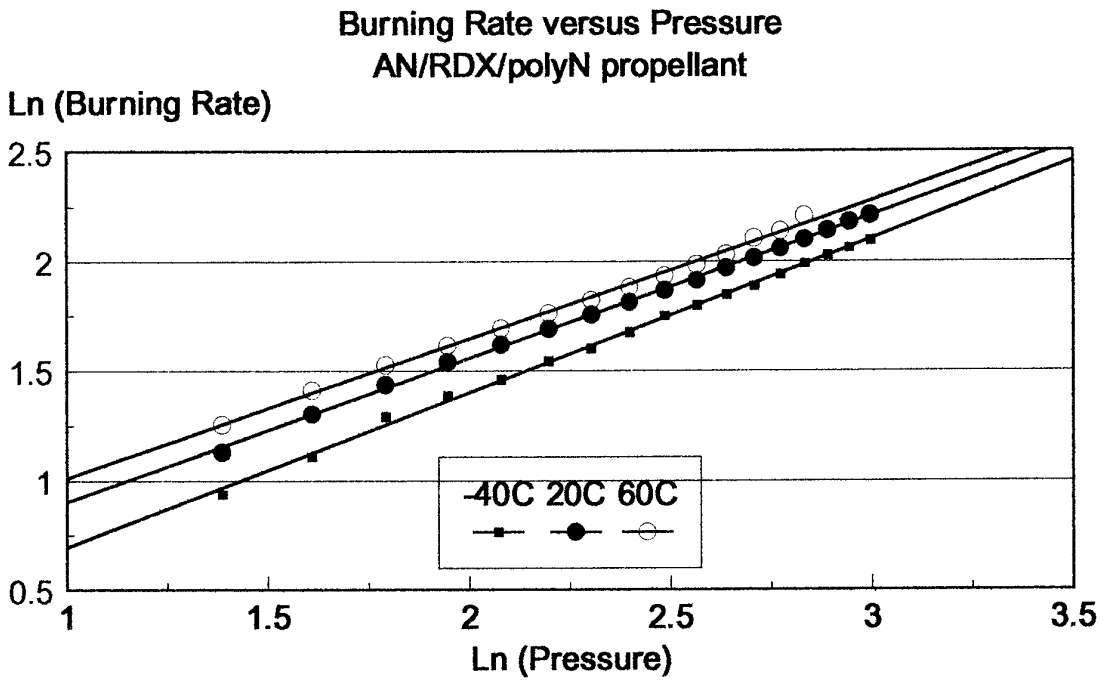



Figure 9

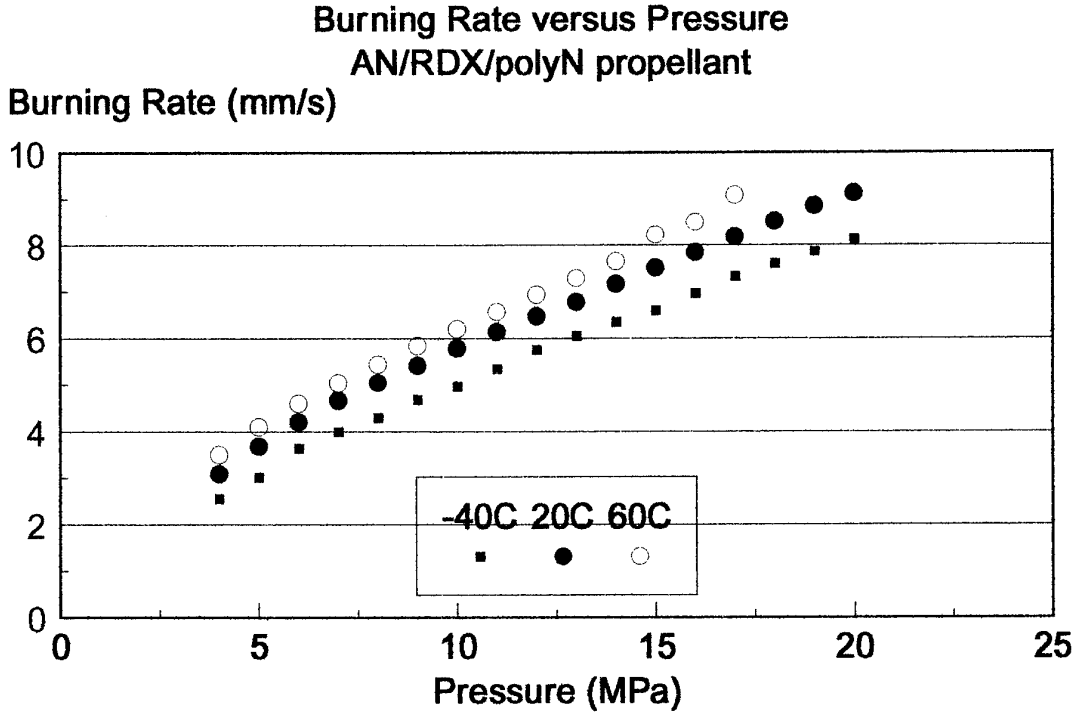


Figure 10

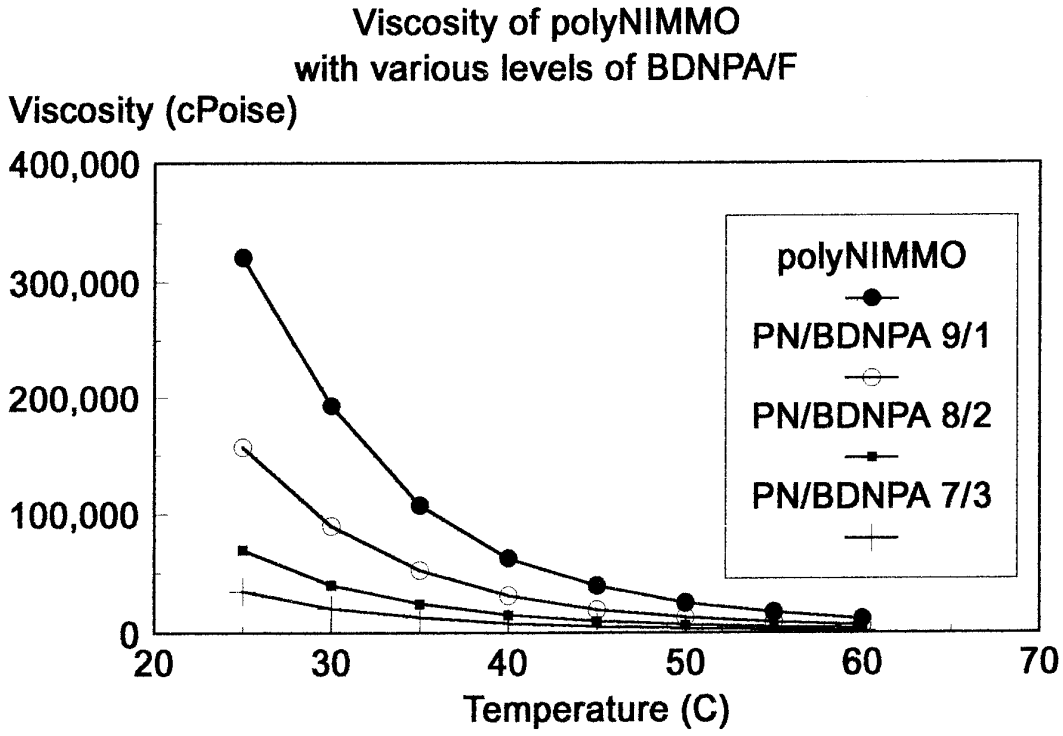
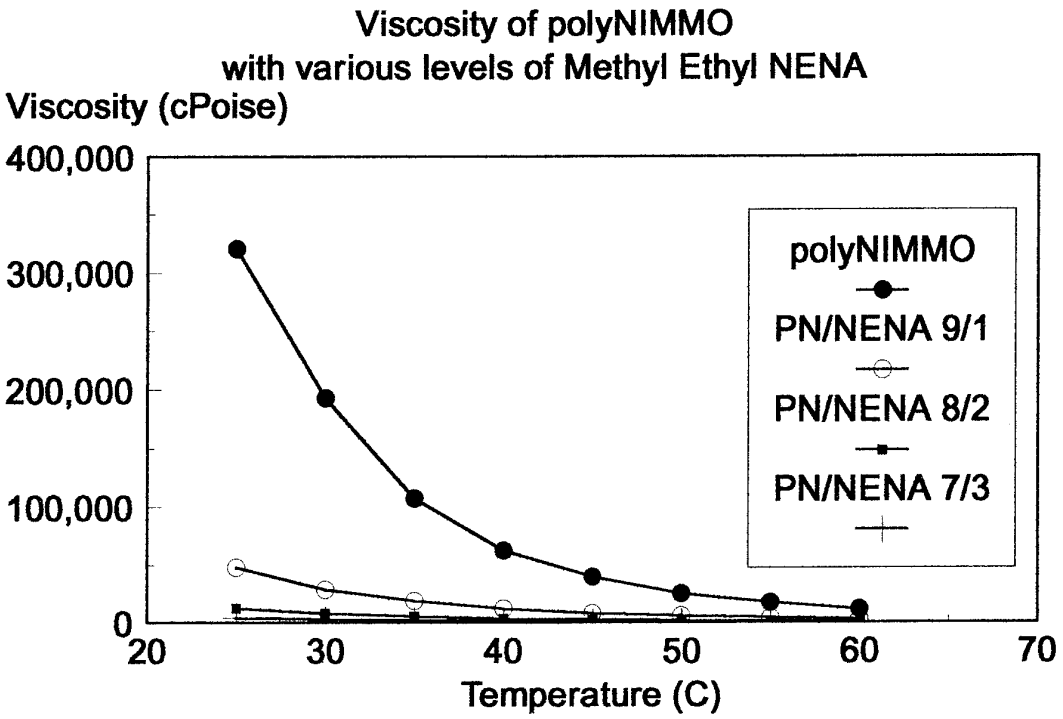



Figure 11



## Discussion

QUESTION BY K. MENKE : Could you not use the PolyNiMMO with a higher molecular weight and functionality to achieve better mechanical properties together with a higher percentage of energetic plasticizers, which also may allow to formulate AN/Poly N -propellants with higher performance ?

ANSWER : As I said in my presentation the work we have carried out to date has been using difunctional polyNIMMO, and that it is our intention in the near future to examine the use of trifunctional polyNIMMO and how this affects the rheology of the cured system. With regard to variations in the molecular weight, changes in this will not only affect the mechanical properties of the cured system, but will also affect the viscosity of polyNIMMO and hence its processability. A balance has to be reached between these factors.

# Use of New Oxidizers and Binders to Meet Clean Air Requirements

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## 1. SUMMARY

The burning of conventional solid rocket propellants introduces various substances into the atmosphere, including such noxious materials as hydrochloric acid and other reactive chlorine compounds, uncombusted fuel species, and toxic heavy metal oxides, as well as lighter metal oxides and alkali metal oxides. These materials can contaminate the natural landscape and water sources, degrade atmospheric quality, and even have the potential to affect atmospheric behavior (e.g., through ozone depletion). Advanced new energetic oxidizers and binders now being investigated, used in conjunction with selected conventional propellant ingredients, will allow the formulation of new propellants that will eliminate nearly all of these contaminants and still possess a high measure of performance. Oxidizers include an inorganic derivative of nitramidic acid and a dense 3-dimensional cyclic nitramine having high oxygen balances and favorable heats of formation. Binders include polyglycidyl and polyoxetane derivatives containing energetic azido or nitrato structures.

## 2. NOMENCLATURE

| | |
|---|---|
| ADN | ammonium dinitramide |
| AN | ammonium nitrate |
| AP | ammonium perchlorate |
| BTTN | butanetrioltrinitrate |
| DMBT | dimethylbitetrazole |
| GAP | glycidyl azide polymer |
| HCl | hydrochloric acid |
| HMX | cyclotetramethylenetetranitramine |
| HNIW | hexanitroisowurtzitane |
| HTPB | hydroxyl-terminated polybutadiene |
| NAWCWPNS | Naval Air Warfare Center Weapons Division |
| NSAN | non-stabilized ammonium nitrate |
| PEP | Propellant Evaluation Program |
| poly-NMMO | poly-nitratomethyl, methyl oxetane |
| PSAN | phase-stabilized ammonium nitrate |

## 3. INTRODUCTION

This paper presents a comparative study of the relative performance and potential atmospheric contamination produced by three typical state-of-the-art solid rocket propellants, and some new "clean" developmental propellants containing two advanced new chlorine-free oxidizers, along with analogous formulations with two conventional oxidizers. Some of the new propellants are largely theoretical, although the ingredients they incorporate do exist. Little to no actual formulation work has been made with the new propellants. However, they contain a practical volume percentage of solids, ranging from 70 to 72% depending on ingredient density, which, from general experience, means that they should be processible. The state-of-the-art composite propellants in this study have a higher volume percentage of solids (76-78%), which reflects their more mature formulating technology. The values shown for performance and exhaust products are calculated values, obtained from the NAWCWPNS PEP, Feb. 1990 upgraded version.

## 4. PROPELLANT TYPES AND INGREDIENTS

The binders, plasticizers, fuels, and oxidizers used in the developmental propellants are listed in Table 1.

**TABLE 1. Developmental Propellant Ingredients.**

| | |
|---|---|
| HTPB | Hydroxyl-terminated polybutadiene, the state-of-the-art composite propellant binder, manufactured by ATOChem, Inc. |
| GAP | Glycidyl azide polymer, a developmental energetic binder produced by 3M Co. |
| Poly-NMMO | Poly-nitratomethyl, methyl oxetane, a developmental energetic binder with a high oxygen content, by Aerojet Solid Propulsion Co. |
| BTTN | Butanetrioltrinitrate, a highly oxygenated energetic plasticizer |
| DMBT | Dimethylbitetrazole, a developmental high nitrogen solid fuel with a high positive heat of formation, used in propellants with oxidizers having high oxygen balances to increase performance, developed at NAWCWPNS |
| AN | Ammonium nitrate solid oxidizer |
| HMX | Cyclotetramethylenetetranitramine solid oxidizer |
| HNIW | Hexanitroisowurtzitane, a dense, high energy solid nitramine oxidizer, developed at NAWCWPNS |
| ADN | Ammonium dinitramide, a developmental high performance solid oxidizer with a high oxygen balance |

A rather narrow selection of binders and oxidizers was used for this limited study. AP oxidizer was not considered because of its chlorine content. AN and HMX oxidizers are

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common non-chlorine oxidizers. HNIW and ADN are energetic new chlorine-free oxidizers. HTPB represents a state-of-the-art hydrocarbon binder with little oxygen content. GAP binder has a higher oxygen content than HTPB, and is quite energetic with its abundant azido-nitrogen content. Poly-NMMO binder is a highly oxygenated binder with a large portion of its oxygen in the form of energetic nitrato groups.

Three state-of-the-art propellants were included in this study for comparison purposes: (a) state-of-the-art space booster propellant—an HTPB formulation with aluminum fuel and AP oxidizer, analogous to that used on such heavy lifters as the Space Shuttle and Titan; (b) state-of-the-art reduced-smoke propellant—containing HTPB binder and AP oxidizer; (c) state-of-the-art double-base propellant—a conventional double base containing nitroglycerin-plasticized nitrocellulose plus chemical stabilizers and a lead compound as a ballistic catalyst.

## 5. PROPELLANT PERFORMANCE AND EXHAUST PRODUCTS

The relative performance values for all propellants in this study are shown in Table 2. The state-of-the-art reduced-smoke propellant is used as the baseline for estimating relative performance among all the propellants in the study. Table 3 contains the noxious exhaust species produced by the propellants on combustion. $CO_2$, $H_2$, $H_2O$, $N_2$, and occasionally $O_2$ are also produced in substantial amounts, but these are not regarded as noxious and are, therefore, not included in the table ($CO_2$ is a "green-house" gas that allegedly causes global warming. It is, therefore, undesirable, but is far less toxic and objectionable than HCl or CO. $H_2$ is combustible, but otherwise unobjectionable, and diffuses rapidly into the upper atmosphere). Some potentially noxious, transitory compounds and radicals that are produced in very minute quantities (e.g., HO, CHN) are also not included in the table. All the exhaust species described in this study occur in the expansion zone of the rocket nozzle, just before ejection from the nozzle exit plane. Some of them partially burn to $CO_2$ and $H_2O$ and possibly other oxides upon exposure to oxygen in the air, but the extent of combustion is not known. Species that are present in "trace" amounts have a concentration of <0.03 kg in the exhaust for every 100 kg of propellant consumed.

## 6. DISCUSSION

The propellants containing only non-stabilized AN oxidizer (NSAN) would probably not be practical in many solid rocket applications, because of the phase changes AN is subject to with varying temperatures. These phase changes, and their accompanying volume changes, can destroy a propellant's physical integrity. Such propellants were included to indicate their potential when, at some future time, an effective PSAN with a small percentage of stabilizer can be successfully developed (present PSANs usually contain substantial amounts of alkali metal compounds, which detract from performance and contaminate the exhaust). NSAN propellants are relatively moderate performers, can be very clean burning when properly formulated, and would tend to have relatively low detonability. AN propellants that are only partially oxidized with NSAN, such as those containing a phase-stable co-oxidizer such as HNIW or ADN, are relatively stable, and are being successfully developed at NAWCWPNS.

HMX is not a true oxidizer, having no effective oxygen balance beyond what is required to combust itself (HMX is stoichiometrically balanced to burn to CO, $H_2O$, and $N_2$, with no oxygen left over). However, with an appropriate binder containing an energetic plasticizer, its performance in propellants is respectable. While propellants with HMX as the major oxidizer are certainly not as "dirty" as AP propellants, which generate HCl in their exhausts, they are not the cleanest burning either, especially when compared to those formulated with the newer oxidizers. Also, HMX propellants tend to be quite detonable.

HNIW has a great deal of potential as a new oxidizer for propellants requiring both high performance and clean burning. HNIW's oxygen balance is not especially high, but in propellants with well-oxygenated binders and plasticizers, a very clean exhaust is obtained together with performance that rivals, and in some cases exceeds, that of the state-of-the-art aluminized AP propellants. The detonability of HNIW propellants tends to be high, on the same order as that of HMX propellants.

ADN is a new oxidizer with a high oxygen balance, rivaling that of AP, but without chlorine. As such, it produces very clean burning in propellants. Its performance in propellants rivals that of HNIW in specific impulse, but is inferior in volumetric impulse (density x Isp) because of its lower density. Its high oxygen balance allows the use of a high energy fuel, DMBT, to good advantage in propellant with a well-oxygenated binder, substantially increasing performance without significantly affecting clean burning characteristics. ADN propellants tend to be detonable, but are probably less so than other nitramine propellants because of the highly over-oxidized, fuel-poor nature of ADN, which tends to reduce detonability of such oxidizers.

## 7. CONCLUSIONS

When selecting solid rocket propellant ingredients, the presence of substantial amounts of oxygen in energetic molecular structures appears to be essential to minimize noxious rocket exhaust species and maintain high performance. This appears to be true not only for the propellant oxidizers used, but for the propellant binder and plasticizer as well. For this reason, propellants made with nitrato-plasticized, highly oxygenated energetic polymers such as poly-NMMO appear to offer a way to satisfy future solid rocket propulsion requirements for high performance and clean exhaust, especially when formulated with new, advanced oxidizers such as HNIW or ADN.

**TABLE 2. Solid Rocket Propellant Type and Relative Performance.**

| Propellant No. | Propellant Type | Relative Performance (State-of-the-Art Reduced-Smoke Propellant = 100%) | |
|---|---|---|---|
| | | Density x Isp | Isp |
| 1 | State-of-the-art aluminized space booster | 111.4 | 106 |
| 2 | State-of-the-art reduced smoke | 100 | 100 |
| 3 | State-of-the-art double base | 93.9 | 97.6 |
| 4 | HTPB/AN | 69.9 | 80.7 |
| 5 | HTPB/HMX | 84.8 | 90.0 |
| 6 | HTPB/HNIW | 97.4 | 95.6 |
| 7 | HTPB/ADN | 90.7 | 98.8 |
| 8 | GAP/AN | 85.1 | 91.2 |
| 9 | GAP/HMX | 99.1 | 98.4 |
| 10 | GAP/HNIW | 109.8 | 103.2 |
| 11 | GAP/ADN | 102.1 | 105.2 |
| 12 | PolyNMMO/BTTN/AN | 88.6 | 93.2 |
| 13 | PolyNMMO/BTTN/AN/DMBT | 90.9 | 95.6 |
| 14 | PolyNMMO/BTTN/HMX | 106.8 | 103.6 |
| 15 | PolyNMMO/BTTN/HNIW | 116.3 | 107.2 |
| 16 | PolyNMMO/BTTN/ADN | 99.8 | 100.8 |
| 17 | PolyNMMO/BTTN/ADN/DMBT | 103.3 | 105.6 |

6.894 MPa chamber pressure exhausted to sea level, at optimum exhaust expansion.

**TABLE 3. Solid Rocket Propellant Noxious Exhaust Products.[a] (kg/100 kg of propellant.)**

| Propellant No. | Pb[b] | C (solid) | CO | $Al_2O_3$[c] | HCl | Cl + $Cl_2$ | $CH_4$ | $NH_3$ | $NO_x$[d] | Total, kg |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | 23.2 | 35.7 | 20.1 | 0.41 | | trace | | 79.4 |
| 2 | | | 7.8 | | 27.0 | trace | | trace | | 34.8 |
| 3 | 1.8 | | 31.3 | | | | | trace | | 33.1 |
| 4 | | | 7.1 | | | | 4.0 | trace | | 11.1 |
| 5 | | 5.5 | 42.2 | | | | 0.9 | trace | | 48.6 |
| 6 | | 0.9 | 54.4 | | | | 0.3 | trace | | 55.6 |
| 7 | | | 18.1 | | | | trace | trace | | 18.1 |
| 8 | | | 3.4 | | | | | trace | | 3.4 |
| 9 | | | 37.2 | | | | 0.03 | trace | | 37.2 |
| 10 | | | 38.1 | | | | trace | trace | | 38.1 |
| 11 | | | 5.2 | | | | | trace | | 5.2 |
| 12 | | | | | | | | | trace | trace |
| 13 | | | trace | | | | | | | trace |
| 14 | | | 28.3 | | | | | trace | | 28.3 |
| 15 | | | | | | | | trace | trace | trace |
| 16 | | | trace | | | | | | 0.07 | 0.07 |
| 17 | | | 1.1 | | | | | | trace | 1.1 |

[a] $CO_2$, $H_2$, $H_2O$, $N_2$, and occassionally $O_2$ are also produced in substantial amounts, but are not considered noxious and are not included. All exhaust species are as they exist in the rocket nozzle expansion cone exit plane, before exposure to air. "Trace" means <0.03 kg occurs in the exhaust for each 100 kg of propellant burned.

[b] Most Pb is elemental, but lead oxide is added.

[c] This includes small amounts of various aluminum chloro-oxides.

[d] $NO_x$ (oxides of nitrogen) is virtually all NO

## Discussion

QUESTION BY A. DAVENAS : What price would be considered acceptable for a new oxidizer for use in a propellant for a tactical system (for instance taking RDX or HMX as a reference) ?

ANSWER : Generally speaking the technology guidelines utilized in the IMAD Program and in the United States, I believe, is that the price should not be significantly higher than other common oxidizers such as AP, HMX and RDX. The cost of the propulsion unit in a US Navy tactical system is small in comparison to the overall cost of the system. The fact that HMX and RDX run in the $ 10- $ 20/pound range and that is double or triple the cost of AP is not significant. It is generally considered that something in the $ 20- $ 30/pound range, would be acceptable. If the performance or signature characteristics merited it, a higher cost to achieve the requirements, perhaps up to $ 50/pound, might be acceptable. However it would depend upon the particular tactical system and the target it is designed to defeat. It should also be noted that the cost of very pure AP can be in the $ 10- $ 15/pound range or higher and this grade of AP is currently in use in some fielded systems.

QUESTION BY A. DAVENAS : What is in your opinion the order of the cost of CL 20 and ADN in mass production ? (for instance taking RDX or HMX as a reference)

ANSWER : It is not possible at this point in time to predict the cost of ADN with any accuracy due to the stage of maturity of the synthesis technology in the United States. We have only recently begun working with this material and there is no ADN work currently ongoing in the IMAD program. A requirement for the 6.4 IMAD program is that in order to use a material, it has to have been scaled up to hundreds of pounds and be commercially available. This is not the case presently and there would be little or no validity in cost projections for mass production of the material until synthesis optimization is completed. ADN also at this point in time is primarily being pursued as a propellant ingredient.
CL 20, on the other hand, is a much more mature technology. The cost given of $800 - $ 900 /pound is an average over the entire production on the IMAD program. The first 100 pound batch cost/significantly more than that price and the last batches were significantly less. There is also a lot of interest in CL 20 as an explosive as well as a propellant ingredient. Therefore the overall projected demand in the United States appears to be significantly higher for CL 20. There are two propulsion companies in the United States, Aerojet and Thiokol, that have scaled up the production and sell this material in bulk quantities. If further work with this oxidizer produces the desired results, the price should be in the $ 15 - $ 30 range or comparable to HMX/RDX.

# Evaluation of Ammonium Nitrate Propellant Emissions

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## 1. SUMMARY

Defence Research Establishment Valcartier has recently completed the exploratory development of a solid rocket propellant based on an ammonium nitrate (AN) oxidizer and a glycidyl azide polymer (GAP). Apart from developing a propellant with good energetic performance, improved safety and low observables, the goal was to obtain a propellant having an exhaust with few harmful emissions. This propellant has now been extensively tested, including the firings of several 70 mm diameter motors, four 200 mm diameter motors, small ballistic test motors inside a closed smoke chamber, and closed bomb tests. Estimates of the exhaust gas composition have been done using a thermochemical equilibrium computer code, and are supported by motor performance data and infrared emission spectra. The smoke chamber firings include mass extinction coefficient measurements of the exhaust smoke, derived from transmissometer data at the visible and 2-14 μm wavelengths. The closed bomb tests provided gas samples for Fourier transform infrared (FTIR) spectrometry and gas chromatography analysis of post-combustion exhaust products. Overall, the results indicated that the combustion of GAP/AN propellants produce exhaust emissions that are less harmful to the environment than those produced by ammonium perchlorate-based propellants. However, mainly because of the presence of zinc oxide in the AN, solid particulates in the exhaust form more primary smoke than a minimum smoke or reduced smoke propellant.

## 2. INTRODUCTION

Many conventional composite propellants, including commercially-successful Canadian propellants and the propellant for the Space Shuttle Solid Rocket Motor, use ammonium perchlorate (AP) as the oxidizer. These propellants give, in general, good energetic performance while being fairly easy to process and reasonably safe (Class 1.3C). Unfortunately, their main drawback is that the combustion of these propellants generates a large amount of hydrogen chloride, as well as some other chlorine compounds. The exhaust is therefore very corrosive and toxic and will not only damage equipment, but is harmful to personnel and other life. Another consequence of AP-based propellant combustion is the formation of secondary smoke. From a military point of view, the existence of any exhaust smoke can betray the launch point and flight path of a missile to the enemy, as well as attenuate electromagnetic signals, both friendly and enemy. While primary smoke is caused by the condensed exhaust products, such as metal oxides and binder particles, secondary smoke is the condensation of water vapour, ambient and/or from the propellant combustion. Hydrochloric acid, resulting from the combination of hydrogen chloride with water, enhances the formation of secondary smoke by lowering the saturation vapour pressure of water. Condensation therefore takes place at higher temperatures and lower relative humidities than when it normally would. When atmospheric conditions favourable to secondary smoke formation exist, as they often do in a maritime environment, secondary smoke can be a more significant problem than that of primary smoke since our measurements indicate that it is more "optically dense" in the infrared and visible regions than primary smoke.

The elimination of the chlorine compounds in the exhaust is therefore a desirable goal for reducing exhaust toxicity, corrosiveness, and compounds that cause secondary smoke. This can be done in two ways: by scavenging the hydrogen chloride and chlorine in the exhaust by additives in the propellant, or by eliminating the AP and replacing it with a chlorine-free oxidizer. For the first method, sodium nitrate added to the propellant reacts with AP products during combustion to form salt. With this method there is a loss in propellant specific impulse ($I_{sp}$) of 15-20 s [1], not all of the hydrogen chloride or chlorine is scavenged, and primary smoke due to the presence of salt particles is produced. In the second method, preferred oxidizer replacements for AP are nitramines such as cyclotetramethylene tetramine (HMX) or cyclotrimethylene triamine (RDX), or ammonium nitrate (AN). If chosen on strictly an energetic basis, HMX and RDX are preferable over AN. Unfortunately, HMX and RDX are explosives with small critical diameters, are hazardous to process, and produce more dangerous propellants. Therefore, since a relatively safe, low vulnerability propellant with little primary smoke was the goal, replacing AP with AN was chosen as the

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method of reducing chlorine compounds in the exhaust. In order to recover some of the loss in $I_{sp}$, DREV's AN propellants use "energetic" GAP as the binder rather than hydroxy-terminated polybutadiene as in its AP-based propellants.

While eliminating AP reduces the problems associated with chlorine compounds in the exhaust, the use of AN introduces two new concerns with the exhaust emissions. The first is due to the fact that during storage at normal temperatures, AN can undergo a phase transition that causes crystal growth. This can result in a deterioration of the mechanical properties of the propellant. By adding a metal oxide to the AN, this phase transition can be stabilized. In addition to losing propellant $I_{sp}$ due to use of phase-stabilizing oxides, these oxides are present in high enough amounts that they could cause some primary smoke. Original DREV formulations used a PSAN (phase-stabilized AN) containing 3.5% nickel oxide. Unfortunately, after we developed some promising formulations, NiO was identified as a potential carcinogen. All subsequent formulations, including those described in this paper, have contained 3% zinc oxide PSAN instead of 3.5% NiO PSAN.

Another potential consequence of AN combustion is the formation of harmful nitrogen compounds, the most important of these being nitrogen oxides (NOx). This is of great concern for air pollution and the ozone layer. In fact, a major design driver for air-breathing combustion systems (gas turbines, automobile engines, furnaces, thermal generating plants, etc.) is the reduction of NOx emissions. There are two ways in which NOx can form. The first is directly from the combustion of the propellant ingredients, especially AN, where the formation of NOx is one of the reaction steps toward complete combustion. The second way is from the combination of oxygen and nitrogen gases at high temperatures, particularly in the afterburning exhaust plume. Since AN propellant exhaust is cooler than AP propellant exhaust, there should not be as much NOx formed from the second method. However there is much more "fuel-bound" nitrogen contained in AN propellants compared with AP propellants, so the first method may be much more important.

After having developed some promising GAP/AN formulations and successfully firing motors containing them, we at DREV have expended considerable effort trying to characterize the exhaust and compare it to that from AP propellants. The first goal was to identify and quantify the gaseous constituents of the exhaust. Unfortunately, direct gas sampling is very difficult to do, given the severe environment in a rocket motor plume. For experimental data from the plumes, we had to rely on FTIR emission spectroscopy, a non-obtrusive measurement technique, but this does not reveal the absolute concentrations of the gases. To estimate these, calculations and closed bomb measurements have had to be done. Next, attention turned to identifying and quantifying the particulates in the exhaust, or smoke. The optical properties of the smoke were measured in the visible and IR regions with a transmissometer. The optical properties were then fed into an electro-optic sensor performance model in order to quantitatively estimate the effect of the smoke on the range of detection of enemy missiles.

In most instances where data for the GAP/AN propellant is given, comparative data for a non-aluminized HTPB/AP propellant are also given. The basic formulation for each is in Table I.

**Table I** Propellant formulations, by weight

| GAP/AN | 0%Al HTPB/AP |
|---|---|
| 69.5% PSAN (includes 3% ZnO) | 87.2% AP |
| 29% plasticized GAP binder | 12% plasticized HTPB binder |
| 1.5% ballistic modifiers (metal compounds) | 0.8% ballistic modifiers (metal compounds) |

## 3. EXHAUST GAS COMPOSITION

### 3.1 Thermochemical Equilibrium Calculations

Because of the high temperatures present in a solid rocket motor combustion chamber, the chemical species present are likely in chemical equilibrium with each other. Furthermore, at these high temperatures and relatively low pressures (as opposed to gun propellant combustion), the gases can be assumed to be ideal. With a computer code such the NASA SP-273 code [2], the chamber conditions and gas composition can be calculated. This code can also be used to predict nozzle exit plane conditions once the gases expand from the chamber through the nozzle, provided several assumptions hold, including isentropic expansion. One problem with nozzle exit plane calculations, however, is that the assumption that the gases are always in equilibrium may not be valid. This is because the gases may forced to expand too quickly through the nozzle compared with the time needed for the chemical reactions to take place to keep the species in equilibrium with each other. Fortunately, the prediction of the nozzle exit plane properties and species can be bounded (if the other assumptions hold) by assuming that the gases remain in equilibrium (infinitely fast reactions) as they expand, or

that the mole fractions of the species are frozen at the chamber composition and remain so through the nozzle (infinitely slow reactions).

### *3.1.1 Major Exhaust Products*

Calculations were performed for each of the two propellants described in Table I, at the values of chamber pressure and nozzle expansion ratio used in actual 70 mm diameter motor firings. Results for the exit plane properties and species, both frozen and equilibrium flow, are listed in Table II. Metal compounds from the ballistic modifiers and gases present in mole fractions less than 0.00005 are not included.

**Table II** Nozzle exit plane properties and species

| **GAP/AN** | | | **0%Al HTPB/AP** | |
|---|---|---|---|---|
| 12.872 MPa | | Chamber Pressure | 11.528 MPa | |
| 16.45 | | Expansion ratio | 5.518 | |
| Frozen | Equil. | Mole fraction | Frozen | Equil. |
| 0.0000 | 0.0077 | $CH_4$ | 0.0000 | 0.0000 |
| 0.1347 | 0.0332 | CO | 0.0977 | 0.0715 |
| 0.0780 | 0.1751 | $CO_2$ | 0.1235 | 0.1501 |
| 0.0000 | 0.0000 | HCl | 0.1841 | 0.1933 |
| 0.3954 | 0.3132 | $H_2O$ | 0.4353 | 0.4259 |
| 0.1394 | 0.2145 | $H_2$ | 0.0472 | 0.0599 |
| 0.0000 | 0.0000 | NO | 0.0016 | 0.0000 |
| 0.2525 | 0.2563 | $N_2$ | 0.0984 | 0.0993 |
| 0.0000 | 0.0000 | OH | 0.0106 | 0.0000 |
| 0.0000 | 0.0000 | $O_2$ | 0.0017 | 0.0000 |
| 690 K | 824 K | Exit Temp | 1555 K | 1697 K |
| 0.0660 MPa | 0.0772 MPa | Exit Pressure | 0.3031 MPa | 0.3171 MPa |

Understandably, there is no HCl in the exhaust products of the GAP/AN propellant, but there is much more $N_2$ gas present than for HTPB/AP. There is also much more $H_2$ gas present in the exhaust of the GAP/AN propellant because it is more fuel rich than HTPB/AP. This $H_2$, along with CO, can contribute to afterburning in the plume trailing the motor. The other main combustion products, including $H_2O$ and $CO_2$, are also present in large amounts for each propellant.

### *3.1.2 Temperatures and Combustion Efficiency*

From Table II, the exit plane temperature for GAP/AN is much lower than for HTPB/AP. While some of the difference may be due to the much greater expansion ratio, there is still a difference of 500 K if the gases for each propellant are expanded identically from 6.9 MPa to 0.1 MPa. Temperatures in the combustion chamber are also much lower for the GAP/AN propellant (2100 K versus 3000 K for HTPB/AP at the chamber pressures given in Table II). In fact, since the GAP/AN temperatures are significantly lower and GAP/AN is more fuel rich than the HTPB/AP propellant, incomplete combustion is more likely with GAP/AN. From performance data of a motor firing, the completeness of combustion can be estimated from the measured and theoretical values of the characteristic velocity (C*) or the $I_{sp}$. Of the two, C* is preferable because it neglects the effects of the nozzle. It is derived from the pressure-time curve of the firing, and is a thermodynamic property of the propellant gases that depends on their temperature and molecular weight. It can be thought of as the ability of a propellant to produce gas. If there is incomplete combustion, larger molecular weight compounds will be present and the measured C* will be lower. In our experience at DREV firing HTPB/AP propellant motors, measured and theoretical C*'s have usually been within a couple of percent (most of which may be attributed to the error on the pressure measurements). We therefore feel that complete combustion and chemical equilibrium conditions are being approached within the combustion chambers of HTPB/AP motors. To determine whether or not complete combustion is being approached in the GAP/AN propellant motors, theoretical and measured values of C* were compared and are shown in Table III. The theoretical C* values for both propellants, were calculated from the NASA code at the same chamber conditions as shown in Table II. The close agreement of the theoretical and measured values is indicative of the completeness of the combustion for both propellants, and indirectly supports the NASA code calculations for the major species concentrations as well. However, significant amounts of minor species (for example NOx concentrations of concern are measured in parts per million) could still be present and not affect the C* values very much.

**Table III** Theoretical and measured C*

| GAP/AN | C* | 0%Al HTPB/AP |
|---|---|---|
| 1369 m/s | Theoretical | 1528 m/s |
| 1378 m/s | Measured | 1498 m/s |

*3.1.3 NOx Formation*

As for the presence of NOx (NO, usually in the highest concentrations, as well as $NO_2$, and $N_2O$), none is indicated in Table II for the GAP/AN propellant and there may be a small amount of NO for the HTPB/AP propellant, depending on the rates of reaction through the nozzle. There is a lack of NOx because these calculations are for chemical equilibrium and assume that all the propellant has reacted completed. Therefore these calculations would only allow the presence of AN based on the NOx being in chemical equilibrium with the other species present, particularly $N_2$ and $O_2$. However, the formation of NOx in this manner ("thermal" NOx) is only important above 1800 K [3]. The low exit plane temperatures in Table II, along with the lack of $O_2$ present, explain the absence of NOx there. If afterburning occurs and raises the temperatures above 1800 K, though, the combination of $N_2$ and $O_2$ may still be responsible for the formation of NOx.

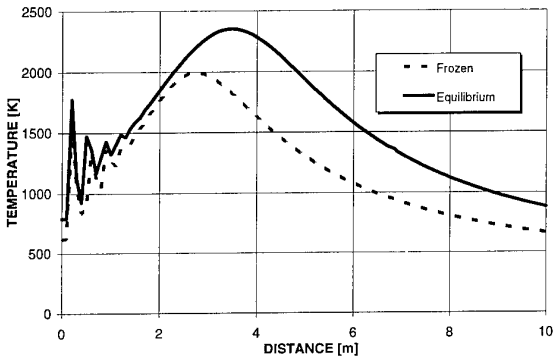



**Figure 1** Predicted centreline temperatures

We never observed steady afterburning during firings of 70 mm diameter GAP/AN motors, and only some intermittent afterburning during one firing. However, the four 200 mm diameter motors that were fired did exhibit steady afterburning. With the British plume code REP-3, we have estimated the temperatures present on the plume centreline and they are shown in Fig. 1. Predictions were done assuming both equilibrium and frozen expansion through the nozzle. With frozen expansion assumed, the temperature on the centreline never exceeds 2000 K, and is above 1800 K for only 1.4 m, which means a residence time subject to temperatures above 1800 K of about 0.001 s. Based on the Zeldovich reaction rate mechanism for thermal NO [4] and assuming maximum temperatures and species concentrations over the 1.4 m, only a few ppm of NO would form. Assuming equilibrium expansion exit plane conditions, however, the peak centreline temperature is higher, and the zone above 1800 K much longer. The residence time of gases in this zone is about 0.004 s, and based on the same "worst-case" assumptions for concentrations and temperatures, up to 500 ppm of NO may form. The prediction of thermal NO is therefore quite dependent on the exit plane conditions, and only better estimates of the temperatures and species at the exit plane and in the plume will improve its accuracy.

## 3.2 FTIR Emission Spectroscopy

Many of the gases present in rocket exhaust plumes emit IR radiation at specific wavelengths; they can therefore be identified if the emissions at their characteristic wavelengths can be measured. In general, the major species can be readily identified, but not their concentrations. The infrared emission spectra from the firings were measured with a Bomem Fast Scan FTIR. This instrument is equipped with two input ports and two detectors. Its optical system is made of a $BaF_2$ beamsplitter and two corner cubes. Spectra were recorded between 1.7 to 5.5 μm (1800-6000 $cm^{-1}$) with 2 $cm^{-1}$ resolution by using InSb detectors. The field-of-view of the instrument is sufficiently wide (20°) for all the IR spectrum of the entire plume to be recorded since the instrument was positioned to the side of the plume 27.9 m away. The data was processed by performing a Fourier transform on the interferograms from the instrument and then dividing them by a reference. This reference is calibrated from the spectra of a blackbody at 700°C, 800°C and 900°C and takes into account the instrument response correction.

IR emission spectra of the GAP/AN and HTPB/AP rocket plumes (70 mm diameter motors) are given in Figs. 2 and 3. The main peaks that could be positively identified are indicated on the graphs. As can be seen, the strongest emission band at 2225 $cm^{-1}$ and the sharp peak at 2375 $cm^{-1}$ are identified as the vibrational mode $\upsilon_3$ of $CO_2$. At shorter wavenumbers (about 2150 $cm^{-1}$), rotational bands of CO overlap with the $CO_2$ band. This structure is not well resolved because it is very close to the limit of the detector and there is more noise in this spectral region. Bands centred around 3430, 3655 and 4010 $cm^{-1}$ correspond to the vibration modes of $H_2O$ and combination modes of $CO_2$ ($\upsilon_1+\upsilon_3$, $2\upsilon_2+\upsilon_3$). In the HTPB/AP spectrum, a rotational fine line structure centred at about 2850 $cm^{-1}$ is observed. This structure

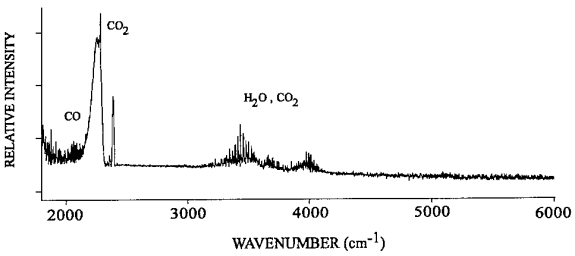



**Figure 2** FTIR spectrum of GAP/AN exhaust

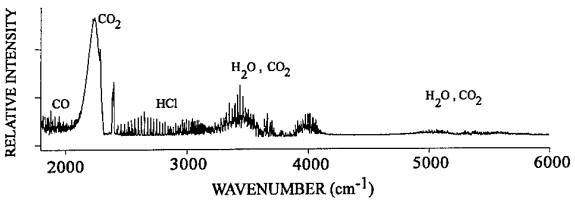



**Figure 3** FTIR spectrum of HTPB/AP exhaust

confirms the presence of HCl during the combustion of these rockets and constitutes a major difference in gas emissions in comparison with the GAP/AN motor.

In the region between 5000 and 5500 $cm^{-1}$, weak bands are observed in the HTPB/AP spectrum. These bands were already observed by Laroche et al [5] in the emission spectrum of a propane flame. They were identified as combination of vibration modes of $H_2O$ and $CO_2$ in accordance with the assignments given by Herzberg [6]. However, these bands were not observed in GAP/AN spectra, which could be explained by the fact that the spectral intensity of this motor is, at least, an order of magnitude lower than the other motor. Therefore, if the flame temperature is lower (as predicted), a lower emission intensity from combustion gases is expected.

### 3.3 Gas Sampling

Since FTIR emission spectroscopy could not reveal absolute values of concentration for the major species, nor identify the minor ones, direct gas sampling of the exhaust plume was attempted. A sampling probe was placed at various distances behind the motor nozzle, and during the firing gases would enter the probe and be drawn into a previously-evacuated vacuum bottle. Unfortunately, our probe would not survive if placed too near the nozzle because of the high temperatures and velocities of the gases there. It was therefore placed more than 2 m downstream; at this distance, the plume has already entrained a substantial amount of air and the exhaust gases are quite dilute. Gas chromatography analysis revealed the presence of $N_2$, $CO_2$, CO, and $H_2O$, all major exhaust products (Table II). No trace compounds, such as NOx, were detected. The only way to reduce the dilution of the sample would be to develop a better probe and sample closer to the nozzle; this was considered to be too difficult and costly with no guarantee of success.

Another method for the experimental identification of trace compounds that was tried was to burn small samples of propellant within a closed bomb [7]. The main drawback of this method is that it does not closely approximate the combustion taking place in a rocket motor chamber. Because the bomb is closed, the sample must be small to limit the pressure rise, but this results in relatively large heat losses from the sample and lower combustion temperatures. It is therefore doubtful that the products could approach chemical equilibrium as in the case of rocket combustion. The expansion of the gases through the nozzle and subsequent afterburning are also not accurately simulated. However, despite these limitations, the exhaust gases are easily collected and even trace compounds are present in sufficient concentrations for analysis.

#### *3.3.1 Apparatus*

The closed vessel is 15.2 cm tall, 3.8 cm in diameter, and has 5 mm thick stainless steel walls capable of withstanding a pressure of 20 MPa (Fig. 4). A 2 g sample of propellant is electrically heated in a crucible within the chamber, and after it ignites and burns, a valve is opened to allow the gases to flow to the instrumentation. Two instruments were used, the first being a Michelson MB100 FTIR spectroscope from Bomem with an adapted gas cell 10 cm long and 7 mm in diameter. An IR source is placed at the end of the cell and the gases in the cell absorb the radiation before it reaches the detector. The concentration of each detectable gas can be derived from how much IR radiation it absorbs at a particular wavelength. The other instrument is a HP 5890 gas chromatograph with a TCD detector. It is equipped with two capillary columns maintained at 50°C to selectively separate the polar gases (such as $CO_2$ and $N_2O$) and the non-polar gases ($N_2$, $O_2$, and CO). The 5A molecular sieve is used to separate each of the non-polar gases, and the polar gases are separated from the rest of the compounds with the poraplot Q column.

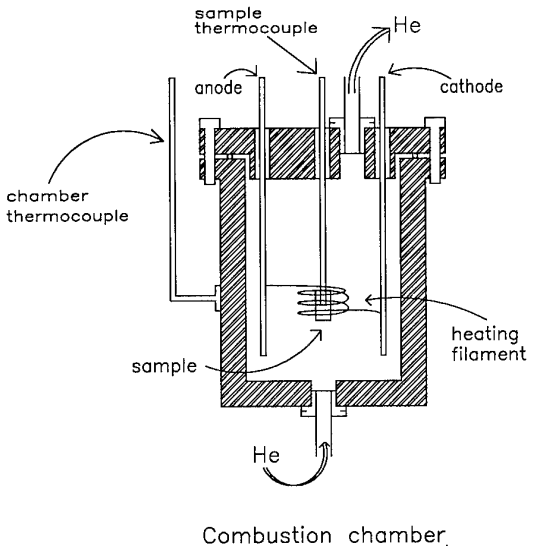



**Figure 4** Closed vessel apparatus

### 3.3.2 *Results*

A typical chromatogram from the closed vessel firings is shown in Fig. 5. The species $O_2$, $N_2$, CO, $CO_2$, $N_2O$, $CH_4$, $C_2H_2$, and $C_2H_4$ were well separated and identified. Because of condensation in the line between the closed vessel and the instruments, water was not quantified. Figure 6 shows an FTIR spectrum of the GAP/AN exhaust products, and in addition to the products seen on the chromatogram, NO and $NO_2$ were identified as well. In the case of the chromatogram, these two compounds probably reacted with the chromatographic column packing.

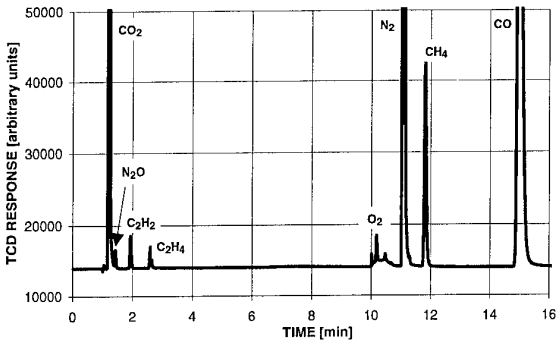



**Figure 5** Chromatogram of GAP/AN combustion products

Hydrogen, a major product of GAP/AN combustion as indicated in Table II, will not show up on the FTIR spectrum because it does not absorb radiation in the IR band used. However, $H_2$ is notably absent from the chromatograph. This can be at least partly explained by the small sample size and consequently lower average temperatures in the closed vessel during combustion due to heat losses. Incomplete combustion is therefore taking place and some of the hydrogen is still present in the hydrocarbons detected such as $CH_4$, $C_2H_2$, and $C_2H_4$.

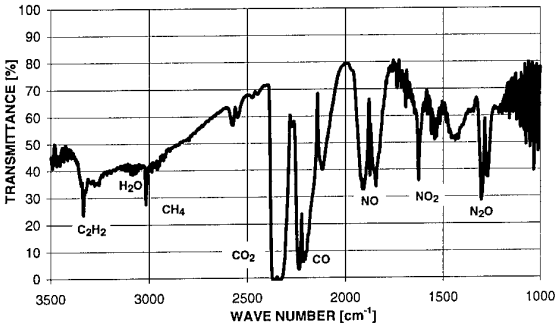



**Figure 6** FTIR spectrum of GAP/AN combustion products

Table IV gives the results of the FTIR method for GAP/AN propellant burning in an inert atmosphere of helium at 0.1 MPa. These results are shown rather than results for a more realistic motor chamber pressure because only at this low pressure were there fairly significant amounts of hydrocarbons and NOx. For comparison, thermochemical equilibrium calculations for the same propellant are also shown. The only compounds shown are those detected by the FTIR; for the calculations, water and $H_2$ were therefore dropped from the post-combustion products so the remaining mole fractions add up to 1.0. The presence of the hydrocarbons and NOx for the FTIR results, as compared to the calculations, prove that complete combustion did not occur in the closed vessel.

**Table IV** Measured and calculated mole fractions (pressure = 0.1 MPa)

| Compound | Calculated | Measured (FTIR) |
|---|---|---|
| CO | 0.27823 | 0.301 |
| $CO_2$ | 0.15952 | 0.228 |
| $N_2$ | 0.56216 | 0.458 |
| NO | 0.00009 | 0.001 |
| $NO_2$ | 0.00000 | 0.000 |
| $N_2O$ | 0.00000 | 0.003 |
| $CH_4$ | 0.00000 | 0.008 |
| $C_2H_2$ | 0.00000 | 0.001 |

The measured results show that major exhaust products are present in amounts comparable to the calculations, demonstrating that high temperatures are achieved at least in some parts of the combustion zone. The products of combustion are then probably quenched by the cool surrounding inert gas, preventing further reactions, while in a rocket chamber they would remain at high temperature and react further to approach chemical equilibrium. Further closed bomb tests were done, at increased pressures and initial propellant temperatures, and in all cases the combustion was improved and the amount of hydrocarbons and NOx diminished. Therefore the amount of NOx formed at realistic rocket motor chamber pressures would be much lower than that shown in Table IV. Table V shows FTIR results of NOx formation versus chamber pressure. As pressure increases, so does combustion efficiency, and the amount of NOx formed decreases. In fact, at 6.9 MPa, a realistic chamber pressure for a rocket, the amount of NOx formed is an order of magnitude less than that formed at atmospheric pressure.

**Table V** Effect of pressure on NOx formation

| Pressure [MPa] | Mole fraction NOx |
|---|---|
| 0.00 | 0.0055 |
| 0.75 | 0.0024 |
| 3.54 | 0.0011 |
| 6.94 | 0.0005 |

Because the combustion of GAP/AN propellant in the closed vessel is less efficient than that in a rocket motor chamber, the amount of NOx formed at 6.9 MPa in the closed vessel can be thought of as a maximum estimate of what would be formed directly from fuel combustion in a rocket. This is also similar to the maximum estimate of the thermal NOx formed in the plume. The maximum total amount of NOx that could possibly be present in the exhaust is therefore about 1000 ppm, based on worst-case conditions.

## 4. PARTICULATE COMPOSITION

### 4.1 Smoke Chamber Measurements

The experimental characterization of exhaust smoke from full-size motor firings is very difficult to do, as demonstrated previously with the characterization of the gases in the plume. While AGARD [8] has recently developed a method to categorize the formation of smoke from propellant combustion based on thermochemical equilibrium calculations, experimental measurements are still necessary to properly characterize the optical properties of smokes. By firing small motors, representative of full-size motors, in a closed chamber, characterization of the smokes' optical properties is much easier and more accurate in the absence of variable atmospheric conditions and dispersion.

#### *4.1.1 Experimental Setup*

The smoke experiments took place at the DREV "silo", a 326 $m^3$ cylindrical chamber. For each test, a small (50 mm diameter and 100 mm long) rocket motor was statically fired in the silo. Each motor contained about 210-240 g of propellant and, to minimize smoke contribution by the igniter, each motor was ignited with cubes or shavings of its own propellant, plus 1 g of BPN (boron potassium nitrate) pellets and an electric match. The small ballistic test motors fired in the chamber are designed to give an approximately-constant chamber pressure throughout the burn time. The chamber pressure chosen for each of the firings was about 10 MPa. Before and during each test, measurements were made of temperature and humidity within the chamber. For the non-aluminized HTPB/AP propellant, motors were fired in both humid (to cause the formation of secondary smoke) and dry conditions. The GAP/AN motor was fired in only the humid conditions since no effect of humidity on smoke formation was expected. The humid conditions were created by wetting down the walls of the silo before the tests; the relative humidity was 93% and the temperature 10.6°C for the mass extinction coefficient results shown. For the dry conditions, the relative humidity was less than 30% and the temperature greater than 13.6°C. After each motor firing, the resulting exhaust was distributed continually throughout the chamber. Transmission readings, taken over a path of 5.7 m, were done spectrally over 2.5-14.5 μm with a chopped Barnes 11-210 infrared reference source and a Barnes 12-550 Mark II radiometer. A He-Ne laser, in combination with a pyroelectric detector, was used to measure the transmission at 0.63 μm (visible). The mass extinction coefficients were then calculated from the transmission readings and the concentration of effluent (difference of the before- and after-firing masses of the motor divided by the chamber volume).

#### *4.1.2 Mass Extinction Coefficients*

The mass extinction coefficient is a physical characteristic that depends on the effluent's optical properties, composition, particle size and shape distributions, and wavelength of interest. In general, mass extinction coefficients must be measured. They are related to the transmission of a particular wavelength or wavelength band through the effluent with the Beer-Lambert Law:

$$T = e^{-\alpha CL}$$

where $T$ is the transmission (fraction of the intensity of the signal which passes through the effluent), $\alpha$ is the mass extinction coefficient of the effluent, $C$ is the concentration of the effluent, and $L$ is the length of the signal path through the effluent. This equation is valid for single scattering, which means that the effluent is dilute enough that any photons that pass through would not be scattered more than once.

Figure 7 shows the calculated mass extinction coefficients for the two primary smokes, non-aluminized HTPB/AP propellant under dry conditions and the GAP/AN propellant under humid conditions. The GAP/AN propellant has somewhat higher mass extinction coefficients at all wavelengths, no doubt due to the greater presence of particulates formed from metallic compounds in it. Most of this is likely ZnO, the AN phase stabilizer present in propellant at about 2.1% by weight.

Figure 8 gives the same mass extinction coefficients for GAP/AN propellant smoke as in Fig. 7, but this time compared to the HTPB/AP propellant fired under humid conditions. Therefore, in addition to the primary smoke, the HTPB/AP propellant exhaust caused the formation of secondary smoke. The formation of secondary smoke is a dynamic process and it continues to form for many seconds, even minutes, after the firing. We began measurements 30 s after firing when the exhaust gases were well mixed in the silo. The radiometer was able to do a sweep of the 2.5-14.5 μm band every minute. The results in Fig. 8 are for the first sweep, or the least smoke. As seen, the mass extinction coefficients of the HTPB/AP smoke under humid conditions are, in general, an order of magnitude higher than the GAP/AN smoke (except for a couple of discrete wavelengths).

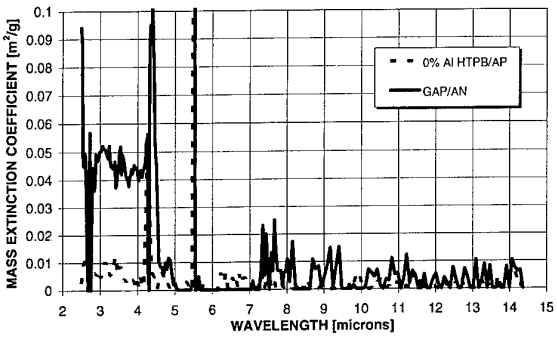



**Figure 7** Mass extinctions coefficients of primary smokes

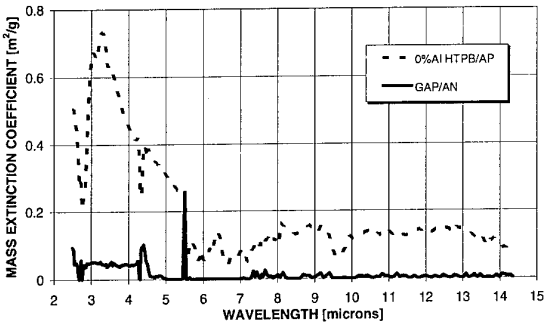



**Figure 8** Mass extinctions coefficients of exhaust smokes, humid conditions

From the spectral mass extinction coefficients, broad-band values were calculated to facilitate comparison between the smokes. They are shown in Table VI along with values at 0.63 μm, representative of the visible range. As already shown in the Figs. 7 and 8, the values for GAP/AN are higher than those for the non-aluminized HTPB/AP propellant primary smoke. However, the values for HTPB/AP propellant smoke under humid conditions are considerably higher than for the GAP/AN smoke.

**Table VI** Mass extinction coefficients

| Propellant | Condi-tions | Mass Extinction Coefficients ($m^2/g$) | | |
|---|---|---|---|---|
| | | 0.63 μm | 3–5 μm | 8–12 μm |
| HTPB/AP | dry | 0.00829 | 0.00749 | 0.001320 |
| GAP/AN | humid | 0.03940 | 0.03866 | 0.003947 |
| HTPB/AP | humid | 6.66859 | 0.45513 | 0.128428 |

### 4.2 AGARD Smoke Classification

From the thermochemical equilibrium calculations previously performed, the species and concentrations at the nozzle exit plane were used to classify the two propellant formulations according to the AGARD method [8]. The AGARDP number for primary smoke was 0.41 for the GAP/AN propellant, giving it a B classification, while the non-aluminized HTPB/AP propellant has a superior A classification. The GAP/AN propellant has an A classification for secondary smoke, however, while the HTPB/AP propellant has an inferior rating of C.

Visual observations confirm these classifications as well, as shown in Figs. 9, 10, and 11. For primary smokes, only small traces of smoke were seen from either the non-aluminized HTPB/AP or the GAP/AN 70 mm diameter motor firings. However, the 200 mm diameter motor firings of the GAP/AN propellant produced an obvious amount of primary smoke (Fig. 9). Under humid conditions, a non-aluminized HTPB/AP 70 mm diameter motor firing (Fig. 10) produced a quantity of secondary smoke that looks (roughly) as optically thick as the primary smoke from the 200 mm diameter GAP/AN motor firing, despite the fact that the HTPB/AP motor emits only half the flow rate of exhaust as the GAP/AN motor (approximately 2.5 kg/s versus 5 kg/s). A 200 mm diameter motor containing non-aluminized HTPB/AP propellant was also fired under humid conditions, and a considerable amount of secondary smoke formed, only part of which can be seen on the right hand side of Fig. 11. Because of the larger size of the motor, the exhaust gases did not cool as quickly to allow secondary smoke to form as for the 70 mm diameter motor firing. Downstream of the bunker in the right of the photograph, a huge cloud of secondary smoke formed that appeared much more optically thick than the primary smoke cloud from the GAP/AN firing. We have never seen the formation of secondary smoke during any of our GAP/AN firings, accomplished under a variety of atmospheric conditions, especially cold, humid ones.

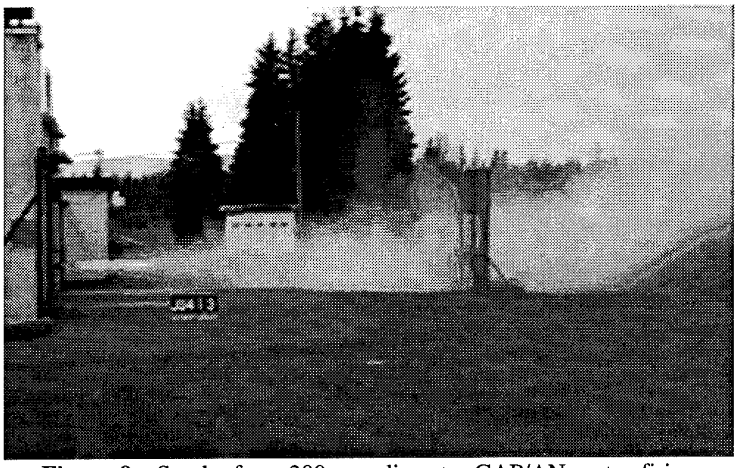


**Figure 9** Smoke from 200 mm diameter GAP/AN motor firing

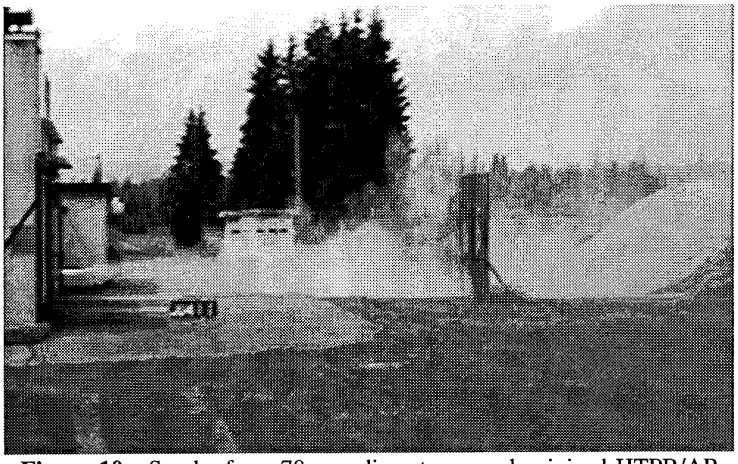


**Figure 10** Smoke from 70 mm diameter non-aluminized HTPB/AP motor firing

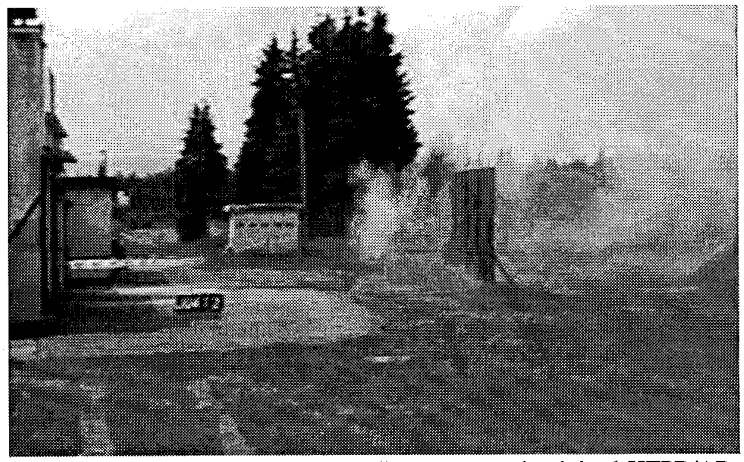


**Figure 11** Smoke from 200 mm diameter non-aluminized HTPB/AP motor firing

### 4.3 Detection Range Calculations

Unfortunately, the mass extinction coefficients, taken by themselves, cannot give a quantitative indication of the consequences of missile smoke. Furthermore, the AGARD smoke classifications are only a general categorization of smokes. In order to quantify the some the effects of exhaust smoke, DREV has recently performed a complex study of the effects of various missile smokes, under both humid and dry conditions on the performance of IRST (infrared search and track) sensors in a maritime environment. A computer simulation (Fig. 12) was performed of a scenario where an enemy missile flies toward a ship. The ship, previously (as well as currently) under attack, has fired up to six missiles and the exhaust smoke from these missiles forms clouds around the ship. These clouds are assumed to be in the vertical plane between the shipboard threat detection sensors and the incoming enemy missile. These clouds grow and disperse with time (R(t)) as they entrain air, and they also rise (H(t)) while they are still buoyant. They may therefore not always remain in the line-of-sight between the threat missile and the sensors, as shown in Fig. 12. From the simulation, the reduction in detection range of the enemy missile due to the presence of these launch clouds was calculated. This gives a quantitative measure of the effect that various exhaust smokes will have on the degradation of performance of the sensors.

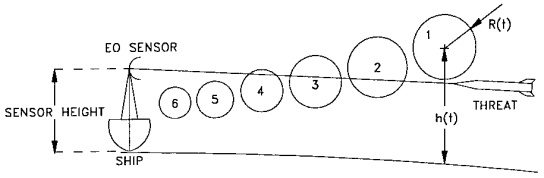



**Figure 12** Detection range scenario for up to six missiles fired

For these detection range calculations, the spectral natures of the threat signatures, the attenuation of these signatures by the atmosphere and the exhaust smoke clouds, and the spectral response of the sensors were all taken into account. Therefore all calculations involving the infrared signal emission and attenuation considered the emission and attenuation at each incremental wavelength in the particular wavelength band of interest. This is because, in general, the intensities of IR emissions vary spectrally, sometimes quite substantially. As these emissions pass through the atmosphere and any smoke present (Figs. 7 and 8), the intensity at each individual wavelength is attenuated to different degrees. Therefore, at the end of the journey when the emissions reach the sensor, the spectral nature of the entire emission (relative intensity at each wavelength) can be quite different than at the source. The total energy that arrives (integrated over the wavelength band of interest) is also different than that which would be calculated if the spectral natures of the emissions and the subsequent attenuation media were ignored and only broad-band values were used. The broad-band values, such as those reported in Table VI, should not be used to calculate sensor performance in this manner.

Calculations were performed for four various atmospheric scenarios, three different threat signatures (solid fuel rocket, liquid fuel ramjet, and turbojet) following sea-skimming trajectories, two different sensors (one operating in the 3-5 μm band and the other in the 8-12 μm), the various propellant smokes, and one, two, or six independent launch clouds present. A reference detection range calculation for no smoke clouds present was also performed; the reduction in detection range due to smoke is calculated with respect to this reference. The calculated detection ranges were very dependent on all of these factors, but in general the reduction in detection range due to the presence of secondary smoke (HTPB/AP propellant under humid conditions) was much higher than for GAP/AN propellant under identical conditions. In some instances, the GAP/AN propellant gave slightly lower detection ranges than the HTPB/AP propellant under dry conditions. Table VII can be thought of as fairly indicative of the results we received. The results in this table are for the calculations using an autumn atmospheric scenario, the 3-5 μm sensor, a solid rocket threat, and smoke from six launch clouds present.

**Table VII** Reduction in detection range

| Exhaust smoke type and conditions | % reduction in detection range |
|---|---|
| 0%Al HTPB/AP, dry | 18.91 |
| GAP/AN, humid | 23.63 |
| 0%Al HTPB/AP, humid | 85.08 |

## 5. CONCLUSIONS

The most obvious environmental benefit of using AN as the oxidizer in solid rocket propellant rather than AP is the lack of HCl and other chlorine compounds in the exhaust. This was confirmed by FTIR emission spectroscopy measurements of the exhaust plumes of 70 mm diameter rocket motors containing GAP/AN and non-aluminized HTPB/AP propellants, and by thermochemical equilibrium calculations.

The production of nitrogen oxides (NOx) is also an environmental concern. However, FTIR emission spectroscopy failed to reveal any in the exhaust from actual GAP/AN motor firings, and direct gas sampling of the plume also failed. Closed bomb tests and calculations demonstrated that there could be some NOx present, either from incomplete combustion of the AN in the propellant or by the combination of nitrogen and oxygen in the afterburning plume. A maximum estimate of 1000 ppm was made, but this is based on several "worst-case" assumptions.

The closed bomb tests at atmospheric pressure revealed, from FTIR absorption spectroscopy and gas chromatography, that some hydrocarbons were present from the incomplete combustion of the propellant. However, apart from NOx, no other harmful compounds were detected.

Because of the presence of zinc oxide in the AN as a phase stabilizer, there are more particulates present in the exhaust of the GAP/AN propellant than in the non-aluminized HTPB/AP propellant. As a consequence, GAP/AN exhaust mass extinction coefficients are somewhat higher than the other smoke. DREV's GAP/AN propellant using 3% ZnO PSAN cannot therefore be considered a minimum smoke propellant, so it has the AGARDP smoke classification of B. To improve its classification, the use of non-stabilized AN (no metal oxides within) is being investigated.

Under humid conditions the GAP/AN exhaust produces no secondary smoke, but the non-aluminized HTPB/AP propellant does. In fact, the mass extinction coefficients of the HTPB/AP smoke under humid conditions are, in general, an order of magnitude higher than the GAP/AN smoke. Therefore, under humid conditions, the GAP/AN propellant is superior to the non-aluminized HTPB/AP propellant with an AGARDS rating of A versus C.

Detection range calculations provided a more quantitative estimate of the effects of the propellant smokes than the AGARD smoke numbers. They indicated that the GAP/AN smoke would reduce the detection range of incoming enemy missiles slightly more than non-aluminized HTPB/AP smoke under dry conditions. However, under humid conditions, the GAP/AN smoke reduced detection ranges much less than the HTPB/AP smoke because secondary smoke would form with the latter.

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## Discussion

QUESTION BY I. MAXEY : Is it the intention of Canada to use the AGARD classification system for exhaust smoke throughout the future characterisation of rockets for Canadian service use?

ANSWER : Certainly, it is the intention of the research community Moreover. I have personally recommended ratification of STANAG 6014 - Rocket Propellant Smoke Classification, which was developed on the basis of the work carried out by WG 21 (AR 287).

QUESTION BY SCHUBERT : Pure AN/GAP propellants produce clean exhaust. The smoke you found was coming from ZnO for Zinck is a smoke producing agent. Perhaps also ballistic modifiers support also smoke production ?

ANSWER : We agreed one hundred percent with this remark and we are currently investigating ways of using non-stabilized AN and "less smoky" ballistic modifier.

# EMISSION SPECTROSCOPY AND PYROMETRY OF PROPELLANT FLAMES AND SOLID ROCKET EXHAUST PRODUCTS

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## Abstract

The developement of solid propellants is a major topic at the institute. For the purpose of getting more insight into the combustion behaviour of solid propellants and the exhaust plume signatures of rocket motors some new spectroscopic and pyrometric devices were developed. In the UV-VIS-region an Optical Multichannel Analyzer (OMA) is used. For the detection of radiation in the IR -region three systems are available ranging from 1.2 to 14.5 μm with a wavelength resolution of about 1% and a scanning rate of 10ms per spectrum. The time resolution of the two colour pyrometer ranges from DC up to 50 kHz and detects fast particles with temperatures above 1000K. In this paper these methods of investigation are described and illustrated in different applications.

## Introduction

Recently, general public interest in enviromental effects like the perturbation of the ozone layer by anthropogenic sources has increased. Besides other man-made compounds the influence of solid rocket motor exhaust to ozone depletion is discussed. International efforts are in progress to qualify and to quantify atmospheric effects of chemical rocket propulsion [1,2].

The standard composite propellant contains typically more than 65% AP and up to 20% Al, using HTPB as binder system. Therefore the major part of the rocket exhaust products are chloric acid and $AL_2O_3$ particles. These particles may also influence the ozone layer. Their size distribution is a function of altitude and was subject of a work in 1991 [6].

Meanwhile a new energetic binder GAP (Glycidil-Acido-Polymer) combined with AN as oxidizer is in discussion to replace the improved propellant formulation based on AP. Some disadvantages like the question of phase stability of AN or the loss in specific impulse should be subject of future investigations. At ICT the focus is on new catalysts and additives. In addition, boron or boron compounds can be used to increase the specific impulse related to volume.

For the determination of reaction mechanism and especially temperatures within the reaction zone and the exhaust of propellants, spectroscopic and pyrometric methods are necessary.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

## Experimental

The standard equipment for the investigation of rocket propellants is a pressure vessel equipped with quartz windows. Tests can be done in oxidizing or inert atmospheres and at pressures up to 40 MPa. The so called optical bomb is essentially designed for basic investigations (see fig. 1). All the test methods described in the following chapter can be applied to this equipement.

A small rocket motor directly connected to a vacuum vessel is used for simulation of secondary combustion at high altitude. The equipment keeps all the residuals after firing in the closed vessel for later analysis. The particles were collected on glass and copper plates at different distances from the nozzle exit plane.

## Measuring methods

In general, both particles and gases are present in the flame or exhaust of a propel-lant. As a consequence we normally expect a superposition of a continuous radiation emitted by particles and of a discrete radiation emitted by atoms and molecules. For the determination of the temperature of the particles and the gases different methods have to be applied.

### Emission spectroscopy in UV-VIS-IR-region

A spectrometer system with an Optical Multichannel Analyzer (OMA) with a spectral range of 200 - 900 nm is used to get a first information about the type of radiation and the atomic or molecular emitters which are present in the reaction zone or in the exhaust.

By means of spectroscopy not only the species participating in the combustion process are identified; from the recorded band spectra of some molecules temperatures can be derived: the intensity distribution of the bands of some molecules (OH, NH, CN, CH) can be calculated as a function of temperature if the molecular data like energy levels and transition probabilities are known. In thermal equilibrium densities of the energy levels are given by a Boltzmannn distribution which is a function of temperature. With a least square fit routine these calculated spectra are fitted to the experimental ones with temperature as fitparameter. It has turned out that this method is reliable and simple compared with time consuming methods like CARS or LIF. In some cases selfabsorption might disturb the temperature estimation.

If the intensity of the emitted radiation of hot particles is much higher than that of the molecules the result is a completely continuous radiation. For the determination of temperature the calculated emission intensity is compared with the measured one; in principle the idea is the same as in the chapter before. The calculated emission is given in this case by Planck's law $B(\lambda,T)$, which has to be multiplied by a factor $\varepsilon$ which is in general a function of wavelength $\lambda$ and temperature T.
By the assumption of grey body radiator with an emissivity independ to the wave-length a 'least square fit' is possible. For a comparison of the calculated and experimental intensity values a quantitative calibration is necessary, which is done by the use of a tungsten filament; temperature and emissivity of this lamp are known.
In the wavelength region up to 800 nm there is nearly no $\varepsilon$ - dependence of wave-length in particle laden combustion zones: in most composite

propellant flames for example it is only a function of temperature. As a result of the fit procedure by means of a corresponding fit routine not only temperature but also emissivity is obtained. Since the spectra are taken at fixed time intervals i.e. at different distances from the propellant surface and for each spectrum the method can be applied, temperature and emissivity can be determined in different burning regions.

For the detection of the radiation in the IR-region two systems are available. First rotating filter wheels combined with different IR-detectors covering the range from 2.5-14μm [5]. A sketch of the principle is depicted in fig. 2 Second, a two colour pyrometer operating in the near infrared region.
IR-spectroscopy is e.g. of importance for the investigation of the afterburning in rocket exhausts: the composition of the reaction products outside of the motor nozzle is changing because of the reaction of excess fuel with oxygen by the entrainment of ambient air. Especially species like $H_2O$ and $CO_2$ are indicators for this effect and increase of the temperature in the rocket plume. Both molecules are emitting in the IR-region.

### Particle temperature

For the determination of the temperature of hot particles (1000-3000K), the emission intensity of which has its maximum in the near IR-region, a two-colour pyrometer is used: The intensity of the continuous radiation emitted from hot particles is described by Planck's law, multiplied by $\varepsilon(\lambda)$. The intensity measurement in two different wavelength regions $\lambda_1$ and $\lambda_2$ which is acquired by a Si/Ge - sandwich detector and the division of the two signals $I_1(\lambda_1)$ / $I_2(\lambda_2)$ yields the temperature of the particle - with the assumption that the emissivity is constant over the detected wavelength range [3].

## Results and Discussion

### Investigation of collected particles

The collected particles were investigated by scanning electron microscopy (SEM). No significant differences were found between the samples on glass or copper plates. Because of the electrical conductivity the samples on copper plates were prefered for SEM analysis.
In general particle obtained from test1 (vessel pressure 20 hPa) were smaller and less deformed as the particles from test 2 (vessel pressure 100 hPa). Besides, the samples of test 2 tends to form large agglomerates. It appears that a higher temperature of the exhaust is responsible for these agglomerates, in which small particles were deformed between large particles. Some representative photographs are shown in fig. 4 and 5.
The particle size distributions in table 1 are obtained by measurements on the SEM images. Only particles on the surface that show a spherical shape were counted.
Explaining the influence of ambient pressure on particle size the expansion factor should play a role on particle formation.

### Spectroscopic temperature estimation

As depicted in fig. 1 two different optical instruments are focussed at the identical local plane of the propellant strand burning downstream. In this way it is possible to compare directly the temperatures measured with the two colour pyrometer and the fitted temperature curve acquired by the OMA [4]. Typical plots of the temperature T and intensity profile $U_{Ge}$ coming from the pyrometric device one can see at the top of figure 5 [7]. Below this the profiles of the intensity I and emission coefficient $\varepsilon$ are shown with the corresponding temperaure evaluated with these data. There is no sigificant difference between the results of the two methods. The advantage in time resolution concerning the two colour pyrometer is evident. The beginning of the pyrometric signal shows no "ground noise". The oscillations are related to the particle displacment coming from the convective flow.

### Afterburning in exhaust plumes

The characterization of solid rocket motor exhaust plumes are of interest for detection and guidance problems. Mainly solid propellant ingredients and the nozzle flow field influences the signature.
An example of increasing temperature caused by afterburning can be seen in the figure 6 and 7. The IR-spectra show the increase of the $H_2O$ and $CO_2$ molecule bands of more than 20% in radiation intensity at greater distance from the nozzle exit plane. This effect was measured at static firing and may change to smaller amounts in flight tests. Assuming constant emissivity over temperature of the $CO_2$ molecule radiation, it can also be used for estimating gas temperature of the exhaust flow.

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| Partical Size | Counts | | Percentage of Total Particles | |
|---|---|---|---|---|
| | Test 1 | Test 2 | Test 1 | Test 2 |
| 0.06-0.20µm | 127 | 59 | 25.4% | 17.4% |
| 0.20-0.33µm | 123 | 70 | 24.6% | 20.6% |
| 0.33-0.47µm | 93 | 45 | 18.6% | 13.2% |
| 0.47-0.61µm | 53 | 34 | 10.6% | 10.0% |
| 0.61-0.75µm | 35 | 27 | 7.0% | 7.9% |
| 0.75-0.89µm | 29 | 29 | 5.8% | 8.5% |
| 0.89-1.03µm | 19 | 20 | 3.8% | 5.9% |
| 1.03-1.17µm | 11 | 15 | 2.2% | 4.4% |
| 1.17-1.31µm | 5 | 9 | 1.0% | 2.6% |
| 1.31-1.45µm | 3 | 8 | 0.6% | 2.4% |
| 1.45-1.6µm | 1 | 6 | 0.2% | 1.8% |
| >1.6µm | 1 | 18 | 0.2% | 5.3% |
| Total Particles | 500 | 340 | | |

Table 1: Size distribution of particles collected in the vessel experiments test 1 and test 2

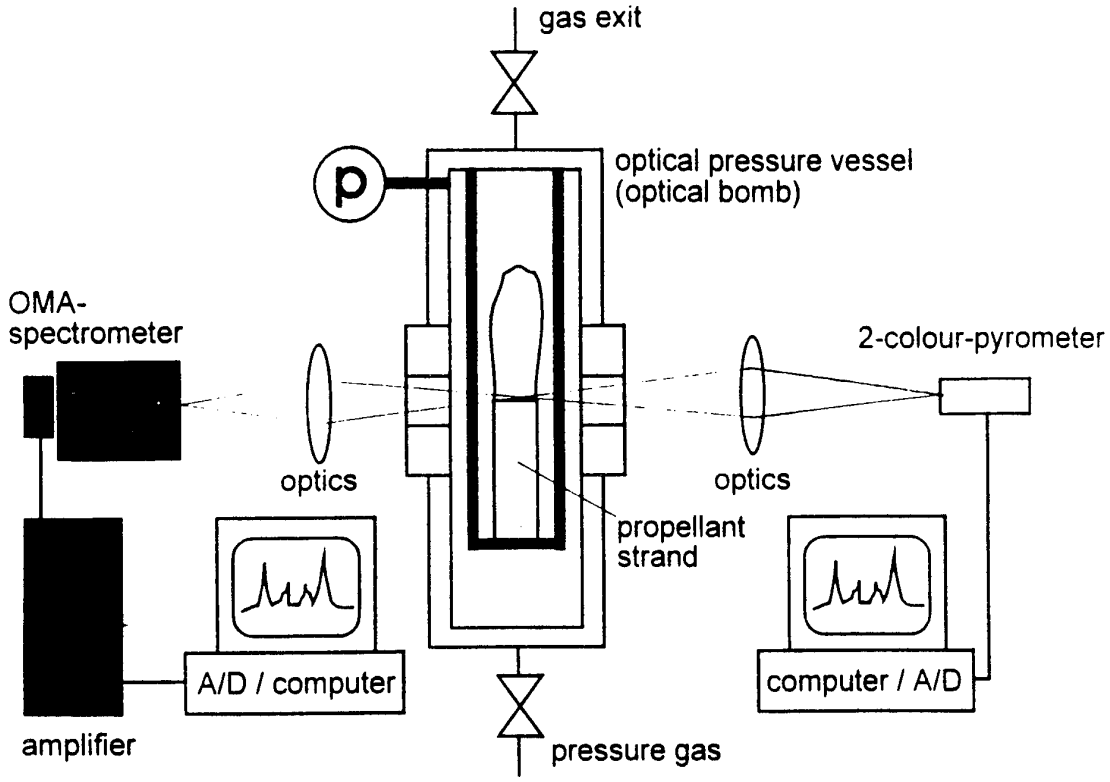



Figure 1 Test equipement for standard investigations of propellants

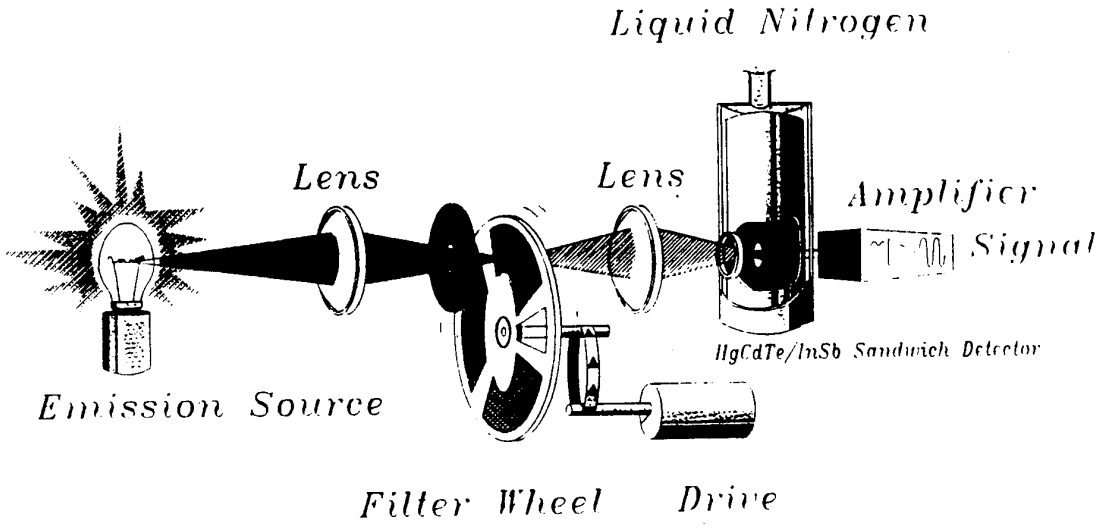



Figure 2 Experimental setup of an IR-spectroscopic device

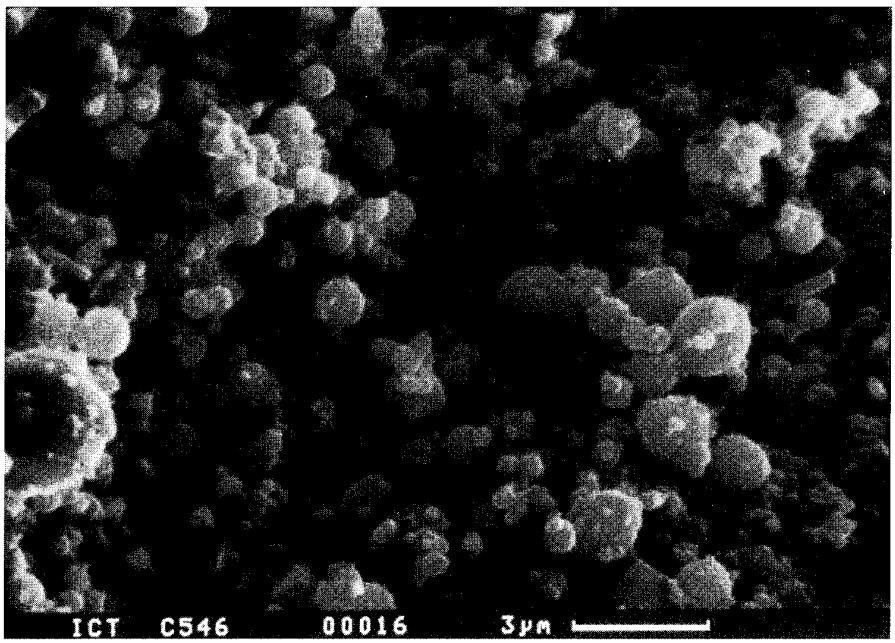



Figure 3 SEM image of alumina particles from test1 at 20 hPa ambient pressure (magnification 6300 : 1)

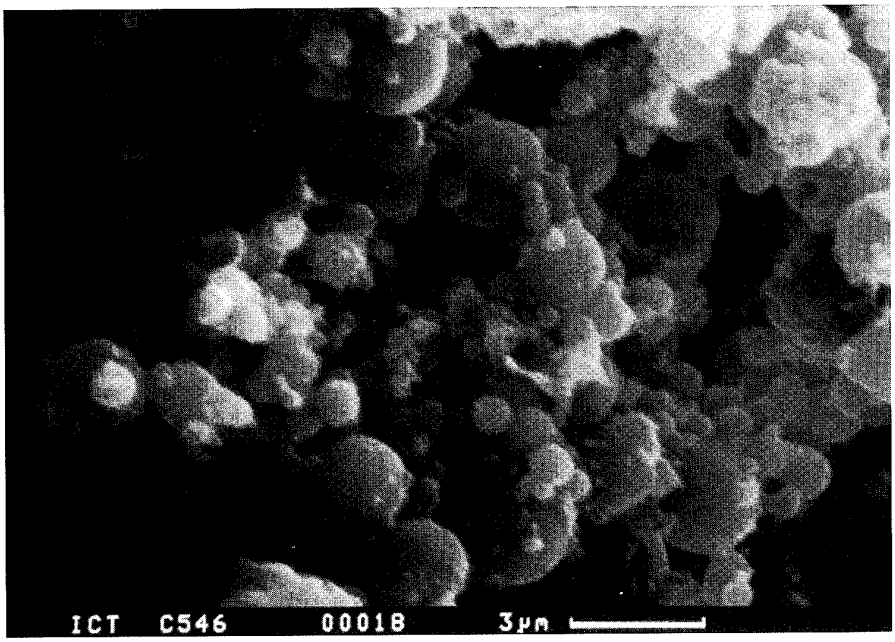



Figure 4 SEM image of alumina particles from test2 at 100 hPa ambient pressure (magnification 6300 : 1)

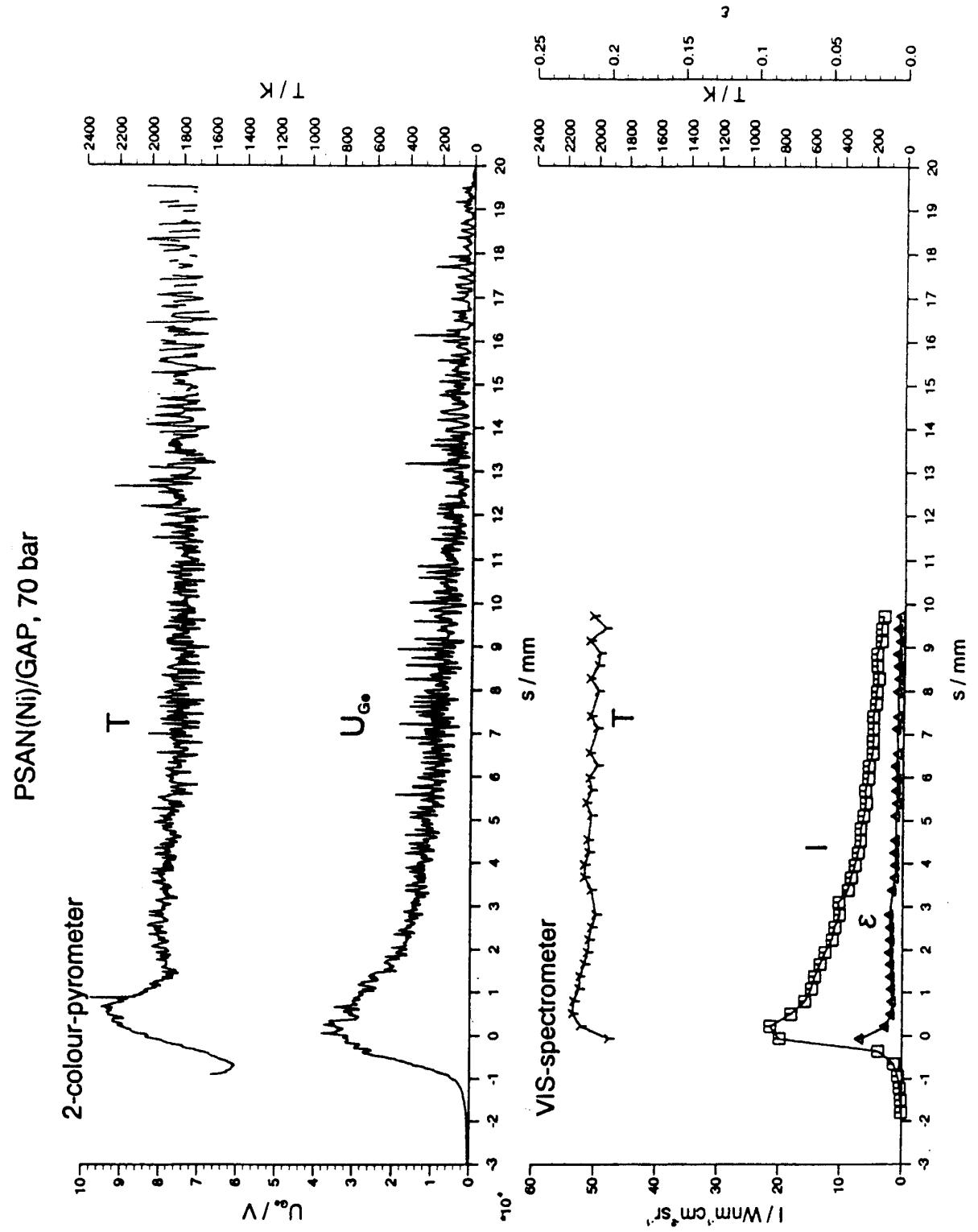



Figure 5 Temperature measurement and calculation of a propellant strand of phase stabilized AN/GAP burnt in the optical bomb shown in fig. 1

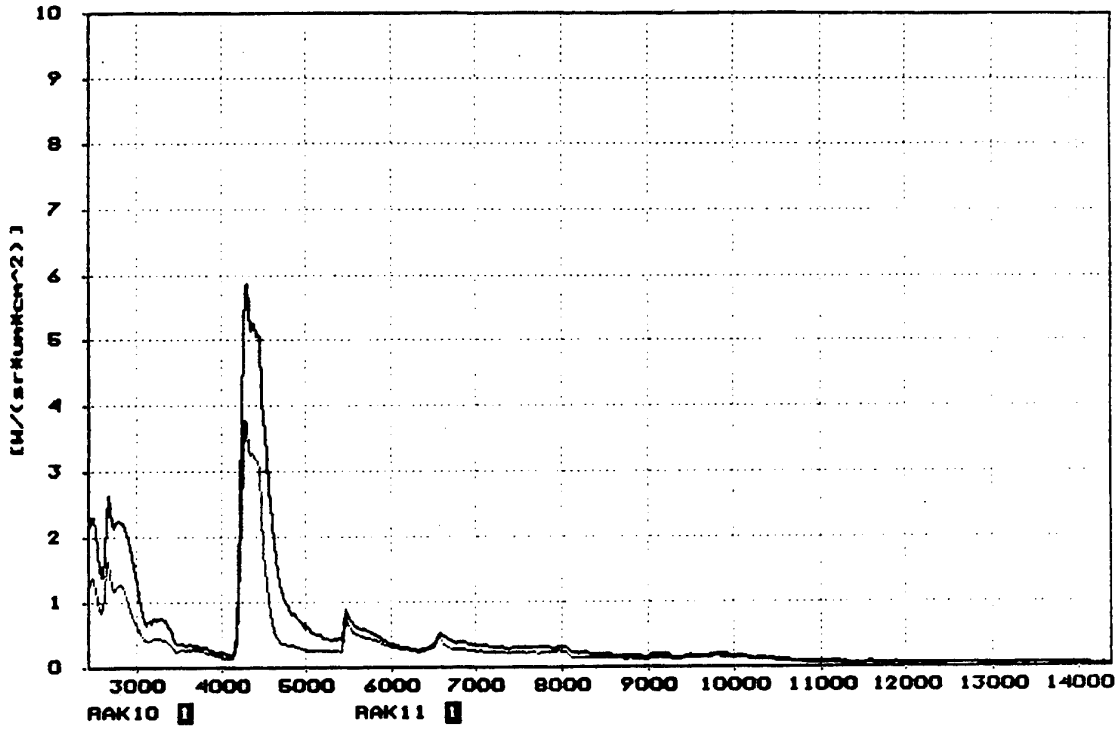



Figure 6 IR-spectrum at 150mm from nozzle exit plane of two composites with different mass flow

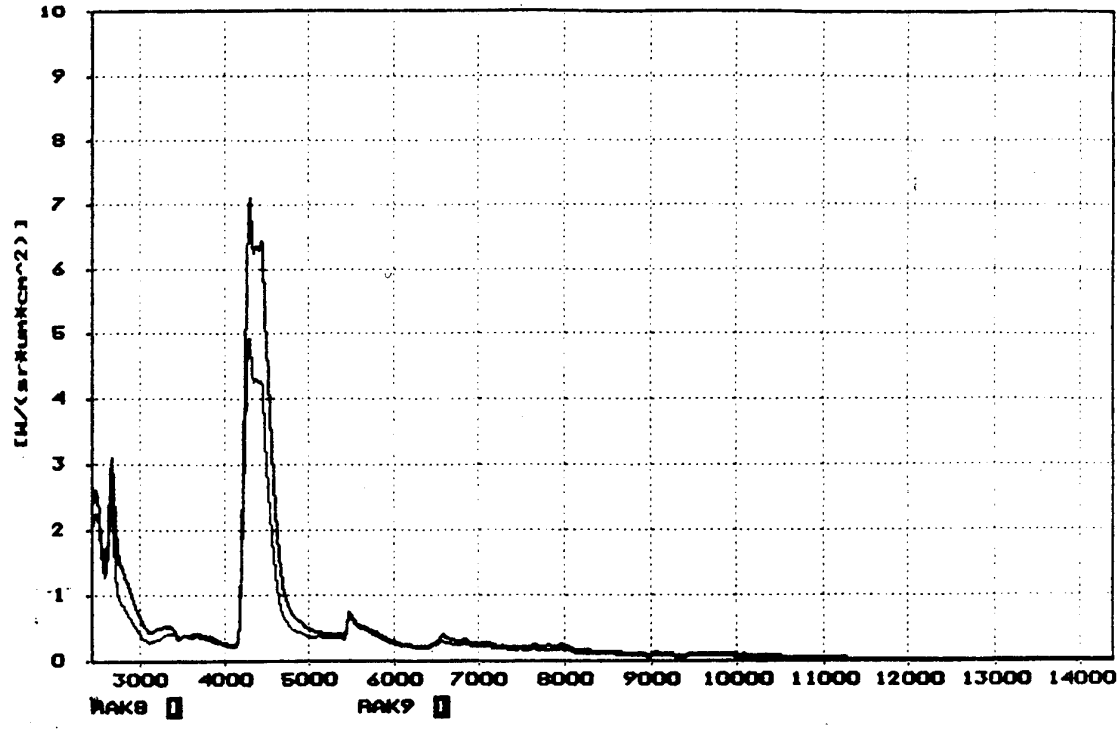



Figure 7 IR-spectrum at 250mm from nozzle exit plane of two composites with different mass flow

# Gas Pollutants From Ammonium Nitrate Based Propellants

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## SUMMARY

Ammonium nitrate (AN) is the base component of a low pollutant propellant, composed by polyurethane (PU) binder, based in hydroxyl terminated polybutadiene (HTPB), a plasticizer (DOA) and a curing agent (IPDI). The impossibility of burning a pure AN-PU propellant of AN concentration of 80% leads to find an additive component in order to increase thermal insulation and decrease the global initial density. Glass microballoons (GMB) have these properties and can be assumed as inert in combustion processes. AN-PU-GMB compositions, with AN concentrations from 80 to 90 %, keeping constant 4% of GMB, were tested.

Theoretical predictions of combustion pollutants were performed using THOR code, assuming thermodynamic equilibrium of combustion products for the minimum value of Gibbs free energy. Predictions shows negligible $NO_2$ concentrations. CO emissions were more important than NO, in a good agreement with classic kinetic models.

Experimental combustion samples were tested in a steel closed explosion chamber of 17 $m^3$. They can be heated in the cases where it was not observed self sustained combustion. The real extinction of propellant of AN concentration of 80%, without GMB, was observed. A transition situation was verified in this composition with GMB. Combustion process of AN-PU-GMB, with AN concentrations of 83%, show heterogeinities, but seems to be relatively stable. Measured combustion temperatures for AN-PU-GMB with AN concentrations of 83% were near 1050 K. Measured values of combustion residues were always less than 3% of initial mass. The exhaust gas system is connected to a NO, CO, $CO_2$, $CH_4$ gas analysers by IR spectroscopy. Measured concentrations of combustion products, corrected by the dilution factor, show very reliable results. For self sustained combustion, measured CO concentrations were higher than NO. In the other cases, NO concentrations being higher than CO, seems to indicate a pyrolisis regime. $CO_2$ and NO were higher than the predicted values. The obtained results prove the validity of test procedures and show the existence of self sustained combustion, at atmospheric pressure, of AN-PU-GMB with AN concentrations of 83%.

## 1. INTRODUCTION

There are many tests and procedures proposed in the bibliography to burn propellants and measure pollutants. Incineration of many kind of energetic materials have been studied: single and double base propellants, TNT, rocket propellants, black powders and metallic oxides, generating pollutants in their gaseous exhaust products (NOx, CO, HCl, HF, SO2, H2S). An example of its mean values can be found in bibliography (vd. Table 1 Folk [1], van Ham [2]).

| Explosive | NOx | SO2 | HCl | H2S |
|---|---|---|---|---|
| Single base | 10 | - | - | - |
| Double base | 19 | - | - | - |
| TNT | 0.01 | - | - | - |
| Rocket prop. | - | - | 25 | - |
| Black powder | - | 0.1 | - | 6-8 |

Table 1 - Toxic gases, in weight %, from combustion products of explosives (Folk [1])

There is a certain inadequacy concerning E.E.C. regulations about the emission of polluting gases such as NOx, SOx, CO and solid ashes. A reference of threshold values, for gaseous exhaust products, in The Netherlands (vd. [2]) can be seen in Table 2.

| Product component | Threshold value [mg/m3] |
|---|---|
| NOx | 70 |
| CO | 50 |
| SOx | 40 |
| HCl | 10 |
| Heavy metals | 1 |
| Cd/Hg | 0.05 |
| PCD´s (dioxines) | 0.1 nanogr. TEQ/m3 |
| Total solid dust | 5 |

Table 2 - Threshold values for gaseous exhaust products in The Netherlands (van Ham [2]).

Partial substitution of ammonium perchlorate (AP) by ammonium nitrate (AN), in a composite propellant, reduces significantly the HCl content in combustion products, reducing pollution due to acid rain. Ammonium nitrate (AN) is the base component of a recent family of gas generators and rocket composite propellants. Those propellants have the same polyurethane binder (PU) of the classic ammonium perchlorate (AP) based composite propellants. This kind of propellant, having lower pollutants concentration, presents a lower flame temperature and specific impulse. In order to reduce these problems many additives have been proposed in the literature (AIAA [3]). There was recent information concerning the existence of metallic oxides as additives to reduce or even avoid phase transition of AN (vd.[4], [5]). The changements of volume, as a function of temperature does not allow a perfect control of combustion characteristics of an AN propellant from the energetic point of view phase IV of AN has a great interest, while phase III presents problems of storage and transportation. Thus the low temperature of transition from phase III to IV (32 ºC) generates new problems. In the open literature is refered the great interest in keeping AN in an extremely dry conditions.

Curing agents, plasticizers, crosslinkers, stabilizers and antioxidants are also important to optimize mechanical and energetic properties (vd. [6]). The aim of the present study is not to optimize compositions, but to evaluate and measure the existence of pollutants in an AN based propellant. Consequently our binder has more simple composition than a final optimized system.

The combustion mechanism of a composite propellant (vd. [7], [6]) depends of vaporization temperature of filler particles and binder's pyrolisis. The impossibility of burning pure AN - PU propellant, with AN concentration standard of 80 % at atmospheric pressure (vd. [8]) and the possibility of burning this propellant at pressures greater than 5 MPa, suggests the great influence of the expansion and heat transfer in this phenomena. The fact of initiation energy to be a function of initial propellant density, leads to find an inert additive component in order to increase insulation and decrease the global initial density.

In our study it was selected an AP/AN-PU propellant as reference, with mass fractions respectively of 40, 40 and 20 %. This propellant composition corresponds to the minimum AP concentration which allows the ignition at atmospheric pressure. For this condition a regression rate less than 1 mm/s has been measured (vd. [8]).

The following text presents:
- characteristics of components and selected compositions of tested AN based propellants,
- predictions of combustion products, using THOR code, to calculate equilibrium compositions of gas and solid species, as a function of propellant initial composition,

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- experimental conditions and pollutant measurements from the propellant combustion, inside a steel closed explosion chamber,
- correlations between theoretical and experimental results in order to discuss the validity of selected compositions and experimental conditions.

## 2. COMPONENTS CHARACTERISTICS AND COMPOSITIONS

### 2.1. Selected components

Glass microballoons (GMB) were used to sensitize emulsion AN explosives, by the generation of hot spots that increases its sensitivity. Its low density (220 kg/m$^3$) and the impossibility to move the air inside its glass hollow shell, allows an increasing global thermal insulation properties. Glass ($SiO_2$) can be considered like an inert in combustion reaction. Consequently it was decided to add a few percent of GMB to our reference AN-PU reactive system and evaluate the possibility of combustion at atmospheric pressure.

The perfect insertion of filler particles in the organic polymeric binder matrix needs an adequate viscosity during processing phases, in order to avoid the generation and/or maintenance of air bubbles, the coating of particles with the binder film and its good dispersion inside the heterogeneous system (vd. [7]).

#### 2.1.1. Filler particles

Three types of filler particles, assumed by suppliers as chemical pure materials, have been used (vd. Table 3). Its particle size distribution, shown in Fig. 1, was established by Laser Diffraction Spectrometry. They were added in dry condition and were stored in an electric heated oven at 60°C.

| Reference and name (supplier) | Density |
|---|---|
| AP - Ammonium perchlorate - NH4ClO4 - (SNPE) | 1950 kg/m3 (TMD) |
| AN - Ammonium nitrate - NH4NO3 - (Nitroazote) | 1720 kg/m3 (TMD 1725 kg/m3) |
| GMB - Glass micro balloons - Silicate glass shell (SiO2) and air inside - (Q-Cel 520 FPS - AKZO-PQ) | Effective - 220 kg/m3 Bulk - 110 kg/m3 |

Table 3 - Selected filler particles.

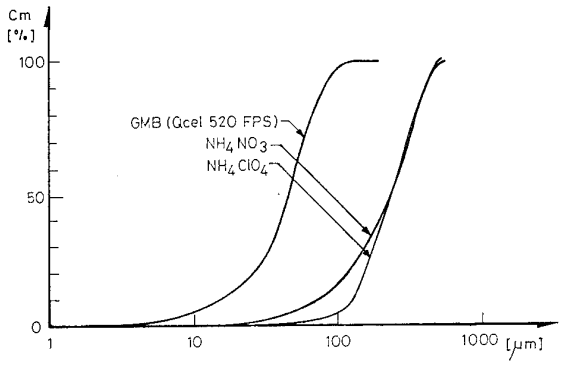



Fig. 1 - Particle size distribution of AP, AN and GMB.

#### 2.1.2. Binder components

The binder components were used directly being assumed as pure chemical products (vd. Table 4). The rheological properties of this binder system has been recently studied [9]. The binder system was composed by 82.57 % of HTPB, 9.17 % of DOA and 8.26 % of IPDI.

| Reference and name (supplier) | Function |
|---|---|
| HTPB - Hydroxyl- terminated polybutadyene - (HTPB R45HT - Elf Atochem) | Pre-polymer |
| IPDI - Isophorone diisocyanate (Merck) | Curing agent |
| DOA - Dyoctil adipate (Fluka) | Plasticizer |

Table 4 - Binder components

#### 2.1.3. Propellant compositions and preparation

Three kinds of propellants were prepared, changing successively the filler nature and its concentration. The AP/AN based propellant was named D1 (donor) and the AN based propellants were named A1, A2, A3 and A4 (acceptors), being A2 to A4 compositions with GMB. Table 5 shows for used mixtures, the molar and mass composition, the equivalence ratio related to the stoicheiometry and measured global density. Air concentration was calculated as a function of measured global density. Tested mixtures including GMB, referred as Ai, are followed in Table 5 by mixtures Ai(AIR) used in theoretical predictions - calculations were done with the same molar composition, not considering the glass of mass of GMB. This allow to evaluate the influence of air, inside GMB, without influence of the inert glass material.

Tested propellant mixtures were prepared under vacuum conditions in a double "z" blades contra rotating mixer (Werner, Inc.). The pre-polymer HTPB was previous mixed with the plasticizer DOA and the solvent (methyl ethyl ketone - MEK) in order to decrease global viscosity allowing a fine coating of particles. The double effect of vacuum and constant mixing of 60°C allows to extracte all the MEK, verified by the global measured mass. When the viscosity of the mixture became constant as a function of time, after many hours of mixing process, the curing agent was added and mixed. The propellant tubes were then filled and cured in a oven at 60°C, during more than 1 day.

| Mixture (AP/AN -PU- GMB) | Molar composition | Mass composition (%) | Equi. ratio | Density |
|---|---|---|---|---|
| **D1 (»40/40-20-0)** | 33.455 AP + 49.116 AN + 12.951 HTPB + .523 DOA + .797 IPDI + .020 AIR | 39.29 AP + 39.30 AN + 17.70 HTPB + 1.94 DOA + 1.77 IPDI + .01 AIR | 2.043 | 1411 kg/m3 |
| **A1 (»80-20-0)** | 98.232 AN + 12.965 HTPB + .523 DOA + .797 IPDI + .030 AIR | 78.57 AN + 17.72 HTPB + 1.94 DOA + 1.77 IPDI + .01 AIR | 2.056 | 1321 kg/m3 |
| **A2 (»76-20-4)** | 94.454 AN + 12.453 HTPB + .502 DOA + .766 IPDI + .075 AIR + 6.410 GMB | 75.55 AN + 17.02 HTPB + 1.86 DOA + 1.70 IPDI + .02 AIR + 3.85 GMB | 1.967 | 1180 kg/m3 |
| **A2 (AIR) (»80-20-0)** | 94.454 AN + 12.453 HTPB + .502 DOA + .766 IPDI + .075 AIR | 78.57 AN + 17.70 HTPB + 1.93 DOA + 1.77 IPDI + .02 AIR | 2.055 | 1157 kg/m3 |
| **A3 (»83-13-4)** | 103.405 AN + 8.147 HTPB + .329 DOA + .501 IPDI + .130 AIR + 6.340 GMB | 82.69 AN + 11.13 HTPB + 1.22 DOA + 1.11 IPDI + .04 AIR + 3.81 GMB | 1.443 | 1071 kg/m3 |
| **A3 (AIR) (»86-14)** | 103.405 AN + 8.147 HTPB + .329 DOA + .501 IPDI + .130 AIR | 85.97 AN + 11.57 HTPB + 1.27 DOA + 1.16 IPDI + .04 AIR | 1.501 | 1049 kg/m3 |
| **A4 (»90-6-4)** | 112.398 AN + 3.783 HTPB + .153 DOA + .233 IPDI + .270 AIR + 6.377 GMB | 89.95 AN + 5.17 HTPB + .57 DOA + .52 IPDI + .08 AIR + 3.83 GMB | .988 | 827 kg/m3 |
| **A4 (AIR) (»94-6-0)** | 112.398 AN + 3.783 HTPB + .153 DOA + .233 IPDI + .270 AIR | 93.42 AN + 5.37 HTPB + .59 DOA + .54 IPDI + .08 AIR | 1.025 | 807 kg/m3 |

Table 5 - Composition, equivalence ratio and initial global density of tested mixtures.

## 3. THEORETICAL PREDICTIONS

### 3.1. Introduction - thermal equation of state

The theoretical prediction of combustion products, using THOR code, is based on theoretical work of Heuzé et al. [10], [11], [12], and later modified (vd. IEPG Reports [13], Campos [14]) in order to calculate the composition and thermodynamic properties of explosive compositions, for Chapman-Jouguet detonation conditions. Several equations of state are used, namely BKW, Boltzmann, H9, H12 and JCZ3 (vd. [14]). Results have been compared within themselves and with results of other codes refered in open literature (Quatuor Code from Heuzé et al. [10], [12], using BKW EoS the TIGER Code [15], [16], and using the KHT EoS the Tanaka Code [17] ). The BKW and H9 EoS are selected for our calculations. The first equation EoS is the most common in bibliography and the second is the natural development of a Boltzmann EoS type with similar results to the KHT and JCZ3 EoS (vd. [14]).

### 3.2. Chemical equilibria conditions

A classical combustion system have generally CHNO system. Using our computer code it is possible to consider up to $m$ atomic species ($m$<20) and form $n$ chemical components with these atomic species ($n$<40). Among these $n$ chemical components, $m$ are considered "basic" chemical components and $n$-$m$ "non basic". The selection "ab initio" of the "basic" chemical components depends on the equivalence ratio $r$ of the mixture, related to the stoicheiometry ($r$=1). These values must be those which are expected to have significant concentrations in final products composition.

For a CHNO system it has been selected (vd. [18], [11], [12]):

- $CO_2$, $H_2O$, $O_2$ and $N_2$ for poor mixtures ($r$<1),
- $CO_2$, $H_2$, $H_2O$ and $N_2$ for rich mixtures ($r$>1) of low initial density and C(s), $CO_2$, $H_2O$ and $N_2$ for rich mixtures of high initial density (initial condensed or solid components). When Cl atomic species is added it must be assumed HCl as a "basic" chemical component.

The mass balance yields a linear system involving $m$ equations. In order to solve the problem it is necessary to add more ($n$-$m$) equations. These $n$-$m$ equilibrium equations are determined by the method of Lagrange multipliers or the equilibrium constants (vd. [19], [20]). Consequently the system of equations is formed by $m$ linear atomic mass balance equations and ($n$-$m$) non linear equilibrium equations.

In order to determine the chemical concentration of $n$ components, for imposed P and T conditions, two methods can been used:

- the chemical affinity method, proposed by Heuzé et al.[10], [11],
- solving first the system composed by the $m$ "basic" components, and secondly adding one by one more components, optimising the relative concentration inside the group reported to the same atomic species, for the minimum value of global Gibbs free energy $G = \Sigma\, x_i\, \mu_i$, being the Gibbs free energy of each component $\mu_i = G_{oi}(T) + R\,T \ln P + R\,T \ln (x_i)$. The values of $G_{oi}(T)$ are the Gibbs free energy as a function of temperature. They are obtained from JANAF Thermochemical Tables [21] and from polynomial expressions of Gordon and McBride [22]. This second method is slower than the first, but avoid numeric problems (vd. Campos [14], [23]).

The solution of composition problems involves simultaneously:

- the thermodynamic equilibrium, obtained with the mass and species balance, and the equilibrium condition $G=G_{min}(P,T,x_i)$, previously described, applying to the condensed phase the model proposed by Tanaka [17],
- the thermal equation of state (EoS),
- the energetic equation of state, related to the internal energy $E = \Sigma\, x_i e_i(T) + \Delta e$, $e_i(T)$ being calculated from JANAF Thermochemical Tables [21] and polynomial expressions of Gordon and McBride [22],
- the combustion regime, being $P_b=P_o$ constant for the isobare adiabatic combustion (equal initial and final total enthalpy $H_b=H_o$) and the Chapman-Jouguet conditions (mass, momentum and energy balances and $dp/dV\,]_S = (P-P_o) / (V-V_o)$ ) for the detonation regime.

The isobare and detonation regimes are kept as limit combustion conditions in order to determine the threshold pollutant concentrations. (vd. Campos [23]).

The selection of components are dependent of atomic initial composition. For a classical CHNO system it is assumed an equilibrium composition of $CO_2$, CO, $H_2O$, $N_2$, $O_2$, $H_2$, OH, NO, H, N, O, HCN, $NH_3$, $NO_2$, $N_2O$, $CH_4$ gases and two kinds of solid carbon (graphite and diamond). When the initial mixture include Cl species HCl and $Cl_2$ are expected in final products. The glass shell of GMB was considered $SiO_2$ in two phases, solid and gas. It is assumed as inert in reaction.

### 3.3. Theoretical results and discussion

Theoretical predictions of isobare adiabatic combustion temperature T and specific volume ratio V/Vo, detonation temperature T and pressure P are respectively presented in Figs. 2 and 3. Combustion and detonation products are respectively presented in Figs. 4 and 5.

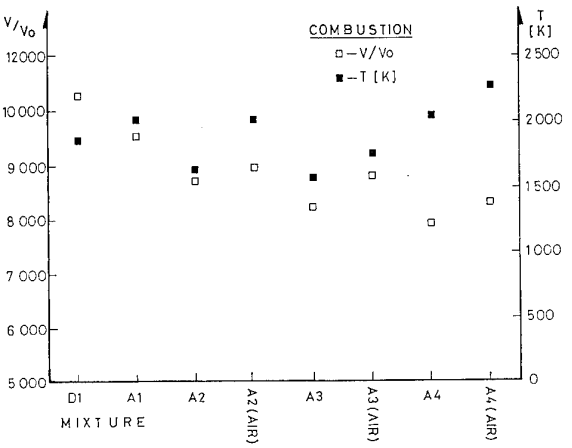



Fig. 2 - Calculated combustion temperature T and specific volume ratio V/Vo.

Analysis of the calculated combustion products allows to conclude:

- there is no influence of EoS selected to predict combustion products; the influence is negligible in detonation regime,
- there is no significant concentration of $Cl_2$, being HCl the chemical component calculated with Cl species in combustion calculations (vd. Figs. 4 and 5),
- calculated combustion temperature of tested mixture are similar, but there is a difference of ≅200 K from mixture Ai with and without $SiO_2$ material, for a final concentration of air (vd. Fig. 2),
- there is no significant concentrations of $NO_2$, being NO the present NOx chemical component, because all the tested mixtures have its equivalence ratio r higher than 1 (vd. Figs. 4 and 5),
- CO emissions are greater than NOx, in good agreement with classic kinetics theory, because all the calculated mixtures have its equivalence ratio higher than 1,
- solid carbon ($C_\beta$) is significant, being its concentration more important in the richest mixtures D1, A1 and A2, in combustion regime.

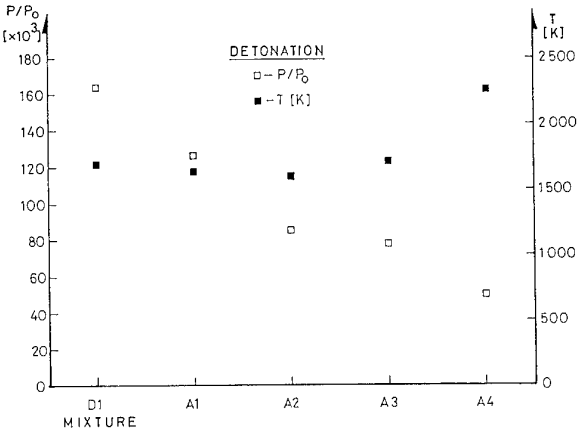



Fig. 3 - Calculated detonation temperature T and pressure P.

## 4. EXPERIMENTAL MEASUREMENTS

### 4.1 Experimental procedures

The sample combustion assembly is composed by a brass tube, with internal diameter of 25.5 mm and 100 mm long, having axially an ignition PMMA tube of 5 mm diameter (vd. Fig. 6). The tube was filled with propellant and kept in a oven at 60 °C more than 1 day. This ignition tube ensures a slow and constant flame progression, inside propellant cylinder, and allows the evacuation of combustion products. The sample tube was placed over an electrically heated metal plate, keeping constant the temperature of propellant (80 °C). The combustion assembly was enclosed inside a steel closed explosion chamber of 17.316 m3 (vd. Fig. 7) previously ventilated by environmental air, in order to keep constant the environmental conditions before each experience.

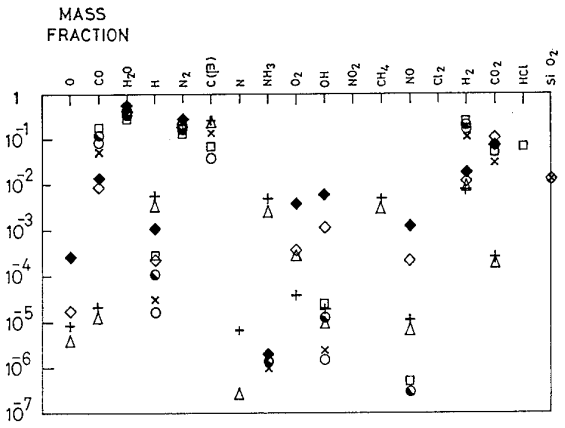



Fig. 4 - Calculated combustion products.

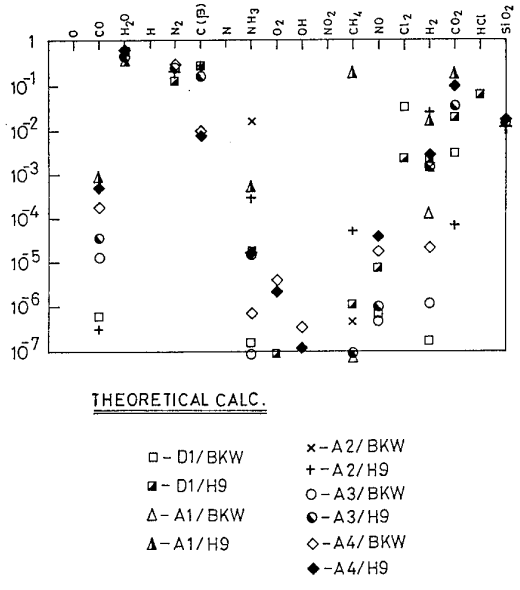



Fig. 5 - Calculated detonation products.

The exhaust gas sampling system consists of a fan connected to a cyclone, a mechanical filter and two columns of silica gel and activated coal. NO, NOx, and CO, $CO_2$, $CH_4$ gas analysers by IR spectroscopy (types MIR 9000 and SEC probe from Emission S.A.) are connected at the end of this exhaust gas sampling system (vd. Fig. 8). The HCl measurement was not performed because the HCl production comes only from propellant D1.

More than one sample tubes were simultaneously burned inside the explosion chamber, in order to correlate the burnt mass and measured combustion products concentration. The measured concentration value was then multiplied by the dilution factor, calculated by the mass ratio between the air, inside explosion chamber, and propellant sample (vd. Campos et al. [23]).

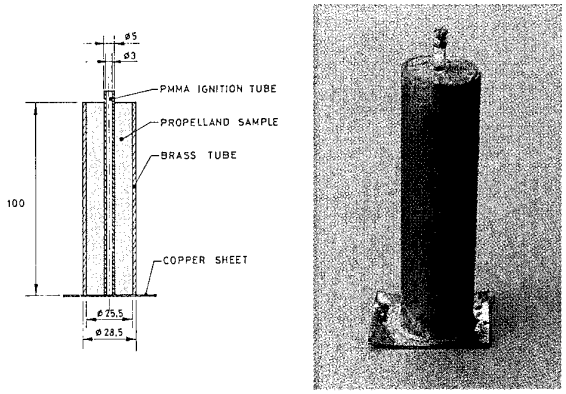



Fig. 6 - Sample combustion assembly.

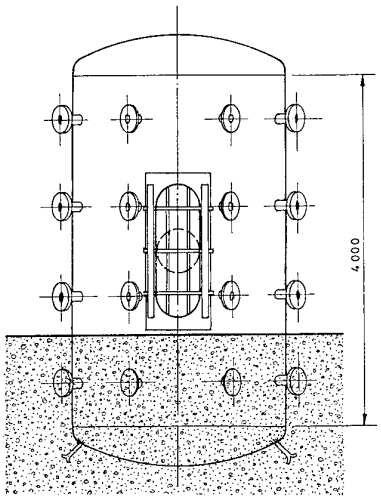



Fig. 7 - Steel closed explosion chamber.

Two other experimental combustion tubes were used (vd. Figs. 9 and 10) designed, respectively, by contact and coaxial combustion samples. The first configuration was suggested by Zarco et al. [24]. The second configuration is obtained changing the ignition PMMA tube by the propellant donor (mixture D1). They were tested with the aim to verify if the acceptor propellant presents or not self sustained combustion. Combustion temperatures were recorded from K type thermocouples, with 100 μm of diameter insulated with alumina, enclosed in a stainless steel 1 mm diameter tube ( delivered by Thermocoax from Philips).

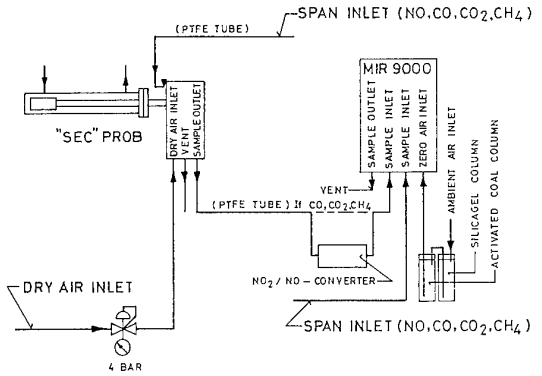



Fig. 8 - NO, NOx, and CO, $CO_2$, $CH_4$ gas analysers by IR spectroscopy.

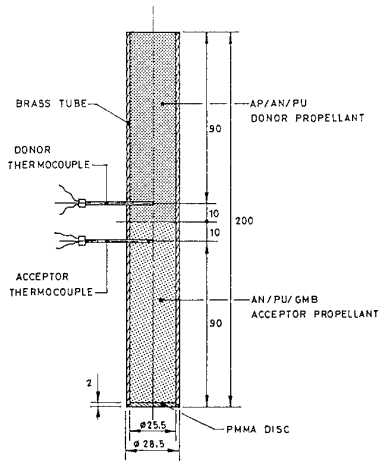



Fig. 9 - Contact combustion assembly.

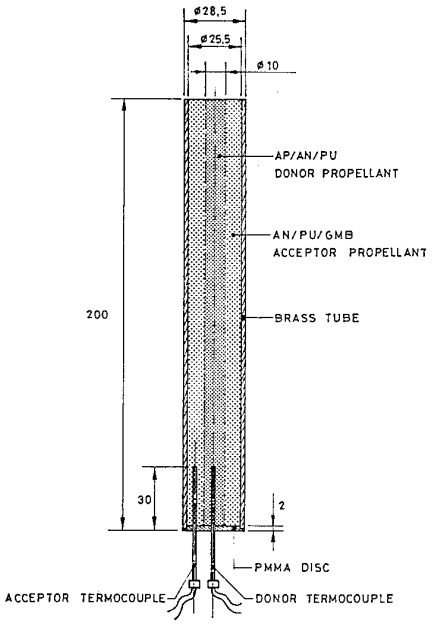



Fig. 10 - Coaxial combustion assembly.

Detonation assembly, was composed by a brass tube with the same internal diameter (25.5 mm) shocked by a plastic explosive donor.

**4.2 Experimental results and discussion**

It was observed the real extinction of combustion for A1 propellant and a transition situation for A2. In order to evaluate combustion products of these mixtures, samples are heated at temperatures up to 200 °C, in order to increase pyrolisis and parcial combustion of these two propellants.

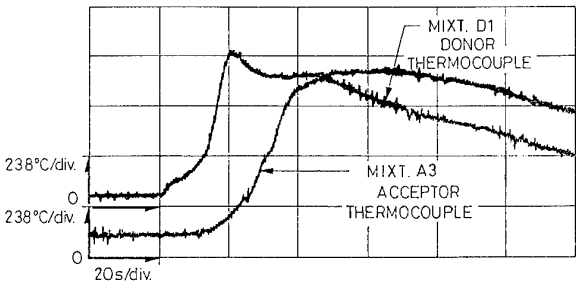



Fig. 11 - Thermocouple records for contact combustion samples.

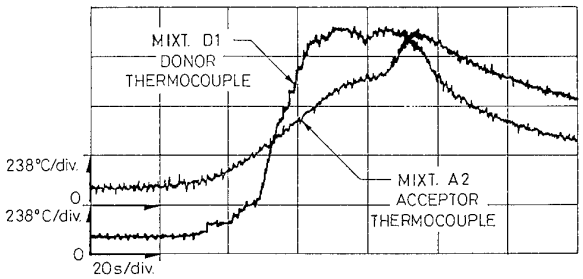



Fig. 12 - Thermocouple records for coaxial combustion samples.

Typical thermocouple records for contact and coaxial combustion samples are shown in Figs. 11 and 12. The self sustained combustion is not very stable, perhaps due to its low density. Combustion of A3 shows heterogeinities (vd. Fig. 13) but seems to be relatively stable. Combustion temperatures of donor propellant D1 are in the range 970 to 1250K. Measured combustion temperatures for A3 were near 1050 K, showing a slow decrease of temperature, after the maximum value be reached. This fact seems to be due to the influence of GMB on internal heat transfer. The measured values of propellants residues are always less than 3% of initial mass, proving the validity of these tests procedures.

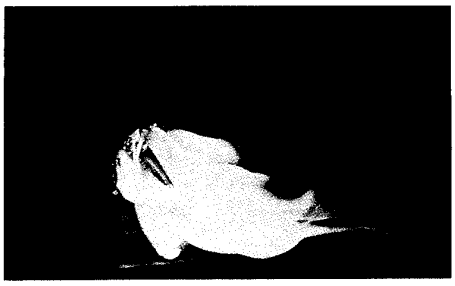


Fig. 13 - Combustion aspect of propellant A3.

Measured products concentration of $CH_4$, $CO_2$, CO and NO, of tested combustion and detonation samples, are presented in Fig. 14. The analysis equipment was configurated to analyse NO concentrations, converting all of existing NOx into NO. Measured concentrations, corrected by the dilution factor, show very reliable results independent of the burned mass of combustion sample. $CO_2$ concentrations were on the limit level of the measurement equipment. Measured CO concentrations were higher than NO, for the cases where it could be observed self sustained combustion (D1, A3 and A4), being in a good agreement with theoretical predictions. In the other cases, NO concentrations higher than

CO, seems to indicate a pyrolisis regime, sustained by the heat transmitted from the electrically heated plate. Correlation with theoretical predictions, assuming $CH_4$ like a transient chemical component for mixtures near stoicheiometry, shows a very good agreement with CO and $CH_4$ measurements. $CO_2$ and NO were higher than predicted values - this fact seems to indicate the effects of recombination and heat transfer to the environmental air. CO and NO measured emissions from contact and coaxial samples confirm the validity of self sustained combustion of A3 mixtures.

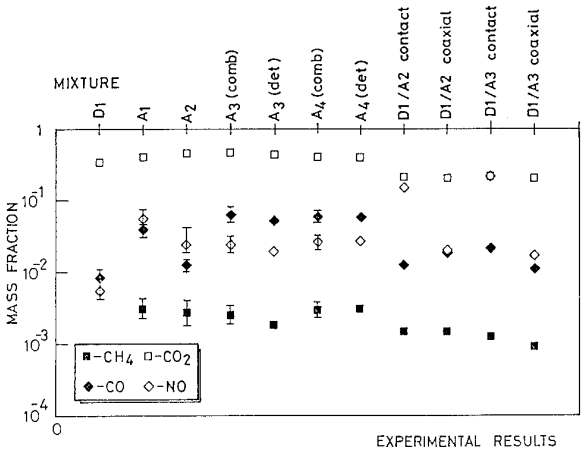



Fig. 14 - Measured concentrations corrected by the dilution factor.

## 5. CONCLUSIONS

Predicted compositions of combustion products, using THOR code, show no significant concentrations of $Cl_2$. Calculated combustion temperatures of tested mixtures were similar, but there was a difference of ~200 K from AN-PU mixture with and without GMB. No significant concentrations of $NO_2$ have been predicted. CO emissions were higher than NOx, which is in a good agreement with classic kinetics models.

It was observed the real extinction of AP-PU propellant of AN concentration of 80% and a transition situation for this composition with GMB. Combustion of AN-PU-GMB propellants, with AN concentration of 83%, shows heterogeinities and it seems to be relatively stable, at atmospheric pressure. Combustion temperatures of donor propellant AP/AN-PU of 40/40-20% were in the range 970 to 1250 K. Measured combustion temperatures for AN-PU-GMB propellant with AN concentration of 83% were near 1050 K. Measured values of propellants residues were always less than 3% of initial mass, proving the validity of these tests procedures.

Measured concentrations of combustion products, corrected by the dilution factor, show very reliable results. Measured CO concentrations were higher than NO, for the cases where it could be observed self sustained combustion, in a good agreement with theoretical predictions. In the other cases, NO concentrations being higher than CO, seems to indicate a pyrolisis regime. Correlations with theoretical predictions, assuming $CH_4$ as a transient chemical component for mixtures near stoicheiometry, show a very good agreement with CO and $CH_4$ measurements. $CO_2$ and NO were higher than the predicted values. The CO and NO emissions of contact and coaxial combustion samples prove the validity of self sustained combustion of AN-PU-GMB propellant with AN concentration of 83%, at atmospheric pressure.

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# PRÉVISION DU BRUIT IMPULSIONNEL DES MOTEURS À TRÈS COURT TEMPS DE COMBUSTION

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**Résumé**

L'onde de choc et le cortège acoustique de haut niveau émis lors du tir d'un missile ou d'une roquette équipé d'un moteur à très court temps de combustion (10 ms) peuvent entraîner un risque de traumatismes auditifs ou extra-auditifs pour les servants d'armes. Pour ces raisons, un ensemble d'outils prévisionnels adaptés, utilisables dès les stades de conception ou d'évaluation d'avant projets pour ces moteurs a été élaboré.

Ainsi, dans le cas des tirs en champ libre, un modèle semi-empirique a été mis au point. Ce modèle est basé sur un modèle d'explosion globale, traitant la génération et la propagation d'ondes de choc générées par une libération isotrope et instantanée d'énergie. Il a ensuite été adapté au cas des moteurs, à partir de résultats expérimentaux traduisant une variation systématique des paramètres de conception.

Enfin, pour les tirs depuis un espace clos simulant le combat en zone urbaine, une étude expérimentale a permis de préciser les mécanismes de formation et de réflexion des ondes de choc sur les parois. Par ailleurs un ensemble d'essais, selon un plan d'expérience faisant intervenir diverses caractéristiques de moteurs et d'organisation d'espace clos, a permis de mettre au point des règles et abaques prévisionnels.

**Liste des symboles**

$a_0$ vitesse du son dans l'air au repos
$A_c$ aire au col
$A_e$ aire en sortie de tuyère
$C$ calibre d'une arme
$C^*$ vitesse caractéristique des gaz de combustion
$C_f$ cœfficient de poussée
$C_v$ chaleur spécifique à volume constant
$E_a$ Energie acoustique
$E_0$ Energie d'explosion
$Leq8, Laeq8$ Niveau de bruits équivalents sur 8 heures, sans et avec pondération A
$M$ masse du projectile
$p_0$ pression atmosphérique de l'air au repos
$p, p_s$ surpression statique
$\overline{P}_s$ surpression statique réduite
$Pch$ pression dans la chambre de combustion
$P_e$ pression statique en sortie de tuyère
$P_a$ pression atmosphérique
$PROP$ pression de rupture de l'opercule
$R$ distance au centre du plan de sortie de la tuyère
$\overline{R}$ distance réduite
$R_s$ rayon d'un choc sphérique
$s$ surface de la sphère de rayon $R$
$t$ temps
$t_a$ temps d'arrivée de l'onde compté à partir du début de libération de l'énergie
$t_f$ temps de fonctionnement du propulseur
$T_g$ température des gaz de combustion
$T_s$ durée de la phase positive du signal de bruit
$U$ vitesse du choc
$V_0$ vitesse maximale du projectile
$V_e$ vitesse des gaz en sortie de la tuyère
$x(t)$ position du projectile
$\gamma$ rapport des chaleurs spécifiques
$\eta(E_0, \theta)$ paramètre d'ajustement expérimental utilisé dans la modélisation de la surpression maximale
$\rho_0$ masse volumique de l'air au repos
$\theta$ azimut

## 1. Introduction

Le tir d'un missile ou d'une roquette équipé d'un moteur à très court temps de combustion (10 ms) donne lieu à l'émission de gaz à des débits relativement élevés (de l'ordre de 10 à 50 kg/s). Ces gaz sont responsables de la formation d'ondes de choc et de cortèges acoustiques de haut niveau.

De plus les contraintes de conception des moteurs de lancement conduisent souvent à des

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écoulements fortement sous-détendus dans le plan de sortie de la tuyère, renforçant les ondes de pression autour du propulseur.

Ces effets sur l'environnement constituent des nuisances pour les servants d'armes ; ils peuvent entraîner des risques de traumatismes auditifs ou extra-auditifs. Ils peuvent aussi occasionner des effets mécaniques par effet de souffle. Afin de prévoir ces effets et de déterminer la zone de l'espace où ils peuvent se produire une étude a été menée par l'ONERA sous l'égide de la DAT (Direction des Armements Terrestres).

## 2. Modélisation du bruit en espace libre : logiciel EXPLOG

### 2.1. Analyse théorique et expérimentale

Considérons un propulseur (figure 1) libérant son énergie essentiellement sous forme d'un jet fortement sous détendu (pression en sortie tuyère très supérieure à la pression atmosphérique). La modélisation de l'onde de souffle générée à l'allumage nécessite une approche différente suivant la zone à laquelle on s'intéresse :

- dans le jet, c'est typiquement un problème d'aérodynamique,

- en avant du propulseur, en champ lointain, l'onde est quasiment acoustique,

- en arrière, en champ lointain, elle est assimilable à celle d'une explosion (chocs forts, onde en N) d'énergie Eo égale à l'énergie totale libérée par le propulseur,

- plus on s'écarte de l'axe du jet, plus les chocs s'affaiblissent, jusqu'à rejoindre le domaine acoustique,

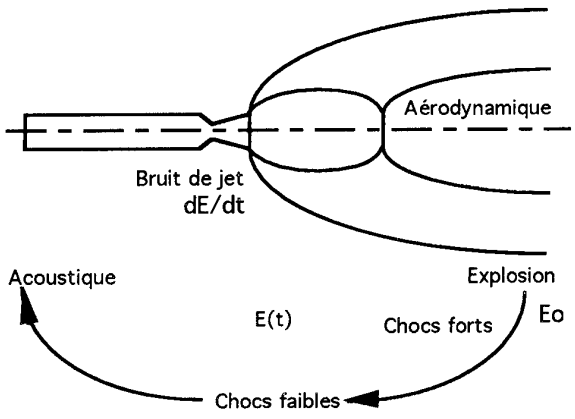



Figure 1 :Onde de souffle générée par un propulseur

- en zone tireur, par contre, on a plutôt à faire à un bruit de jet supersonique de nombre de Mach relativement élevé, pour lequel le débit d'énergie est alors le paramètre déterminant,

- enfin en zone intermédiaire, il faut prendre en compte, le mieux possible, la loi de libération de l'énergie.

C'est à partir du modèle d'explosion que nous avons développé notre modélisation.

#### 2.1.1. Modèle de l'explosion

##### *2.1.1.1. Surpressions maximales*

Une explosion correspond à une libération d'énergie instantanée qui engendre une onde de souffle d'amplitude finie (voir figure 2). On suppose, qu'en dehors du front de choc, le fluide est calorifiquement parfait et non visqueux, et on considère qu'il n'y a pas d'échanges de chaleur avec l'extérieur.

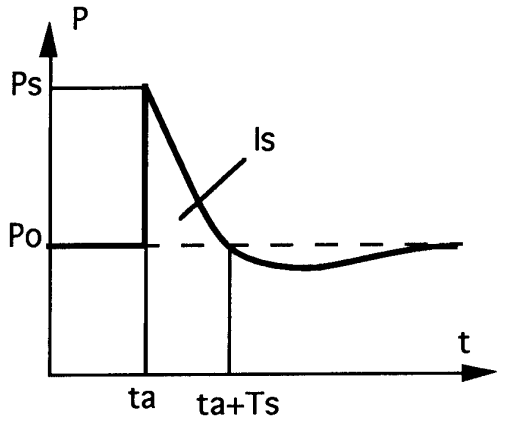



Figure 2 : Evolution de la pression de l'air lors du passage d'une onde de choc.

Les différentes grandeurs caractéristiques d'une onde de souffle générée par une explosion idéale (ponctuelle, isotrope, dans l'air au repos et sous des conditions normales de pression et de température) ont été compilées par Baker [1].

Elles sont réduites à l'aide de $E_0$ (énergie d'explosion) et des quantités $p_0$ et $a_0$, pression et vitesse du son, relatives à l'air au repos. Les paramètres du modèle de Baker que nous avons utilisés sont donnés dans le tableau 1. Pour les valeurs numériques on se reportera à Baker [1].

| Paramètre | Symbole | Equation |
|---|---|---|
| Distance réduite | $\overline{R}$ | $\left(Rp_0^{1/3}\right)/E_0^{1/3}$ |
| Surpression crête réduite | $\overline{P_s}$ | $P_s/p_0$ |
| Vitesse du choc | $\overline{U}$ | $U/a_0$ |
| Temps d'arrivée | $\overline{t_a}$ | $\left(t_a a_0 p_0^{1/3}\right)/E_0^{1/3}$ |
| Durée de la phase positive | $\overline{T_s}$ | $\left(T_s a_0 p_0^{1/3}\right)/E_0^{1/3}$ |

Tableau 1 : paramètres du modèle de Baker

Pour les chocs faibles, l'approximation acoustique conduit à la forme asymptotique suivante :

$$\overline{P}_s = \frac{0{,}1153}{\overline{R}}$$

*2.1.1.2. Energies "acoustiques"*

On peut également estimer l'énergie de l'onde à partir du modèle de Baker (figure 3) :

- dans l'expression de l'énergie "acoustique ", que l'on supposera valable quelle que soit l'intensité des chocs, voir[4],

$$E_a = 4\pi R_S^2 \int_{t_a}^{t_a+T_s} \frac{p^2(t)dt}{\rho_0 a_0}$$

on peut approximer l'évolution de la surpression $p(t)$ par l'équation de Friedlander,

$$p(t) = P_s\left(1-\frac{t}{T_s}\right)\exp\left(-\frac{bt}{T_s}\right)$$

- il vient alors,

$$E_a = \frac{4\pi R_S^2 P_S^2 T_s}{\gamma p_0}\left(\frac{2b^2-2b+1-e^{-2b}}{b^3}\right)$$

soit en coordonnées réduites,

$$E_a = E_0\left[\frac{\pi \overline{P}_S^2 \overline{T}_s \overline{R}_S^2}{\gamma}\left(\frac{2b^2-2b+1-e^{-2b}}{b^3}\right)\right]$$

- l'approximation acoustique,

$$\overline{P}_s = \frac{0{,}1153}{\overline{R}};\ \overline{T}_s \cong 1;\ b \cong 3{,}5$$

permet de déduire l'asymptote de cette courbe,

$$E_a = 0{,}012 E_0$$

On notera que les valeurs de $E_a$ sont supérieures à cette valeur asymptotique, elles prennent donc en compte une autre forme d'énergie qui sera dissipée dans le milieu environnant lors de la propagation de l'onde et qui ne constitue pas à proprement parler de l'énergie acoustique. Nous ne parlerons donc que de l'énergie "acoustique" (entre guillemets) dans la suite de l'article.

*2.1.1.3. Modélisation*

Dans le modèle prévisionnel proposé, le cas d'une explosion est pris en compte en considérant une énergie d'explosion égale au produit de la masse d'explosif par l'énergie spécifique de l'explosif, une libération quasi-instantanée de cette énergie (quelques pas de temps de calcul) et une répartition isotrope.

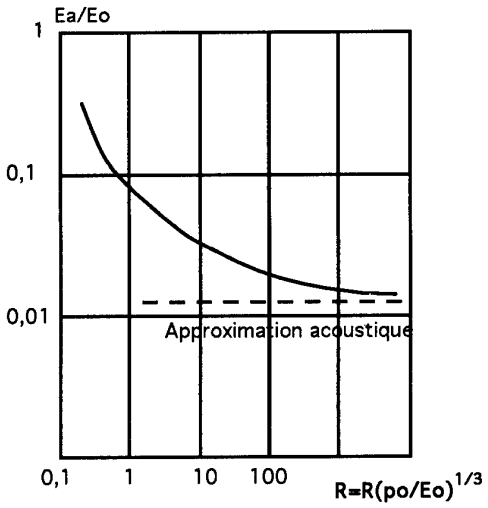



Figure 3 : Explosion. Calcul de l'énergie "acoustique"

2.1.2. Modélisation pour un propulseur

On constate expérimentalement qu'un modèle d'explosion peut servir de guide à l'analyse d'une telle onde de souffle : lois de similitude de Hopkinson et Sach, modèle de Baker.

Quelles analogies existe-t-il avec une explosion ?

- Tout d'abord nous avons généralement à faire à des propulseurs à courts temps de combustion. La libération de l'énergie est donc relativement rapide et, en première approximation, nous pouvons l'assimiler à celle d'une explosion.

- En champ lointain, les dissymétries sont très atténuées et l'explosion peut être considérée comme isotrope.

Nous utilisons le modèle de Baker [1] pour décrire cette explosion.

Quelles sont les différences avec une explosion ?

Elles apparaîtront surtout en zone proche et en zone intermédiaire, c'est à dire à des distances pour lesquelles le temps d'arrivée de l'onde est inférieur ou égal au temps de fonctionnement du propulseur.

- La libération de l'énergie ne peut plus être considérée comme instantanée, il faudra définir à chaque instant une énergie équivalente d'explosion : E(t).

- Par ailleurs, du fait de la présence du jet, la répartition de l'énergie est fortement directionnelle et il faudra introduire dans le modèle une distribution azimutale $f(\theta)$.

- Enfin les propulseurs étant généralement tirés d'une certaine hauteur au-dessus du sol, il faudra prendre en compte la réflexion par le sol.

*2.1.2.1. Modélisation en champ lointain*

*Prise en compte de la libération progressive de l'énergie*

L'énergie équivalente d'explosion est prise égale à l'énergie libérée depuis l'instant de la désobturation de la tuyère jusqu'au temps d'arrivée de l'onde de souffle au point de mesure considéré :

$$E(t_a) = \int_0^{t_a} Pch(t) \frac{A_c C_v T_g}{C^*} dt$$

avec :

$T_g$ température des gaz de combustion

$C^*$ vitesse caractéristique des gaz de combustion

$C_v$ chaleur spécifique à volume constant

$Pch$ pression dans la chambre de combustion

$A_c$ aire au col

A partir de cette valeur de l'énergie, on déduit des abaques de Baker les caractéristiques du choc : Ps et U à la distance R déterminée par la relation :

$$R = \int_0^{t_a} U(t) dt$$

Un programme de calcul itératif permet de déterminer à chaque instant le champ de pression Ps(R).

Afin de valider la méthode proposée, l'application en a été faite dans le cas où la libération de l'énergie est de la forme :

$$E(t) = at$$

car dans ce cas il existe une solution analytique établie dans l'hypothèse des chocs forts [2]. Nous avons étendu cette solution au cas des chocs intermédiaires en adoptant la méthode de Jones [3].

Il a été constaté un accord satisfaisant avec la solution analytique, à la fois pour les temps d'arrivée et les surpressions, jusqu'en zone intermédiaire.

*Prise en compte des effets asymétriques*

La répartition azimutale n'étant pas connue, les effets de cette dissymétrie sont pris en compte de façon semi-empirique, à partir des résultats des mesures effectuées au cours de l'étude paramétrique [4] et des formules semi-empiriques relatives à des canons proposées dans la littérature [5], [6], [7].

Le choix de la fonction de répartition est explicité dans [4]; la forme retenue est :

$$f(\theta) = 0{,}513\left[0{,}75\left(\cos\theta + \sqrt{\cos^2\theta + 16/9}\right)^3\right]$$

*Prise en compte de la réflexion par le sol.*

Lorsque l'onde de souffle rencontre obliquement le sol, que l'on suppose rigide, on peut considérer qu'il se forme une onde réfléchie qui paraît issue d'une source symétrique par rapport à la surface du sol.

A partir d'une certaine valeur de l'angle formé par le vecteur de l'onde incidente et le plan réflecteur, l'onde incidente et l'onde réfléchie fusionnent en une seule onde dite "onde de Mach", qui se déplace parallèlement à ce plan; au-dessus de la zone de Mach, les deux chocs restent distincts. Les limites de la zone de Mach sont estimées en fonction de l'énergie libérée et des paramètres géométriques à partir d'abaques expérimentales. Dans cette zone, on calcule la surpression en lui attribuant une énergie double :

$$E'(t) = 2E(t)$$

*2.1.2.2. Modélisation en zone proche*

*Energies "acoustiques".*

L'analyse des résultats expérimentaux a permis d'établir une corrélation entre l'énergie "acoustique " mesurée, la loi de libération de l'énergie du propulseur et la répartitition azimutale de cette énergie.

On a montré [4] qu'elle pouvait se mettre sous la forme :

$$\frac{dE_a}{ds} = k \frac{E(\bar{R})}{4\pi \bar{R}^2} f(\theta)$$

En ajustant cette expression aux résultats expérimentaux, en zone proche, on a déterminé la valeur de k :

$$k_{exp} \cong 0{,}0314$$

*Surpressions maximales*

La comparaison expérience-calcul (modèle d'explosion), en considérant une répartition azimutale de l'énergie similaire à celle observée pour les canons, a montré qu'en champ lointain (ta>>tf) les surpressions calculées recoupent bien les valeurs expérimentales; toute l'énergie libérée contribuant à la formation d'un choc unique.

Partant des résultats pour les énergies "acoustiques", pour lesquelles on a montré qu'une même distribution azimutale pouvait, en zone proche, être appliquée aux différents propulseurs considérés, on a pu corréler l'état de formation du choc (surpression maximale) et l'énergie génératrice.

Le rapport $\eta$ , de la surpression maximale expérimentale sur la surpression maximale calculée suivant la méthode utilisée en zone lointaine, moyenné en zone proche, est en effet très bien corrélé avec le produit de l'énergie totale libérée et de la fonction de répartition f(θ). (figure 4).

L'interprétation de ce facteur $\eta(E_0, \theta)$ est la suivante : le facteur $\eta$ est lié aux processus de formation de l'onde de choc, au regroupement plus ou moins rapide des ondes de compression. On constate que ce regroupement s'effectue d'autant plus rapidement que l'énergie est importante. Il eût été possible d'appréhender ces

phénomènes d'une façon plus théorique, cependant cette démarche aurait dépassé largement les limites de cette étude; aussi nous nous contentons d'utiliser au mieux cette relation $\eta(E_0,\theta)$ dans notre modèle prévisionnel.

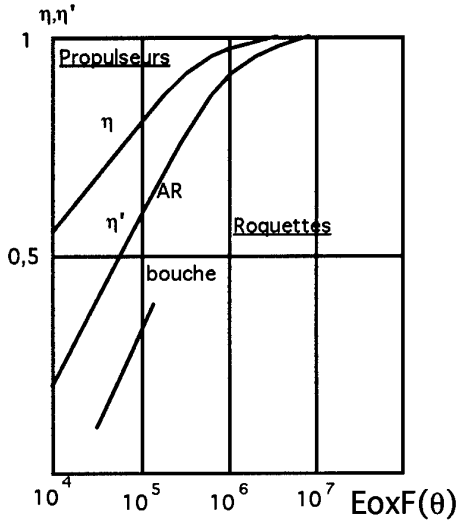



Figure 4 : Variation de $\eta$ en fonction de l'énergie libérée.

*2.1.2.3. Prise en compte des paramètres secondaires*

Il a été montré [4] que les paramètres de fonctionnement des propulseurs :
- pression de rupture de l'opercule PROP
- pente de montée en pression dans la chambre dPch/dt
- conditions de détente de la tuyère ε, Pe ou Ve

pouvaient être considérés comme secondaires dans la mesure où ils n'agissent notablement sur le champ de surpression qu'en zone très proche.

La prise en compte de ces paramètres, dans le modèle, est purement expérimentale; les influences sont supposées indépendantes et cumulatives.

Elle se traduit par une altération locale du terme correctif η utilisé pour la modélisation de la surpression maximale en zone proche :

$$\eta(E) = \eta_0(E).\alpha(\overline{R},\theta).\beta(\overline{R},\theta).\gamma(\overline{R},\theta)$$

avec,

$\alpha(\overline{R},\theta)$ influence de la pente de montée en pression dans la chambre

$\beta(\overline{R},\theta)$ influence de la pression de rupture de l'opercule

$\gamma(\overline{R},\theta)$ influence des conditions de détente de la tuyère

L'état de référence de η a été défini en fonction du propulseur REF utilisé pour cette étude expérimentale, avec les caractéristiques de fonctionnement suivantes :

dPch/dt = 2,11 $10^{10}$ Pa/s

PROP = 6,5 $10^6$ Pa

Pe = 2 $10^6$ Pa

En zone proche et en dehors du jet, il s'avère qu'une meilleure corrélation est obtenue en considérant, comme paramètre caractéristique des conditions de détente, la pression statique Pe dans le plan de sortie tuyère.

L'ajustement expérimental en zone proche conduit aux expressions suivantes pour les coefficients :

$$\alpha = 1 + 1,6.10^{-11}\left(\frac{dPch}{dt} - 2,1.10^{10}\right)$$

$$\beta = 1 + 1,57.10^{-8}\left(PROP - 6,5.10^{6}\right)\left(\frac{2,3}{\overline{R}} - 1\right)$$

$$\gamma = 1 + 0,044(\theta - 1,22)(\pi - \theta)\left(\frac{2,3}{\overline{R}} - 1\right)\ln\left(\frac{P_e}{2.10^6}\right)$$

L'influence des ces paramètres est supposée nulle en zone lointaine; leur influence en zone intermédiaire est prise en compte par l'interpolation zone proche-zone lointaine.

Pour les énergies "acoustiques", l'influence de ces paramètres secondaires est nettement inférieure à la précision des mesures ou des valeurs prédites; elle n'est pas prise en compte dans la modélisation.

2.1.3. Modélisation pour un lance-roquette

Le modèle proposé a été développé pour décrire l'onde émise à l'arrière d'un propulseur. Dans le cas d'un lance-roquette, on doit également tenir compte du déplacement de la roquette dans le tube de lancement et de l'onde générée à l'avant du tube.

Pour déterminer la cinématique de la roquette, on fait les hypothèses suivantes :

- Les forces de frottement dans le tube sont supposées négligeables.

- Le coefficient de poussée

$$C_f = \left[\frac{V_e}{C^*} + \frac{A_e}{A_c}\left(\frac{P_e - P_a}{Pch}\right)\right]$$

est supposé constant; ceci n'est vrai que dans le cas où $P_e >> P_a$.

La masse $M$ de la roquette est supposée constante et égale à la masse de la partie inerte + la moitié de la masse du propergol ; cette dernière étant faible devant la masse totale.

La cinématique de la roquette est alors déduite de la loi de poussée :

$$F(t) = M\frac{d^2x(t)}{dt^2} = C_f A_c Pch(t)$$

Une première intégration de F(t) conduit à :

$$M\frac{dx(t)}{dt} = C_f A_c \int_0^t Pch(t)dt$$

$C_f$ est déterminé expérimentalement à partir de la mesure de la vitesse maximale Vo de la roquette à la sortie du tube :

$$C_f = \frac{MV_0}{A_c \int_0^{T_f} Pch(t)dt}$$

Une deuxième intégration permet d'obtenir la loi de déplacement.

Expérimentalement on constate que la répartition azimutale de l'énergie "acoustique" au niveau de l'onde arrière, en dehors de la zone balayée par le jet, est très peu perturbée par la présence du tube de lancement; le modèle est donc utilisable comme précédemment.

On constate, par ailleurs, que l'onde de bouche est beaucoup moins directive que l'onde AR; en particulier dans la zone tireur, elle est pratiquement isotrope. L'intérêt de la modélisation prévisionnelle étant essentielle en zone tireur, nous en limiterons l'application à cette zone et nous utiliserons une répartition isotrope de l'énergie.

Par contre, le champ des surpressions maximales de l'onde AR est légèrement perturbé par la présence du tube. Ce dernier, en modifiant les processus de formation des chocs, conduit à une certaine atténuation. Après corrélation des résultats obtenus avec différents types de lance-roquette, comme dans le cas d'un propulseur, on a montré que ces phénomènes peuvent être pris en compte dans la modélisation, par un facteur $\eta'$ (figure 4) que l'on applique après détermination de la surpression maximale.

Remarque:

Il s'est avéré, au cours de l'étude expérimentale, que la prévision des caractéristiques de l'onde de bouche était extrêmement délicate, voire impossible, sans une étude approfondie de la balistique intérieure prenant en compte le profil de la roquette et la variation de l'aire d'éjection des gaz à la bouche.

Ici, on a supposé que l'ajustement du plan de sortie tuyère dans le tube de lancement était parfaitement étanche et que le débit des gaz de combustion à la bouche passait brutalement de 0 à la valeur correspondant au débit de la roquette à l'instant de sa sortie de tube de lancement.

Les valeurs des paramètres de l'onde de bouche ainsi déterminées seront donc des valeurs approchées majorant les phénomènes réels.

## 2.2. Degré de confiance des valeurs prédites

Comme on l'a vu précédemment, aucune théorie simple ne permet de décrire l'ensemble des phénomènes qui régissent la formation et la propagation d'une onde de souffle. Aussi, la modélisation prévisionnelle proposée repose en grande partie sur l'exploitation de résultats expérimentaux, que ce soit pour le modèle de Baker ou pour son adaptation au cas des lance-roquettes.

Le degré de confiance des valeurs prédites est, par conséquent, directement lié à la précision des mesures et de l'exploitation qui en a été faite. Il ne peut être véritablement établi que dans le cas des propulseurs et des lance-roquettes (onde AR uniquement); pour les autres types d'armes, on considérera actuellement que la modélisation proposée donne un ordre de grandeur généralement majorant des grandeurs caractéristiques de l'onde de souffle.

### 2.2.1. Surpressions maximales

La précision sur la détermination expérimentale de la surpression maximale est liée à :

- la reproductibilité des mesures,

- la reproductibilité des essais.

La réalisation d'un grand nombre d'essais et leur exploitation ont permis de préciser et d'interpréter les écarts importants parfois au cours des essais. Ainsi, les capteurs utilisés sont généralement fidèles mais pas interchangeables malgré toutes les précautions prises lors de l'étalonnage des chaînes d'acquisition. De même la reproductibilité des essais, notamment pour les mesures effectuées en zone proche, est absolument tributaire des processus de formation des chocs (regroupement des ondes, réflexions...), lesquels sont fortement aléatoires.

Une estimation globale de l'erreur expérimentale à laquelle on peut s'attendre pour l'exploitation de la surpression maximale peut atteindre 20 à 30%, c'est à dire 2 à 3 dB. Toutefois, pour un grand nombre d'essais, et en corrélant les résultats obtenus pour différents capteurs, on peut déterminer une valeur moyenne très significative, avec un écart type inférieur à 1dB.

Ces valeurs moyennes sont, en zone lointaine et pour $\theta<90°$ , en bon accord avec le modèle proposé. En zone proche, la prise en compte des paramètres secondaires et du terme correctif assure un accord modèle-expérience satisfaisant pour l'ensemble des propulseurs étudiés ; les écarts-type sont inférieurs à 2dB, en dehors de la zone balayée par le jet.

La figure 5a indique, sous forme de zones centrés sur les valeurs moyennes, le degré de confiance à accorder aux valeurs prédites par le code EXPLOG.

Pour les roquettes, un degré de confiance ne peut être défini que pour les grandeurs caractéristiques de l'onde AR; il est tout à fait comparable à celui défini pour un propulseur.

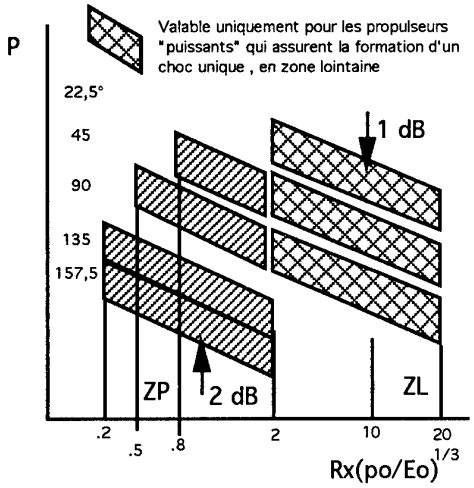



Figure 5a : degré de confiance des valeurs prédites (surpressions)

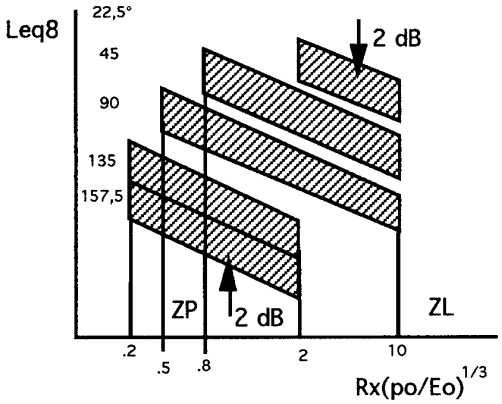



Figure 5b :degré de confiance des valeurs prédites (énergies)

2.2.2. Energies "acoustiques"

La précision que l'on peut attendre des déterminations expérimentales de ces énergies est liée, comme pour les surpressions maximales, à la précision des enregistrements de bruit et à la reproductibilité des essais.

Au niveau des enregistrements, il faut tenir compte des problèmes de vibrations et de dérive des capteurs qui deviennent cruciaux, dans ce cas, puisqu'ils sont traduits directement en niveaux équivalents d'énergie.

Au niveau de la reproductibilité des essais, les phénomènes de formation des chocs, en zone proche, sont également plus cruciaux puisque leur caractère aléatoire intervient quadratiquement.

Au cours de l'étude expérimentale, une élimination plus drastique des mesures inexploitables a été nécessaire et l'analyse statistique a été rendue plus délicate. L'estimation globale de l'erreur expérimentale pour cette grandeur varie de 5 dB en zone intermédiaire jusqu'à 10 dB en zone proche. Toutefois, une exploitation plus poussée de ces mesures : recherche de corrélations et analyse semi-théorique, réduit cette incertitude à 1 ou 2dB autour de valeurs moyennes alors significatives.

En zone proche, les relations empiriques, utilisées pour la prévision de cette grandeur, assurent, pour l'ensemble des propulseurs, une cohérence à moins de 2 dB près.

La figure 5b présente, sous forme de zones centrées sur les valeurs moyennes calculées, le degré de confiance à accorder aux valeurs prédites par le code EXPLOG

2.2.3. Energies "acoustiques" filtrées A et nombre de coups autorisés

Les paramètres physiologiques de l'onde de souffle ont été définis par le "Comité Bruits d'Armes". Le comité regroupe au niveau national des ingénieurs, médecins, physiologistes et opérationnels concernés par les problèmes des bruits d'armes.

Les paramètres :
- énergie "acoustique" filtrée dBA,
- nombre de coups autorisés sans protection,
- nombre de coups autorisés avec simple protection,
- nombre de coups autorisés avec double protection,

ont été estimés en exploitant systématiquement les résultats des essais réalisés à l'ETBS. Cette exploitation a consisté à appliquer à chaque signal enregistré, et notamment à sa répartition spectrale, différentes fonctions de transfert spécifiques: courbe dBA ou courbes spectrales d'atténuation d'une simple ou d'une double protection.

Cette estimation s'est révélée assez difficile compte-tenu du caractère aléatoire des résultats expérimentaux; notamment en ce qui concernent les énergies "acoustiques" filtrées dBA.

Dans le cas des propulseurs et des lance-roquettes, l'atténuation dBA (=Leq8-LAeq8) dépend essentiellement de l'état de formation des chocs:

- en zone proche, la succession des ondes de compression donne au signal un caractère haute fréquence et l'influence du filtrage dBA est assez limité (1 à 2 dB),

- par contre, en zone lointaine, lorsqu'un choc unique est formé (cas des propulseurs à forte énergie libérée: LIB, REF...), l'atténuation dBA est maximale, de l'ordre de 10 à 12 dB.

En l'état actuel, nous avons choisi de rechercher des majorantes en minimisant l'atténuation dBA à 2 dB pour tout type d'arme, et ce, uniformément sur tout l'environnement.

En ce qui concerne la prise en compte des filtres dBA+PS (protection simple) et dBA+DP (double protection), on constate, sur les valeurs déterminées expérimentalement, un meilleur regroupement de ces valeurs sur la totalité de l'environnement et, avec une précision de ± 2 dB, on peut attacher une valeur unique à l'atténuation de ces filtres, quelque soit le type d'arme

considéré : petit, gros ou moyen calibre, propulseur ou roquette.

dBA+PS --> -27±2 dB

dBA+DP --> -37±2 dB

Pour le calcul des nombres de coups autorisés , on utilise les valeurs précédemment déterminées :

$$N_A = 10^{\frac{L_0-(Leq8-dBA)}{10}}$$

$$N_{PS} = 10^{\frac{L_0-(Leq8-dBA+PS)}{10}}$$

$$N_{DP} = 10^{\frac{L_0-(Leq8-dBA+DP)}{10}}$$

avec $L_0$ : 90 dB, valeur limite recommandée par le Comité Bruit d'Armes [8].

Les nombres de coups ainsi déterminés sont donc des minorants que l'utilisateur pourra adapter en fonction de sa propre déontologie; notamment dans le cas "sans protection" pour lequel on a nettement joué la sécurité en utilisant la valeur minimale de l'atténuation.

## 2.3. Limites du modèle

2.3.1. Modélisation d'un propulseur ou d'un lance-roquette

Avant de fixer des limites de validité du modèle proposé, il convient de rappeler dans quel cadre il a été développé :

il s'agissait de modéliser l'onde de souffle générée à l'allumage d'un petit propulseur de combat, dont le fonctionnement se caractérise par :

- un court temps de fonctionnement, de l'ordre de 10 ms,

- une mise en pression rapide de la chambre, environ 2 ms,

- une tuyère très fortement sous-détendue, et donc une pression assez importante dans le plan de sortie tuyère, $2.10^6$ Pa,

- une pression de rupture de l'opercule relativement importante pour assurer un allumage rapide du chargement, $8.10^6$ Pa,

toutes ces caractéristiques de fonctionnement étant propices à la formation d'une onde de souffle importante.

Au cours de l'étude paramétrique, le balayage des paramètres a été effectué autour des valeurs initiales et dans des domaines relativement limités :

| | | |
|---|---|---|
| 5 | < tf | < 20 ms |
| $50\ 10^8$ | < dPch/dt | < $400\ 10^8$ Pa/s |
| $3\ 10^5$ | < Pe | < $5\ 10^6$ Pa |
| 20 | < PROP | < $150\ 10^5$ Pa |
| 0,06 | < Eo | < 4,6 MJ |

pour l'onde de bouche , les domaines sont plus étroits

| | | |
|---|---|---|
| $2\ 10^5$ | < Pe max | < $15\ 10^5$ Pa |
| 0,03 | < E'o | < 0,25 MJ |

Il convient donc, pour s'assurer d'un degré de confiance suffisant, de ne pas trop sortir de ces domaines.

De même, la totalité de l'espace autour du propulseur n'ayant pas toujours été caractérisé, on se reportera à la figure 5 pour connaître les zones où un degré de confiance à pu être défini.

Remarque : le cas limite PROP=0, fonctionnement sans opercule, ne peut être appréhendé par un modèle d'explosion, la pente de montée en pression étant, surtout avec un allumage par le fond arrière, trop faible pour assurer la formation d'un choc unique.

2.3.2. Modélisation d'une explosion

Pour ce qui est des explosions, on se reportera à Baker; il semble qu'il n'existe théoriquement aucune limite à la validité du modèle. On évitera cependant de considérer le cas d'une explosion nucléaire où les phénomènes lumineux compliqueraient singulièrement le modèle prévisionnel.

## 2.4 Comparaison du modèle avec les résultats expérimentaux

2.4.1 Propulseur PM5

Le propulseur PM5 est un très petit propulseur mis au point pour les besoins de l'étude. Il contient 16 g de propergol et délivre une poussée de 3800 N pendant 12 ms.

Pression crête (figure 6)

La pression crête est très bien prédite en zone proche. En zone lointaine, ce propulseur ne conduit pas à la formation d'un choc unique , la modélisation surestime donc les grandeurs caractéristiques de l'onde de souffle dans cette zone.

Energie (figure 7)

Malgré des résultats expérimentaux insuffisamment nombreux pour assurer un degré de confiance acceptable (en particulier à 45° pour lequel on ne dispose que de 3 points expérimentaux), l'accord expérience-calcul est assez bon pour les Leq8.

2.4.1 Lance-roquette REF

Le lance-roquette REF est équipé d'un propulseur délivrant une poussée de 68 kN pendant 10 ms.

Pression crête (figure 8)

On observe un très bon accord des résultats pour l'onde arrière, en dehors de la zone balayée par le jet, laquelle est particulièrement étendue pour ce lance-roquette.

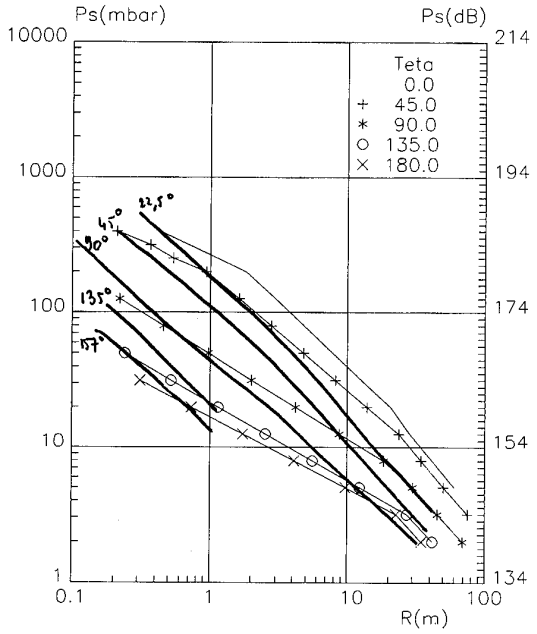



Figure 6 : Pression crête pour le propulseur PM5

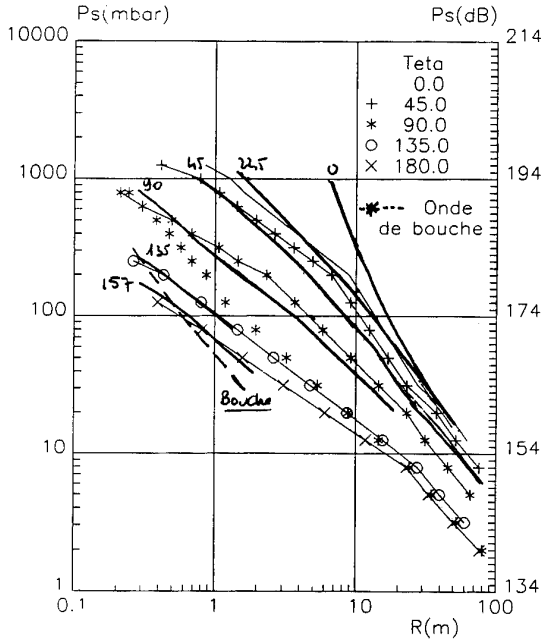



Figure 8 : Pression crête pour le lance-roquette REF

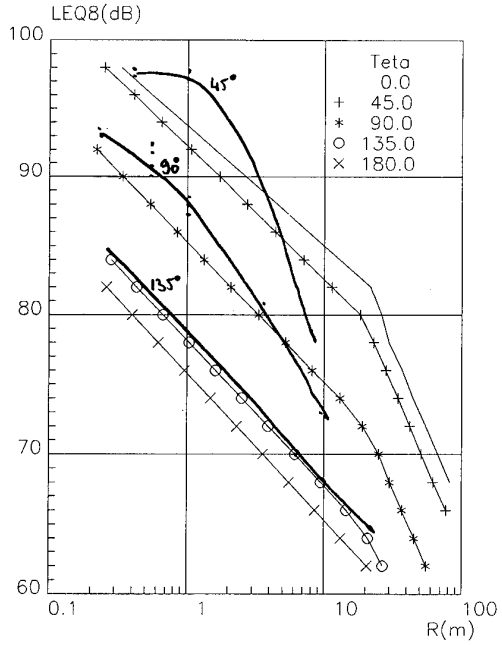



Figure 7 : Leq8 pour le propulseur PM5

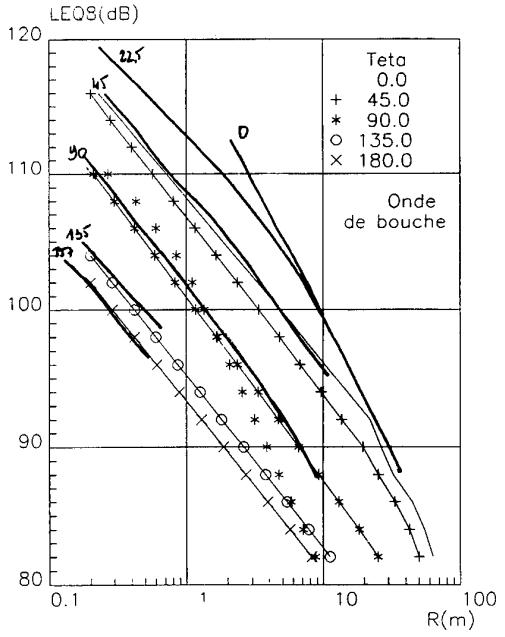



Figure 9 : Leq8 pour le lance-roquette REF

Par contre l'accord est médiocre pour l'onde avant, qui est fortement surestimée par le calcul en raison de la libération progressive des gaz à la bouche, et ceci, avant la sortie du projectile.

Energie (figure 9)

Très bon accord des résultats, sauf dans la zone balayée par le jet.

## 3. Etude de l'onde de souffle en abri clos

### 3.1. Introduction.

La formation de l'onde de souffle en abri clos est liée aux réflexions multiples de l'onde incidente sur les différents murs de l'abri.

L'étude expérimentale de cette onde, effectuée à l'aide de la construction progressive de l'abri, a permis d'élucider certains des phénomènes qui conduisent à la formation de l'onde: notamment,

la réflexion sur le mur AR dont l'importance est prépondérante dans la configuration de tir qui a été adoptée. On a pu également constater que globalement il se créait une certaine homogénéisation du niveau de bruit dans tout l'abri.

Cependant, compte-tenu de la complexité des phénomènes, l'établissement de corrélations précises entre ce niveau de bruit et les différents paramètres influents a nécessité une étude plus complète.

Une campagne d'essai a donc été réalisée, où l'on a cherché à préciser l'influence de la géométrie de l'abri, de l'implantation de l'arme, du revêtement des murs et de l'ameublement sur les caractéristiques de l'onde de souffle; le but final, après exploitation des résultats expérimentaux, étant de définir un outil semi-empirique prévisionnel basé sur la corrélation de ces caractéristiques et les temps de réverbération relatifs aux différentes configurations de l'abri.

### 3.2. Etude expérimentale.

L'objet de cette étude était de déterminer expérimentalement le champ acoustique autour d'un propulseur équipé de différentes charges de propergol solide à très court temps de combustion, tiré en différentes configurations d'abri clos, afin d'en déduire un outil de prévision des niveaux de bruit en fonction des paramètres étudiés [9].

Essais réalisés.

On a cherché à préciser les influences de :
- la géométrie de l'abri ( diminution de volume, rapprochement du mur AR ),
- l'implantation de l'arme, site et azimut,
- l'ameublement et le revêtement mural de l'abri.

5 géométries de l'abri ont été caractérisées :
- 5 x 4 m, abri dit "nominal",
- 5 x 3,5 m,
- 5 x 3 m,
- 4 x 3,5 m,
- 3 x 3 m.

6 implantations différentes de l'arme ont été caractérisées dans la configuration nominale de l'abri :
- site normal, azimut normal,
- site normal, azimut + 18 °,
- site normal, azimut + 30°,
- site normal, azimut - 40°,
- site - 45 °, azimut normal,
- site + 30 °, azimut normal.

2 types d'ameublement ont été installés dans l'abri nominal :
- table 150x73x75 au centre de l'abri,
- table au centre + armoire 121x57x209 remplie de chiffons près de la porte.

2 types de revêtement mural ont été testés :
- moquette collée sur béton,
- mousse alvéolaire collée sur béton,

( les autres essais ayant toujours été réalisés sur béton nu ).

La position des capteurs dans l'abri est indiquée sur la figure 10.

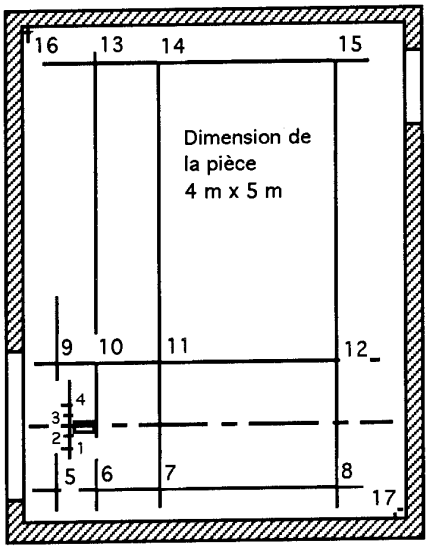



Figure 10 : Position des capteurs dans l'abri.

### 3.3. Analyse des résultats.

3.3.1. Homogénéisation du champ de surpression.

Quelle que soit la configuration de tir, on observe une bonne homogénéisation des surpressions crête et des énergies "acoustiques" (figure 11).

Il est difficile d'attribuer la dispersion autour des valeurs moyennes à la seule inhomogénéité du champ de surpression; de la même façon il est impossible d'estimer l'erreur liée aux mesures et à leur exploitation. On constate toutefois que l'homogénéisation est meilleure pour les niveaux équivalents filtrés dBA qui, eux, sont moins sensibles aux dérives lentes des capteurs (dérives thermiques ou vibrations des supports).

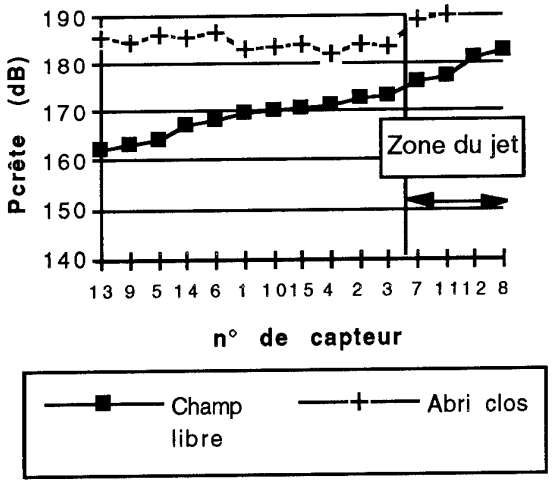



Figure 11 : Pression crête. Comparaison des mesures en champ libre et en espace clos.

3.3.2. Influence des différents paramètres de l'abri.

*3.3.2.1. Influence du volume.*

L'influence de la configuration géométrique de l'abri dans le cas d'un tir de lance-roquette peut avoir deux origines:

- la variation du volume réverbérant, qui agira directement sur le temps de réverbération et les niveaux d'énergie acoustique,

- la variation de la distance tuyère-mur AR, qui agira sur la surpression crête maximale laquelle, on l'a vu précédemment [4], correspond à la réflexion de l'onde sur le mur AR.

Or, les résultats obtenus montrent clairement que ni l'un ni l'autre de ces paramètres n'a d'influence notable sur les caractéristiques de l'onde de souffle; en niveaux moyens et en dispersion autour de ceux-ci, les résultats sont tout à fait comparables quelque soit le volume de l'abri.

En ce qui concerne les énergies acoustiques, l'influence très minime du volume de l'abri confirme que la façon dont est calculée l'énergie "acoustique" ne conduit pas au calcul exact de la seule énergie acoustique mais prend en compte l'énergie du choc qui est dissipée lors de la propagation de l'onde dans le milieu ambiant; cette énergie qui est prépondérante en zone proche n'est en rien influencée par les phénomènes de réverbération.

En ce qui concerne la surpression crête, l'influence de la distance tuyère-mur AR, mise en évidence précédemment [10], est , dans l'abri complet, contrecarrée par l'effet de "tunnel" qui renforce l'onde réfléchie par les réflexions sur les murs latéraux; cet effet étant d'autant plus important que la profondeur de l'abri (distance mur AR- mur AV) est grande.

En conclusion, l'influence du volume de l'abri telle qu'elle a été étudiée lors de ces essais est inférieure à la dispersion intrinsèque des mesures et semble tout à fait secondaire quant à la caractérisation physioacoustique des armes tirables en abri clos.

*3.3.2.2. Influence du revêtement mural.*

Pour l'étude de ce paramètre, deux types de matériaux ont été choisis:

- une moquette, afin d'être représentatif d'une pièce d'habitation "confortable",

- une mousse alvéolée, comme cas extrême permettant d'étendre le domaine exploré et d'être sûr d'une réelle absorption sonore.

Les résultats obtenus montrent que:

- La surpression crête est absolument insensible au type revêtement mural, l'efficacité d'absorption des différents matériaux utilisés devant être parfaitement négligeable pour des bruits type "onde de choc".

- Les mêmes remarques sont valables pour les niveaux d'énergie "acoustique": Leq8. Une légère influence, de 0,4 dB et de 1,5 dB respectivement pour la moquette et pour la mousse, est cependant décelable en valeurs moyennes; mais celle-ci est de l'ordre de grandeur de la dispersion des résultats autour de ces valeurs moyennes.

- Quant aux énergies "acoustiques" filtrées dBA, une influence notable peut être observée avec la moquette (2 dB) et surtout avec la mousse (5,5 dB).

Couplés au filtrage dBA, très efficace pour les basses fréquences, ces matériaux, notamment la mousse, apparaissent idéaux pour atténuer la réverbération en abri clos.

En résumé, on peut dire que l'atténuation du bruit, grâce à un revêtement mural adapté, restera très limitée, eu égard aux matériaux classiques de la construction urbaine actuelle.

*3.3.2.3. Influence de l'ameublement.*

Que l'ameublement soit de type écran (table) ou absorbant (armoire remplie de chiffons), l'atténuation du bruit est très locale, uniquement à l'abri des éléments constitutifs de l'ameublement.

Une très légère atténuation (1 dB), sensiblement uniforme pour l'ensemble de l'abri est observée, à la fois, pour les Leq8 et les LAeq8, lorsque l'ameublement est constitué d'une table et d'une armoire ( soient 4 m2 de surface très absorbante).

Cette influence est toutefois négligeable devant l'imprécision globale des mesures.

*3.3.2.4. Influence de la position de l'arme.*

Quelle que soit la position de l'arme, le champ acoustique en abri clos est fortement homogénéisé par rapport à ce qu'il est en champ libre. On peut donc utiliser les mêmes critères de comparaison basés sur les valeurs moyennes des capteurs situés en dehors de la zone balayée par le jet et l'on constate que ni l'azimut ni le site n'ont d'influence notable sur les différentes caractéristiques du bruit, seule une légère atténuation (1 à 2 dB) en fonction du site est observée à la fois sur les pressions crêtes, les Leq8 et les LAeq8.

**3.4. Conclusions.**

Au cours de l'étude expérimentale en abri clos, on a pu vérifier que, quelle que soit la configuration de l'abri ou la position de l'arme, le niveau de bruit, pression crête ou énergie "acoustique", s'homogénéisait dans tout l'abri en dehors de la zone balayée par le jet.

De cette étude il ressort également que les influences des différents paramètres: volume de l'abri, revêtement mural, position de l'arme, sont tout à fait secondaires et généralement inférieures à la dispersion des résultats expérimentaux.

La seule influence notable concerne le revêtement mural en mousse de polyuréthane alvéolée, avec une atténuation de 5,5 dB sur le niveau d'énergie "acoustique" filtrée dBA, mais ce matériau n'est absolument pas représentatif des revêtements muraux des constructions urbaines actuelles.

Actuellement, il n'est donc pas possible d'établir un outil prévisionnel pour les bruits de ces armes en abri clos, sinon l'abaque semi-empirique déjà proposée précédemment [4] et construite autour du paramètre essentiel qui est l'énergie totale libérée par le propulseur (figure 12).

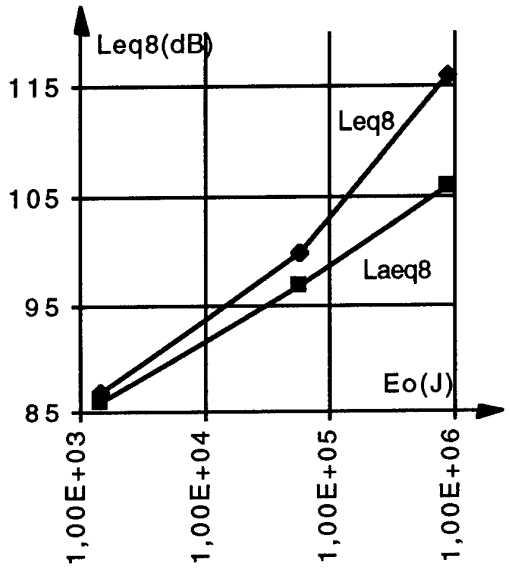



Figure 12 : Niveaux de bruit dans un abri clos : influence de l'énergie libérée.

## Conclusion générale

Une modélisation de l'onde de souffle produite par les propulseurs à court temps de fonctionnement en espace libre a été mise au point. Cette modélisation est suffisamment précise pour pouvoir être utilisée comme outils de comparaison de différents systèmes au stade de la conception ou de l'évaluation de systèmes d'armes.

Notre tentative de mise au point d'outils prévisionnels d'estimation du bruit en espace clos nous amène à dire que le volume de l'espace clos, la position de l'arme dans l'abri et la nature de l'ameublement n'ont que très peu d'influence sur le bruit en espace clos. Dans notre étude, seule la nature du revêtement (mousse alvéolée) a eu une influence sur les énergies filtrées "A" (atténuation de 5,5 dB).

Le paramètre déterminant l'énergie "acoustique" en espace clos est l'énergie libérée à la bouche de l'arme.

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# NOISE ASSOCIATED TO ROCKET ENGINE TESTING AND NOISE REDUCTION MEASURES TAKEN ON DASA'S TEST FACILITIES IN OTTOBRUNN

by

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## ABSTRACT

The presented paper explains the environmental implications of noise, resulting from rocket testing, by means of an evaluation performed within the scope of the development tests of cryogenic liquid propellant engine components foreseen for the Ariane V launcher. An analysis of the different noise sources is carried out and the measures taken to perform noise reduction are presented. Finally, an outlook over the noise reduction measures in preparation for the case of other engine components, presently in development at DASA, is also given.

## 1. INTRODUCTION

One of the most important environmental aspect of rocket engine testing is related to the level of noise during the hot runs to be carried out in the course of engine and/or engine components development.

On DASA's rocket engine test facility in Ottobrunn, the problematic nature of noise is enhanced by the presence of a settlement in the immediate vicinity of the testing area.

In order to protect the inhabitants of settling areas, situated in the vicinity of industrial zones, from intolerable immisions, german legislation has issued, over the years, prescriptions which define noise limits to be observed under precise conditions.

Some development tests performed on the facilities meet those rules at once, others display a noise level which, without precaution, would be situated beyond the legal limits. For the latter case, technical measures have to be taken, in view of reducing the noise level associated with the tests to an acceptable value.

## 2. MAIN CONCLUSIONS

The organized noise phenomenon observed in the frequency range around 2 khz (4.4) [a, for the human ear, quite disagreeable frequency, on the ground of the high sensitivity of the former, in the range 1250 - 5000 HZ - see A-weighting on Fig. 9], corresponding to the acoustic excitation (combined transversal - longitudinal mode) of the outlet section of the flare stack, downstream of the baffle unit, could be suppressed by dismounting the latter, which in the case of rocket engine testing is not as indispensable (because of $GN_2$-purging of the exhaust gas pipe, prior to ignition) as it is in the case of activities related to the petrochemical industry.

One of the most important conclusion of our analysis is that in the general case of stochastic (i. e. not organized) noise associated with rocket engine testing, we are confronted with several sources (4.4), which, for the most part, are also distributed on the test area and consequently complicate the problem of noise reduction. Moreover, it can be that two or more of those sources relatively lie near from each other, as far as the radiated sound level is concerned. Therefore, only their fine evaluation can help to determine the most intensive one, upon which all efforts have to be concentrated, in view of obtaining a noticeable noise reduction.

The analysis, carried out in the frame of the general investigation of this problem (4.4), showed that fluctuation of combustion pressure within the gas generator belongs to the most effective sources we have to counteract and leads to a fluctuation of pressure in the exhaust pipe (A-measurement point on Fig. 14, situated at proximity of the bottom section of the flare stack) of ca 178 dB (wrt 2 E-5Pa), corresponding to a sound level of some 85 dB (A) at B-measurement point, situated at a height of 5 m, 300 m away from the facility, near the settlement area.

Overall noise sound level reduction, achievable by means of an adapted sound absorber [(4.5), Fig. 15)], installed at floor level, near the bottom section of the flare stack, has theoretically been estimated to some $\Delta L_{max} \approx 10$ dB (A) and finally achieved an actual value of quasi 8 dB (A), which enabled to meet the prescription of 50 dB (A), defined in ref. 6.3, and therefore to solve the noise problem arisen in conjunction with the testing of the LOX-turbopump of the Ariane-V-launcher on the P59-3 facility.

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## 3. PROSPECT FOR THE FUTURE

Fig.19 shows a large sound absorber manufactured in view of damping the immissions resulting from the hot testing of the combustion chamber developed within the scope of the EQHHPP-Project*. As can clearly be seen on this figure, we have to deal here with a semi-mobile equipment, which can be adapted to the diverse test cells used in the frame of this program and related activities.

Notice that design is such as principally absorbing the "transversal" noise oscillation, moreover general oscillation level is lowered by means of an "ejector effect" of the exhausting jet (air aspiration between the baffles).

As far as new rocket engines or engine components are concerned, direction of DASA's propulsion department has decided to already include noise reduction activities to the planning phase of the corresponding projects, in order the official noise prescriptions are met as of the first hot run. Among others, within the scope of a new hydrogen/oxygen-gas generator activity, it is foreseen to lead the exhausting gas jet, via gas pipe, inside a water pool complex, in view of using the difference of acoustic impedance between water and surrounding air, to prevent a large noise immission on the facility.

## 4. TECHNICAL ASPECTS

### 4. 1 Specimen under Test

The specimen under test is the liquid oxygen turbo-pump of the future Ariane V-launcher (maiden-flight foreseen for 1995), whose main characteristics are the following (6.1):

- Mass : 185 kg
- Rotation speed : 13800 RPM
- Turbine power : 3.8 MW
- Pump inlet pressure : 3 bar
- Pump outlet pressure : 155 bar
- Flowrate : 231 kg/sec
- Turbine gas inlet pressure : 60 bar
- Turbine gas inlet temperature : 875 K

(Pump-developer is FIAT-AVIO, Italy, Turbine-developer is VOLVO, Sweden)

The turbine is powered by means of the combustion gas provided by the gas-generator (Fig. 2), whose main technical characteristics are the following (6.1):

- Mass : 40 kg
- Operating pressure : 93 bar
- Mixture ratio : 0.9
- Mass-flow : 9.2 kg/sec

(Gas generator- developer is SEP, France)
This component is fed by means of liquid oxygen (LOX) and liquid hydrogen ($LH_2$) provided by the test facility.
For special testing (such as, among others, investigation of the cavitation behaviour of the LOX-pump), the combustion gas of the gas generator is replaced by cold gas hydrogen ($GH_2$) in provenance of a HP-reservoir, which after throttling through the control valve directly powers the turbine.

### 4.2 Test facility and corresponding geographical location

The pertaining test-facility (6.2) has been erected at the beginning of the seventies (P59-1) to carry out the development tests of the combustion chamber of the 3rd stage (LOX, $LH_2$) of the Ariane I-launcher and is equipped with high-pressure (HP-) vacuum isolated run tanks (LOX, $LH_2$), HP-pressurization reservoirs ($GN_2$, GH2), low-pressure (LP-) storage tanks (LOX, $LH_2$) and all the control, safety and auxiliary functions which enable the hot run operation of a cryogenic combustion chamber under sea-level or altitude simulation conditions.

The facility has been modified in the mid-eighties (new feed-system, new control organs) in order of allowing hot run development tests of the Ariane V's gas generator (P59-2), respectively further extended (new vacuum isolated feed-system, new test cell, LP-run tank, LP-catch tank, new control organs, etc...) at the end of the eighties (Fig. 3), to permit development tests of the LOX-turbopump of the Ariane V-launcher (P59-3).

The configuration resulting from the association between specimen (LOX-TP) and facility (P59-3) is summarized on Fig. 4. The mass-flow of combustion gas stemming from the gas generator is subdivided into two parts, one foreseen for the LOX-TP the other for the $LH_2$-TP [The Vulcain engine (6.1) has only one gas generator for two turbopumps], which, on the P59-3 facility, is simulated by means of a Venturi nozzle.
The mass flow through the LOX-TP's turbine amounts to a value of 3.0 - 4.0 kg/sec. After throttling by means of another Venturi nozzle placed at the outlet of the turbine, the gas flow is routed to a gas exhaust pipe, where it meets with that part of the gas generator flow (3.8 - 5.2 kg/sec) which has not been used by the turbine drive.
The resulting gas mass-flow (6.8 - 9.2 kg/sec) sensibly at a temperature of 500 K and under a static pressure of 1 bar is routed to the flare stack (Fig. 5), where it is burnt (visible flame, Fig. 6) at a height of some 23 meters above the ground floor.

As already mentioned (4.1), in special cases, turbine of LOX-TP can also directly be powered by means of cold $GH_2$-flow (mass-flowrate around 5.0 kg/sec).

The test facility is located some 300 meters away, northward from a purely settling area. Although facility and settlement are separated by a large screen of trees, the settlers are submitted to serious noise immissions during the performance of hot test runs. Particularly the noise stemming from the stack (not only necessarily the flame noise!) is at stake, although, due to the design of the latter, the main part of the immission at that level takes place in the vertical and not in the horizontal direction, but at the considered height, the damping effect of the wood is quasi reduced to nothing.

### 4.3 Sensitivity of Ear an legal Prescriptions

Fig. 7 shows an overview of the human hearing surface, as a function of frequency. This area is limited at the bottom by the "stimulus threshold" and at the top by the "threshold of pain". Only the operational points (P, f), whereby P' is the amplitude of the corresponding sine-wave, lying at the interior of this surface, can be perceived by the normal human ear.
Fig. 8 respresents the curves of "ISO-sound loudness level" (German: Kurven "gleicher Lautstärke"), expressed in "phons", v. s. frequency, for a sine-wave pressure oscillation, as perceived by human ear. To the contrary of the physical parameters such as sound pressure level, sound power density, etc.., the sound loudness level is not a physical but a physiological parameter, which is measured in "phons", defined as

$$20 \log_{10} \frac{P}{P_o}$$

whereby $P_o$ = 2 E-5 Pa, at frequency of 1000 HZ (at this frequency, sound level, expressed in "dB", and sound loudness, expressed in "phons", are identical). Thanks to the present diagram, the sound level or the sound power density necessary, in order to produce a certain sound loudness, at a given frequency, can simply be determined, without computation.

In most of the cases involving industrial noise brought in connection with human ear, however, the sounds to be generally considered, display a continous frequency spectrum and relatively rarely involve a single frequency alone, therefore Fig. 8 cannot easily be used.

In order to cope with this difficulty, instead of determining the monochrome sound level, a "weighted" sound level is measured, using for this measuring devices consisting at least of the three following elements: first, of an adapted microphone, second, of a signal amplifier (whereby amplifier gain is a function of frequency, in a way trying to represent, as nearly as possible, sensitivity of human ear, with respect to that variable, but which today is more understood as a convention, allowing to perform reproducible measurements under similar conditions), third, of a rectifier unit, associated with a certain time constant [Ref. (6.5)]. Quite clearly, the variable gain v. s. frequency function as well as the rectifying and filtering ones can today easily be realized by means of the computer. In that case, the hardware apparatus is reduced to a microphone and recording device.

In view of realizing the variable amplifier gain v. s. frequency (approximation of ear sensitivity), so called "A"-respectively "B" - and "C"-weighting procedures have been implemented by means of a passive RC-network comprising a certain number of poles along the real frequency axis.

In the conventional case of industrial noise evaluation, the "A"-weighting procedure [dB(A)] is generally employed. If we look at the corrections taken into acount by this procedure, we remark that the most crucial part of a noise frequency spectrum (assuming a constant power density) is situated in the range 1000 - 5000 HZ (Fig. 9), with maximum sensitivity between 2000 and 3150 HZ. Therefore, this is the frequency range upon which we, among others, must concentrate our attention during the definition and implementation of noise counter measures.
In order to understand the prescriptions issued by legislation, we must now remind a certain number of definitions:

-"A"- weighted sound level

$$L_A = 20 \log_{10} \frac{P}{P_o} \text{ dB(A)} \quad \text{[Ref. (6.5)]}$$

(reference pressure $P_o$ = 2. E-5 Pa, independent of frequency)

-"F"-weighting time procedure (F = Fast): means that time constant in rectifier unit is low and therefore that measurement of (some) peaks is possible ($L_{AF}$), [Ref. (6.4)]

- "L"$_m$: Mean value of measurement during time duration T

$$L_m = 10 \log_{10} \left( \frac{1}{T} \int_o^T 10^{0.1\, L(t)}\, dt \right) \text{ dB(A)} \quad \text{[Ref. (6.4)]}$$

- Correction factor for mean value during the day

$$K_T = 10 \log_{10} \frac{T}{3600.16}$$

[Test duration T = 20 sec yield $K_T$ = - 34,6 dB(A)]

- "Effective"-sound level during the day

$$L_{"eff"} = L_{AFm} + K_T$$

- Rating level of immission [Ref. (6.3)] respectively [Ref. (6.4)]:

$$L_r = L_{AFm} + K_T - 3\text{dB(A)} + \Delta L$$

Substraction of 3dB(A), which was initially foreseen to compensate for inaccuracies of measuring devices, has to be understood today as a pure convention [Ref. (6.3)].

$\Delta$L-handicap takes into account structure of the noise to be investigated (presence of harmonic sound components, presence of peaks and their periodicity, etc...). In our case, the value $\Delta L$ = 1dB(A) has been assessed as satisfactorily.

According to legislation [Ref. (6.3)], maximum tolerable level of immissions, for the case of a pure settlement, shall be 50dB(A) during the day and 35dB(A) during the night, whereby the latter has a duration of 8 hours ($10^{00}$p.m - $6^{00}$a.m), i. e.

$$L_r \leq 50 \text{ dB(A) during the day}$$

$$L_r \leq 35 \text{ dB(A) during the night.}$$

Additionally to this, on bavarian territory, immission peak value of a single event, as short as it may be, during the day ($(6^{00}$a.m - $10^{00}$p.m) shall not surpass general value defined for day-time by more than 30dB(A) [Ref. (6.4)] i.e:

$$L_{AF} \leq 50 \text{ dB(A)} + 30 \text{ dB(A)} = 80 \text{ dB(A)}$$

### 4.4 Level of Noise associated to the Tests, Analysis of the related Noise Sources

One of the main sources of noise, identified during the performance of a LOX-TP's test on the P59-3 test facility, presented an unpleasant screeching character, very similar to the phenomenon of the high frequency instability, encountered in the combustion chamber or rocket engines [Ref. (6.9)].

Carrying out of a LOX-TP's test using cold gas ($GH_2$-) drive, enabled to identify this phenomenon as the acoustic excitation of the stack outlet section, by means of the interaction of the cold gas flow, and its associated turbulences, with the baffle unit, installed shortly upstream of stack outlet cross-section.

Considering Fig. 11, we notice the presence of a discrete frequency line around 1890 HZ (time 7.6 sec), whose amplitude, first increases, then decreases and soon disappears, while another discrete frequency line in the range 1475 HZ is generated, whose amplitude, at first relatively low (corresponding to the fading away of the 1890 HZ-line), continuously increases and, as of a time value of around 11 seconds, is stabilized.

If we closely look at Fig. 11, we remark a certain drift v. s. time of both discrete frequency lines (both frequency values are slightly getting lower).

We were able to correlate downward frequency drift with the temperature decrease of the cold hydrogen gas in the HP-$GH_2$ reservoir, due to the isentropic depressurization of the latter during test.

If we try to modellize the stack outlet section by means of a relatively simple $2^{nd}$ order system, we notice, first, that damped frequency decreases when damping coefficient increases, second, that damping coefficient augments, when temperature is lowered, due to the influence on the sound velocity, which also diminishes with temperature.

Those remarks are sufficient to explain the observed phenomenon, on condiction gain G(s) of the equivalent control loop (Fig. 12), for the discrete frequency oscillation, is not constant v. s. frequency (if gain were constant, we would then observe several acoustic modes at a time and the low frequency ones would be preponderant).

L. Crocco, [Ref. (6.8)], has put in evidence the existence of a characteristic time during combustion instability. For a given acoustic mode of a combustion chamber (or similar resonator unit), with the frequency f = 1/T, the order of magnitude of this characteristic time lies around $\theta \sim T/2$.

We were able to identify a characteristic time for the stack outlet section, with an order of magnitude of
$\theta = (250 \pm 50)$ E - 6 second, defined by the ratio (d/u), with d being the distance between the baffle blades and u the velocity of exhaust gas in the corresponding section of the stack.

With this explanation, a preferential gain for the equivalent control loop can be defined, according to Crocco, as $G(s) = n [1- \exp(-\theta s)]$, where n is the so called pressure interaction index and s the complex frequency.

By so doing, we can represent the variation of n (or better of a n-compound) v. s. value of characteristic time, and, we obtain the diagram shown on Fig. 13, which is sufficient to explain the registered phenomenon.

Note that, on the ground of the boundary condition at the stack outlet cross section (P' = o), we are confronted with the genesis of standing waves, consisting of combined (transveral - longitudinal) modes (Fig. 20). The dismantling of the baffle unit leading to the supression of those standing waves (4.5) has demonstrated the exactness of the present analysis.

In order to be able to reduce the sound level corresponding to the continuous part of the noise spectrum (Fig. 18) in the range between some hundred and eight thousand Hertz, it has been necessary to proceed to a fine analysis of the different noise sources, with the assistance of Müller-BBM GmbH, which disposes of special computer programs as well as of the background know-how [Ref. (6.7)] as far as characterization of industrial noise and the measures to be taken, in view of reducing the corresponding sound level of the related immissions, are concerned.

Fig. 10 represents a summary of the noise level and its distribution on the facility, as resulting from the analysis carried out, and also shows the corresponding associated immissions near of the settlement area.

Condensing the obtained results of the investigation, we can enounce the following conclusions:

Main sources of noise on the facility are:

- The "internal" noise within the piping system, principally composed of the intrinsic gas generator noise and the noise of the pressure reducing organs, such as Venturi orifices [together around 145 - 148 dB(A)]

- The combustion noise at flare head [131 - 132 dB(A)]

- The flow noise of exhaust gas in piping and flare stack radiated by the outlet flare head [126 - 131 dB(A)]

- The external noise of components and pipe radiated by the corresponding casing [129 - 132 dB(A)].

Those results translated into matter of emissions near of the settlement area, produce the following sound level

- Internal source of noise: up to 89 dB(A)
- Remaining sources of noise: up to 82,5 dB(A)

Noise reduction measures must consequently consider in priority the abatement of the internal noise level.
This goal can be achieved by means of an ad'hoc sound absorber, as shown in subparagraph 4.5.

### 4.5 Improvement achieved by Noise Reduction Measures

First noise reduction measure consisted in dismantling the baffle situated in the outlet section of the stack respectively in progressively increasing the cross-section there, by means of the insertion of a 6-degree divergent.

The improvement brought by this measure in the near field (protection wall) can be seen on Fig. 18. The organized noise component in the form of a discrete frequency around 2 KHZ (corresponding to the excitation of the outlet section of the stack, downstream of the baffles) has disappeared and a mean sound level reduction $\Delta L_{AFm} = 3.5$ dB(A) has been achieved.

Unfortunately, due to several causes (among others, the increase of damping coefficient with frequency), the reduction registered in the near field led to no sensible improvement of the situation in the settlement area (B-point measurement on Fig. 14).

Nevertheless, we had then the demonstration that the noise part due to flow fluctuation in the gas exhaust pipe (proportional to the $n^{th}$ power of mean flow velocity, with n = 6 - 8), was not the main noise source on the facility, since in the opposite case, due to the insertion of the divergent into the outlet section of the stack, an improvement by an order of magnitude of 6 - 7 dB(A) could have been expected.

Second noise reduction measure consisted, after the identification of the combustion pressure fluctuation within the gas generator as one (together with the throttling of pressure in the gas exhaust pipe, by means of the Venturi orifice) of the main noise sources, in inserting the ad'hoc sound absorber (Fig. 15) in the pertaining section of the hot gas exhaust pipe (Fig. 14) at the ground floor level, shortly before the beginning of stack, respectively the location of A-measurement point [Ref. (6.10)].

Since, as can be seen on Fig. 18, the main part of the mean "A"-weighted sound level spectrum, as measured near of the settlement area, lies in the range 1 - 8 KHZ, the sound absorber was conceived to reduce the pressure fluctuation in this range in such a way, that the corresponding overall mean sound level reduction could reach a maximum theoretical value $\Delta L_{AFm} \approx 10$dB(A).
The absorber (Fig. 15) consists of a central (same diameter as gas exhaust pipe) perforated sheetmetal pipe surrounded by 12 resonator chambers tuned for the above mentioned frequency range. The hot gas flowing to and fro between central pipe and resonator chambers loses its fluctuation energy within the bores of the perforated metallic sheet (upper frequency part of spectrum), respectively inside a metallic wool compound (remaining part of spectrum), embedded within the resonator at ca mid-radius distance of the device's axis, by converting it into heat.

Fig. 16 shows the improvement introduced by the sound absorber by comparing the spectra of the pressure fluctuation measured at point A, by means of a dynamic quartz transducer, with and without sound absorber. Maximum pressure fluctuation (around 2 KHZ) coincides with a transversal eigen-mode of the exhaust pipe, somewhere at the outlet level of the gas generator. As for that part of the spectrum above 4 KHZ, it corresponds to the turbulent flow fluctuations in the exhaust gas pipe. In the range 0.8 - 4.0 KHZ, pressure fluctuation in the pipe, measured at point A, has been reduced by a factor of 2 - 5 representing 6 - 14 dB. (It has to be remarked here, that those values neither take into account combustion noise of the flare stack nor turbulence noise generated by the gas flow in the stack itself).

The improvement occasioned by the insertion of the sound absorber, as determined at measurement point B, near of the settlement area, and displayed on Fig. 17 shows that, as far as spectrum of mean sound level is concerned, effectiveness is even better than the one registered by means of pressure measurement at point A.

Downward of 500 HZ, we notice no change between the two (with and without absorber) configurations. This is understandable, since this part of spectrum mainly corresponds to the combustion noise of the flare stack.

The reduction of mean sound level in the range 0.5 - 5.0 KHZ increases from 2 - 21.5dB(A) and has still a value of 10dB(A) at 8 KHZ.
Global mean noise reduction level amounts to more than 7dB(A) and the very disagreeable part of the spectrum, due to human ear sensitiveness in the corresponding frequency range (1 - 5 KHZ), has drastically been reduced.

## 5. ACKNOWLEDGEMENTS

The authors wish to thank the direction of DASA's propulsion technology department for permission to publish this paper as well as the technicians (H. Faulhaber) who have carried out the acoustic measurements and a large part of the previously conducted investigation.

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* EQHHPP = "Euro-Quebec Hydro-Hydrogen Pilot Project"

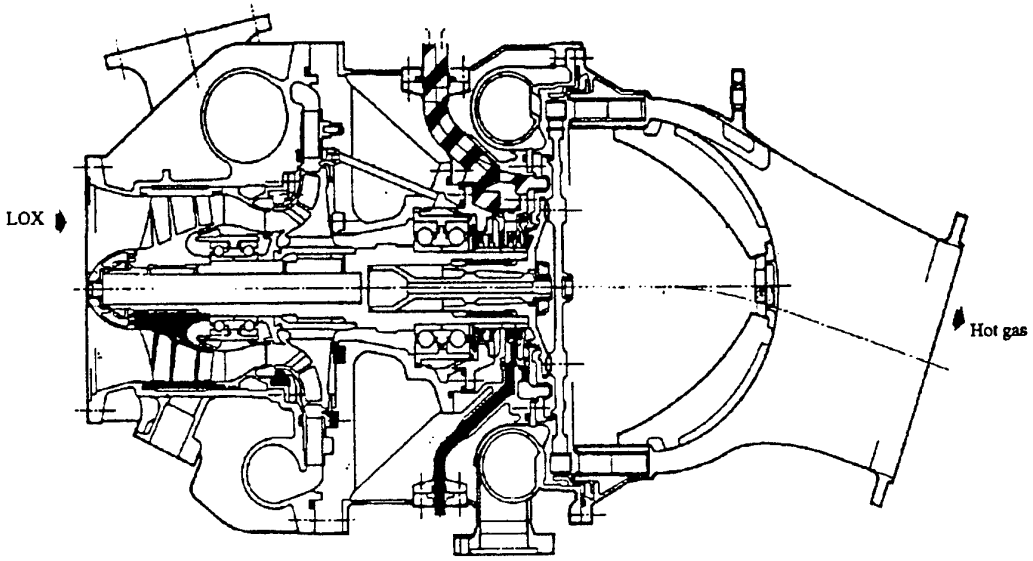



Fig. 1: LOX-turbopump of the Ariane V-launcher (Ref. 6.1)

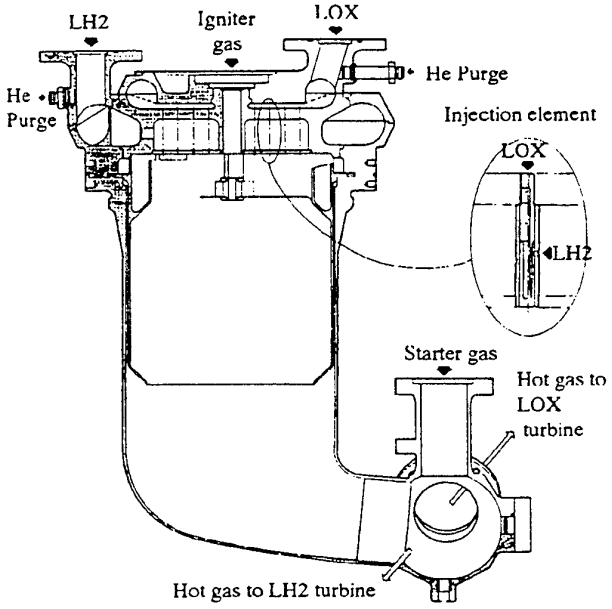



Fig. 2: Gas generator of the Ariane V-launcher (Ref. 6.1)

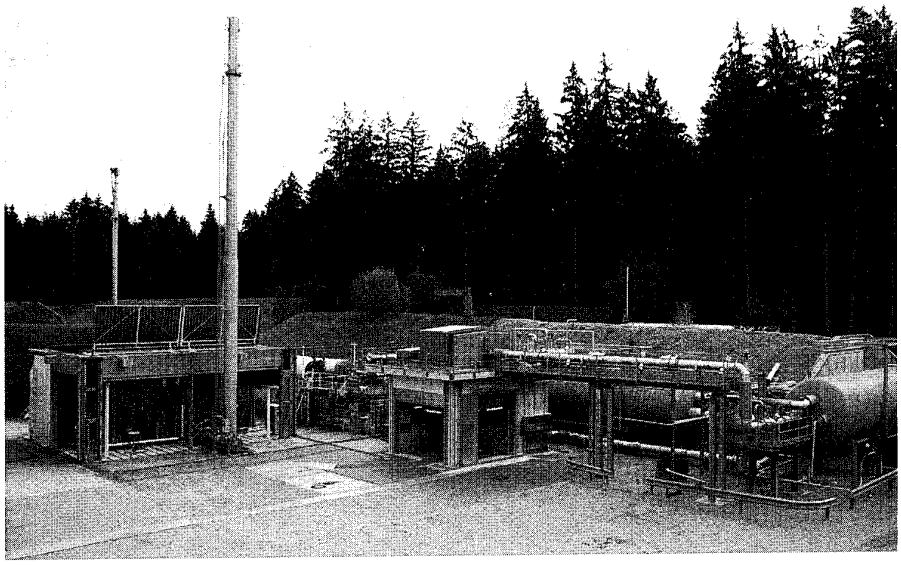


Fig. 3: General view of P59-3 Test facility

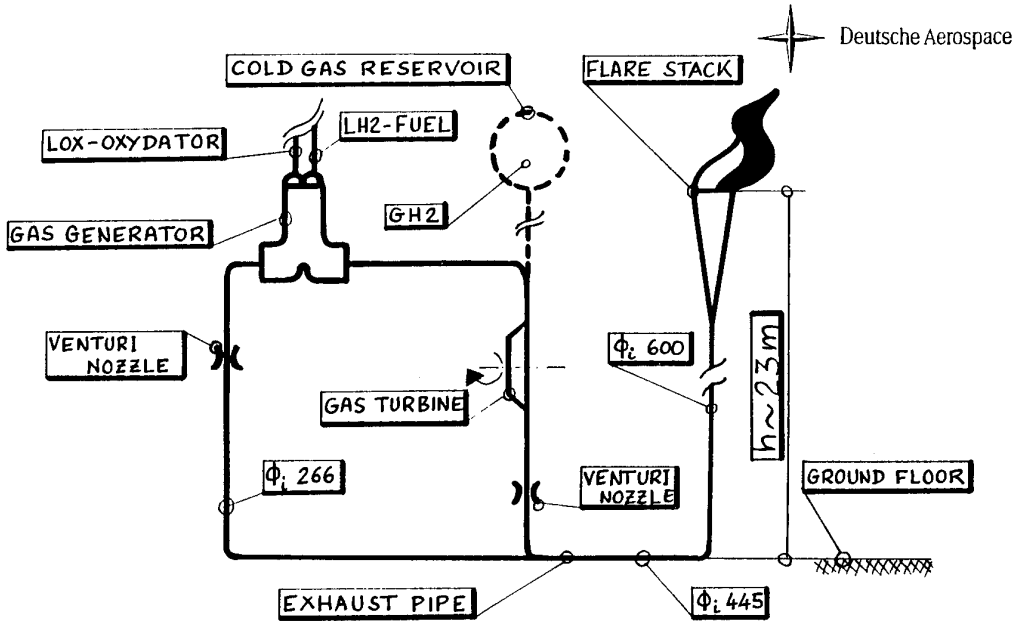



Fig. 4: Simplified configuration of P59-3 Test facility

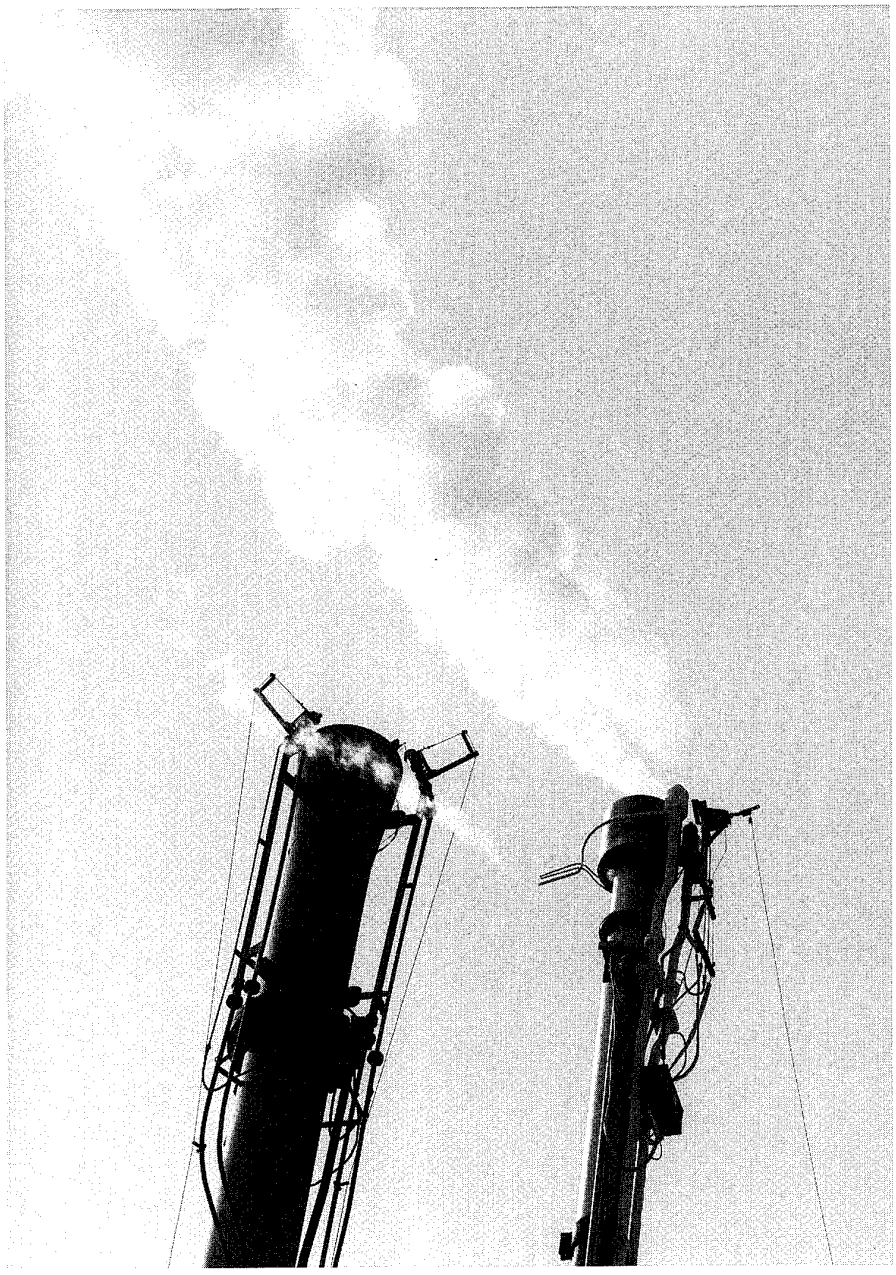


**Fig. 5, Fig. 6: Detailed view of the flare stack at rest**

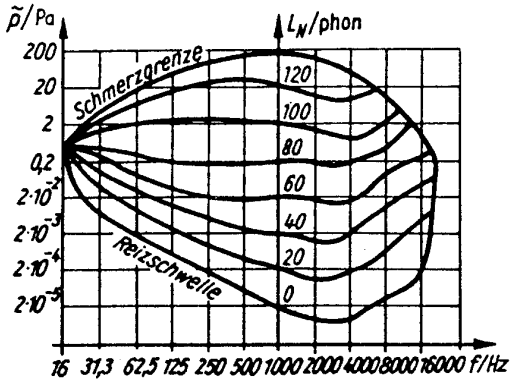



Fig. 7: Hearing surface with stimulus threshold and threshold of pain v. s. frequency [Ref. 6.6)]

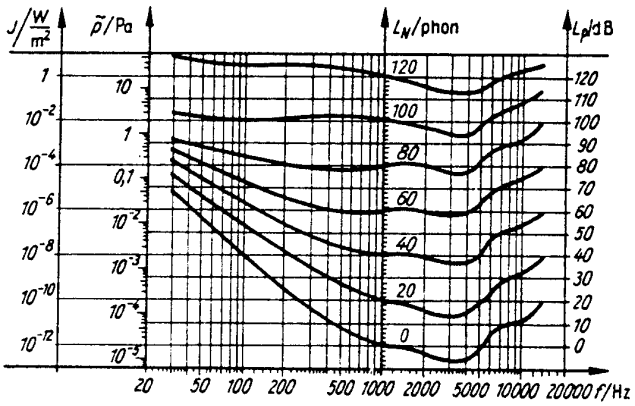



Fig. 8: Curves of ISO-loudness level as a function of frequency for the human ear [Ref. (6.6)]

| Nenn-frequenz *) in Hz | Exakte Frequenz *) in Hz | A-Bewer-tung | B-Bewer-tung | C-Bewer-tung |
|---|---|---|---|---|
| 10 | 10,00 | −70,4 | −38,2 | −14,3 |
| 12,5 | 12,59 | −63,4 | −33,2 | −11,2 |
| 16 | 15,85 | −56,7 | −28,5 | − 8,5 |
| 20 | 19,95 | −50,5 | −24,2 | − 6,2 |
| 25 | 25,12 | −44,7 | −20,4 | − 4,4 |
| 31,5 | 31,62 | −39,4 | −17,1 | − 3,0 |
| 40 | 39,81 | −34,6 | −14,2 | − 2,0 |
| 50 | 50,12 | −30,2 | −11,6 | − 1,3 |
| 63 | 63,10 | −26,2 | − 9,3 | − 0,8 |
| 80 | 79,43 | −22,5 | − 7,4 | − 0,5 |
| 100 | 100,0 | −19,1 | − 5,6 | − 0,3 |
| 125 | 125,9 | −16,1 | − 4,2 | − 0,2 |
| 160 | 158,5 | −13,4 | − 3,0 | − 0,1 |
| 200 | 199,5 | −10,9 | − 2,0 | − 0,0 |
| 250 | 251,2 | − 8,6 | − 1,3 | − 0,0 |
| 315 | 316,2 | − 6,6 | − 0,8 | − 0,0 |
| 400 | 398,1 | − 4,8 | − 0,5 | − 0,0 |
| 500 | 501,2 | − 3,2 | − 0,3 | − 0,0 |
| 630 | 631,0 | − 1,9 | − 0,1 | − 0,0 |
| 800 | 794,3 | − 0,8 | − 0,0 | − 0,0 |
| 1 000 | 1 000 | 0 | 0 | 0 |
| 1 250 | 1 259 | + 0,6 | − 0,0 | − 0,0 |
| 1 600 | 1 585 | + 1,0 | − 0,0 | − 0,1 |
| 2 000 | 1 995 | + 1,2 | − 0,1 | − 0,2 |
| 2 500 | 2 512 | + 1,3 | − 0,2 | − 0,3 |
| 3 150 | 3 162 | + 1,2 | − 0,4 | − 0,5 |
| 4 000 | 3 981 | + 1,0 | − 0,7 | − 0,8 |
| 5 000 | 5 012 | + 0,5 | − 1,2 | − 1,3 |
| 6 300 | 6 310 | − 0,1 | − 1,9 | − 2,0 |
| 8 000 | 7 943 | − 1,1 | − 2,9 | − 3,0 |
| 10 000 | 10 000 | − 2,5 | − 4,3 | − 4,4 |
| 12 500 | 12 590 | − 4,3 | − 6,1 | − 6,2 |
| 16 000 | 15 850 | − 6,6 | − 8,4 | − 8,5 |
| 20 000 | 19 950 | − 9,3 | −11,1 | −11,2 |

Fig. 9: Decibels' A-Weighting [dB(A)] table v. s. frequency, according to Ref. (6.5)

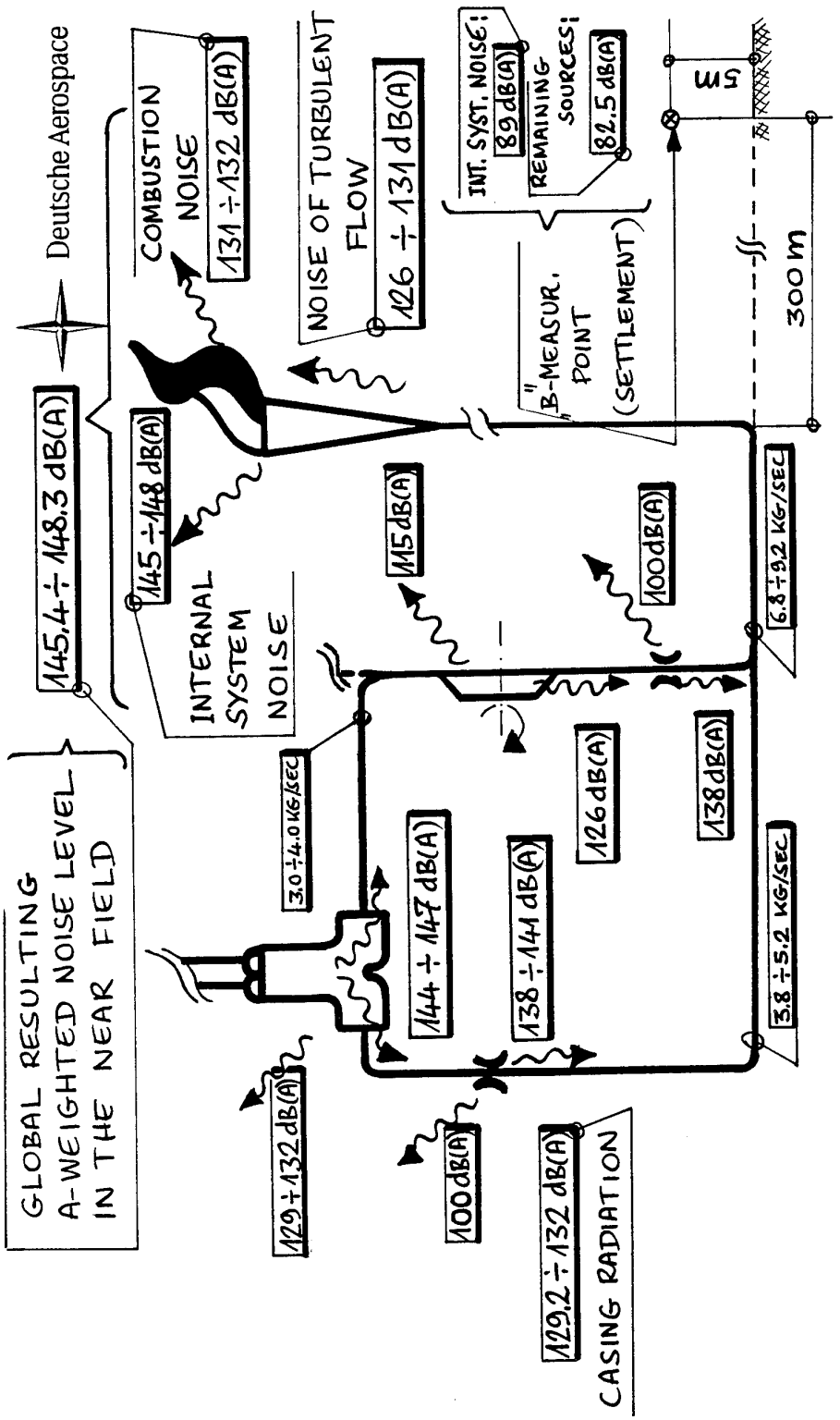



**Fig. 10:** Level (and distribution) of noise on facility P59-3, associated to the LOX-TP's tests, and corresponding noise level near of settlement

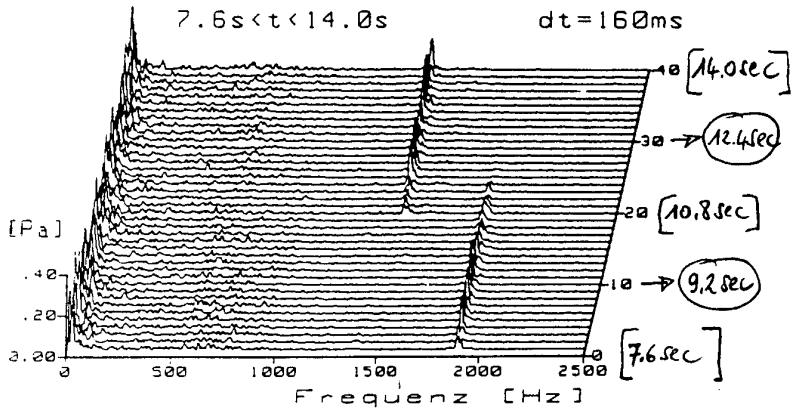



**Fig. 11:** Frequency analysis for cold (GH2) - gas drive (outlet section of stack in the baffles-configuration)

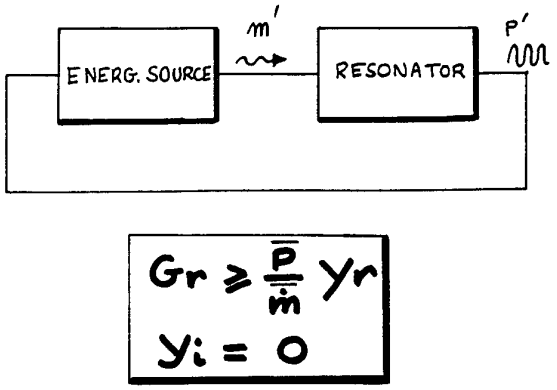



**Fig. 12:** Equivalent control loop for discrete frequency oscillation in outlet section of stack, downstream of baffle-unit

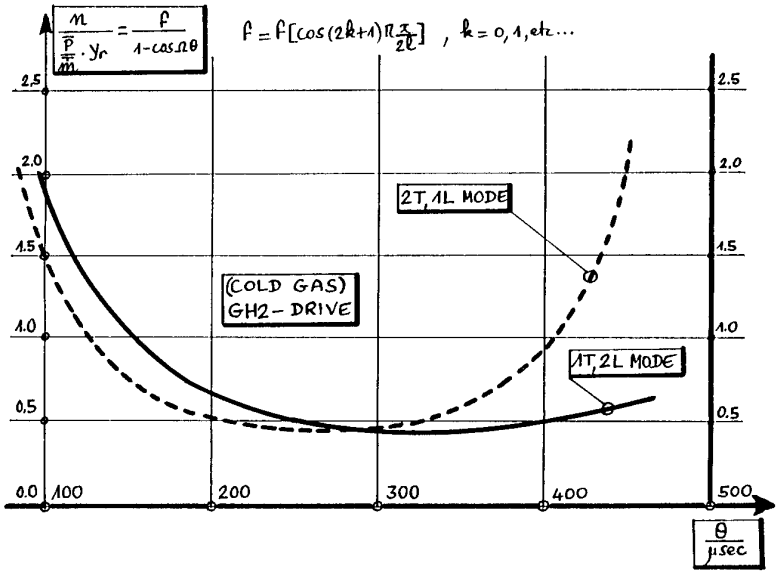



**Fig. 13:** Variation of pressure interaction index n v. s. characteristic time $\theta$

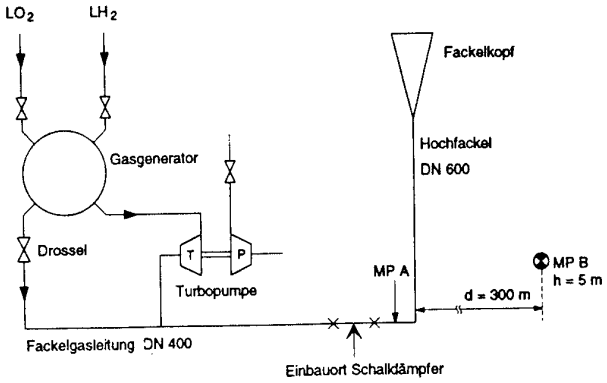



Fig. 14: Location of sound absorber on facility as well as A-respectively B-measurement point

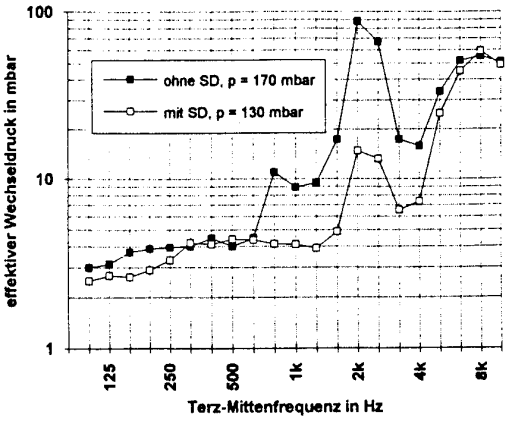



Fig. 16: Effective pressure fluctuation (point A of gas exhaust pipe) with and without sound absorber, as a function of frequency

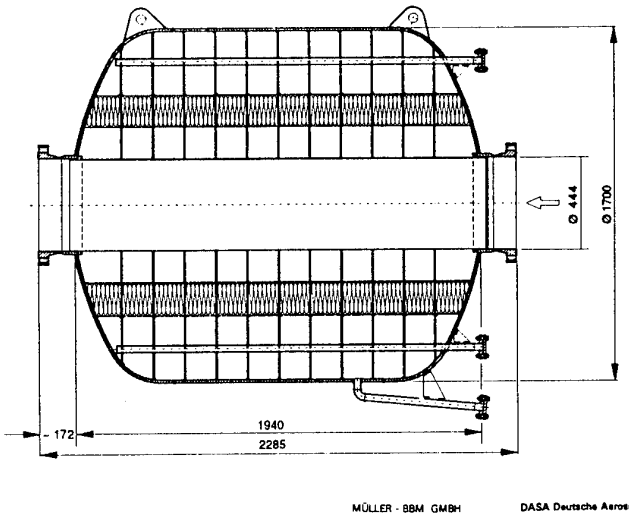



Fig. 15: Cut through - and size of sound absorber

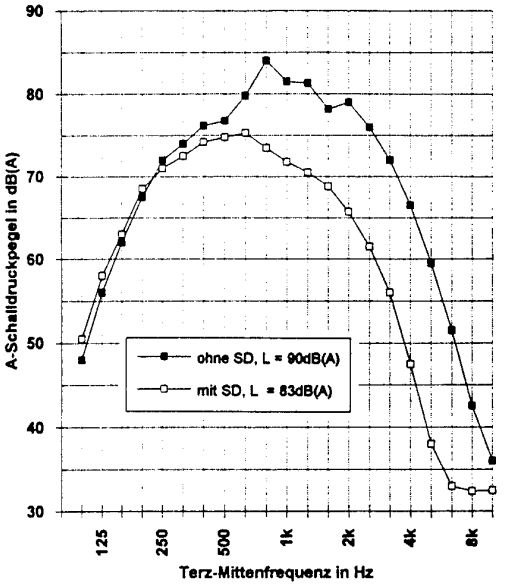



Fig. 17: Mean "A"-weighted sound level $L_{AFm}$ v. s. frequency, as measured at point B (settlement) with and without sound absorber (gas generator flow-rate: m ~ 8.5 kg/sec, test duration ~ 20 sec)

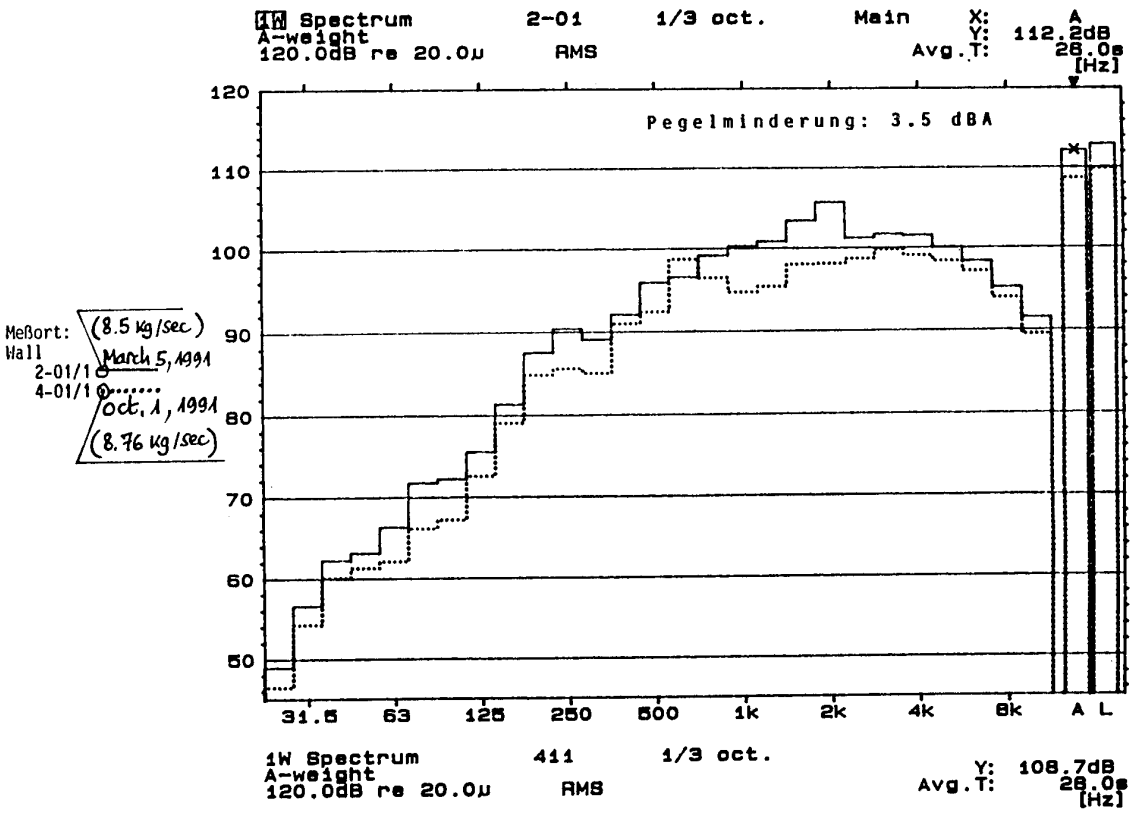



**Fig. 18:** Mean "A"-weighted sound level $L_{AFm}$, near of facility, prior (March 5, 1991) and posterior (October 1, 1991) to baffles' dismantlement and increase of exhaust pipe's outlet cross-section

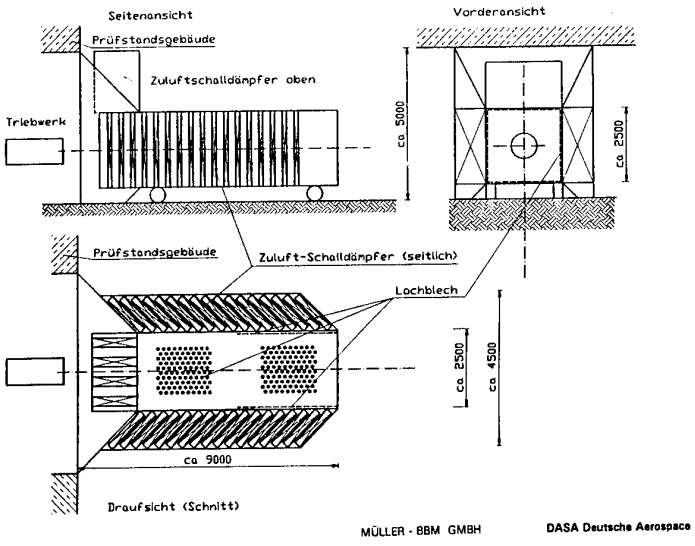



**Fig. 19: Semi-Mobile sound absorber equipment for EQHHPP-test facility**

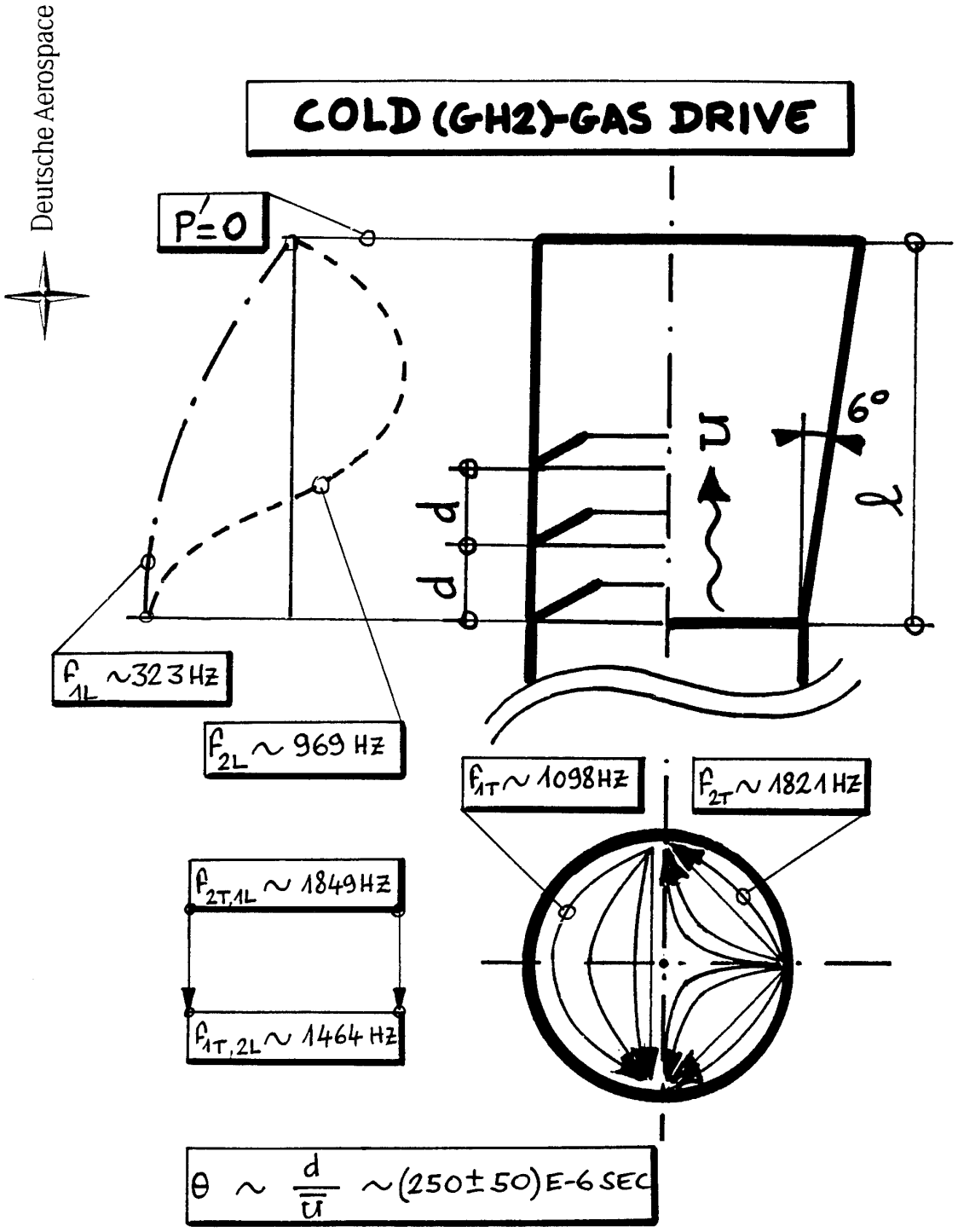



Fig. 20: Schematic representation of stack outlet section (in the baffles-configuration) with standing acoustic wave.

# *BANC DE TIR POUR MOTEUR FUSEE A PROPERGOL SOLIDE A IMPACT SONORE REDUIT SUR L'ENVIRONNEMENT*

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## RESUME

Cette conférence présente une réalisation de l'établissement SNPE de SAINT MEDARD pour le tir sans nuisance sonore pour l'environnement de moteurs à propergol solide à grand débit constituant des émetteurs sonores d'une très grande puissance.

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## 1 - GENERALITES

Le développement et la production de moteurs à propergol solide qui constituent l'activité principale de l'établissement nécessite de procéder à de nombreux tirs au banc : plusieurs milliers par an.

Ces tirs émettent systématiquement des gaz de combustion, du rayonnement et du bruit et occasionnellement des projections et du souffle.

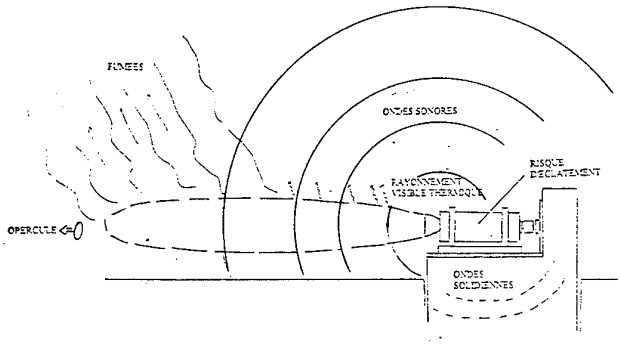



**Figure 1 : Emissions d'un tir dans l'environnement**

Lorsque ces tirs sont effectués sur les bancs d'essais usuels à l'air libre, ces émissions vont dans l'environnement et peuvent devenir des nuisances.

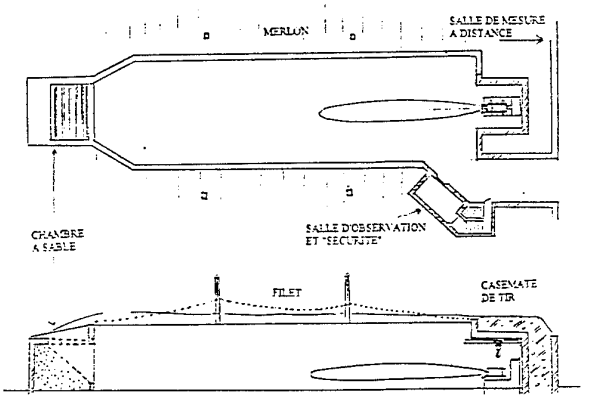



**Figure 2 : Banc d'essais à l'air libre**

Ces nuisances sont plus ou moins tolérables selon leur nature et leur intensité qui sont fonction à la fois des caractéristiques des moteurs testés et de l'environnement lui-même.

Les émissions de gaz ne posent pas de problèmes majeurs soit qu'elles ne soient pas perceptibles et peu nuisibles : cas des propergols double base, soit qu'elles soient visibles : cas des propergols composites mais suffisamment diluées aux limites de l'établissement pour ne pas créer de dommage. Leur faible durée et leur relativement faible volume limitent également l'impact perçu.

Pour les projections systématiques : opercule, ou accidentelles : éclatement de moteur, des protections lourdes ont été aménagées pour en arrêter la majorité : ouvrage en béton armé, mur caisson, butte de

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

sable. Un filet en métal à haute résistance mécanique et chimique complète la protection. Ces dispositifs donnent satisfaction.

Il n'en est pas de même pour le bruit. Les niveaux d'émission peuvent être très importants et la conception de ces bancs n'a aucun effet d'atténuation ; au contraire, la plupart des surfaces rencontrées dans les stands étant parfaitement réverbérantes, le niveau sonore peut s'en trouver renforcé dans certaines directions.

Compte tenu du spectre des fréquences émises, ces bruits se propagent à très grande distance.

Deux évolutions ont modifié les conditions d'acceptation de la situation par la population voisine de l'établissement :

- la première est une augmentation notable du nombre de tirs très bruyants et des niveaux sonores émis. Elle est liée à l'évolution des programmes et notamment à la production en masse d'un moteur de roquette de 100 kg de propergol composite.

- la seconde est une évolution de l'environnement : le nombre d'habitants dans la zone située à moins de 2 km des stands est de plusieurs milliers, certains tolérant de moins en moins les tirs les plus bruyants et surtout n'acceptant pas d'augmentation de cette nuisance.

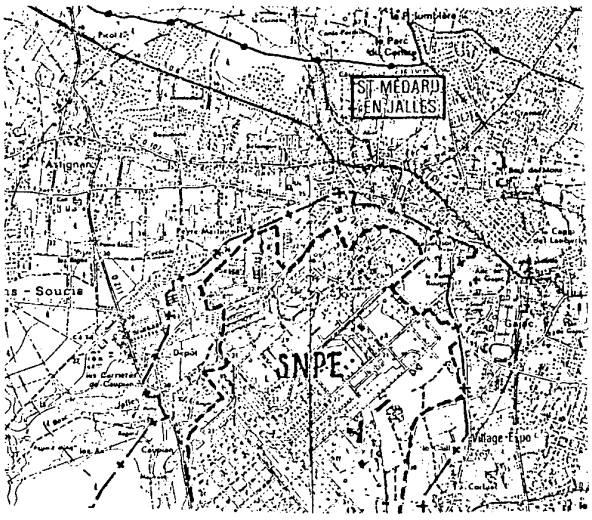



**Figure 3 : Environnement de l'usine**

Un règlement fixe les seuils à ne pas dépasser. Ces seuils sont très bas et ne sont bien respectés que pour les moteurs dont le débit instantané ne dépasse pas 20 à 25 kg/s.

L'arrivée de programmes d'études et de développement de moteurs à grand débit de 30 à 100 kg/s et le démarrage de la production de masse de moteurs du programme MLRS conduisant à une augmentation importante du nombre de tirs très bruyants n'auraient pas permis de respecter ces règlements.

En l'absence, à proximité de l'usine, de bancs d'essais utilisables, l'établissement a pris la décision de construire un banc de tir insonorisé donnant la garantie à moyen terme et long terme du maintien de l'activité tir quelle que soit l'évolution de la réglementation. Compte tenu des plaintes qui n'auraient pas manquer d'être émises, notre activité tir aurait pu être interdite ou limitée. Cette perspective n'était pas acceptable.

## 2 - OBJECTIFS ET DONNEES POUR LA CONCEPTION DU BANC DE TIR INSONORISE

Le banc en projet devait satisfaire aux conditions suivantes :

**Pour les tirs :**

permettre le tir de moteur ayant des débits massiques instantanés pouvant atteindre 100 kg/s avec des tuyères courtes donc peu adaptées. La durée de ces tirs est de quelques 1/10ème de secondes à quelques secondes. Les variations de débit sont extrêmement rapides. Les gaz du jet sont à haute température : > 2000°C avec post-combustion : l'extension de la "flamme" peut atteindre 20 m. Ces gaz contiennent jusqu'à 20 % d'acide chlorhydrique qui s'hydrate rapidement dans l'air humide pour donner un brouillard acide très corrosif lorsqu'il est concentré.

La vitesse d'éjection très élevée : ~ 2000 m/s conduit à un entraînement important d'air frais par effet "Venturi".

**Pour l'environnement :**

limiter l'impact sonore sur l'environnement c'est à dire ne pas dépasser 50 à 70 dBA en limite d'établissement selon le classement en zone de bruit des espaces limitrophes. Cette valeur tient compte des niveaux effectifs, de l'émergence sonore des tirs, de l'effet éventuel de fréquence pure et de leur nombre journalier. A la source, les tirs les plus bruyants à l'air libre génèrent un niveau sonore de 175 dB ce qui donne en limite de propriété des niveaux de 95 dB avec une forte émergence. Le nombre de tirs ne doit pas être limité par la nuisance sonore résiduelle.

**Autres contraintes :**

les dispositifs d'insonorisation ne doivent pas perturber les mesures effectuées sur les tirs (pressions, poussées, ..), ils doivent résister sans dégradation à l'onde de choc émise au moment du désoperculage dont la puissance a été estimée équivalente à celle de la détonation de 375 g de TNT. Le banc doit également assurer la protection de l'environnement contre les projections (systématiques : opercules, occasionnelles : explosion de moteur). Il doit résister sans dommage notable à une explosion dont le niveau supérieur a été fixé à un équivalent TNT de 5 kg. La cadence des tirs de contrôle faiblement instrumenté doit pouvoir atteindre au moins 2 tirs à l'heure.

## 3 - LE CHOIX DE LA SOLUTION

Différentes solutions ont été envisagées.

Les solutions basées sur la technique des silencieux utilisés sur les armes à tube ont été évaluées et éliminées car elles ne répondent pas au problème posé. Elles sont peu performantes et peu adaptables à la variété des tirs à prendre en compte.

Les solutions basées sur l'absorption du bruit par des gouttelettes d'eau sont difficilement réalisables à l'échelle envisagée : l'importance des débits et des vitesses des jets conduit à des débits d'eau très importants et à des installations annexes d'alimentation en eau et de séparation de l'eau des gaz en sortie de grande dimensions donc coûteuses.

La solution qui a été finalement retenue consiste à effectuer le tir dans un volume limité par des parois épaisses et lourdes qui ne communique avec l'atmosphère extérieure que par deux immenses pièges à son qui ne laissent pas passer le bruit tout en assurant la circulation des gaz.

La société Boet, sélectionnée pour ses compétences dans le domaine de l'insonorisation a développé et réalisé cette solution.

## 4 - DESCRIPTION DU BANC INSONORISE REALISE

### 4.1. La structure

Le banc d'essai proprement dit est logé à l'intérieur d'une structure lourde en béton armé composée d'un couloir horizontal surmonté à chaque extrémité d'une tour verticale contenant les silencieux.

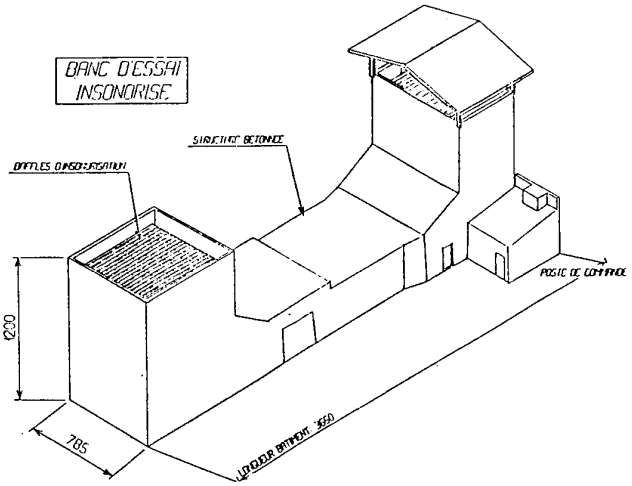



**Figure 4 : vue extérieure du banc**

La structure en béton armé a été calculée pour :

- avoir une inertie suffisante assurant la non transmission des bruits de l'intérieur vers l'extérieur : insonorisation passive,

- résister aux surpressions et dépressions internes engendrées par les écoulements dus au tir sans dégradation,

- résister aux effets de l'explosion d'un moteur sans endommagement notable.

De cet ensemble de contraintes, c'est la deuxième qui a été dimensionnante et qui a conduit à une épaisseur minimum de 40 cm. En effet, ce type de tir en local semi-clos génère du fait de l'importance des débits instantanés, de leur vitesse et de leur variation très rapide, des turbulences énormes et des ondes de chocs. Les contraintes thermiques interviennent peu du fait de la forte inertie de la structure et de la brièveté des émissions.

### 4.2. Les baffles d'insonorisation

Les baffles d'insonorisation placées dans les tours d'extrémité constituent les éléments actifs de l'insonorisation.

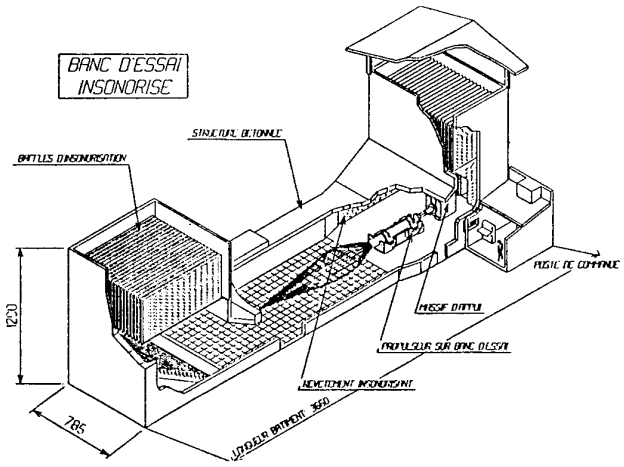



**Figure 5 : Vue en coupe du banc**

Ces baffles sont constituées de caissons parallélépipédiques minces en métal perforé garnis de laine de roche d'une densité bien choisie.

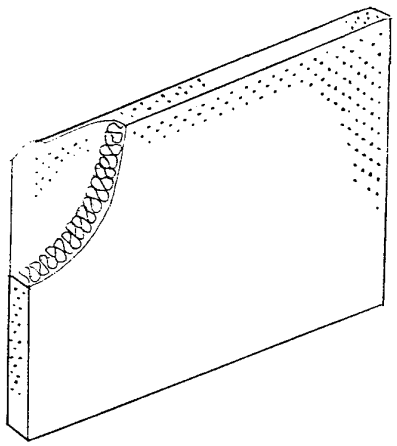


**Figure 6 : Caisson insonorisant**

Ces caissons sont solidement fixés dans les tours avec des espacements réguliers et calibrés. Ils constituent à la fois l'élément actif de l'insonorisation et le point faible du dispositif car il sont soumis à de fortes contraintes mécaniques et à l'action corrosive de l'acide chlorhydrique.

### 4.3. Les équipements annexes

#### 4.3.1. Les portes

Pour l'exploitation du banc de tir il est nécessaire d'assurer la circulation des personnes, des équipements et des moteurs à tester avec leur moyen de transport.

Trois portes ont été installées : deux petites permettant le passage des personnes et une grande pour le passage des produits. Ces portes, en position fermée, doivent satisfaire aux mêmes contraintes que la structure. Cet objectif a été obtenu en réalisant des portes en caissons d'acier solidement fixés à la structure avec un système de joints gonflables assurant une parfaite étanchéité. Ces portes sont très lourdes mais elles ne sont fermées qu'en l'absence de toute personne à l'intérieur du banc. Elles ne sont donc pas un obstacle à la fuite des opérateurs pendant les montages.

#### 4.3.2. Dispositif d'arrêt des projections

Il est composé des parois lourdes déjà présentées et sous le piège à son de sortie d'une série de gradins en maçonnerie munis d'alvéoles. Cette disposition permet d'éviter le rebond vers le haut, c'est à dire en direction des caissons d'insonorisation des projections accélérées par les jets du moteur qui pourraient les endommager. Cette disposition en gradin a également été adoptée pour verticaliser le flux de gaz.

#### 4.3.3. Insonorisation complémentaire

Les parois de l'espace situé sous la tour d'entrée d'air et autour du banc de tir proprement dit sont garnies de matériaux absorbants retenus par des plaques perforées.

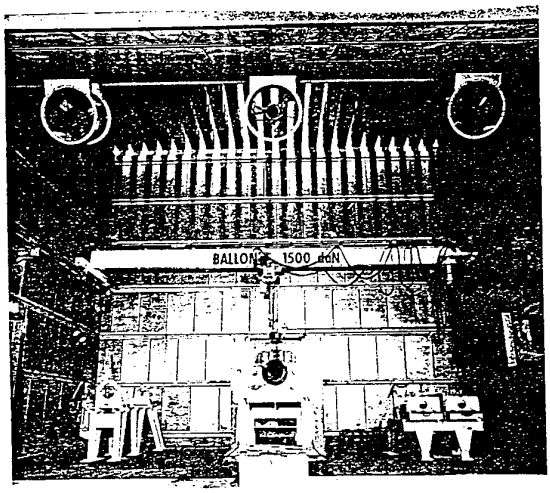



**Figure 7 : Vue du volume d'entrée**

Cette protection n'existe que dans cette zone qui n'est pas exposée aux gaz de combustion et aux turbulences les plus fortes. Elle contribue à l'insonorisation et surtout limite les phénomènes de réflexion d'ondes qui pourraient perturber les mesures.

### 4.3.4. Ventilation forcée

Une ventilation forcée du volume interne a été montée pour évacuer rapidement les gaz de combustion encore présents après le tir afin de limiter leur action corrosive et de permettre le travail des opérateurs peu de temps après les tirs.

Cette ventilation d'un dévit de 65.000 $m^3/h$ est mise en service avant chaque tir pour amorcer l'écoulement des gaz.

### 4.3.5. Le local de commande

Compte tenu de l'excellente protection apportée par la structure du banc, le local de commande a été placé juste à côté. Un hublot garni de verre feuilleté permet d'observer les tirs. Les câbles de mesure et les lignes de mise à feu qui vont du banc à la salle de commande et d'exploitation des tirs cheminent dans des caniveaux avec des chicanes et un garnissage de sable.

### 4.3.6. Le banc de tir proprement dit

Il s'agit de bancs classiques. Le massif est conçu pour des poussées jusqu'à 90 000 daN ; il peut recevoir aussi bien un banc à lame qu'un banc à glissière pour les mesures de pression et de poussée ou un banc à berceau fixe et mors de serrage pour les mesures de pressions seules.

## 5 - LES PERFORMANCES OBTENUES

Les objectifs fixés par le cahier des charges ont été atteints et même dépassés.

Les mesures de bruit ont été effectuées dans des conditions rigoureuses de qualité : matériel agréé et étalonné, mode opératoire bien défini, conditions d'environnement comparables pour des tirs de moteurs identiques sur banc à l'air libre et sur le banc insonorisé.

Ces résultats sont spectaculaires tant au niveau des mesures effectuées qu'au niveau des appréciations portées par le personnel chargé de la réalisation des tirs.

Les mesures effectuées aux points de référence ont donné des niveaux très inférieurs au seuil fixé.

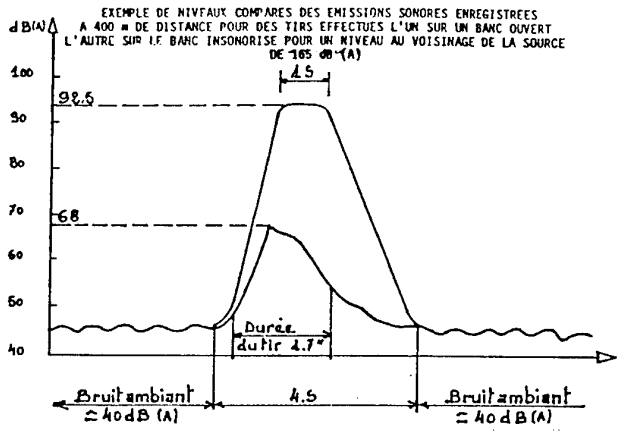



**Figure 8 : Enregistrements comparés**

A proximité du stand (40 m), on a mesuré des niveaux inférieurs à 90 dB, là où en l'absence de protection il y aurait eu plus de 110 dB.

Ces niveaux sont suffisamment bas pour

- que la personne chargée des tirs puisse se tenir dans la salle de commande sans porter de casque antibruit et y mener une conversation normalement,

- que la circulation des personnes à proximité du stand soit permise sans restriction et sans précaution particulière.

Par ailleurs la signature sonore des tirs a été profondément modifiée dans un sens qui la rend moins gênante :

- disparition quasi totale des fréquences les plus élevées,

- durée de l'émergence réduite,

- évolution de la puissance sonore plus progressive.

Le bruit résiduel perçu est sourd, sans effet de choc et donc mieux toléré.

Ces performances ont conduit à améliorer les conditions et les coûts d'exploitation. En effet l'absence de nuisance à l'extérieur du stand a permis :

- de regrouper dans le local de commande, la mise à feu, les mesures et leur exploitation ce qui donne des gains de temps sur les procédures avant et après tir,

- de placer à proximité du stand les installations de conditionnement thermique des moteurs pour les tirs en température (tir à chaud et tir à froid). Cette disposition réduit notablement les délais entre sortie de conditionnement et tir.

L'événement majorant redouté pour la tenue de l'installation : l'explosion d'un moteur, s'est produit une fois. Le banc de tir proprement dit a été sévèrement endommagé mais l'enceinte de confinement n'a subi que des dommages légers et les conséquences sur l'environnement ont été négligeables.

## 6 - LES POINTS FAIBLES

Cette réalisation a permis d'obtenir les résultats escomptés mais en l'absence de référence (il s'agissait d'une première) quelques insuffisances sont apparues à l'usage.

Tout d'abord, il s'est avéré que l'étude avait sous estimé les contraintes de pression lié à la turbulence extrême des écoulements. Il en est résulté des déformations de la structure qui, à l'usage, aurait pu conduire à sa dégradation prématurée. Il a fallu la renforcer et accroître son inertie.

Une conséquence de ces déformations a été une dégradation des liaisons entre les caissons d'insonorisation et la cheminée de sortie.

Ce fait, ajouté à une qualité insuffisante des soudures des caissons a conduit à une dégradation assez rapide des premiers caissons qu'il a fallu remplacer. Les travaux de renforcement des structures lourdes et d'amélioration de la fixation des caissons d'insonorisation ont maintenant conduit à un fonctionnement stable du système avec des performances encore améliorées.

On peut donc dire que cette réalisation a répondu aux objectifs que nous nous étions donnés. Elle supprime une des émissions, perçue comme la plus gênante par l'environnement : le bruit inhérent au principe même des moteurs fusées. Cette suppression a permis de maintenir sur le site de Saint Médard à proximité des équipes de recherches, de développement et de contrôle, l'activité de tir au banc, activité indispensable en propulsion. Les performances obtenues permettraient même de mener cette activité avec une proximité plus grande des habitations ce qui donne une garantie durable pour le maintien de l'activité "tir" sur ce site.

Cette réalisation a valu à la SNPE un prix de l'environnement 1991 pour l'industrie.

**Réf.** : Arrêté et instructions du 20 août 1985
J.O. du 10 novembre 1985

# CARACTERISATION DU FLUX THERMIQUE ET ESTIMATION DES RISQUES DE BRULURES AUTOUR DES MOTEURS A TRES COURT TEMPS DE COMBUSTION

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## Résumé

Le flux thermique autour des moteurs de missiles ou roquettes est lié à l'éjection d'une quantité importante de gaz chauds au cours du tir et peut constituer une nuisance importante.

Outre les risques d'inflammation de l'environnement immédiat (végétation...), ces effets peuvent entraîner des risques de brûlures pour les servants d'armes.

Afin de mieux prendre en compte ces effets, une étude a été menée en vue de mettre au point un outil prévisionnel des risques de brûlures, adapté au cas des moteurs à court temps de fonctionnement.

Ainsi, une méthodologie de caractérisation du flux thermique dans le jet des moteurs a été étudiée. Elle a été élaborée de façon à tenir compte des spécificités suivantes :

- temps de réponse très brefs adaptés à la rapidité des phénomènes,
- tenue mécanique aux projections d'imbrûlés dans le jet,
- représentativité des flux thermiques dans la peau,
- distinction entre flux convectifs et radiatifs.

En complément, un modèle thermique de la peau a été étudié. Il est basé sur le modèle de peau de Stolwijk et Hardy et permet le calcul du profil de température dans les diverses couches de la peau : épiderme, derme et tissus sous-cutanés. Une loi de destruction des cellules en fonction de la température a été dérivée des travaux de Henriques et Stoll et adaptée.

Cet outil permet la prévision des risques de brûlures autour des moteurs ; il peut en particulier être utilisé pour délimiter les zones à risques, pour les tirs en champ libre ou en espace clos.

## Liste des symboles

| | |
|---|---|
| $C$ | chaleur spécifique de la peau |
| $E$ | énergie d'activation |
| $h$ | cœfficient de transfert thermique |
| $H_a$ | enthalpie d'ablation |
| $K_0$ | facteur pré-exponentiel de la loi d'Arrhénius |
| $q$ | flux thermique à la surface de la peau |
| $Q$ | flux thermique imposé |
| $R$ | constante universelle des gaz |
| $t$ | temps |
| $T_a$ | température d'ablation |
| $T_i^t$ | température du nœud i à l'instant t |
| $T_r$ | température ambiante |
| $T_s$ | température de surface |
| $T_\infty$ | température de l'écoulement libre |
| $\lambda$ | conductivité thermique des couches cutanées |
| $\rho$ | masse volumique |
| $\sigma$ | constante de Stefan-Boltzmann |
| $\Omega$ | paramètre caractérisant l'état d'une cellule |

## 1. Introduction

Le tir d'un missile ou d'une roquette donne lieu à l'émission de gaz de combustion chauds à des débits relativement élevés (de l'ordre de 10 à 50 kg/s). Ces gaz chauds sont susceptibles d'enflammer l'environnement immédiat (végétation) et constituent également un risque de brûlures pour les servants d'armes.

Afin de prévoir ces effets et de déterminer la zone de l'espace où peuvent se produire des brûlures cutanées une étude a été menée par l'ONERA sous l'égide de la DAT (Direction des Armements Terrestres).

## 2. Méthodologie de l'étude

### 2.1. Le phénomène physique étudié

Le problème qui se pose est de déterminer une zone de sécurité pour les servants d'armes autour du lanceur. Pour cela, il faut être capable d'estimer les traumatismes que peut provoquer le fonctionnement d'un propulseur.

Les mesures physiques effectuées par l'ONERA [1] sur les jets de gaz chauds issus d'un propulseur à court temps de combustion ont permis de préciser la nature de l'agression thermique ; celle-ci est caractérisée par :

- une durée courte d'environ 10 ms,

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

- une forte intensité, puisque des densités de flux thermiques dépassant 1 kW/cm2 ont été enregistrées,

- une nature essentiellement convective, la part du rayonnement étant estimée à moins de 4 % du flux de chaleur total.

### 2.2. La méthodologie de l'étude

Pour déterminer la zone de sécurité, l'approche suivante a été retenue :

- l'agression est caractérisée à l'aide de fluxmètres qui mesurent au cours du temps le flux thermique entrant dans le capteur.

Dans les conditions de mesures, ce flux de chaleur est assimilable au flux de chaleur entrant dans la peau.

- l'évolution de la température dans la peau est ensuite calculée au cours du temps.

- un modèle de dégradation des cellules permet d'estimer la mortalité des cellules constituant la peau et donc d'estimer le risque de brûlures.

## 3. La mesure du flux thermique

### 3.1. Les capteurs

Les phénomènes provoqués par le fonctionnement du propulseur sont de courte durée (quelques ms), il faut donc disposer de capteurs ayant un temps de réponse de l'ordre de la milliseconde. D'autre part la température d'arrêt des gaz de propulsion est couramment comprise entre 2000 et 3000 K, il faut donc que les couches superficielles du capteur résistent au contact avec les gaz chauds. La mesure de flux est faite à l'aide de capteurs [2] à élément calorimétrique de silice. Le flux est déduit de la température d'un revêtement thermométrique mince en platine. Un schéma des capteurs est présenté sur la figure 1.

### 3.2. Nature du flux thermique mesuré

Pour que la mesure soit utilisable pour le calcul ultérieur il faut pouvoir assimiler le flux reçu par le capteur au flux reçu par la peau. Le flux thermique de convection entre un fluide et un obstacle placé dans l'écoulement dépend :

- des propriétés thermocinétiques du fluide,

- de la géométrie de l'obstacle,

- des propriétés thermocinétiques de l'obstacle.

Le premier aspect est pris en compte en effectuant la mesure de flux dans l'écoulement réel. Le deuxième est pris en compte en disposant les capteurs dans des obstacles de même géométrie que les parties du corps que l'on désire simuler. Le troisième aspect est pris en compte indirectement de la façon suivante :

le flux de chaleur convectif entre les gaz et le capteur (ou la peau) peut s'écrire :

$$q = h(T_\infty - T_s)$$

le coefficient de transfert de chaleur $h$ entre le gaz et le capteur est identique au coefficient de transfert de chaleur entre le gaz et la peau.

La température du capteur varie au plus de quelques centaines de degrés au cours d'un essai d'une durée de quelques millisecondes. Le rapport des effusivités de la peau et de la silice est tel que si la température du capteur varie de 100 °C au cours d'un essai, la température de la peau varierait de 130 °C.

La température de l'écoulement étant voisine de 2200 °C, elle est identique que l'on soit en présence du capteur ou de la peau. La différence $T_\infty - T_s$ ne varie donc quasiment pas quand on passe du capteur de silice à la peau. En conséquence le flux de chaleur mesuré par le capteur est très voisin de celui que recevrait la peau dans le même écoulement.

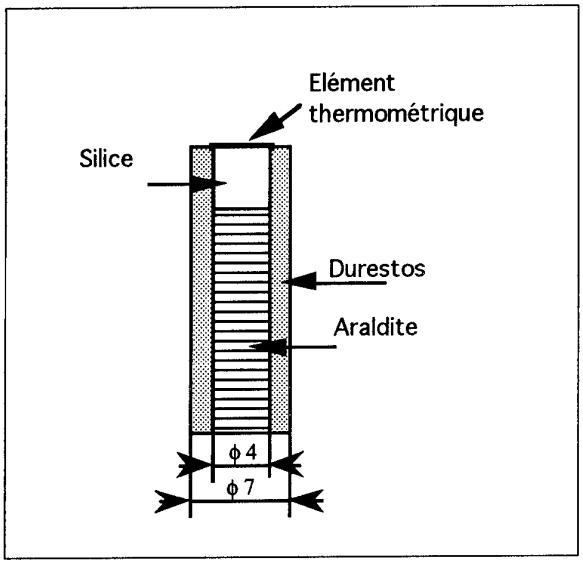



Figure 1 : Schéma d'un capteur de flux

## 4. Le calcul de l'effet de l'application d'un flux thermique à la peau

### 4.1. La position du problème

L'application d'un flux thermique à la peau se traduit par un échauffement superficiel de la peau. La chaleur diffuse dans la peau et il s'établit un profil thermique fonction du temps. Les cellules constituant la peau sont sensibles à la température et vont être détruites d'autant plus rapidement que la température sera plus élevée.

Le problème de l'évaluation des brûlures se décompose donc en deux sous-problèmes :

- D'abord l'estimation de l'échauffement des tissus créé par l'agression,

- Ensuite, l'estimation des dégradations cellulaires consécutives à cet échauffement.

## 4.2. Estimation de l'échauffement cutané par modèle numérique

### 4.2.1. Structure de la peau

La peau est un ensemble de tissus extrêmement complexe comme on peut le voir sur la figure 2. On peut distinguer l'épiderme et le derme. L'épiderme, le plus extérieur, a avant tout un rôle de protection mécanique et d'isolement thermique des tissus et des organes vis à vis de l'extérieur.

L'épiderme est d'une épaisseur variable suivant l'individu et l'emplacement du corps considéré : de quelques dizaines de microns à environ 200 microns. On peut distinguer diverses couches en partant de l'extérieur, ces couches sont orientées parallèlement à la surface extérieure de la peau, mais elles présentent des ondulations parfois importantes, notamment en ce qui concerne la plus profonde, à la jonction derme-épiderme.

Cette couche, dite couche germinative, ne comporte en épaisseur qu'une cellule. Elle repose sur une membrane, dite membrane basale, qui marque la séparation des deux zones, derme et épiderme. Les cellules de l'épiderme sont générées au niveau de la couche germinative et, en vieillissant, elles se déplacent vers l'extérieur jusqu'à devenir des cellules pratiquement mortes au niveau de la couche cornée (voir figure 2).

Le derme est constitué de tissus conjonctifs traversés par un réseau dense de capillaires sanguins, un réseau lymphatique et un réseau nerveux. Par ailleurs, dans le derme sont implantés les glandes sudoripares, les glandes sébacées et les poils. Ces systèmes constituent une extension de l'épiderme dans le derme car ils sont enveloppés par les cellules basales.

### 4.2.2. Schématisation de la peau : Modèle thermique de Stolwijk et Hardy [3]

La modélisation d'un système aussi complexe que la peau nécessite des schématisations et des simplifications importantes. Du point de vue des transferts thermiques, le modèle le plus évolué et le mieux adapté au problème est celui de Stolwijk et Hardy. Le modèle réduit l'ensemble de la peau à 4 couches d'épaisseurs différentes. Dans chaque couche les propriétés thermophysiques sont supposées constantes. Les couches sont les suivantes :

- la couche cornée,
- la couche de cellules basales,
- la couche vasculaire sous-cutanée,
- une couche graisseuse profonde.

Les épaisseurs et les propriétés thermophysiques de ces couches sont données sur le tableau n°1. Afin de prendre en compte les différences entre la peau des différentes régions du corps, deux configurations ont été utilisées : un épiderme mince, correspondant à la peau de l'avant-bras, et un épiderme épais correspondant mieux au tronc (régions dorsales).Dans le premier cas, l'épaisseur des deux premières couches est de 40 microns pour chacune d'elles, dans le second de 100 microns.

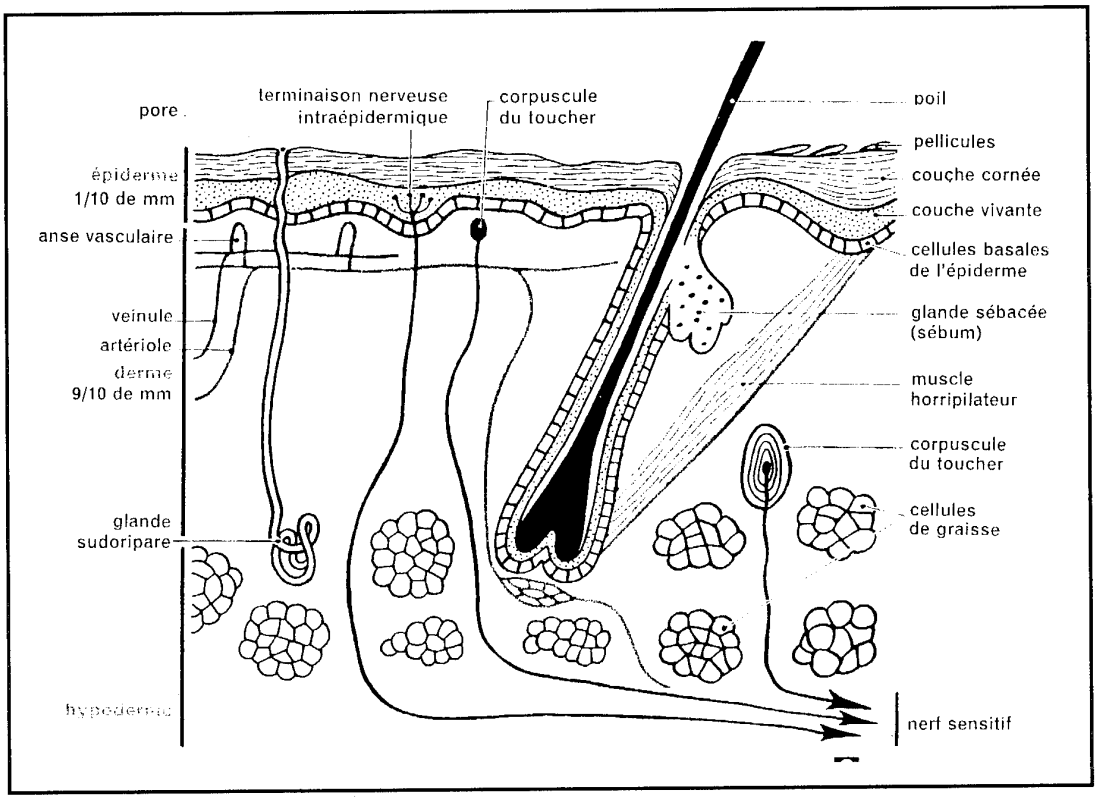



Figure 2 : Structure de la peau

| Nature de la couche | Epaisseur (mm) | | Conductivité W/(m.K) | Chaleur spécifique J/(kg.K) | Masse spécifique kg/m$^3$ | Diffusivité m$^2$/s | Effusivité J/(m$^2$.s$^{1/2}$.K) |
|---|---|---|---|---|---|---|---|
| | peau mince | peau épaisse | | | | | |
| Couche cornée | ,04 | ,1 | ,21 | 3600 | 1200 | $4{,}86.10^{-8}$ | 950 |
| Couche des cellules basales | ,04 | ,1 | ,42 | 3600 | 1200 | $9{,}72.10^{-8}$ | 1340 |
| Couche vasculaire sous-cutanée | ,6 | ,6 | ,42 | 3600 | 1200 | $9{,}72.10^{-8}$ | 1340 |
| Couche graisseuse profonde | 10,0 | 10,0 | ,167 | 2300 | 920 | $7{,}90.10^{-8}$ | 595 |

Tableau 1 : Schématisation de la peau : modèle de Stolwijk et Hardy

D'autre part, étant donnée la gamme restreinte de température, les propriétés thermophysiques sont supposées indépendantes de la température.

Enfin, le seul mécanisme considéré pour le transfert thermique est la conduction. Dans une certaine mesure la conductivité de la couche vasculaire prend en compte le phénomène de convection sanguine. Cettè propriété doit être considérée comme une propriété efficace.

Les flux appliqués à la peau étant d'origine convective ou radiative dans l'infrarouge, on peut admettre que l'énergie est déposée tout à fait en surface. L'effet combiné de la carbonisation des couches les plus superficielles de l'épiderme et de l'écoulement extérieur de gaz très chauds, sans doute chargés de particules, est supposé être une desquamation de ces couches superficielles. Tout se passe donc comme si l'on avait ablation avec une enthalpie d'ablation nulle. La température de surface choisie pour le calcul numérique est $T_a = 700\,K$, valeur compatible avec les mesures effectuées par Knox et al [4]et Ross et al [5].

On suppose, par ailleurs, la peau initialement isotherme et à 300 K, ce qui correspond à une température d'épiderme exposé à une ambiance fraîche.

4.2.3. Formulation mathématique du problème

La propagation de la chaleur dans la peau est supposée monodimensionnelle. L'équation a résoudre avec des propriétés thermiques variables dans l'espace, s'écrit :

$$\rho(x)C(x)\frac{\partial T}{\partial x} = \frac{\partial}{\partial x}\left[\lambda(x)\frac{\partial T}{\partial x}\right]$$

La condition initiale exprime la température dans la peau :

$$T(x,0) = T_0 = 300\,K$$

Les conditions aux limites sont :

$$-\lambda(0)\left(\frac{\partial T}{\partial x}\right)_{x=0} = q(t)$$

pour la condition sur la paroi externe qui reçoit le flux entrant $q(t)$ et :

$$\left(\frac{\partial T}{\partial x}\right)_{x=e} = 0$$

pour la condition sur la paroi interne où le flux de chaleur est nul (approximation du milieu semi-infini).

4.2.4. Résolution de l'équation de la chaleur

L'équation de la chaleur est résolue par la méthode des différences finies c'est à dire que les opérateurs différentiels sont approximés par les expressions suivantes :

$$\frac{\partial T}{\partial x} = \frac{T_{i+1}^t - T_{i-1}^t}{2\Delta x}$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{T_{i+1}^t - 2T_i^t + T_{i-1}^t}{(\Delta x)^2}$$

$$\frac{\partial T}{\partial t} = \frac{T_i^{t+\Delta t} - T_i^t}{\Delta t}$$

$\Delta x$ étant la largeur d'un intervalle d'espace et $\Delta t$ le pas de temps.

*4.2.4.1. Point courant*

L'équation du point courant se met sous la forme :

$$T_i^{t+\Delta t} = T_i^t\left[1-\frac{F_i}{\lambda_i}\left(\lambda_{i-\frac{1}{2}}+\lambda_{i+\frac{1}{2}}\right)\right]$$

$$+T_{i-1}^t F_i\frac{\lambda_{i-\frac{1}{2}}}{\lambda_i}+T_{i+1}^t F_i\frac{\lambda_{i+\frac{1}{2}}}{\lambda_i}$$

avec $F_i=\dfrac{\lambda_i}{\rho_i C_i}\dfrac{\Delta t}{(\Delta x)^2}$

*4.2.4.2. Conduction pure*

En absence d'ablation, les conditions aux limites s'écrivent (méthode de la tranche fictive) :

$$T_1^{t+\Delta t} = T_1^t\left[1-F_1\left(1+\frac{\lambda_{1+\frac{1}{2}}}{\lambda_1}\right)\right]$$

$$+T_2^t F_1\left(1+\frac{\lambda_{1+\frac{1}{2}}}{\lambda_1}\right)+2\frac{\Delta x}{\lambda_1}F_1 q(t)$$

avec $q(t)$ = flux imposé -flux radiatif émis.

$$q(t)=Q(t)-\sigma\left(T_1^4-T_r^4\right)$$

avec $\sigma = 5{,}7.10^{-8}$ unités S.I.

pour la paroi extérieure et

$$T_n^{t+\Delta t} = T_n^t\left[1-F_n\left(1+\frac{\lambda_{n-\frac{1}{2}}}{\lambda n}\right)\right]$$

$$+T_{n-1}^t F_n\left(1+\frac{\lambda_{n-\frac{1}{2}}}{\lambda_n}\right)$$

pour la paroi intérieure.

*4.2.4.3. Conduction avec ablation*

Lorsqu'il y a ablation le flux entrant $q(t)$ s'écrit

$q(t)$ = flux imposé -flux radiatif émis - flux bloqué par l'ablation.

$$q(t)=Q(t)-\sigma\left(T_a^4-T_r^4\right)-\rho H_a\frac{ds}{dt}$$

La paroi est en x = s et n'est pas nécessairement sur un point du maillage. Deux quantités sont à calculer :

- l'épaisseur ablatée entre les instants $t$ et $t+\Delta t$ : $\Delta s$,

- la température au temps $t+\Delta t$ du premier point du maillage sous le front d'ablation: $T_s^{t+\Delta t}$.

Si l'ablation vient à s'annuler, c'est à dire si la vitesse d'ablation devient négligeable, le problème redevient un problème de conduction pure. Les abscisses des points du maillage sont recalculées à partir de la nouvelle surface, avec le même pas d'espace que précédemment.

## 4.3. Estimation des dégradations cellulaires par modèle numérique

4.3.1. Les données de Henriques

L'élévation de température a un effet destructif sur les cellules vivantes. La nécrose des tissus correspond à la brûlure. Les premiers travaux sur la cinétique de cette thermodégradation ont été effectués à la fin de la seconde guerre mondiale et publiés en 1947 par Henriques et Moritz [6]. Ils provoquaient des brûlures chez le porc et sur l'homme par application d'une thermode isotherme maintenue a température constante par circulation d'eau chaude (brûlure par conduction), ou par immersion de l'animal dans une enceinte isotherme à température contrôlée (brûlure par convection). Les cellules intéressées par l'étude étaient celles de la couche basale, au niveau de la jonction derme-épiderme.

L'état de la cellule, déterminé par analyse histologique, peut être caractérisé par un paramètre $\Omega$ qui est nul lorsque la cellule est intacte et égal à 1 lorsqu'elle est totalement nécrosée.

L'ensemble des expériences menées par ces auteurs leur a permis de proposer une loi de cinétique de dégradation [7], du type loi d'Arrhénius :

$$\frac{d\Omega}{dt}=K_0\exp\left(-\frac{E}{RT}\right)$$

Dans cette relation, $\Omega$ est le facteur caractérisant l'état d'avancement de la dégradation cellulaire, $t$ le temps, $E$ une énergie d'activation, $R$ la constante universelle des gaz ($R$ = 8,32 J/(mole.K)), $T$ la température absolue en Kelvin et $K_0$ une constante.

Les auteurs proposent pour l'énergie d'activation et pour la constante $K_0$ les valeurs suivantes :

$E$ = 627800 J/mole

$K_0$ = $3{,}1.10^{98}$ $s^{-1}$

L'évolution du taux de dégradation, $d\Omega/dt$, avec la température est représenté sur la figure 3. On peut ainsi voir que la destruction totale d'une cellule portée à une température constante de 49 °C intervient en 100 s. Lorsque la température passe à 60 °C il suffit d'une seconde, et lorsqu'elle atteint 65 °C, ce temps se réduit à 0,03 seconde.

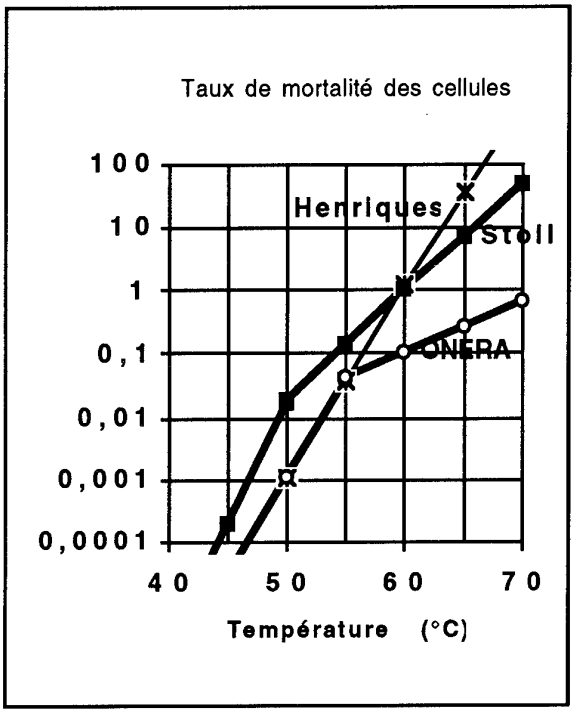



Figure 3 : Evolution du taux de dégradation des cellules en fonction de la température.

4.3.2. Les données de Stoll

Des travaux plus récents de Stoll et Green [8], correspondant à des brûlures provoquées par une lampe à filament de tungstène (brûlure par rayonnement), conduisent à des lois de cinétiques différentes, mais relativement proches. Elles sont également représentées sur la figure 3. Ces auteurs proposent :

$$T < 50°C : \frac{d\Omega}{dt} = 7{,}9.10^{119} \exp\left(-\frac{753300}{RT}\right)$$

$$T > 50°C : \frac{d\Omega}{dt} = 3{,}5.10^{56} \exp\left(-\frac{360700}{RT}\right)$$

Il est à noter que ces lois ont été obtenues à des températures cutanées superficielles n'excédant pas 60 °C, et que l'on sera amené dans le logiciel BRULUR à les utiliser au-delà, donc à les extrapoler.

4.3.3. Les données utilisées par l'ONERA

Au cours de l'étude des effets thermiques des propulseurs sur le personnel [1], l'ONERA a utilisé les lois de dégradation cellulaire de Henriques et de Stoll. La loi retenue a été la loi de Henriques car elle avait été élaborée à partir d'essais mettant en jeu des flux convectifs. Elle a cependant fait l'objet d'une modification au delà de 55 °C lui conférant une pente plus proche de la loi de Stoll. Cette modification a donc consisté à diminuer la vitesse de mortalité pour des températures élevées (supérieures à 55 °C). La loi proposée par l'ONERA est finalement la suivante :

$$T < 55°C : \frac{d\Omega}{dt} = 3{,}1.10^{98} \exp\left(-\frac{627800}{RT}\right)$$

$$T > 55°C : \frac{d\Omega}{dt} = 4{,}6.10^{25} \exp\left(-\frac{167400}{RT}\right)$$

Remarque

Il semble qu'au niveau cellulaire, la dégradation causée par la température et conduisant à la mort de la cellule soit essentiellement liée à l'altération des protéines [7]. Ceci semble corroboré par le fait que les énergies d'activation dont on vient de parler sont du même ordre de grandeur que celles déterminées in vitro pour l'altération des protéines. Ainsi, par exemple : pour l'inactivation thermique de l'invertase, à pH = 4 : E = 460 kJ/(mole.K), pour l'inactivation de la peroxidase : E = 791 kJ/(mole.K), ou pour la dénaturation de l'albumine de l'oeuf : E = 552 kJ/(mole.K).

### 4.4. Estimation de la gravité des brûlures

La gravité des brûlures est liée essentiellement à la profondeur des lésions et à leur étendue. Ce dernier paramètre est généralement évalué en % de la surface totale de peau de l'individu. Une brûlure superficielle peu étendue est bénigne, une brûlure profonde et étendue, grave. L'étendue de la brûlure ne dépend pas que des conditions locales imposées à la peau, mais du volume total où ces conditions sont possibles.

La profondeur des lésions ne dépend que des conditions locales. C'est ce paramètre qui est estimé à l'aide du logiciel BRULUR et sur lequel repose la notion de volume dangereux, dont les limites correspondent à un seuil de gravité de brûlure à déterminer.

Il existe plusieurs systèmes de gradation de la gravité des brûlures en rapport avec la profondeur des lésions. Ces systèmes reposent sur un ensemble de critères cliniques tels que l'aspect, la couleur, la souplesse et la sensibilité des tissus superficiels, l'adhérence de l'implantation des poils, l'existence ou non de phlyctènes et de critères histologiques.

Pour schématiser, on peut distinguer les brûlures bénignes du premier degré. Elles correspondent à une lésion des seules cellules de l'épiderme, sans atteinte de la membrane basale. L'épiderme peut se reconstituer sans intervention chirurgicale. Les brûlures du second degré, même superficielles, font partie de brûlures graves nécessitant des soins bien adaptés en milieu hospitalier, étant donné les risques élevés d'infection que présentent les tissus nécrosés. Le second degré superficiel ou commençant correspond à l'apparition de nécroses transépidermiques locales. Lorsque la totalité de la membrane basale est détruite y compris les invaginations liées aux racines des poils et aux glandes sudoripares, le troisième degré est atteint. Dans ce cas l'autoreconstruction de l'épiderme est impossible si la brûlure est

étendue et il est nécessaire de recourir aux greffes.

Pour effectuer le diagnostic de la gravité de la brûlure, nous considérons l'évolution du paramètre $\Omega$ dans la peau à la fin du phénomène de propagation de la chaleur. Nous utilisons la terminologie du modèle de Stolwijk et Hardy.

Nous considérons que tant que la couche cornée est seule atteinte, soit $0 < \Omega \leq 1$ dans la couche cornée, la brûlure est du premier degré.

A partir du moment où la couche des cellules basales est atteinte, $0 < \Omega \leq 1$ dans la couche des cellules basales , la brûlure devient du second degré.

Dès que la couche basale est entièrement détruite, soit $\Omega = 1$ dans la couche des cellules basales, la brûlure est du troisième degré.

## 5. Utilisation du modèle

### 5.1. Ecriture d'un logiciel

Le modèle qui vient d'être décrit a donné lieu à l'écriture d'un logiciel de prévision de la gravité des brûlures cutanées : le logiciel BRULUR [9].

### 5.1. Zone de danger à l'arrière d'un propulseur

Au cours du fonctionnement d'un propulseur un jet de gaz chauds est éjecté à l'arrière. Les lois de flux sont mesurées en différentes positions à l'arrière du propulseur. Un exemple de loi de flux idéalisée est donné sur la figure 4. Les lois de flux étant mesurées en une quinzaine de points à l'arrière du propulseur, on calcule pour ces points l'état de la peau qui serait exposée au flux thermique mesuré. On identifie ainsi les points de l'espace où peut se produire une brûlure du second degré. Par interpolation ou extrapolation on définit alors la zone de l'espace pour laquelle il y risque de brûlure au second degré. Cette zone a la forme d'un cône dont l'axe coïncide avec l'axe du propulseur (voir figure 5).

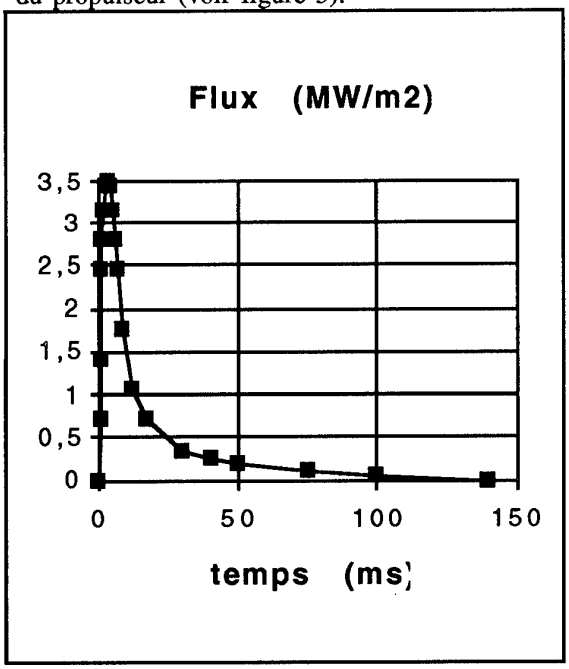



Figure 4 : Loi de flux idéalisée.

### 5.2. Sensibilité du modèle à certains paramètres [10]

5.2.1. Sensibilité au flux d'entrée

Au cours de l'utilisation du logiciel il est apparu que celui-ci était assez sensible à une variation du flux d'entrée. Une variation du flux entraînant

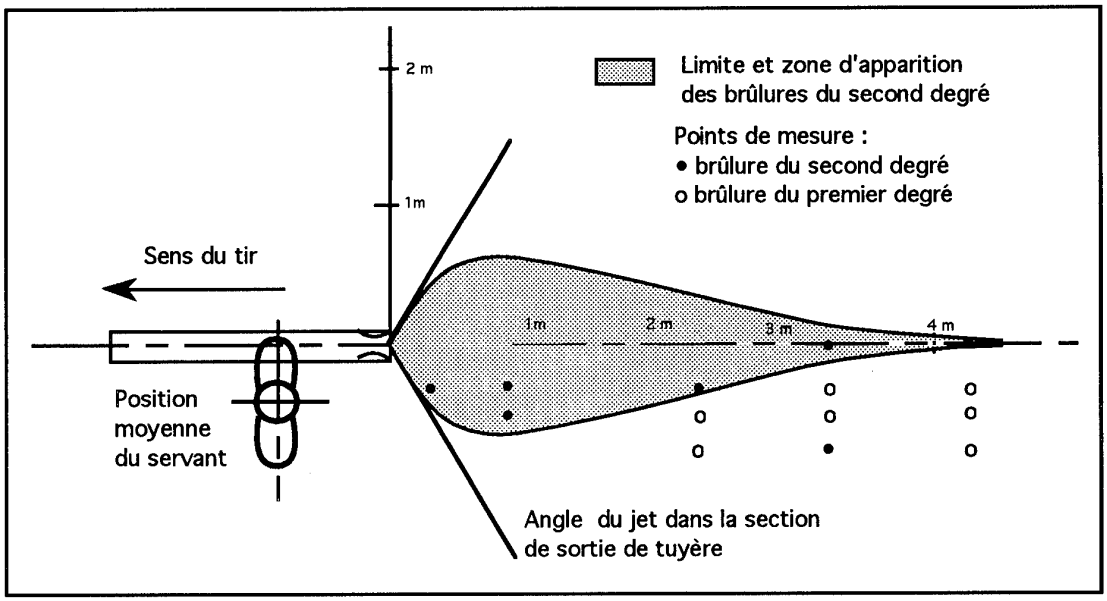



Figure 5 : Répartition spatiale de la zone d'apparition des brûlures du second degré.

une variation du même ordre de grandeur de la profondeur de la brûlure.

5.2.2. Sensibilité à la température initiale

Le code est très sensible au choix de la température initiale de la peau. Pour une variation de 3 °C de la température initiale de la peau la profondeur de la brûlure varie de 2 à 7 % pour les cas qui ont été testés. La sensibilité est d'autant plus importante que la brûlure est de faible profondeur.

5.2.3. Sensibilité aux pas de discrétisation en temps et en espace

Le logiciel est assez peu sensible aux variations du pas de temps, pourvu qu'il reste suffisamment petit pour prendre en compte les variations du flux. D'autre part, pour obtenir une précision suffisante sur le résultat de calcul, il faut que chaque couche contienne au moins 4 à 5 nœuds. Si cette condition est réalisée, le logiciel est également peu sensible au pas d'espace.

D'autre part, pour assurer la stabilité numérique du calcul il est nécessaire que la relation

$$F_i = \frac{\lambda_i}{\rho_i C_i} \frac{\Delta t}{(\Delta x)^2} < 0,5$$

soit vérifiée pour chacune des couches de la peau

5.2.4. Sensibilité à la température d'ablation

Les résultats sont apparus très peu sensibles à la température d'ablation, ce qui est heureux compte tenu de l'incertitude importante sur son estimation.

## 6. Conclusion

Un logiciel de simulation de l'atteinte de la peau lors d'une agression thermique a été mis au point. Ce logiciel utilise comme donnée le flux thermique mesuré par de petits capteurs faciles à mettre en œuvre.

Le logiciel est basé sur une modélisation du transfert thermique dans la peau et sur une loi de dégradation cellulaire qui permet d'estimer l'état des cellules après exposition à l'agression thermique.

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# ROCKET ENGINES AND ECOLOGICAL PROBLEMS

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## Introduction

Creation and employment of rocket engines and ecological problems are known to be poor compartible. Nevertheless, we must aspire to this ideal situation. All specialists recognize the effect of the combustion products of liquid- and solid- fuell rocket engines on the Earth in the local aspect. But, among the scientists, so far there is no generally-acceptable point of view as to whether or not the rocket engines affect on the Earth's environment in the global aspect. The paper analyses this problem, and presents a new unusual and unexpected point of view.

## Impacts of Rocket Engine Combustion Products

Big variety of rockets (from small ones to very heavy rockets - "Space Shuttl" and "Energia") results in big diversity of rocket engines.

The liquid rocket engines use as fuel components: nitric acid ($HNO_3$), nitrogen tetroxide ($N_2O_4$), petroleum pil, unsymmetrical dimethil hydrazine (UDMH, $(CH_3)_2 N_2H_2$ ), hydrazine hydrate ($(NH_2)_2 H_2O$), tonka - 250 ($(CH_3)_2 C_6H_3 NH_2$ (50%) + $(C_2 H_5)_3 N$ (50%)), mixture propellants (for example, UH25), liquid hydrogen, liquid oxygen and others. Exhausts of these engines contains carbon dioxide (the main greenhous gas), NO, CO, water vapour, and propellant components. Acid, tetroxide, UDMH, hydrazine hydrate are exhausted especially at the launch of a rocket, at testing of rocket engines, and at working of the turbopump rocket engines (with turbine gas exhausting).

The solid rocket engines are used two types of propellant: composite propellants (the basic type), and ballistite propellants produced axhaust gas containing $CO_x$, $NO_x$, chlorine, Al, chlorides, chloric acid, sulphate acid, sulphates, and small hard particles (for example, the Shuttle side-mounting boosters produce several

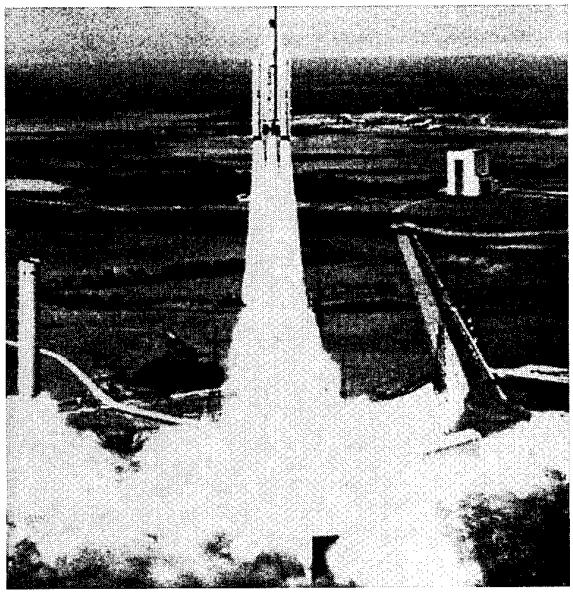


Fig. 1. The launching pad.

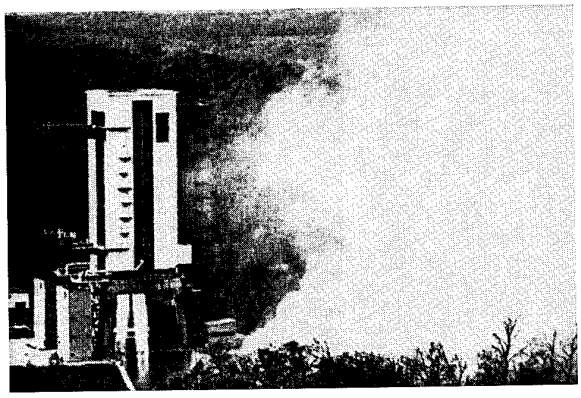


Fig. 2. Testing of the rocket engine.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

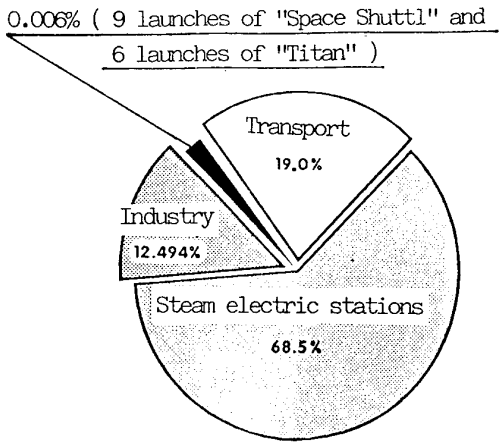



Fig. 3. Annual blow-out of substances effecting formation of acid rains in the atmosphere of the continential region of the USA.

tons of chloric acid and hard particles per second). The exhausted components is known to be dangerous for the environment. The most important ecological impacts include as follows.

1. The pollution and contamination of the territories adjacent to a launching pad ( which can be vast for the heavy-lift rockets, Fig. 1).
2. The pollution and contamination of the territories adjacent to a testing stand especially when the combustion products are exhausted in atmosphere directly ( Fig. 2 ).

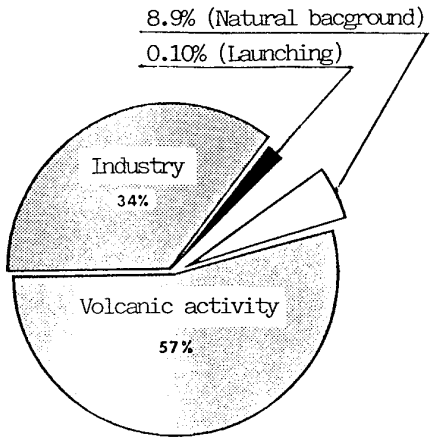



Fig. 4. Annual blow-out of substances effecting atmospheric ozone destruction.

3. The formation and acid rainfalls in vast areas adjacent to launching complexes. For example, Fig. 3 presents the data showing annual blow-out of substances effecting formation of acid rains in the USA [ 1 ]. Besides, we must understand that rocket and propellant productions are included in the three other parts.
4. The exausted products of liquid and solid rocket engines ( chlorine, chlorides, chloric acid, aluminium oxide, small hard particles ) cause depletion of the ozone layer. Fig. 4 shows annual blow-out of substances effecting atmospheric ozone destruction [ 1 ].
5. The very hot and powerful jets exhausted from engines of heavy-lift rockets can cause atmospheric instabilities and formation of cyclonic patterns. This impact is believed to be dangerous for unsteady weather regions.
6. The exausted products containing $CO_2$ ( the main greenhous gas ), $NO_2$ promote to distortion of the greenhous effect. This impact can be appreciable in consequence of numerous launches of big rickets.

The factors 1 - 3 and 6 are especially dangerous for northen regions because of very vulnerable and sensitive northen nature.

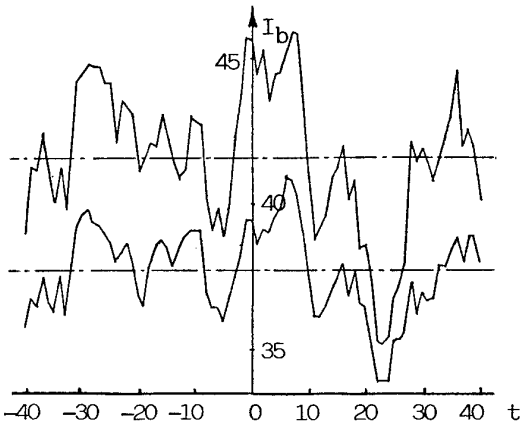



Fig. 5. Average-statistical data showing change of $I_b$ for the equipotential surface $0.5 \cdot 10^5$ Pa ( $I_b$ - the Blinova's index; t - time (day&night) counted from the average-statistical launch of "Space Shuttl" ).

The above-mentioned factors have the local (1-3) and global (4-6) effects.

There are some important questions having a lot of public and practice interest. It is interested to know whether or not the exhausted products emitting into the atmosphere will give fearful local and global impacts. As to the local impacts, scientists agree that the "local acid and toxicity effects are limited to within a half mile of the launch pad ..." [2]. The global impact is concerned with respect to the decreasing concentration of ozone only. Among scientists, so far there is no generally-acceptable point of view as to whether or not the exhaust of rocket engines affect on the Earth's environment in the global aspect [1 - 3]. Moreover, the AIAA conference ("A Chemical Rocket Propulsion and the Environment", June 1991) have confirmed the well-known point of view that rocket engines do not produce a dangerous effect on the Earth and the environment. A.McDonald [2] affirmed, "... there were no data presented to the contrary".

However, we have disposed of so data, which will be analysed further in this paper.

## Heavy-lift Rocket Launches: The Unexpected Detrimental Impacts

The launching of a heavy-lift rocket causes formation in troposphere, stratosphere, and

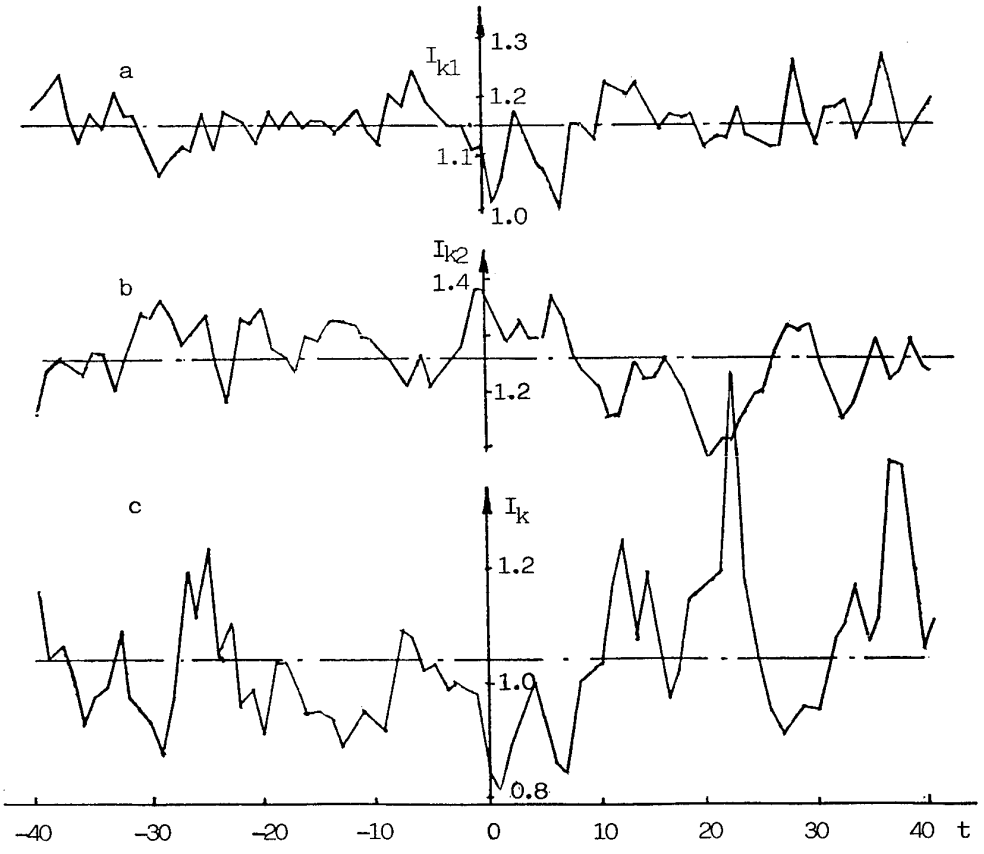



Fig. 6. The non-central and non-normalized statistical mutual correlation functions of the "Space shuttle" launches in Florida in 1981 - 1985 ( $I_k$ - the Kats' index for the equipotential surface $0.5 \cdot 10^5$ Pa and the average latitude range; t - time, the same as in Fig. 5; a - $I_{k1}$ - the meridional circulation index; b - $I_{k2}$ - the zone cirkulation index; c - $I_k$ - the overall index ).

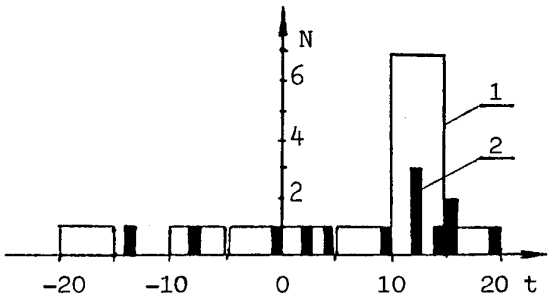



Fig. 7. The Kats' index ( 1 - the average five-day&nights overall Kats' index for the realizations; 2 - a day&night maximum values of the overall Kats' index for the realizations; t - time, the same as in Fig. 5).

lower mesosphere of a huge wake. It overall mass for heavy rockets equals approximately 0.75 of the full rocket mass. For example, "Saturn - 5" had the full launching mass $m_0$ = 2,800—3,000 t with the construction mass $m_c$ = 180 t.Therefore, the full wake mass was more than 2,600 - 2800 t. "Space Shuttl" has $m_0 \approx$2,000 t. Two solid propellant engines exhaust to the atmosphere up to the height 100 km 300 t of small hard particles, sulphates, and water vapour (700 t), which can produce 3,800 t of sulphate acid.

The engines of the heavy-lift "Energia" produce 2,000 t water vapour. These huge wakes can promote dangerous processes in the atmosphere [4]:

- formation in troposphere of a lifting convective flow, which has huge heat energy;
- interaction of combustion products with the convective flow, and formation of a huge sulphuric acid cloud;
- turbulent and heat diffusion of this cloud;
- transfer of the cloud by wind;
- interaction of this cloud with moist layers in troposphere;
- arising unsteady zones in troposphere;
- formation of a cyclonic pattern;
- sinking of the cloud from stratosphere to troposphere causing fluctuation modes in vertical direction; this effect can stimulate an earthquake.

S. Ribnikov [4 - 6] has analysed many statistical data for launchings of "Saturn - 5", "Space Shuttl", "Energia. The results of his analysis are presented here in Fig. 5 - 9.

Fig. 5 presets the results of the average-statistical data showing change of the Blinova's index $I_b$ |7| before and after the average-statistical launch of "Space Shuttl". The Blinova's index defines the intensity of zone atmospheric circulation. The sharp changes of $I_b$ coincide with the changes of average atmospheric pressure in the zone. The change of pressure acts onto the underlying zone of lithosphere, and can cause seismic processes. The graph displays the 1.5-multiple increase of $I_b$ and the 29-th (day&night) period after the average-statistical launch.

Fig. 6 presents the average-statistical Kats' index [8] for the 1-st region (the northen part of the Atlantic Ocean, Europe, and the part of west Asia) for the equipotential surface $0.5 \cdot 10^5$ Pa ( $35^o$ - $70^o$ of latitude North ). The curves

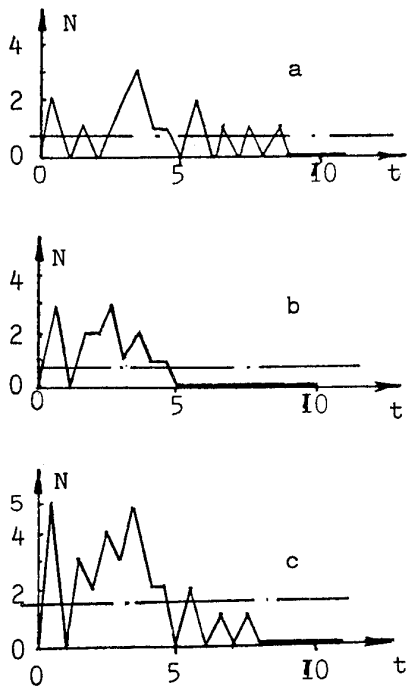



Fig. 8. The summer (a), winter (b), and overall (c) graphs of the cyclones formed in the big region with the center at the east Florida's coast ( t - time, the same as in Fig. 5 ).

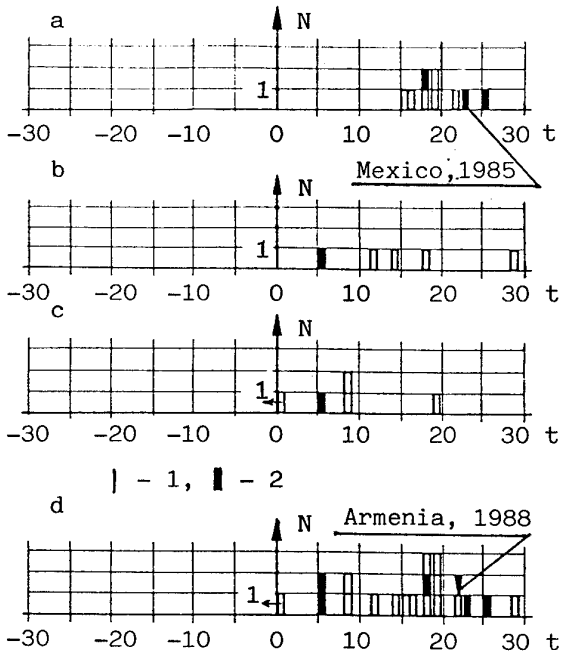



Fig. 9. The powerful and most powerful earthquakes for the three America's regions: a - Mexico, b - California, c - Alaska, d - the overall graph ( 1 - a powerful earthquake, 2 - a a most powerful earthquake; t - time, the same as in Fig. 5).

indicate onto the growth of atmospheric macroturbulence after the average-statistical launch.

The combined graphs of the overall Kats' index ( for 13 realizations, for the 1-st region, and for summer ) are presented in Fig. 7. The first graph shows average five-day&night values. The second one defines the average-day&night Kats' index. These graphs indicate that the wind has turned to north for t = 10 - 15 day&nights.

Fig. 8 shows the suumer, winter, and overall graphs of the cyclones formed in the big region with the center at the east Florida's coast after the average-statistical launch of "Space Shuttl". The graphs display increasing of cyclone formation ( more than one additional cyclone per a average-statistical launch ).

Very important data are presented in Fig. 9. The powerful ( $M \geq 6$ ) and most powerful ( $M \geq 7$ ) earthquakes are shown as function of time before and after the launchings of "Saturn - 5" and "Space Shuttl" for the three seismic regions: Mrxico, California, Alaska. Eighteen powerful earthquakes ( including five most powerful ones) have occured in a month after the launchings. Besides, the Armenia's earthquake ( 1988 ) is shown here. It occured in 22 day&nights after the launch of "Energia - Buran".

## Conclusion

The data presented here gives very important information. At first sight it may seem to be a very dispirted ones. But, it is clear that the problem is not researched sufficiently yet. Therefore, having many reliable data, we will can formulate suitable recommendations ( for example, in respect of a launching pad place ). Nevertheless, we assume that some steps may be made at present ( for example, development of new less dangerous propellans; rejection from dangerous solid propellants; conversion to engine testing stands without exhaust of combustion products into atmosphere directly ).

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# Destruction of Propellant Wastes Using Molten Salt Oxidation

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## 1. ABSTRACT

Molten Salt Oxidation (MSO) is a safe and environmentally acceptable technology for the disposal of energetic waste materials. Initial experiments carried out more than 20 years ago have been supplemented recently with additional work and process improvements. Destruction of energetic materials is nearly quantitative under the current design conditions. The applicability to specialized ordnance wastes is currently under study. These wastes contain a series of chemical elements that are inappropriate to feed to more conventional destruction devices such as incinerators.

## 2. INTRODUCTION

Molten Salt Oxidation (MSO) is a safe and environmentally acceptable thermal treatment process for many materials including waste streams. Figure 1 displays a typical system schematic. For the treatment of ordnance materials as a waste stream, the materials are catalytically destroyed in a molten bed of inorganic salts, such as sodium carbonate. The waste materials are injected in a suitable form, usually with air (for oxidation), below the surface of a molten salt bed at 800 to 1000°C. The high temperature and catalytic character of the molten salt bed causes the thermal decomposition and oxidation of the waste material. The products of thermolysis are readily controlled by adjustment of the fuel-air mixture in the feed system. Typically, carbon and hydrogen go to carbon dioxide and water, respectively, while nitrogen is released as pure gaseous nitrogen or trace levels of nitrogen oxides. Halogens are converted to the corresponding halide salts in the salt bath, while metals are converted to metal oxide ash, alkali oxide complexes, or the elemental metal, depending on the oxidation potential of the metal, and are retained in the melt. The efficiency of the oxidation is a function of the feed rate, salt temperature, and fuel-to-air ratio used in the operation. Destruction efficiencies greater than 99.999% have been achieved by careful control of these variables.

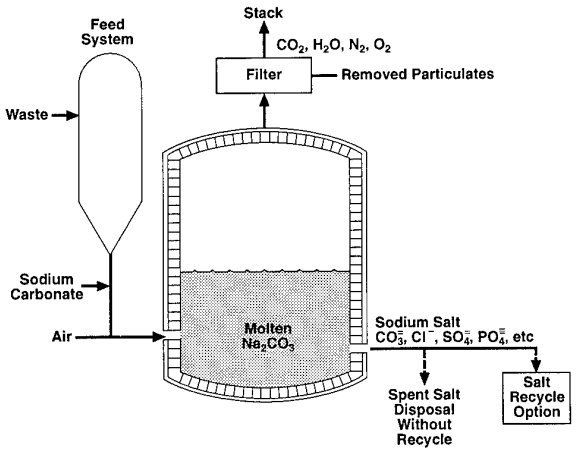



**Figure 1. Molten Salt Oxidation System**

The MSO process for a wide spectrum of applications has been demonstrated on laboratory (1-10 lb/hr), pilot (100-300 lb/hr), and demonstration (2000 lb/hr) scales. Over the last 30 years MSO has been tested and operated for the disposal of explosives and propellants, chemical warfare agents, hazardous wastes and radioactive wastes, flue gas desulfurization, coal gasification, and other applications.

MSO offers the potential benefit of application as a recycling process or for recovery of metals, chemicals, and heating value from various feed stocks. Recovery of silver metal from photographic negatives (1-2 wt% silver) has been demonstrated in processing more than 10,000 lbs of negatives. The silver recovered was 4 nines pure and accepted by the San Francisco Mint without additional refining. Similarly, copper, lead, and aluminum recovery have been demonstrated on the bench scale. Vanadium oxide recovery from crude oils also has been demonstrated. Molten salt gasification of Kraft black liquor has shown that MSO technology can both produce a combustible fuel gas and achieve good sulfur reduction to sulfide. Gasification of a large number of materials has shown that MSO is an excellent technology for the conversion of organics to a clean, low-BTU fuel gas, permitting the recovery of the heating value in many otherwise difficult-to-handle materials. In summary, MSO spent salt can be processed to recover metals or salt compounds, and the off-gas can be processed to recover the heating value.

## 3. PREVIOUS EXPERIENCE WITH MSO DESTRUCTION OF ORDNANCE ITEMS

Rocketdyne has examined the suitability of MSO for the destruction of solid propellant and explosive compositions since 1972.

The first program was carried out under U.S. Navy funding and was designed to determine the parameters for rapid,

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nondetonating destruction of typical propellant compositions and explosive materials in the DOD inventory. Full propellant compositions were chosen for this study instead of discrete ingredients to be representative of the actual materials in the inventory needing disposal. The seven propellant compositions, four explosive compositions, and four pure materials used in these tests are listed in Table 1.

**Table 1. Composition of Ordnance Materials**

| Composition ID | Ingredients | Composition (wt %) |
|---|---|---|
| **Composite Propellants** | | |
| Propellant A | AP/Al/HTPB | 72/13/15 |
| Propellant B | AP/PBAN/Epoxy curative | 75/19/5 |
| Propellant C | AP/PTFE/VITON/Al | 50/15/15/20 |
| Propellant D | RDX/BDNPA-BDNPF/PEG/TDI | 75/19/5/1 |
| **Double-Based Propellants** | | |
| Propellant E | AP/HMX/NG/NC/Al | 5/26/32/15/18 |
| Propellant F | NC/NG/DEP/Inerts | 30/35/10/5 |
| Propellant G | NC/TMETN/TEGDN/Inert | 46/41/10/3 |
| **Explosives** | | |
| Composition B | RDX/TNT | 60/40 |
| HBX-3 | RDX/TNT/Al/wax | 31/29/35/5 |
| H761 | RDX/Al/wax/Graphite | 62/35/2/1 |
| H762 | HMX/Ca-resinate/Graphite/Zn stearate | 97/1.5/1/0.5 |
| TNT | TNT | 100 |
| Tetryl | Tetryl | 100 |
| RDX | RDX | 100 |
| HMX | HMX | 100 |

In more than 600 tests with these materials at scales from 5 to 1000 grams, the energetic materials were destroyed without detonation or any other serious incident.

To determine the effect of temperature on the course of the oxidative destruction process, mixed salt beds were prepared with lithium, sodium, and potassium carbonates (1:1:1) for temperatures from 500 to 800°C, and sodium and potassium carbonate (1:1) for temperatures from 800 to 1000°C. Initial small-scale tests determined that destruction speed and efficiency were improved with increasing temperatures, so that larger scale tests were carried out with the binary mixture at 800°C.

In all of the tests, these solid energetic materials were introduced directly to the molten salt bed. Two modes of addition were investigated. Initially, the materials were dropped onto the surface of the salt bed with and without added combustion air, where they were observed to burn cleanly with luminous flames. The second (and preferred) mode of addition was mechanical injection of the materials below the surface of the melt. This subsurface injection with added air was most successful in the case of small samples (<100 grams) relative to the size of the melt bed of halogen-containing compositions. Subsurface destruction of larger samples (250-1000 grams) generated large volumes of gaseous products that caused ejection of molten salt from the crucible. Subsequent work has shown that this reaction behavior is readily eliminated by control of feed rate.

In small-scale tests, the off-gases were collected in sampling bags and were analyzed for $CO_2$, CO, $NO_x$, hydrocarbons, HCl, and HF (if appropriate) so that quantitative measures of the mass of pollutant per mass of energetic could be determined. The evolution of HCl and HF were noted only in the tests where halogenated propellants were oxidized on the surface of the molten salt or for large samples that exceeded the capacity of the salt bed. In these cases, escape of the acid gases was too fast to be scrubbed by the basic salt bed. $NO_x$ evolution rates depended on the temperature of the process, the type of propellant, and the amount of air (or oxygen) added to the oxidation zone. Reducing the amount of combustion air resulted in lowered $NO_x$ levels, but at the expense of increased $CO/CO_2$ ratios. Samples of the salt bed indicated that the metals (Al and Zn) were retained in the salt bed as their oxides. These data are qualitative because the oxides were not uniformly dispersed in the salt, making a truly representative sample impossible to obtain. Typical emission levels for these energetics are illustrated in Table 2.

**Table 2. Emission Levels From Treatment of Energetic Materials**

| Species Measured | Level Emitted (per tons of propellant) |
|---|---|
| $NO_x$ | 5 kg/mt |
| CO | 2-15 kg/mt |
| Hydrocarbons | 0.5-5 kg/mt |
| Halogens (as HCl & HF) | <4 kg/mt |

Halogen-containing materials present an additional problem that will need to be addressed before a large-scale plant is put into operation. With subsurface feed of the materials, the carbonate salts effectively scrub any acidic gases (i.e., HCl and HF). While NaCl is benign in the MSO environment, NaF is reactive at the 1000°C operating temperture and causes attack of the MSO unit ceramic liner. One solution to overcome this problem is to add calcium carbonate to the molten salt bath, preferentially forming calcium fluoride. It has been shown that calcium fluoride effectively ties up the fluorine, thereby preventing reaction with the refractory liner. Sequestering the fluoride in this fashion significantly prolongs the life of the MSO reactor and can dramatically reduce the level of HF in the off-gas.

On the basis of these data, a plant was designed for the destruction of a simple aluminized propellant (Propellant A) at a rate of 200 lb/hr. It is estimated that the cost of destruction would be $0.78/lb. This estimate included the cost of the MSO unit and its feed systems along with operating costs, but did not include the cost of removing the propellant or explosive from containment, reducing the solid materials to a size suitable for feeding the MSO unit, or the subsequent disposal of the used salts. These additional costs are expected to less than double the total costs, but are dependent on the specific ordnance items being treated.

In recent studies, data were acquired on the destruction of individual propellant and explosive species. Furthermore, a means of destroying a liquid stream of energetic materials under controlled conditions was addressed as the waste stream from propellant formulation operations is frequently such a solution or slurry. A series of tests was undertaken to determine the best means of feeding such a stream and measuring the effluents from such a stream fed to a pilot-scale MSO unit.

It was readily determined that typical gun propellant materials could be solubilized because the cellulosic binders (nitrocellulose and cellulose acetate butyrate) are readily soluble in a variety of solvents including acetone. More extensive studies were needed and were conducted to determine a means of dissolving typical polyurethane propellant systems. The preferred solvent system consisted of mono-ethanolamine, which chemically broke the polymer matrix and isopropyl alcohol/toluene to dissolve the residual mass. Both types of solubilized propellants were pumpable thin slurries of the residual insoluble solids such as AP, Al, RDX, and HMX. Typical total concentrations of the energetic materials in the solvent are less than 10%.

Baseline MSO tests with the two solvent systems were initiated as well as tests with an acetone solution of nitrocellulose and a slurry of RDX in acetone. The liquid feed was introduced below the surface of the molten salt with an excess of combustion air to ensure complete destruction of the organic feed. The initial results of these tests indicate that this method of destruction is practical and will be environmentally acceptable. Under oxidizing conditions, the nitrogen-containing feeds had measured emissions of less than 30% $NO_x$ and greater than 70% $N_2$. Similarly, levels of CO have been low and could be controlled by increased operating temperature and adjustments to the combustion air stoichiometry.

## 4.0 FUTURE APPLICATIONS OF MSO

The Rocketdyne work clearly demonstrates that MSO technology is generally well suited for the destruction of propellant materials. However, there are cases where it would not be the method of choice. Examples include the destruction of materials that are efficiently and cleanly burned to harmless species such as $CO_2$, $N_2$, and $H_2O$, such as hydrazines, nitrogen tetroxide, and nitrocellulose-based gun propellants. In these instances, greater efficiency can be achieved by processes such as controlled combustion in rotary kiln incinerators. Another example using an alternative method is the simple solid propellants containing aluminum, ammonium perchlorate, and hydroxy-terminated polybutadiene. Current technology such as water jet demilitarization and recovery of the AP values is considered a more suitable approach than destruction of the propellant as waste in these instances.

Several other "specialized" areas of ordnance wastes especially lend themselves to the use of the MSO process, whereas alternate processes are expected to result in unsatisfactory and unacceptable gaseous emissions. These include:

a. Liquid-propellant oxidizers containing high levels of fluorine ($ClF_3$, $ClF_5$, $BrF_5$).
b. Liquid-propellant fuels based upon boron hydrides ($B_2H_6$, $B_5H_9$, and $B_{10}H_{14}$ – derivatives).
c. Explosives containing terminal dense, energetic groups ($-SF_5$ and $-CF(NO_2)_2$).
d. Chemical intermediates such as $NF_3$ and $N_2F_4$.
e. Smoke compositions containing elemental phosphorus, sulfur, hexachloroethane, and others.
f. Flare compositions containing high levels of fluorinated polymers and metals such as magnesium.

Table 3 illustrates the typical byproducts formed and the relative amount of carbonate salt required based upon each molar unit of the specific element present.

**Table 3. Carbonate Requirements for Selected Elements**

| Element | Byproduct | θ* |
|---|---|---|
| B | $Na\ BO_2$ | 4.90 |
| P | $NA_3PO_4$ | 5.13 |
| S | $Na_2S/Na_2SO_4$ | 3.31 |
| F | $CaF_2$ | 2.63 |
| Br | NaBr | 0.66 |

*Grams of carbonate/gram of element

An additional area where the MSO process can be used is for beryllium propellants and beryllium metal/hydride wastes. The bulk of the propellant ingredients would be converted in the same manner as previously observed for aluminized propellants, whereas the beryllium species would be converted to BeO and $Na_xBe_yO_z$.

Many older double-base propellants contain lead (Pb) burn rate modifiers. Use of MSO for processing these systems introduces an added parameter into the operation, that is, the dissociation of the molten PbO into gaseous $Pb_xO_y$ off-gases. Thermochemical equilibrium calculations indicate that the degree of dissociation (D) can be expressed by the equation:

$$D = 5.1 \times 10^6 \exp[-27145/RT].$$

If the level of dissociation is to be maintained below 1%, an operating temperature below 612°C would be required. This would suggest the use of mixed carbonates and slower feed rates to maintain the same kinetics of destruction of other ingredients.

## 5.0 SUMMARY

The Molten Salt Oxidation (MSO) process is well-suited for application to a wide spectrum of specialized ordnance wastes. Many of the more standard types of ordnance wastes are more efficiently treated by other processes even though the MSO process would be very useful in treating such wastes.

## Discussion

QUESTION BY H. SCHUBERT : Do you measure dioxin concentration in the exhaust ?

ANSWER : Dioxin measurements have not been made in the exhaust stream of an MSO unit to date, but this very significant data will be available soon. The DOE has commissioned MSO work to be done at three of its separate national laboratories to get independent, third party data on DRE's of halogenated feeds, dioxin and furan formation, and products of incomplete combustion, IC's. This data is to be made available in the next six to eight months.

QUESTION BY H. SCHUBERT : What is the maximum particle size you can accept if you have a solid feeding system and explosive materials ?

ANSWER : The present feed system and injection design constrains would limit the maximum particle size to approximately 0.5 inches or 1.3 centimeters. Conceptual modifications to the feed system design may be able to increase this limit to 1.0 inch (2.5 centimeters) or larger depending on the inside diameter of the salt reactor. Tests have been done with the maximum sized individual pieces in the 1 to 2 kg range.

QUESTION BY H. ROSENDORFER : Can you tell something about the ratio of carbons produced per unit of waste material in the MSO process ?

ANSWER : The oxidation of carbon in the waste fed a MSO process produces the same ratio of carbon dioxide per unit of waste material as in conventional incineration processes with the exception that conventional processes, in general, would require the use of auxiliary fired carboneous fuel, increasing the amount of carbon dioxide per unit waste. As to the neutralization of acid gas components in the waste feed, in the MSO process carbon dioxide is released when the acid gas components react with the alkaline carbonate salt. Whether or not this adds a net burden or carbon dioxide to the environment over conventional incineration depends on many factors such as whether the carbonate source is naturally mined or synthetic, the source of alkaline reagent used in the conventional process, the amount of acid gas components in the waste feed, etc... One would need very specific examples of feed material and process operation to make a meaningful comparison.

# A COMPLETE RESOURCE RECOVERY SYSTEM FOR SOLID ROCKET PROPELLANTS*

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## 1. SUMMARY

Open burn and open detonation (OB/OD) are currently the methods of choice for disposal of Class 1.1 and Class 1.3 explosive materials. OB/OD methods dispose of the combustion by-products through dispersal into the air and the burial of any residual ash with no recovery of materials other than possibly scrap metal. This paper describes a system which controls emissions to regulatory requirements or below, recovers materials for reuse or recycling, and is designed to be an environmentally acceptable alternative to OB/OD.

This three step process removes the energetic material from its container using high pressure water; desensitizes the removed material, making it suitable for thermal treatment; and then disposes of the remaining material in a specially designed incineration system. Test operations completed to date using Class 1.3 solid rocket propellant have demonstrated that this process can recover approximately 90% of the starting mass, providing revenue to offset the cost of operation. Recovered materials were ammonium perchlorate (70%) and aluminum oxide (20%) in these tests. The waste stream is the 25% salt solution from the caustic scrubbers which amounts to approximately one gallon (3.8 $dm^3$) per 250 pounds (113 kg) of material thermally treated.

All tests have been conducted under the auspices of research, development and demonstration permits granted by federal, state, and local agencies. System development has proceeded along a logical course consisting of equipment development, worst case testing, and optimization. The current status of the system development is shown in Table 1. A fully permitted facility is planned to be operational in 1995.

## 2. INTRODUCTION

Open burn and open detonation (OB/OD) have been the traditional disposal methods for energetic materials because of the flame temperatures produced or the danger of detonation associated with these types of material. These methods produce clouds of noxious materials which can produce adverse environmental impacts in the disposal area as a result of the effects of local weather patterns and the structure of the disposal site. Over the years, many improvements have been made in our ability to predict local weather conditions and to construct burn pads that will contain the effects of the resultant residue; however, air emissions remain unchanged and the cost of maintaining the burn areas continues to increase.

**Table 1. Development and demonstration of the Resource Recovery System Was completed in 1993**

| Technology | Development | Worst Case | Optimization |
|---|---|---|---|
| Propellant Removal | | | |
| Class 1.3 | √ | √ | √ |
| Class 1.1 | √ | √ | 8/93 |
| Feed Preparation | | | |
| Class 1.3 | √ | √ | √ |
| Class 1.1 | √ | √ | 5/93 |
| Thermal Treatment | | | |
| Class 1.3 | √ | √ | √ |
| Class 1.1 | √ | √ | 7/93 |

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By 1986, Aerojet recognized that increasing urbanization and changes in air quality standards would create more and more restrictions on new and existing OB/OD disposal sites. A project was initiated at that time to develop an environmentally acceptable alternative to OB/OD for the disposal of the rocket propellant waste which is a natural consequence of our solid rocket motor manufacturing business located east of Sacramento, California. This foresight has been born out by the limitations being imposed on many OB/OD sites in the United States, including cessation of OB/OD operation in the San Francisco Bay area by January of 1995.

Aerojet had been developing a clean burning, negative pressure incinerator for the nuclear industry in the late 1970s to provide volume reduction through incineration of lightly contaminated materials such as paper garments, rubber gloves, and the like.[1] In addition, Aerojet had experimented with high pressure water as a means of removing propellant from rocket motors as early as 1964, and proceeded to develop the technique as a production process which has been in constant use since 1978. What remained to be done was marry the two technologies to achieve the desired alternative to open burn.

## 3. ALTERNATIVE DISPOSAL TECHNOLOGIES

Disposing of solid rocket motor propellants presents many challenges if the method selected is to be environmentally successful. Not only must the measured emissions meet the regulatory requirements, but the cost, complexity, and potential hazards and risks posed by the process itself must be considered. Basically there are three steps: removal from the container, preparation for disposal, and disposal.

### 3.1 Removal

Removal of propellant from its container can be accomplished in many ways: cryogenic fracturing, crushing, mechanical disassembly, mechanical removal, solvation, steam, high pressure fluids, etc. Aerojet has used both mechanical and high pressure water techniques successfully as production methods for more than 15 years. Studies were completed in 1980 on solvation techniques which were proved to work, but were slow and required elaborate process equipment. Other methods were evaluated at the laboratory level and found to be unacceptable for reasons of risk, cost, and/or efficiency when compared to the baseline system using high pressure water.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

### 3.2 Preparation

Preparation for disposal involves rendering the materials nonhazardous and environmentally neutral, if the material is to be disposed of by land filling, or rendering it capable of thermal treatment to reduce the volume and alter the nature of the material to meet environmental standards. Most approaches evaluated to date attempt to accomplish this step by reducing the reactivity and ignitability of the materials through the use of supercritical fluid extraction, chemical and electrochemical oxidation and reduction, dilution, solvation, microbic digestion, and others. An evaluation of these various methods resulted in the development of a water-based system that combines several of these techniques which will be described more thoroughly in Section 4.2.

### 3.3 Disposal

"Disposal of materials", as used in this text, means an environmentally acceptable end point in the treatment process which removes the material from further considerations. A number of methods have been proposed or put into place that attempt to accomplish this end: land fill; road patching material; super-critical water oxidation; cogeneration of energy; microbic digestion; and the various incinerator designs using grates, fluidized beds, hearths, and rotary kilns. Aerojet investigated the various techniques and settled on a fixed hearth incinerator as offering the best result as discussed in Section 4.3.

## 4. AEROJET DISPOSAL TECHNOLOGY

As noted in the preceding discussion, Aerojet has settled on a water-based feed preparation system that is compatible with the fixed hearth incinerator developed by Aerojet to thermally treat desensitized solid propellants. These choices were made for several reasons: safety; environmental compliance; efficiency; and both capital and operating costs, as discussed below. Figure 1 provides an overview illustration of the entire process.

### 4.1 Removal

Experiments with high pressure water have shown that controlled streams of water at pressures between 5,000 psig (34.5 MPa) and 10,000 psig (68.9 MPa) can efficiently cut and remove the various solid propellants currently in service. Various orifice sizes ranging from 0.067 inch (1.7 mm) to 0.100 inch (2.54 mm) in diameter were successfully tested at pressures up to 15,000 psig (103.4 MPa) using translating and stationary test configurations.

To determine the initiation thresholds for the various materials, test samples were provided to the University of Missouri at Rolla where a test devised by Professor David Summers, called the Derringer Test, was performed. The results indicated that the pressures selected were well below the initiation energy level required to ignite or detonate the materials, when using water, which is consistent with the experimental data and operational experience generated by Aerojet. Aerojet continued this work under U.S. Navy Contract N00174-92-C-0031 to demonstrate this technology on Class 1.1 solid propellants currently in the U.S. Navy disposal inventory. Additional propellant types have been procured from other sources, including full scale motors, to demonstrate the proven Class 1.3 removal technique on Class 1.1 materials.

### 4.2 Preparation

Because of the different propellant formulations and materials used, Aerojet has tested four different approaches for propellant desensitization: water extraction, chemical neutralization, electrochemical conversion, and dispersion. Since the latter three are the subject of patent applications, only the water extraction method will be discussed at this time.

As shown in Fig. 2, the removal ("hogout" facility) is tied to the feed preparation equipment so that the transfer of solid and liquid materials can be accomplished in an efficient manner. By using a reverse flow of fluid, low concentrations of residual water-soluble materials will be found in the solid materials exiting the process. Optimization experiments[2] based on Taguchi Methods® were conducted to determine the type of cutters, shaft speeds, pumping rates and solution concentrations to use in the process.

A similar system is used for the Class 1.1 material with the additional desensitization step added. When required, treatment is continued using chemical, electrochemical, and dispersal methods to ensure that the resultant feed preparation material is suitable for thermal treatment.

When treating solid propellants that use ammonium perchlorate (AP) as an oxidizer, useful quantities of AP can be recovered.

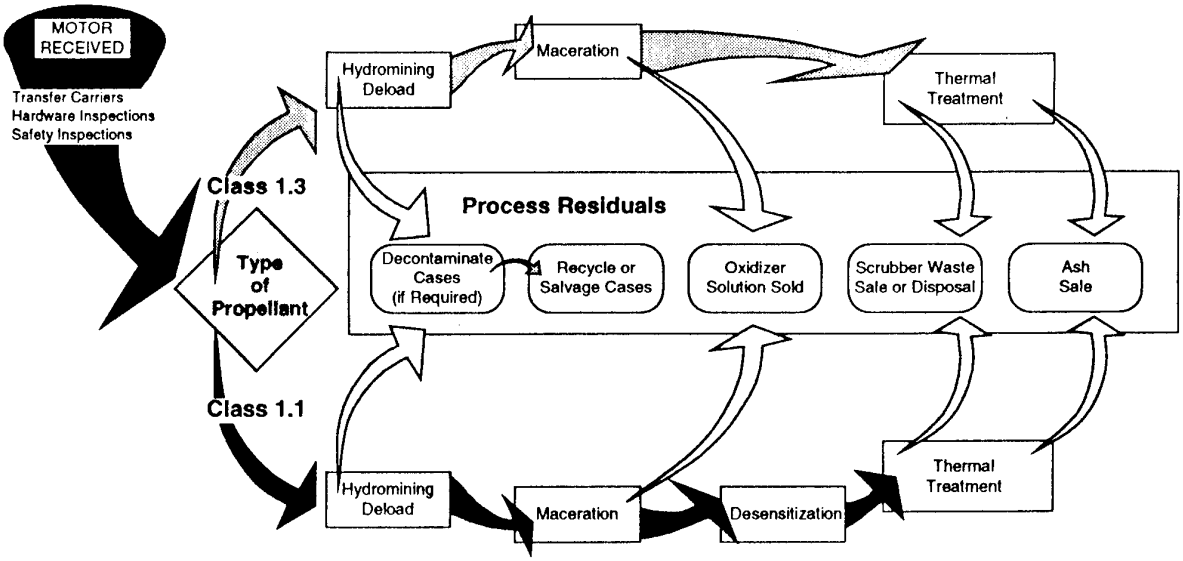



**Figure 1. Aerojet's Resource Recovery System is Designed to Safely Treat Solid Rocket Propellants and Other Energetic Materials**

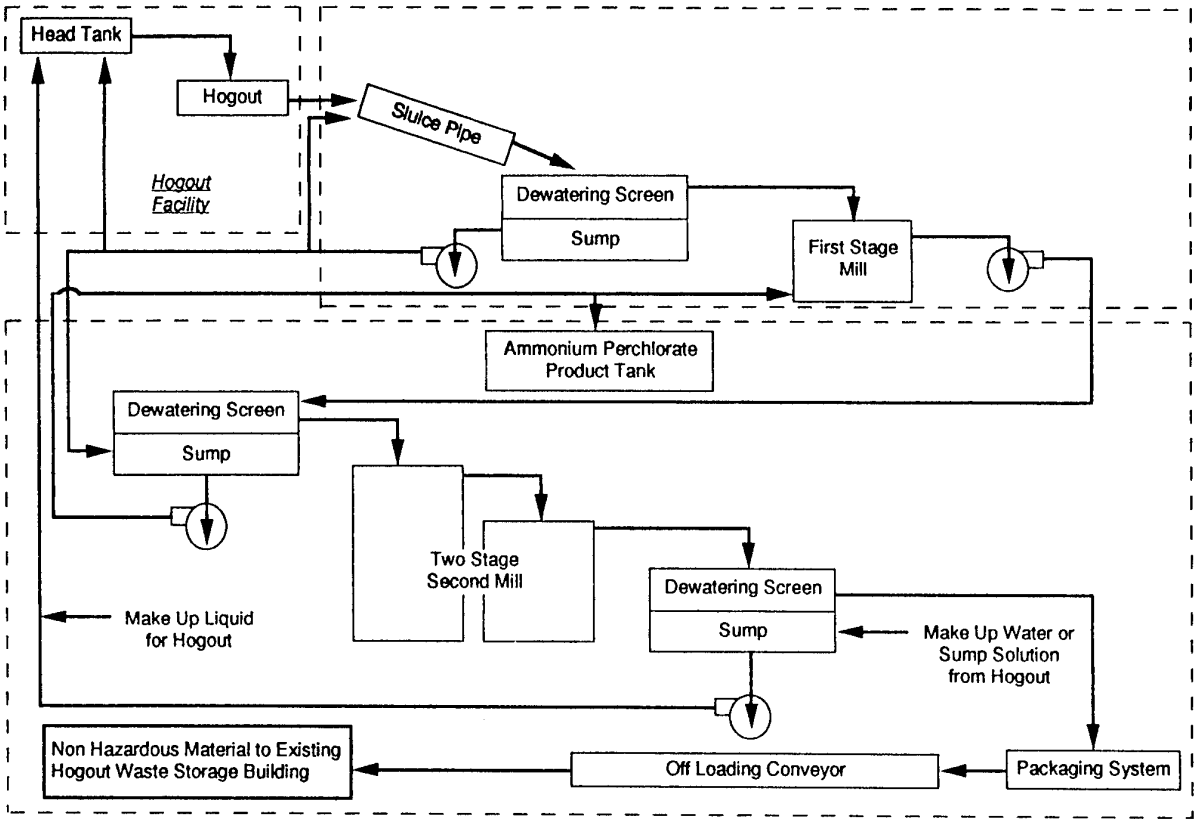



**Figure 2. Flow schematic for the solid rocket propellant removal and feed preparation system**

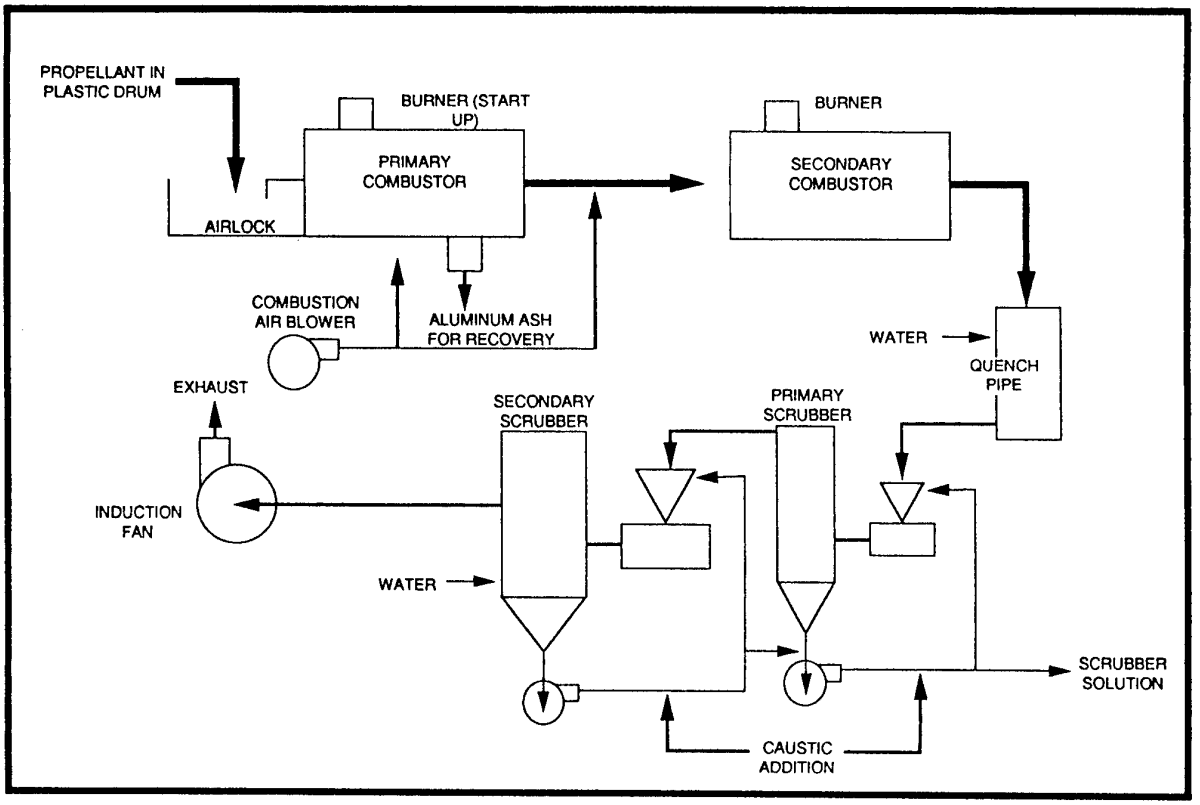



**Figure 3. Schematic of the propellant thermal process (PTP) system**

Tests have shown that more than 90% of the available AP can be recovered and recycled using this system. The extraction efficiency can be controlled so that up to 15 wt.% of the AP can be left in the solid material if required for thermal treatment efficiency.

### 4.3 Disposal

In the Aerojet Resource Recovery System, elimination of the remaining solid material left over from the feed preparation process is accomplished by the Propellant Thermal Processor (PTP) which is an incineration system especially designed for this purpose. As noted in the prior discussion, this is a fixed hearth unit designed to operate under negative pressure to eliminate fugitive emissions. It is a two stage, controlled air incinerator which is fully instrumented with a computerized control system designed to ensure fail/safe operation and optimum operating conditions, including negative air pressure, air flow, temperatures and wet off-gas cleanup system caustic levels and pH. The primary chamber operates under air limiting conditions at approximately 1010°C while the secondary chamber operates at high excess air (about 100%) at approximately 1150°C. It is equipped with tandem liquid scrubbers that provide scrubbing efficiencies capable of limiting particulates to less than 1.0 micron with a 95% efficiency at 0.5 micron, a necessity imposed by its original design for the nuclear industry where HEPA filters were required on the output.

Backup electrical power is supplied by an electric generator driven by an engine that operates on the same fuel as the incinerator burners. In addition, compressed air can be provided from either of two compressors to ensure uninterrupted availability. Other key equipment elements are also provided with alternative sources to ensure that any interruption of power, fuel, or incineration cycle can be smoothly transitioned to an emergency shutdown if required. To guard against other potential types of system failure, critical circuits are hard wired to the control panel so manual control can be exercised when all else fails. Figure 3 is a schematic of the PTP.

Another optimization test series, using propellant feed material containing 15 wt.% AP (feed preparation upper limit), was completed in November 1991 to determine the optimum operating parameters that will minimize those emissions controlled by regulations. This was preceded by a "worst case" equipment test in November 1990, when propellant containing ~37 wt.% AP was used as the feed material for the PTP. Both tests showed that the equipment was capable of controlling emissions to acceptable levels, and that optimization of feed material charge size, feed rate, moisture content, and fuel selection could produce significant reductions in gaseous emissions and particulates (Table 2) while allowing for improvements in feed rate. When optimized for minimum production of dioxins and furans, the feed stream was computed to be composed of 30 pound (13.4 kg) charges in 5 gal (19-liter) polyethylene containers containing ~40 wt.% moisture introduced at a feed rate of 250 pounds (113.6 kg) per hour for desensitized propellant containing approximately 15 wt.% AP.

Figure 4 provides an indication of how the production of dioxins and furans are affected by the presence of particulate matter in the PTP gas stream.[3] The correlation coefficient for the linear regression shown is 0.876, which is quite good. Figure 5 is a graphic presentation of the related experimental data analysis illustrating how Taguchi Methods® can provide valuable insight into the effect of operating parameters on such things as the production and minimization of dioxins and furans.

**Table 2. Comparison of Selected Test Results Shows That Significant Emission Reductions Can Be Achieved Through Fuel Choice and the Selection of Feed Stream Parameters**

| Item | November 1990 | November 1991 | |
|---|---|---|---|
| Fuel | Propane | Propane | Natural Gas |
| Feed Rate (kg/hr) | 86.2 | 109.3 | 138.8 |
| Charge Size (kg) | 18.1 | 13.6 | 13.6 |
| Moisture (wt.%) | 50 | 37 | 44 |
| AP (wt.%) | 37 | 15 | 15 |
| Emissions (kg/hr) | | | |
| CO | <0.004 | 0.002 | <0.004 |
| NOx | 0.45 | 0.37 | 0.50 |
| Particulate | 0.046 | 0.015 | 0.014 |
| THC | 0.007 | <0.007 | <0.006 |
| Dioxins/Furans (kg/hr) | | | |
| Cal. EPA TEFs | $1.48 \times 10^{-9}$ | $9.25 \times 10^{-10}$ | $1.48 \times 10^{-9}$ |
| U.S. EPA TEFs | $2.34 \times 10^{-10}$ | $1.41 \times 10^{-10}$ | $2.38 \times 10^{-10}$ |
| International TEFs | — | $2.70 \times 10^{-10}$ | $3.92 \times 10^{-10}$ |

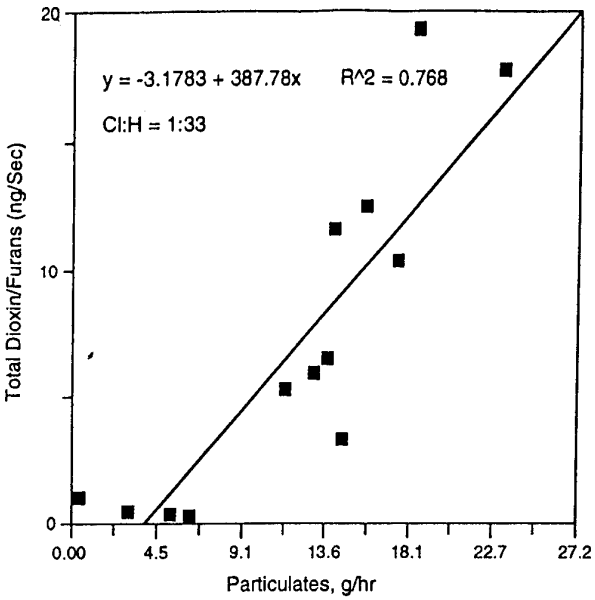



**Figure 4. Formation of Dioxins and Furans Correlated with Particulates**

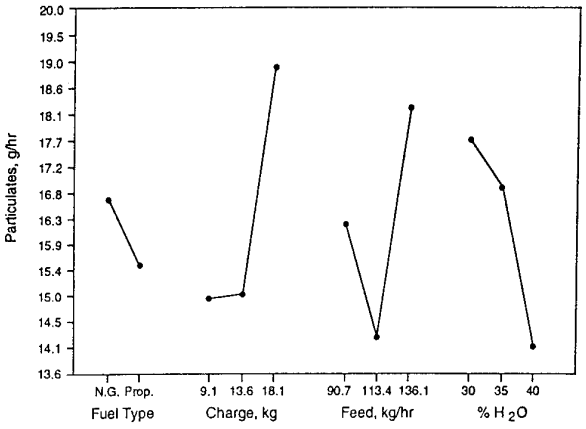



**Figure 5. Analysis of Factor Levels for Particulate Production**

When thermally treating aluminized solid propellant, over 98% of the aluminum is retained as alumina which is the ash left over from the incineration of the propellant binder/fuel material. Tests to date have shown that the recovered alumina is an acceptable material for recycling to manufacturers as a raw material for insulators, grinding compounds, and other products that use aluminum oxide.

Selection of principal organic hazardous constituents (POHCs) to demonstrate destruction and removal efficiency (DRE) for this incinerator during a trial burn was based on the requirements contained in the Code of Federal Regulations 40 CFR 270.62(b)(4), and 40 CFR 261, Appendix VIII, and the presence of these, or similar, materials in the waste to be fed to the incinerator.

After careful consideration of various Appendix VIII compounds, 1,3,5-trichlorobenzene and tetrachloroethene (commonly referred to as perchloroethylene) were selected as the POHCs. The reasons for selecting these compounds include their thermal stability ranking, similarity to various propellant constituents, commercial availability, chlorine content, and the establishment of standard sampling and analytical procedures. Tetrachloroethene is a volatile, Class 2 compound, with a thermal stability ranking of 39, while 1,3,5-trichlorobenzene is a semivolatile, Class 1 compound with a thermal stability ranking of 30-31. Classes 1 and 2 are predicted to be the most difficult to destroy of the seven Classes. Both compounds have been experimentally validated and used as DRE compounds in other trial burns.

The desensitized propellant fed to the PTP during the trial burn was spiked with 1,3,5-trichlorobenzene and tetrachloroethene. Each POHC was dispensed into 29.6 ml polyethylene bottles. Thirty grams of the trichlorobenzene, a solid, were added directly to the bottles, while the 30 grams of liquid tetrachloroethene were added to bottles containing an adsorbent using a precision repeating Eppendorf syringe. This simulated the density of the material normally fed to the incinerator.

These bottles were stored in the laboratory at 5°C until needed for the trial burn; they were then inserted through a small hole cut in the lid of the 19-liter containers of desensitized propellant and fed into the PTP during testing as part of the charge. The containers of desensitized propellant were preweighed while being packaged at the propellant desensitization processor and the weight was recorded on a process log sheet. From this information, the amount of feed charged to the unit during sampling could be determined. Results are summarized in Tables 3 and 4 based on three runs at each residence time during the Trial Burn which was completed in August of 1993.

**Table 3. Tetrachloroethene Destruction and Removal Efficiencies (DRE)**

| | SCC Residence Time (sec) | Emission Rate (kg/hr) | Input Rate (kg/hr) | DRE (%) |
|---|---|---|---|---|
| Condition 1 | 1.14 | $6.03 \times 10^{-6}$ | 0.233 | 99.9974 |
| Condition 2 | 1.48 | $5.29 \times 10^{-6}$ | 0.220 | 99.9976 |

**Table 4. 1,3,5-Trichlorobenzene Destruction and Removal Efficiencieds (DRE)**

| | Residence Time (sec) | Emission Rate (kg/hr) | Input Rate (kg/hr) | DRE (%) |
|---|---|---|---|---|
| Condition 1 | 1.14 | $1.09 \times 10^{-8}$ | 0.233 | 99.999995 |
| Condition 2 | 1.48 | $1.04 \times 10^{-8}$ | 0.220 | 99.999995 |

## CONCLUSION

A viable alternative to open burn/open detonation (OB/OD) exists today. This paper has described a complete system capable of providing an effective and efficient means of disposing of energetic and hazardous materials: It meets all environmental requirements, it provides for material recovery, it completed development and demonstration in August of 1993 with additional trial burns of Class 1.1 and Class 1.3 materials, and it will be fully permitted and operational in 1995 at costs that are estimated to be competitive with the total wraparound costs (including site remediation) associated with OB/OD disposal methods.

## ACKNOWLEDGMENTS

Successful projects are made possible by dedicated people and organizations with unique and complementary skills. Principals in the success of this program are: Stan Spas, Don Kunkle, Ren Rindone, Terry Poole, Mike Broussard, and Felix Chen for their technical expertise; Don Holkestad, Ron Hedges, Jay Glad, and Marvin Young for their ability to organize and direct technical efforts; Karen Gunderson, Roberta Tassey, Anitra Brosseau, and Pete Mendenhall for managing to successfully traverse the often confusing realm of environmental regulations and reporting requirements; and Clean Air Environmental, Inc., Steiner Environmental, and Radian Corporation for their professional execution of their third party roles in emissions data collection, analyses, and report preparation.

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2. MADHAV S. PHADKE, "Quality Engineering Using Robust Design", Prentice Hall, Englewood Cliffs, New Jersey (1989).

3. STELLAN MARKLUND, "Dioxin Emissions and Environmental Imissions. A Study of Polychlorinated Dibenzodioxins and Dibenzofurans in combustion processes", Printing Office of Umeå University, Umeå, Sweden (1990)

## Discussion

QUESTION BY R. PESCE-RODRIGUEZ : Can you give more details on the desensitization process used in your resource recovery system ?

ANSWER : The energetic material is reduced in size (maceration) below its critical diameter and then mixed in water with a desensitizing material to prevent agglomeration of the energetic material. This process uses plain water as the working/mixing medium through out.

QUESTION BY A. DAVENAS : What is the type of 1-1 propellant you can treat ; does it include binders with nitrate plasticizers ? Do you have a special treatment of the effluents in this case ?

ANSWER : We have treated NEPE (SICBM), NC/NG, CMDB, and explosives based on HMX and RDX. Our process is essentially a zero effluent process with the water being used as the processing medium and subsequently introduced into the incinerator as part of the desensitized energetic material.

QUESTION BY ROSENDORFER : I would like to know more about the commercial balance between cost for the recycling of propellant ingredients and the price for these products in selling them to reusers.

ANSWER : Each situation would provide a different set of answers, however, some general comments may be helpful. Our analysis has shown that a self funding (i.e. profitable) demilitarization process is limited to the recovery of materials at a cost that does not exceed the cost of existing virgin materials for the same application unless the process is subsidized. A 5,000 metric ton facility (yearly processing capacity) can process class 1.3 material at $ 1.50 US/kg and class 1.1 material at $ 3.00 US/kg, net cost.

# RECLAIMED AND VIRGIN AMMONIUM PERCHLORATE VARIATIONS AND HOW THEY AFFECT SOLID PROPELLANT PROPERTIES

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## ABSTRACT

Ammonium perchlorate (AP) reclaimed using the water dissolving technique developed by Thiokol Corporation was compared with the two U.S. manufactured APs in a polybutadiene-acrylic acid-acrylonitrile terpolymer (PBAN) propellant formulation. The reclaimed AP was directly substituted for the virgin materials and natural variances for the propellant mixes were established in the areas of processing, mechanics, and ballistics. The PBAN propellant formulations were scaled up to the 30-gallon mix size and 70-pound Ballistic Test & Evaluation System (BATES) Motors were cast and fired. In addition an 800-pound Super BATES motor was fired. Analyses of the reclaimed and virgin AP samples were performed to identify the chemical properties variability's. Results proved that reclaimed AP has the potential to be reused in the solid-rocket-motor industry.

## INTRODUCTION

When solid rocket motors (SRM's) have reached their service life or been scheduled for demilitarization they must be disposed of. With the increase in environmental regulations and the enactment of more stringent standards, the old method of SRM disposal, open burning/open detonation is becoming unacceptable. Various demilitarization technologies have been or are being developed. These technologies range from total destruction to partial reclamation of SRM's and motor grains. Ammonium perchlorate (AP), the main oxidizer used in Class 1.3 propellants, has been identified and demonstrated as a recyclable material. The U.S. Environmental Protection Agency (EPA) ranks recycling second to source reduction as their preferred method of waste management. The propellant can be removed from the motor case by processes such as hydromining, ammonia washout and cryofracturing. Once separated, the water soluble AP can be recovered and undergo recrystallization into the original product. As with any recycling program, the primary concern is having a market for the reclaimed material. Since the solid rocket industry currently controls 99% of the AP market, it is the most probable user for reclaimed AP.

On May 4, 1988 one of the two U.S. AP manufacturers, Pacific Engineering & Production Company of Nevada (PEPCON) was destroyed in an explosion. PEPCON later rebuilt under the name of Western Electrochemical Company (WECCO), however, at the time, the explosion reduced the U.S. capacity to produce AP by 50%. With this reduction in supply, production level missile systems which were qualified to use only PEPCON material had to be requalified using material from the remaining AP vendor, Kerr McGee. From these studies, we learned that ammonium perchlorate had varying properties depending on which vendor manufactured it. A direct substitution of one material for the other was not feasible. Systems undergoing requalification to use both materials, discovered that intraformulation ingredient percentage changes were necessary for the substitution to work. However, they did not know which characteristic differences were critical to obtaining identical propellant.

## OBJECTIVES

The objective of this paper is to show how AP reclaimed using the Thiokol process and recrystallized at the WECCO facility compares with virgin AP in a polybutadiene-acrylic acid-acrylonitrile terpolymer (PBAN) propellant formulation. To meet this objective, we compared the chemical, physical, processing, ballistic and mechanical properties of the reclaimed AP propellant to the virgin Kerr McGee and WECCO AP formulations. In addition, doping studies were conducted to determine the effects of contaminants on propellant properties and problems encountered when scaling-up from 1-gallon mixes to 30-gallon mixes were investigated.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

## RESULTS

Data from the 1-gallon mixes indicated that the reclaimed AP mix properties were better or within the values of the two virgin AP mixes in the areas of viscosity, 2"x4" motor burn rate, maximum stress, and strain at maximum stress. However, the reclaimed AP mixes had a higher 2"x4" motor burn rate exponent and a higher initial modulus than the other AP mixes. Since these mixes were performed at the ingredient percentages optimum for the Kerr McGee AP, room for tailoring with the WECCO and reclaimed APs still exists.

Data from the 30-gallon mixes indicated that the reclaimed AP mix properties were the same or within the values of the two virgin AP mixes in the areas of 2"x4" motor burn rate, maximum stress, strain at maximum stress, and initial modulus. However, the burn rates for the 70 and 800 pound BATES firings were higher but within a correctable percentage of 4.1%.

Results from the chemical analysis indicated the reclaimed AP had higher values for the following anions: chloride, fluoride, nitrate, and phosphate. The purity (in terms of perchlorate assay) of the reclaimed AP was 0.2% less than that for the virgin APs. Cation analysis resulted in higher values for the following cations: Al, Ba, Ca, K, P, Si, and Sr. No organic contaminates were detected for the virgin or reclaimed AP.

The effects of adding dopants to the mixes varied, but the two most dramatic results were caused by the anions of nitrite and fluoride. The mixes made with $KNO_2$ exhibited the "Brownie Mix Anomaly". The propellant experienced outgassing, voids, grain growth and never completed the cure cycle. End-of-Mix viscosity was the only value obtainable from these mixes. The mixes containing KF yielded propellant exhibiting small slits. The values for burn rate and exponent were the lowest of the doped mixes. For the mechanical properties values, the initial modulus and strain were the highest and lowest, respectively.

## TECHNICAL DISCUSSION

Since most solid rocket systems were qualified to use Kerr McGee ammonium perchlorate, we used this material as our baseline. We analyzed all our propellant ingredients according to the contractor's specifications. We then made a few mixes to learn the limits of our system as compared with the contractor's system and made adjustments. When we felt our technique was perfected, we made lot set mixes (a series of mixes to find the optimum percentages of each ingredient within specification limits to hit target burn rates and mechanical properties). Then we made 21 mixes. Each mix had the same ingredients except for the AP. The first seven mixes had Kerr McGee AP, the next seven had WECCO AP, and the last seven had reclaimed AP. After each set of seven mixes was complete, we prepared a 30-gallon mix using the same materials.

### CHEMICAL ANALYSIS OF VIRGIN AND RECLAIMED AP

Chemical composition studies of the APs were performed to investigate the differences in the reclaimed and virgin materials. The levels of specific anions, cations (see Tables and Figures 1 & 2) and organic species were analyzed. Anionic species were analyzed using an Ion Chromatograph (IC), cationic species were analyzed using an Inductively Coupled Plasma Emissions Spectrometer (ICP), and organic species using a Fourier Transform Infrared Spectrometer (FTIR). Before the samples were run through the FTIR, carbon tetrachloride was used to extract organics from the AP. Results from the chemical analysis indicated the reclaimed AP had higher values for the following anions: chloride, fluoride, nitrate, and phosphate. The purity (in terms of perchlorate assay) of the reclaimed AP was 0.2% less than that for the virgin APs. Cation analysis resulted in higher values for the following cations: Al, Ba, Ca, K, P, Si, and Sr. No organic contaminates were detected for the virgin or reclaimed AP.

**Table 1 Anion Analysis of AP Samples Reclaimed Using the Thiokol Process**

| Anions, % | Kerr McGee | WECCO | Reclaimed |
|---|---|---|---|
| bromate | 0.0000 | 0.0000 | 0.0000 |
| chlorate | 0.0058 | 0.0000 | 0.0000 |
| chloride | 0.0053 | 0.0013 | 0.0177 |
| chlorite | 0.0000 | 0.0000 | 0.0000 |
| chromate | 0.0000 | 0.0000 | 0.0000 |
| fluoride | 0.0000 | 0.0014 | 0.0021 |
| iodide | 0.0000 | 0.0000 | 0.0000 |
| nitrate | 0.0004 | 0.0000 | 0.0181 |
| nitrite | 0.0000 | 0.0000 | 0.0000 |
| perchlorate | 99.7000 | 99.7000 | 99.5000 |
| phosphate | 0.0000 | 0.0000 | 0.0436 |
| sulfate | 0.0000 | 0.0000 | 0.0000 |

**Table 2. Cation Analysis of AP Samples Reclaimed Using the Thiokol Process**

| Cations (ppm) | Kerr McGee | WECCO | Reclaimed |
|---|---|---|---|
| Al | 1.330 | 1.060 | 7.162 |
| As | 0.000 | 0.000 | 0.000 |
| B | 0.000 | 0.000 | 0.000 |
| Ba | 3.396 | 0.000 | 3.630 |
| Bi | 0.000 | 0.000 | 0.000 |
| Ca | 738.70 | 768.00 | 1444.00 |
| Cd | 0.000 | 0.000 | 0.000 |
| Co | 0.000 | 0.000 | 0.000 |
| Cr | 0.000 | 0.000 | 0.000 |
| Cu | 0.000 | 0.000 | 0.000 |
| Fe | 1.330 | 3.012 | 2.075 |
| K | 24.580 | 52.530 | 509.700 |
| Li | 0.000 | 0.000 | 0.000 |
| Mg | 6.434 | 7.220 | 6.803 |
| Mn | 0.000 | 0.000 | 0.000 |
| Mo | 0.000 | 0.000 | 0.000 |
| Na | 180.300 | 46.570 | 133.900 |
| Ni | 0.000 | 0.000 | 0.000 |
| P | 376.200 | 350.000 | 437.400 |
| Pb | 0.000 | 0.000 | 0.000 |
| Si | 14.260 | 13.220 | 18.170 |
| Sn | 0.000 | 0.000 | 0.000 |
| Sr | 0.735 | 0.618 | 0.758 |
| Ti | 0.000 | 0.000 | 0.000 |
| V | 0.000 | 0.000 | 0.000 |
| Zn | 0.218 | 0.000 | 0.000 |

LOT SET MIXES

Lot set mixes used Kerr McGee AP. The series of mixes performed is shown in Table 3. When making this series we plotted burn rate versus iron oxide content and maximum stress versus PBAN polymer as a percentage of the binder system to obtain the optimum percentages of these materials. The results indicated that the optimum percentage of iron oxide was 0.22% to achieve a burn rate of 0.362 inches/second. The optimum percentage of PBAN polymer as a percentage of the binder system was 86.8% to achieve a maximum stress of 110 psi.

**Table 3. Lot Set Mix Percentages**

| PBAN Polymer % | Percent Iron Oxide % |
|---|---|
| | |
| 85.8 | 0.2 |
| 85.8 | 0.3 |
| 85.8 | 0.4 |
| 87.2 | 0.2 |
| 87.2 | 0.3 |
| 87.2 | 0.4 |

TARGET MIXES

We performed target mixes after the "lot set" mixes to prove that the plotting system worked. Using the 86.8% PBAN polymer, we achieved a maximum stress value of 124.22 +/- 2.60 psi. Since we wanted a value of 110 psi, we increased the percentage of PBAN polymer to 86.9% when making the variance mixes. We achieved a burn rate of 0.3632 +/- 0.001 inches/second and decided to stay with the 0.22% iron oxide.

VARIANCE MIXES

Seven mixes each were made using the Kerr McGee AP, the WECCO AP, and the reclaimed AP. The reclaimed AP used in these mixes was recovered by Thiokol Corporation from three current propellant formulations and reprocessed through the WECCO facility. The propellant properties screened were end-of-mix (EOM) viscosity, 2"x4" motor burn rate and exponent, maximum stress, strain at maximum stress, and initial modulus. We did not have the rheometer software to obtain potlife data during the variance mixes, but did acquire it later in the project.

Mixing and EOM Viscosity. Forty-four propellant batches were made in a 1-gallon Baker-Perkins flush bottom mixer. When the mixes were complete, EOM viscosity readings were taken using a Physica Rheolab model MC20 viscometer. The viscosity samples were conditioned to 145$^{O}$F and EOM viscosities were taken at the following shear rates: 0.03, 0.06, 0.25, 0.50, and 1.00 reciprocal seconds. Two full tensile slabs and eight 2"x4" motors were cast from each mix. The samples were cured at 140$^{O}$F for 96 +\- 4 hours and post cured at ambient temperature for seven days before testing. Viscosity properties for each set of seven variance mixes were averaged to give an overall value for the specific type of AP used. The reclaimed AP yielded the lowest EOM viscosity and WECCO the highest. (see Table 4 and Figure 3).

**Table 4. End-of-Mix Viscosities of 1-Gallon Mixes**

| Type of AP | Viscosity at 145$^{O}$F and 1.0/second |
|---|---|
| | |
| Kerr McGee | 16.10 +/- 0.34 kp |
| | |
| WECCO | 19.69 +/- 1.78 kp |
| | |
| Reclaimed | 12.62 +/- 4.85 kp |

Burn Rate Data. Eight 2" x 4" motors were cast and fired at ambient temperature and the following pressures: 400, 500, 600, 700, 800, 900, and two at 1000 psi. The data was reduced to obtain burn rates at the given pressures and plotted to give a linear curve fit. From this curve fit we took the burn rates at 1000 psi for the database pressure. Burn rates and exponents for each set of variance mixes were averaged to give an overall value for the type of AP used. The data showed good agreement between the virgin and the reclaimed material. The pressure exponent values for the 2" x 4" motors were slightly higher with the reclaimed AP (see Table 5 and Figure 4).

**Table 5. 2" x 4" Burn Rate and Exponents of 1-Gallon Mixes (at 1000 psi and ambient temp)**

| Type of AP | Burn rate, in/sec | Exponent |
|---|---|---|
| | | |
| Kerr McGee | 0.4252 +/- 0.0031 | 0.3212 +/- |
| | | |
| WECCO | 0.4166 +/- 0.0057 | 0.3278 +/- 0.0147 |
| | | |
| Reclaimed | 0.4233 +/- 0.0054 | 0.3339 +/- 0.0002 |

Mechanical Properties. Twelve Class C dogbone samples were stamped from the two full tensile slabs and tested on a United Mechanical Properties tester. The samples were conditioned at 77°F for four hours and then pulled at 2 inches per minute using a 500-pound load cell. The effective gage length used for the calculations was 2.6 inches. The maximum load applied was around 20 pounds. Maximum stress, strain at maximum stress, and initial modulus were measured for each sample and averaged for each mix. Then the seven mixes from each series were averaged to give an overall value for each type of AP. The data showed the reclaimed values to be within those of the virgin material with the exception of a higher initial modulus (see Table 6 and Figures 5-7).

WECCO Mixes. Variance mixes using the WECCO AP kept all aspects of mixing and testing consistent with those used during the Kerr McGee variance studies.

Reclaimed AP. When making the reclaimed AP variance mixes, the EOM viscosities were too high for proper casting. To compensate for this, we increased the AP addition mixes were too high for proper casting. To compensate for this, we increased the AP addition steps from four to six and increased AP addition mix time from 55 minutes to 85 minutes.

**Table 6. Mechanical Properties of 1-Gallon Mixes (at 77°F and 2 in/min)**

| Type of AP | Max stress (psi) | Strain @ Max stress (%) | Initial modulus (psi) |
|---|---|---|---|
| | | | |
| Kerr McGee | 128.76 +/- 4.24 | 37.00 +/- 1.10 | 639 +/- 35 |
| | | | |
| WECCO | 115.41 +/- 1.14 | 37.30 +/- 1.80 | 588 +/- 13 |
| | | | |
| Reclaimed | 118.57 +/- 4.66 | 37.20 +/- 1.30 | 655 +/- 24 |

SMALL SCALE DOPED MIXES

Doped mixes were made to show the interaction or tolerance of the propellant formulation to the contaminants found in the reclaimed AP when compared with the virgin material. The dopants were compounds of the anions and cations (with the exception of silica) identified in the chemical analysis. Dopants were added to the baseline mixes at concentrations ranging from 0.1 to 3%. The effects varied, but the two most dramatic results were caused by the anions of nitrite and fluoride. The mixes made with $KNO_2$ exhibited the "Brownie Mix Anomaly". The propellant experienced outgassing, voids, grain growth and never completed the cure cycle. End-of-Mix viscosity was the only value obtainable from these mixes. The mixes containing KF yielded propellant exhibiting small slits. The values for burn rate and exponent were the lowest of the doped mixes (see Tables 7 and 8 and Figures 8 and 9).

* "Brownie Mix Anomaly"

- Power outage, data lost

Mechanical Properties. Twelve Class C dogbone samples were stamped from the two full tensile slabs and tested on a United Mechanical Properties tester. The samples were conditioned at 77°F for four hours and then pulled at 2 inches per minute using a 500-pound load cell. The effective gage length used for the calculations was 2.6 inches. Maximum stress,

strain at maximum stress, and initial modulus were measured for each sample and averaged for each dopant. For the mixes containing KF, the values for initial modulus and strain were the highest and lowest, respectively (see Table 9 and Figures 10-12).

**Table 7. End-of-Mix Viscosities/Pot-life of 1-Gallon Doped Mixes**

| Type of Dopant | Viscosity at 125°F and 1.0/second | Pot-Life (hrs.) (40 kp @ 1 sec-1) |
|---|---|---|
| NONE | 15.13 | > 16 |
| $KPO_4$ | 15.09 | 12.12 |
| $KNO_2$ | 9.59 | * |
| $KNO_3$ | 14.62 | 10.01 |
| KF | 15.91 | 8.03 |
| $KSO_4$ | 13.49 | 7.98 |
| $CaPO_4$ | 16.75 | - |
| $AlPO_4$ | 18.81 | 8.57 |
| $BaClO_4$ | 16.81 | 9.61 |
| Silica | 17.73 | 7.92 |

**Table 8. 2"x4" Burn rate and Exponent of 1-Gallon Doped Mixes (at 1000 psi and ambient temp)**

| Type of Dopant | Burn rate, in/sec | Exponent |
|---|---|---|
| NONE | 0.4096+/ 0.0146 | 0.2931 +/- 0.0184 |
| $KPO_4$ | 0.3907 +/- 0.0049 | 0.3085 +/- 0.0233 |
| $KNO_2$ | * | * |
| $KNO_3$ | 0.3915 +/- 0.0048 | 0.2851 +/- 0.0248 |
| KF | 0.3059 +/- 0.0108 | 0.2542 +/- 0.0469 |
| $KSO_4$ | 0.3972 +/- 0.0043 | 0.3145 +/- 0.0224 |
| $CaPO_4$ | 0.3965 +/- 0.0029 | 0.2896 +/- 0.0154 |
| $AlPO_4$ | 0.3975 +/- 0.0053 | 0.3199 +/- 0.0270 |
| $BaClO_4$ | 0.4087 +/- 0.0052 | 0.2975 +/- 0.0296 |
| Silica | 0.4038 +/- 0.0057 | 0.2857 +/- 0.0299 |

30-GALLON MIXES

One 30-gallon mix was made with each type of AP. The contractor's procedures for a 50-gallon mix were used. All steps were kept consistent with the original procedures when using the Kerr McGee and WECCO propellants. When using the reclaimed AP propellant, the AP addition mix times were increased to be consistent with the 1-gallon mixes. Six half-gallon cartons, two strand slabs, eight 2"x4" motors, five 4"x8" motors, and three 70-pound BATES motors were cast from each mix.

Burn Rate Data. Eight 2"x4" motors were fired at the same conditions as the 1-gallon mix motors. The data from these motors were used to calculate nozzle sizes for the 70-pound BATES motors. Burn rates for these motors are shown in Table 10 and Figure 13.

**Table 9. Mechanical Properties of 1-Gallon Mixes (at 77°F and 2 in/min)**

| Type of Dopant | Max stress (psi) | Strain at Max Stress (%) | Initial Modulus (psi) |
|---|---|---|---|
| NONE | 125.83 +/- 1.46 | 37.00 +/- 0.90 | 607 +/- 22 |
| $KPO_4$ | 126.51 +/- 0.69 | 34.20 +/- 1.60 | 650 +/- 25 |
| $KNO_2$ | * | * | * |
| $KNO_3$ | 103.94 +/- 1.30 | 41.50 +/- 0.60 | 455 +/- 10 |
| KF | 133.59 +/- 2.62 | 24.10 +/- 1.20 | 718 +/- 17 |
| $KSO_4$ | 122.71 +/- 0.93 | 35.50 +/- 0.40 | 649 +/- 20 |
| $CaPO_4$ | 133.62 +/- 1.16 | 35.60 +/- 1.70 | 646 +/- 19 |
| $AlPO_4$ | 105.00 +/- 4.18 | 37.60 +/- 2.00 | 549 +/- 26 |
| $BaClO_4$ | 129.52 +/- 1.56 | 36.20 +/- 0.018 | 627 +/- 21 |
| Silica | 136.20 +/- 1.50 | 37.00 +/- 0.90 | 607 +/- 22 |

**Table 10. Burn rates of 30-Gallon Mixes (in/sec at 1000 psi and 60°F)**

| Type of AP | 2" x 4" Motors | 70-Pound BATES |
|---|---|---|
| | | |
| Kerr McGee | 0.4217 +/- 0.005 | 0.393 +/- 0.002 |
| | | |
| WECCO | 0.4136 +/- 0.006 | 0.390 +/- 0.002 |
| | | |
| Reclaimed | 0.4204 +/- 0.004 | 0.406 +/- 0.003 |

Mechanical Properties Twelve Class C dogbone samples were stamped from the half-gallon cartons and tested at the same conditions as the 1-gallon mix dogbones. The data indicated that the reclaimed AP values were the same or within the values of the two virgin AP mixes. Mechanical properties for these mixes are shown in Table 11 and Figures 14-16.

**Table 11. Mechanical Properties of 30-Gallon Mixes (at 77°F and 2 in/min)**

| Type of AP | Max Stress (psi) | Strain at Max Stress (%) | Initial Modulus (psi) |
|---|---|---|---|
| | | | |
| Kerr McGee | 114.13 +/- 1.40 | 30.50 +/- 0.60 | 760 +/- 30 |
| | | | |
| WECCO | 104.88 +/- 1.21 | 35.50 +/- 1.00 | 795 +/- 40 |
| | | | |
| Reclaimed | 110.30 +/- 2.02 | 35.50 +/- 1.20 | 769 +/- 29 |

RECLAIMED AP BATES MOTOR FIRINGS

70-POUND BATES MOTOR FIRINGS

Three 70-pound Ballistic Test & Evaluation System (BATES) motors containing RSRM propellant (TP-H1148) utilizing reclaimed ammonium perchlorate were manufactured at Thiokol Corporation's Wasatch facility under the AP Reclamation Study program. The motors were static-fired at Phillips Laboratory's Test Area 1-32 facility. The data from each motor firing was collected from two independent pressure transducers (A & B). The first motor fired (347A-10) experienced an anomalous trace between approximately 1.25 and 2.25 seconds that was attributed to a blockage of both transducer ports. The two remaining motors performed nominally and were used to calculate the performance (see Table 12). The performance of the reclaimed AP motors was averaged and compared with an average of 14 historical BATES motor firings of virgin AP TP-H1148 propellant contained in the "Corporate Knowledge Database" at PL (see Table 13).

The average burn rate of the reclaimed AP motors was 0.442 ips at 958 psia, the target value was 0.423 ips at 1000 psia. This value was within the 3-sigma control limits as were the reported and theoretical specific impulse values of 294 and 316-lbs*sec/lb., respectively and motor efficiency at 93.2 percent.

800-POUND BATES MOTOR FIRING

An 800-pound BATES motor containing the same propellant as the 70-pound motors was static fired at Phillips Laboratory's Test Area 1-32. The data shows good agreement with the 70-pound data in pressure and burn rate, however, the isp and efficiency data are lower than expected. It is believed this is due to an over range of the load cell, caused by ringing in the thrust stand at motor ignition. We are attempting to calculate a correction factor to reflect the true values at this time (see Table 14).

**Table 14. 800-Pound BATES Motor Performance Data (at 1000 psi and ambient temperature)**

| Motor Number | 347L-001 |
|---|---|
| | |
| Propellant Weight (lbs.) | 784.99 |
| | |
| Expansion Ratio (A/A*) | 9.353 |
| | |
| Ave Pressure (psia) A/B | 971.7 / 972.5 |
| | |
| Ave Thrust (lbs.) A/B | 29000.47 / 29040.42 |
| | |
| Action Time | 6.190 / 6.191 |
| | |
| Burn Rate Ave (ips) A/B | 0.429 / 0.429 |
| | |
| Delivered Specific Impulse (lbs*sec/lb.) A/B | 228.664 / 229.052 |
| | |
| Delivered Specific Impulse (vacuum)(lbs*sec/lb.) A/B | 246.873 / 247.276 |
| | |
| Report Specific Impulse (vacuum)(lbs*sec/lb.) A/B | 260.784 / 260.784 |
| | |
| Theoretical Specific Impulse (vacuum)(lbs*sec/lb.) | 316.018 |
| | |
| Efficiency A/B | 87.399 / 87.542 |

**Table 12. 70-Pound BATES Motor Performance Data (at 1000 psi and ambient temperature)**

| Motor Number | 347A-10 | 347A-11 | 347A-12 |
|---|---|---|---|
| Propellant Weight (lbs.) | 73.83 | 73.78 | 73.40 |
| Expansion Ratio (A/A*) | 9.952 | 9.966 | 10.377 |
| Ave Pressure (psia) A/B | 872.2 / 869.5 | 949.7 / 945.2 | 971.3 / 967.7 |
| Ave Thrust (lbs.) A/B | 3898.08 / 3899.89 | 3835.96 / 3835.96 | 3971.32 / 3973.98 |
| Action Time | 4.609 / 4.607 | 4.620 / 4.620 | 4.532 / 4.532 |
| Burn Rate Ave (ips) A/B | 0.451 / 0.451 | 0.429 / 0.429 | 0.455 / 0.455 |
| Delivered Specific Impulse (lbs*sec/lb.) A/B | 243.343 / 243.352 | 243.259 / 243.252 | 245.179 / 245.242 |
| Delivered Specific Impulse (vacuum)(lbs*sec/lb.) A/B | 259.781 / 259.703 | 263.818 / 263.988 | 266.115 / 266.394 |
| Report Specific Impulse (vacuum)(lbs*sec/lb.) A/B | 296.022 / 296.122 | 293.505 / 293.619 | 295.103 / 295.418 |
| Theoretical Specific Impulse (vacuum)(lbs*sec/lb.) | 316.018 | 316.018 | 316.018 |
| Efficiency A/B | 93.672 / 93.704 | 92.876 / 92.912 | 93.352 / 93.491 |

**Table 13. 70-Pound BATES Motor Performance Data, Historical TP-H1148 vs. Reclaimed AP (at 1000 psi and ambient temperature)**

| | HISTORICAL DATA | | | | RECLAIMED AP DATA | |
|---|---|---|---|---|---|---|
| Data Parameters | AVE | STD DEV | 3S LCL | 3S UCL | AVE | STD DEV |
| Propellant Weight (lbs.) | 72.74 | 0.844 | 70.21 | 75.27 | 73.59 | 0.190 |
| Expansion Ratio (A/A*) | 9.98 | 0.292 | 9.10 | 10.85 | 10.152 | 0.185 |
| Ave Pressure (psia) A/B | 956.18 | 62.52 | 768.62 | 1143.74 | 958.48 | 11.03 |
| Ave Thrust (lbs.) A/B | 3759.80 | 68.567 | 3554.10 | 3965.50 | 3901.40 | 71.252 |
| Action Time | 4.738 | 0.1281 | 4.354 | 5.122 | 4.576 | .0440 |
| Burn Rate Ave (ips) A/B | 0.391 | 0.0186 | 0.335 | 0.447 | 0.442 | 0.0130 |
| Delivered Specific Impulse (lbs*sec/lb.) A/B | 244.80 | 3.578 | 234.07 | 255.53 | 244.23 | 0.978 |
| Delivered Specific Impulse (vacuum)(lbs*sec/lb.) A/B | 294.86 | 1.805 | 289.44 | 300.27 | 294.41 | 0.849 |
| Theoretical Specific Impulse (vacuum)(lbs*sec/lb.) | 317.10 | 2.535 | 309.49 | 324.70 | 316.02 | 0.000 |
| Efficiency A/B | 92.99 | 0.417 | 91.74 | 94.24 | 93.16 | 0.264 |

## CONCLUSIONS

The propellant property results from this study proved the PBAN propellant selected could be made with reclaimed AP and still achieve mechanical properties within the specification limits for this formulation. However, the results showed that reclaimed AP does not act as a direct replacement for either Kerr McGee or WECCO AP to achieve the necessary ballistic properties. Therefore, subscale qualifying mixes are necessary to determine the correct percentage of ingredients to achieve the desired properties when using reclaimed AP. It might also mean opening up the specification for unground to ground AP ratio to achieve the target ballistic properties. Also, with the high levels of sodium and potassium detected, reclaimed AP would not be a candidate for tactical applications unless these levels could be reduced.

## RECOMMENDATIONS

The studies undertaken in this project should be extended to other propellant systems such as HTPB binder based formulations. In addition, work in this area should continue by defining the maximum level of chemical contamination that can be tolerated before propellant properties suffer. It should also define the effect of aging, friability and sphericity on the properties of reclaimed AP propellants.

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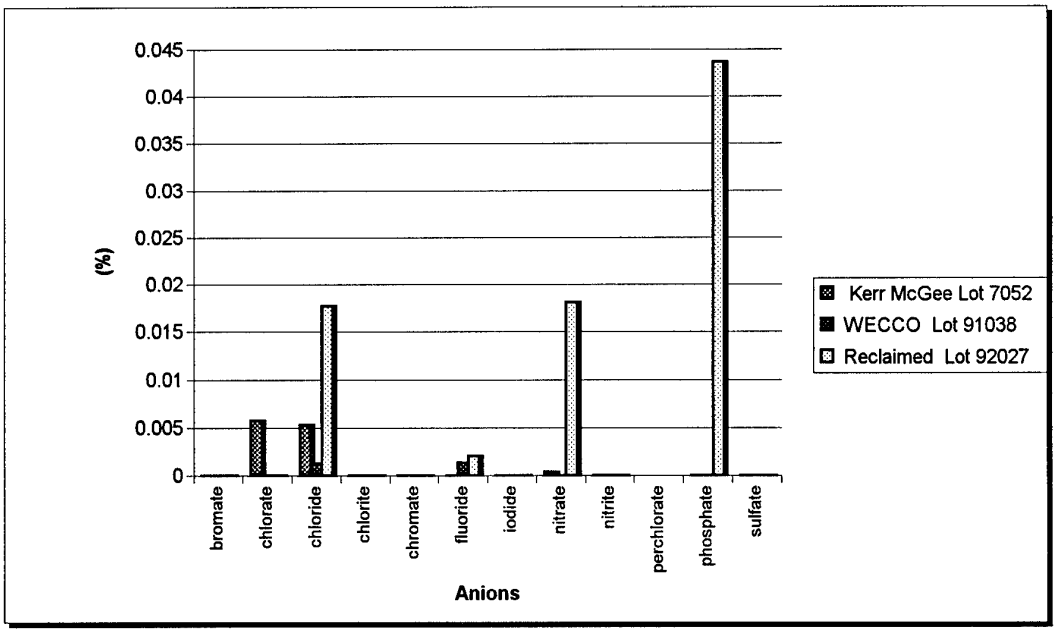



**Figure 1. Anion Analysis of Reclaimed AP Samples (Thiokol Process)**

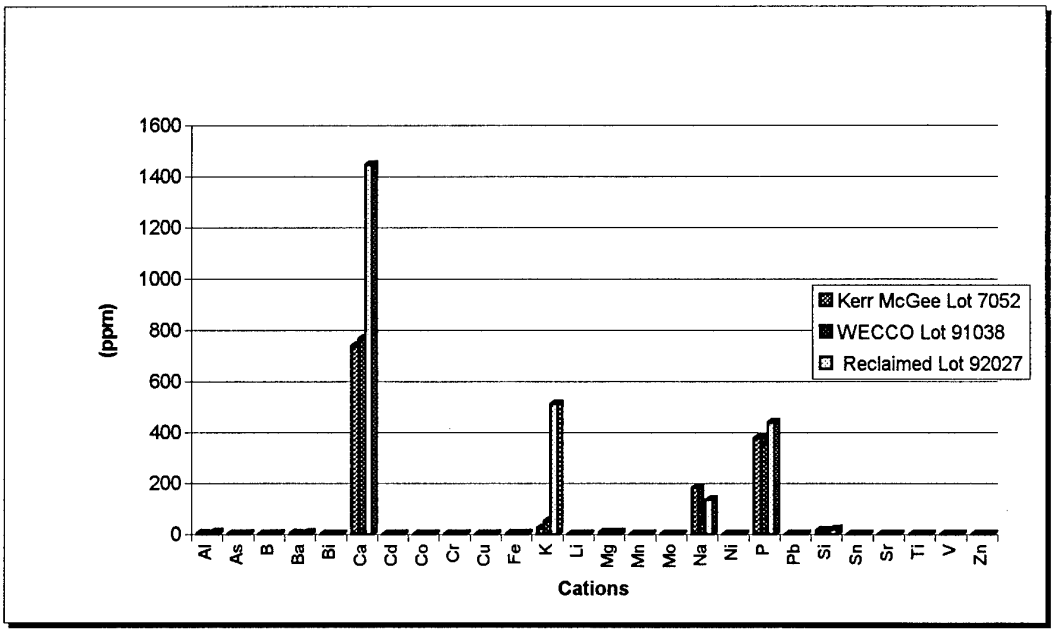



**Figure 2. Cation Analysis of Reclaimed AP Samples (Thiokol Process)**

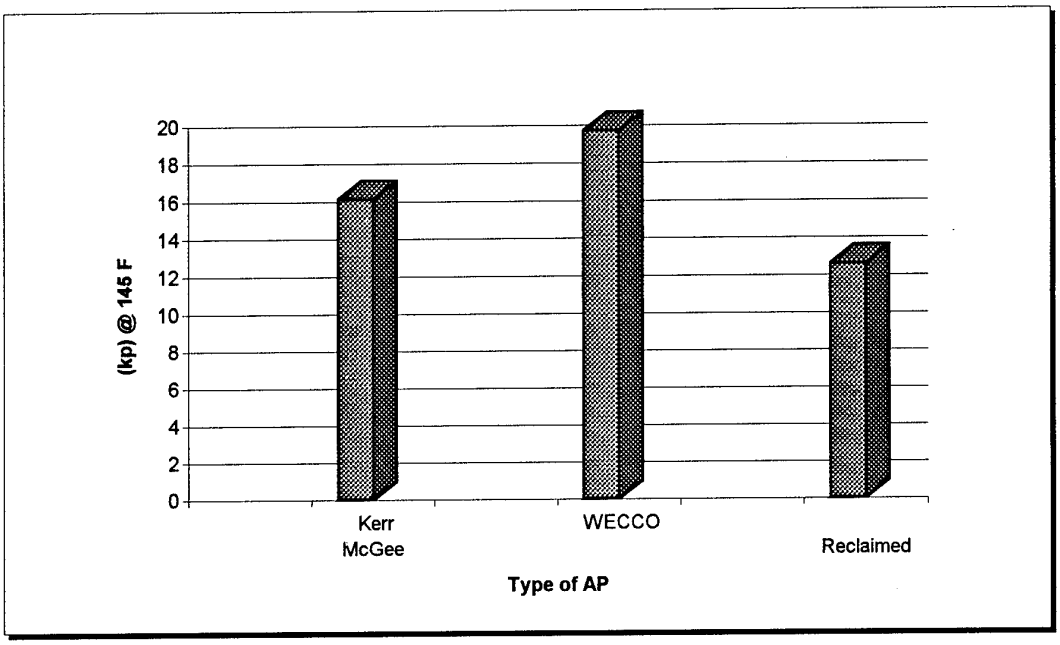



**Figure 3. End-of-Mix Viscosity vs. Type of AP**

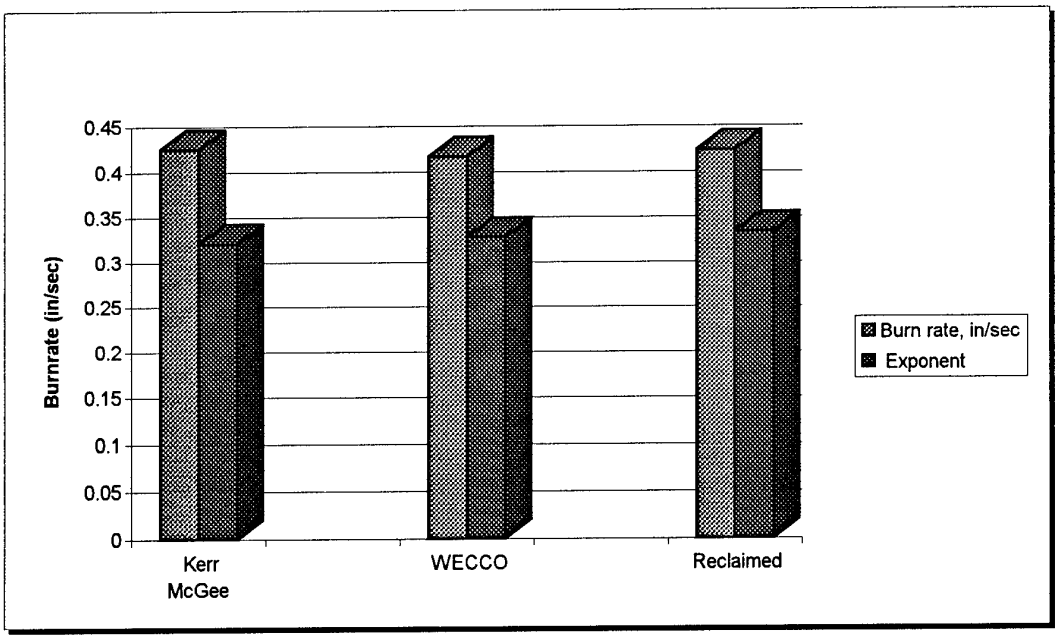



**Figure 4. 2x4 Burn rate and Pressure Exponent vs. Type of AP**

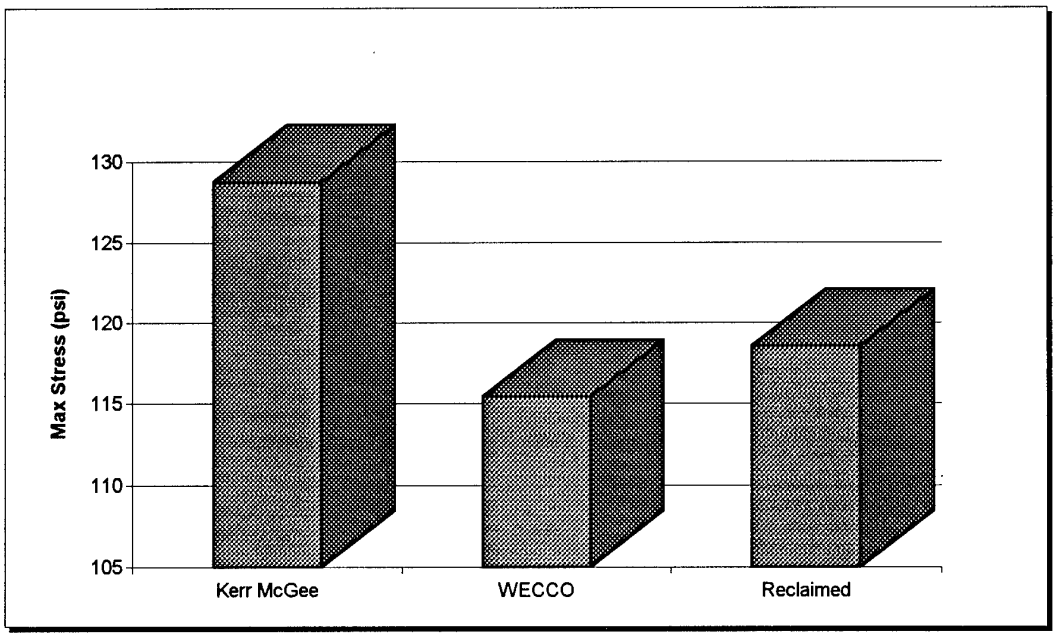



**Figure 5. Max Stress vs. Type of AP (1-Gallon Mixes**

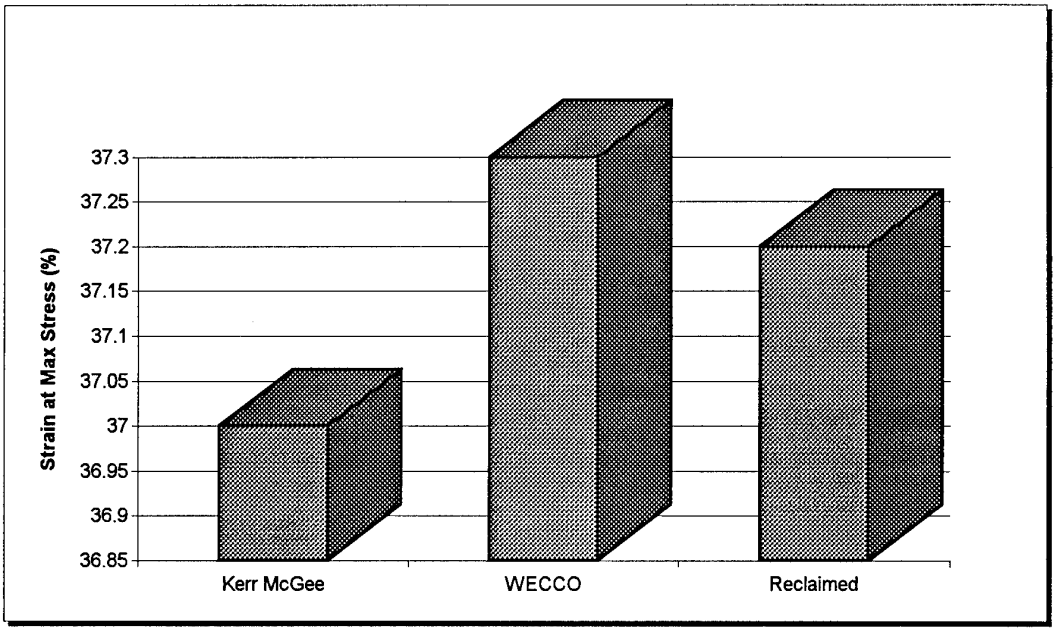



**Figure 6. Strain vs. Type of AP (1-Gallon Mixes)**

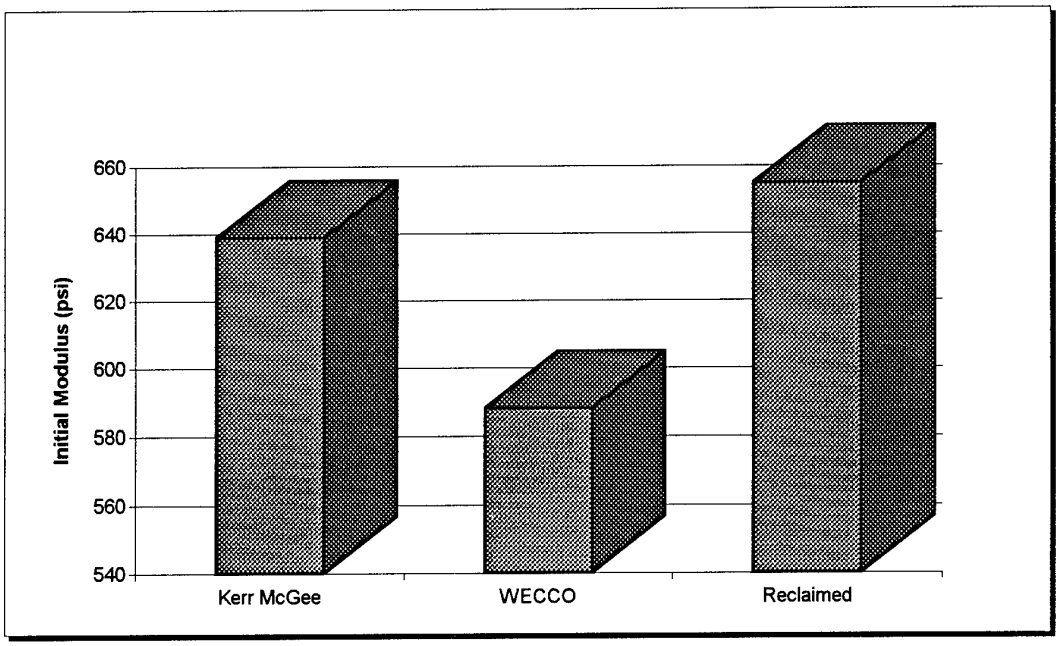



**Figure 7. Modulus vs. Type of AP (1-Gallon Mixes)**

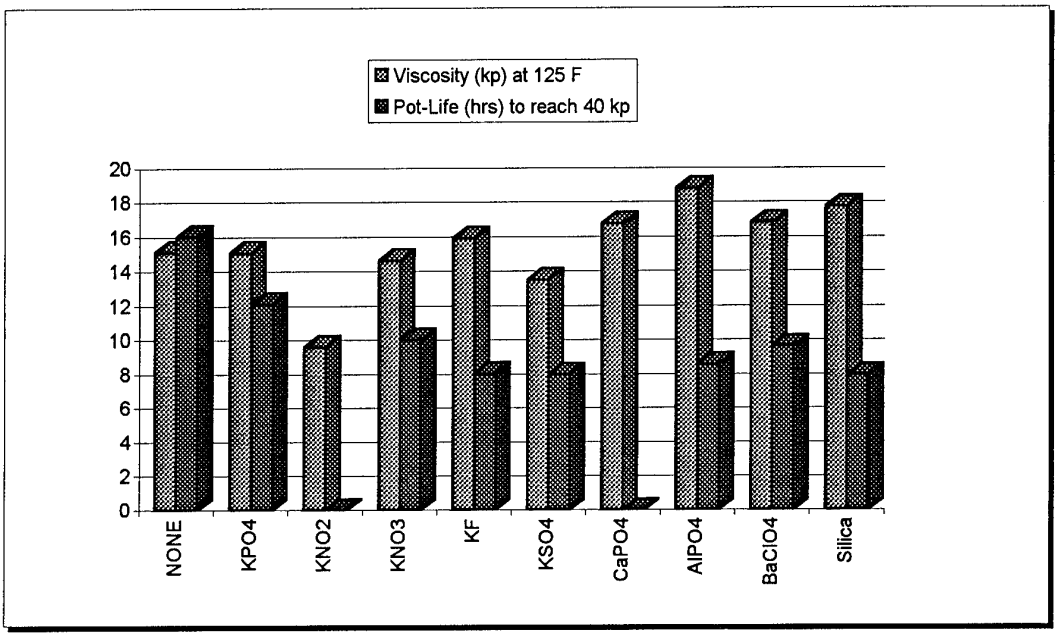



**Figure 8. End-of-Mix Viscosity & Pot-life vs. Dopant**

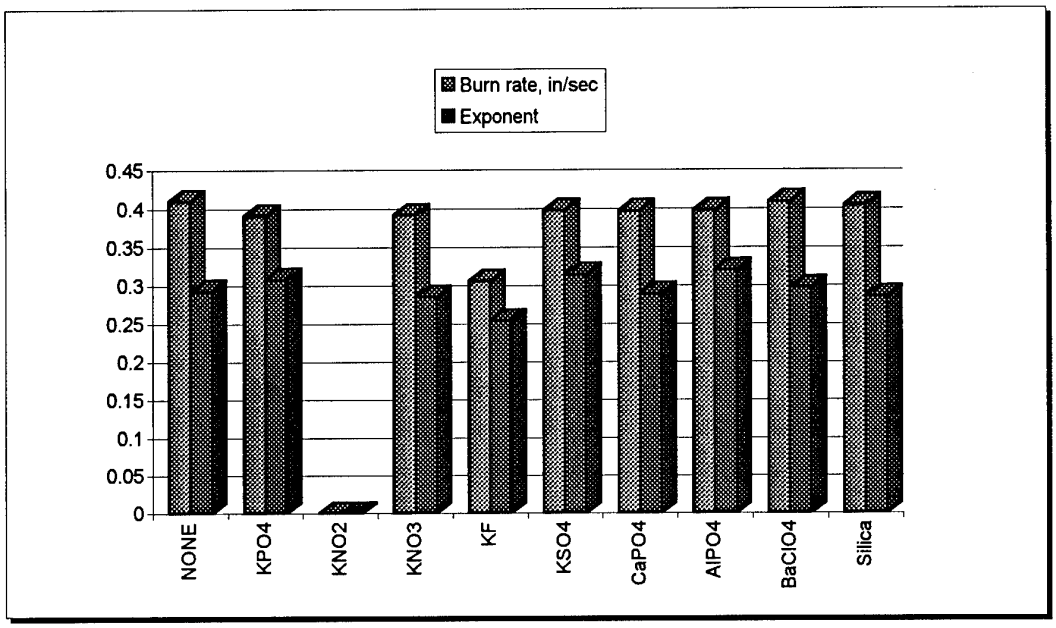



**Figure 9. 2x4 Burn rate & Pressure Exponent vs. Dopant**

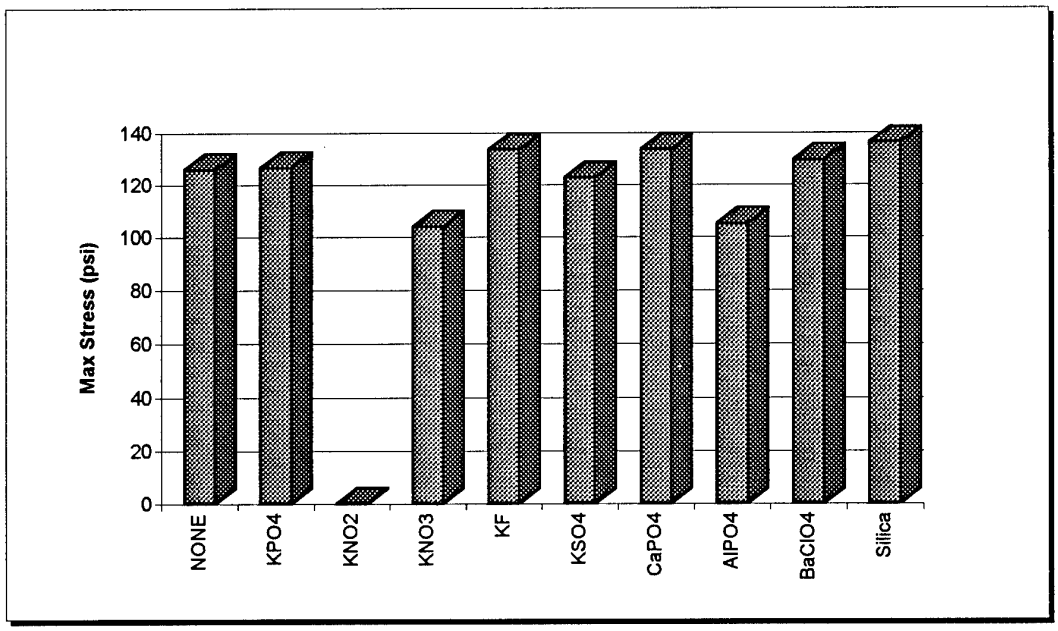



**Figure 10. Max Stress vs. Dopant**

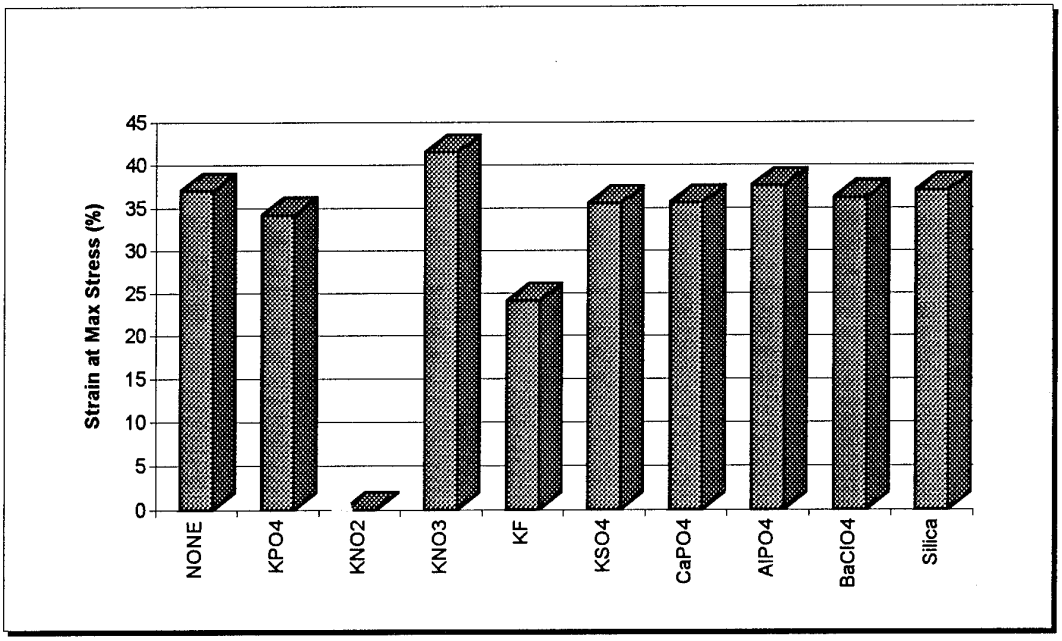



**Figure 11. Strain at Max Stress vs. Dopant**

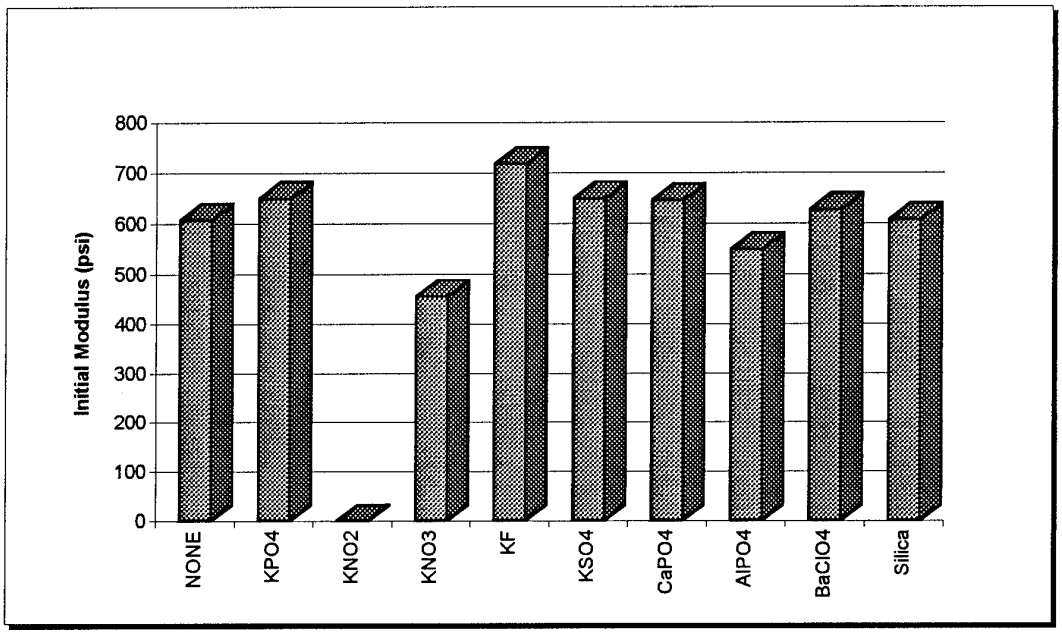



**Figure 12. Initial Modulus vs. Dopant**

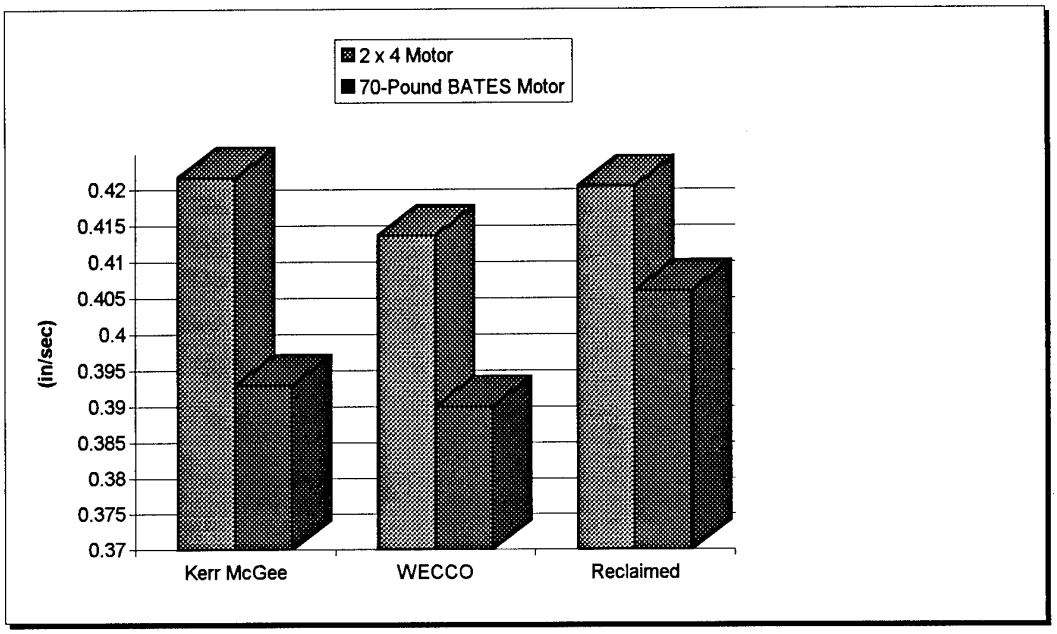



**Figure 13. 2x4 Motor & 70-Lb. BATES Motor Burn rate vs. Type of AP (30-Gallon Mixes)**

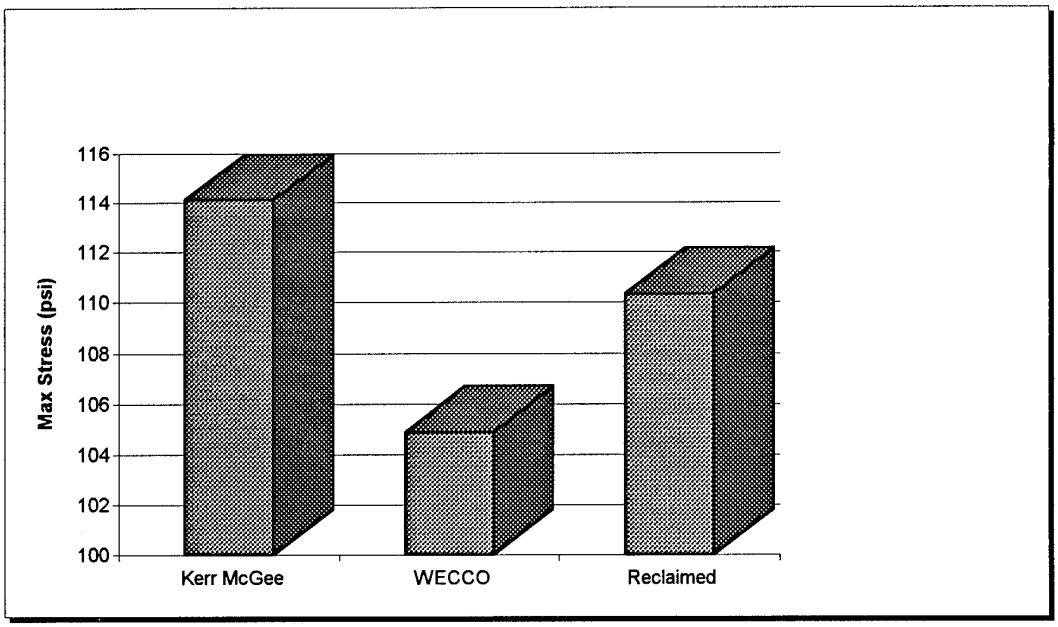



**Figure 14. Max Stress vs. Type of AP (30-Gallon Mixes)**

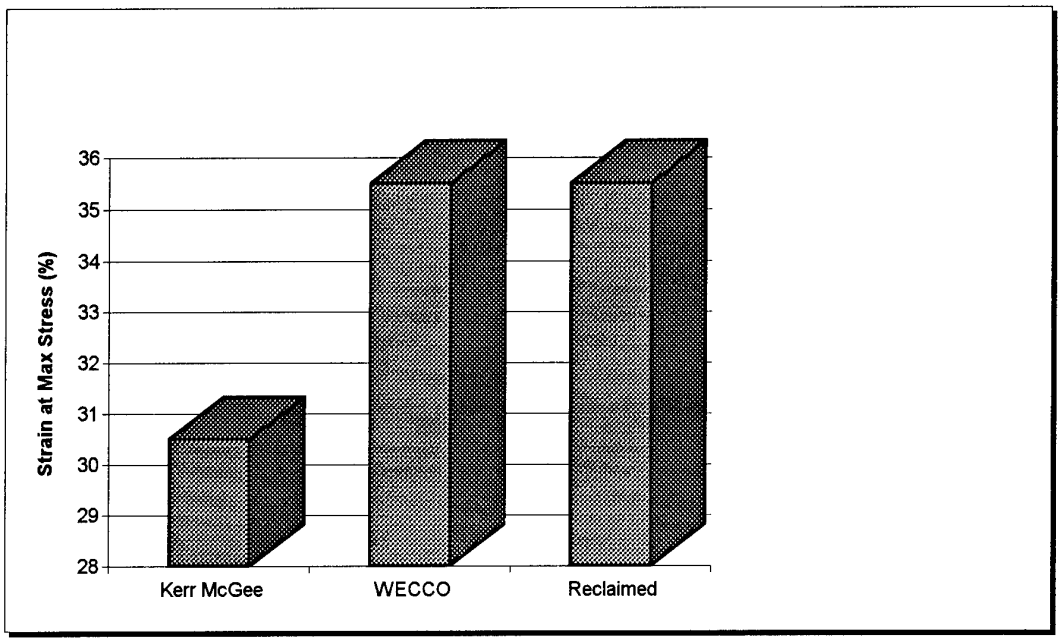



**Figure 15. Strain at Max Stress vs. Type of AP (30-Gallon Mixes)**

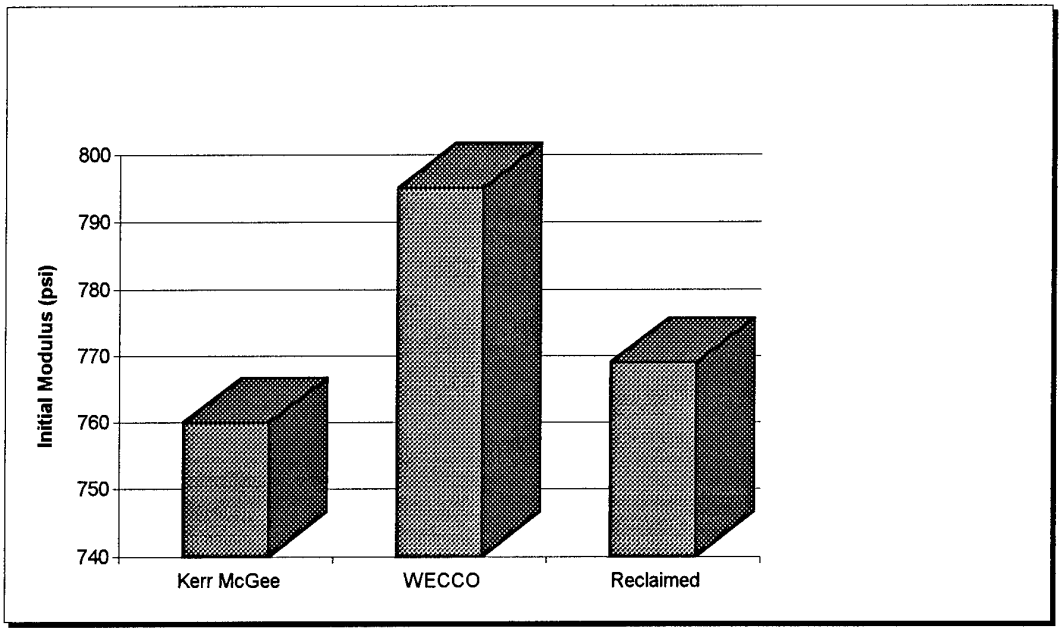



**Figure 16. Initial Modulus vs. Type of AP (30-Gallon Mixes)**

## Discussion

QUESTION BY D.W. BROWN : What does the parameter "circularity" mean ?

ANSWER : This was the measure of how spherical the particles were. It was measured by analyzing an optical microscope image with a KEVEX analyst model 800 microanalyzer.

QUESTION BY D.W. BROWN : What pentrite sizes can be produced ?

ANSWER : Our AP was 200 μ . I don't know if WECCO will recrystallize down to a smaller size. We typically grind our AP to get sizes below 200 μ .

QUESTION BY SCHUBERT : Do you have information about the reproductibility of the data you measure of the virgin and reclaimed AP propellants ?

ANSWER : For the burn rate data on "2x4" motors, each data point is the average of 8 test firings. For mechanical properties, each data point is the average of 12 runs. The standard deviations looked good for all the tests.

QUESTION BY T. ROSENDORFER : Was the reclaimed AP initially WECCO or Ken Mc Gee material or a mixture of both ?
ANSWER : It was WECCO AP from Thiokol propellant.

QUESTION BY T. ROSENDORFER : What is the source for the rather high impurities in the reclaimed AP, i.e. Na, K, P, Ca ?

ANSWER : The Ca and P levels no doubt came from the tri calcium phosphate anti caking agent in the virgin APS. The levels were concentrated during the reclamation process. The other impurities could be salts from the washout water.

QUESTION BY A. DAVENAS : Could you relate the differences in propellant rheology between reclaimed and virgin AP to their particle size distribution ?

ANSWER : In the case of the PBAN propellant used in this study, the particle size distributions were comparable, therefore, I would conclude all things being equal, the reclaimed AP shape being more circular resulted in its lower viscosity. However, you are correct, particle size distribution has a definite effect on propellant rheology, mechanical properties and ballistics.

QUESTION BY A. DAVENAS : Could the Ca and PO4 impurities be attributed to the TCP used as anticaking agent ?

ANSWER : Yes, I am positive that this is the source of the higher levels.

# *DESTRUCTION DES MOTEURS FUSEE A PROPERGOL SOLIDE AVEC RECUPERATION DES MATIERES ENERGETIQUES A HAUTE VALEUR AJOUTEE*

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## RESUME

Cette Conférence présente le procédé de destruction des moteurs à propergol composite solide adopté par SNPE, minimisant les rejets dans l'eau et dans l'atmosphère tout en permettant la récupération des matières premières les plus coûteuses.

## INTRODUCTION

Le respect d'une législation de plus en plus contraignante vis-à-vis de l'environnement conduit aujourd'hui tout industriel à prendre en charge la destruction, avec un minimum de nuisances, des déchets et produits qu'il génère avec le souci de recycler les composants à haute valeur ajoutée.

SNPE s'attache, pour cette raison, à développer de nouveaux procédés de destruction des moteurs en fin de vie et des déchets de propergol solide.

La voie choisie consiste en la découpe du chargement en copeaux par utilisation d'un jet d'eau à haute pression (couteau hydraulique). Le perchlorate d'ammonium (P.A.) est ensuite extrait par macération dans l'eau et récupéré par cristallisation laissant un résidu inerte . Le traitement proposé permet ainsi d'éviter les tirs sommaires et l'incinération à l'air libre qui génèrent de forts dégagements d'acide chlorhydrique dans l'air.

## 1 - LE CONTEXTE

### 1.1 - Les nuisances sur l'environnement

*Rejets aqueux :*

La récupération de la structure des moteurs arrivés en fin de vie nécessite la vidange du propergol qu'ils contiennent. Cette opération, réalisée par découpe au jet d'eau haute pression, génère une pollution importante de l'eau rejetée.

En effet, le perchlorate d'ammonium contenu dans le propergol est partiellement dissous dans l'eau de découpe et entraîne une pollution en ions $NH_4^+$ et $ClO_4^-$.

Pour la vidange d'un chargement de 20 tonnes on retrouve 1 tonne d'ions $NH_4^+$ dans les eaux de découpe.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

*Rejets gazeux :*

Les déchets générés par la mise en oeuvre des propergols solides sont d'une part les déchets de fabrication (reste de malaxage, éprouvettes de contrôle, copeaux et déchets divers provenant de l'usinage.....) et d'autre part (pour 90%) les déchets issus de la vidange au jet d'eau haute pression des moteurs en fin de vie.

Ces déchets sont aujourd'hui brûlés à l'air libre.

Cette incinération entraîne de fortes nuisances au point de vue de l'environnement : les déchets issus de la vidange d'un chargement de 20 tonnes dégagent au brûlage 2 tonnes d'acide chlorhydrique dans l'air. On a aussi dégagement de vapeurs nitreuses et de poussières notamment d'alumine.

### 1.2 - L'évolution de la réglementation

La volonté de tous les pays industrialisés de renforcer la protection de l'environnement se traduit, en Europe, par l'établissement de nouvelles directives sur les rejets aqueux et gazeux.

Ces directives seront applicables aux produits pyrotechniques et conduiront, en particulier, à l'interdiction du brûlage à l'air libre des déchets de propergol solide (ceci à court terme).

### 1.3 - Les nouveaux procédés développés

L'ensemble des fabricants de propergol solide s'est attaché à réduire l'impact de leur activité sur l'environnement.

Aux Etats Unis THIOKOL et AEROJET ont développé des installations de récupération du perchlorate d'ammonium contenu dans les déchets suivi d'une incinération des résidus avec lavage des fumées.

En Europe MUIDEN réalise également une incinération de ses déchets avec lavage des fumées.

SNPE également soucieuse du respect de l'environnement a orienté son effort vers un procédé de récupération du P.A. contenu dans les déchets de propergol solide et vers un traitement "propre" des résidus inertes obtenus.

## 2 - PROCEDE DEVELOPPE PAR SNPE

### 2.1 - Récupération du perchlorate d'ammonium

Comme on a pu le voir précédemment la vidange au jet d'eau des chargements constitue le principal générateur de déchets de propergol composite. C'est pourquoi l'étude s'est orientée en priorité sur le traitement de ces déchets.

Le perchlorate d'ammonium contenu dans le propergol se retrouve à deux niveaux :

- dans les eaux de découpe : sur 1 tonne de produit découpé (contenant initialement 70% de P.A.) 300 kg environ de perchlorate passe dans l'eau.
- dans les morceaux découpés : sur 1 tonne découpée on retrouve les 400 kg de perchlorate restant.

Les deux postes étant équivalents du point de vue de la quantité de perchlorate à récupérer, ils ont été tous les deux pris en considération.

***a) Récupération du P.A. contenu dans les eaux de découpe :***

- Concentration des eaux en PA

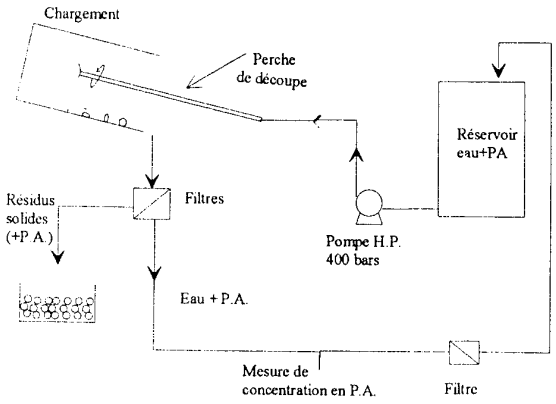
Les eaux de découpe en sortie de l'atelier de vidange sont aujourd'hui très faiblement concentrée en perchlorate du fait de la grande quantité d'eau nécessaire à la découpe : 1 tonne de propergol découpé conduit à 50 $m^3$ d'eau chargée à environ 10 g/l de P.A.. Le coût de récupération du P.A. est alors trop élevé.

La solution retenue consiste donc à recycler l'eau de découpe de façon à l'amener à une concentration telle que la récupération du P.A. qu'elle contient soit aisément et économiquement réalisable.

Cette concentration a été cependant limitée à 150 g/l de façon à éviter tout risque de cristallisation dans l'installation

La vidange d'un chargement contenant 20 tonnes de propergol composite conduit, si l'on suppose que 50% du P.A. part dans l'eau de découpe, à utiliser 50 $m^3$ d'eau initialement propre et qui se charge jusqu'à 150 g/l en P.A..

Voici un schéma de l'installation :




Cette nouvelle configuration a entraîné des études de procédé et de sécurité qui ont conduit à un changement de conception de la pompe haute pression, à la mise en place de filtre sur l'eau et à la mesure en continu du taux de P.A. dans l'eau.

• Recyclage du P.A.

A partir des eaux concentrées à 150 g/l de P.A. il est nécessaire de réaliser une opération de cristallisation de façon à pouvoir réutiliser le P.A..

Pour ce faire l'eau est tout d'abord amenée à une concentration de 500 g/l par évaporation dans un évaporateur à couche mince, puis envoyée pour recristallisation sur le site de fabrication du P.A.

***b) Récupération du P.A. contenu dans les morceaux issus de la découpe :***

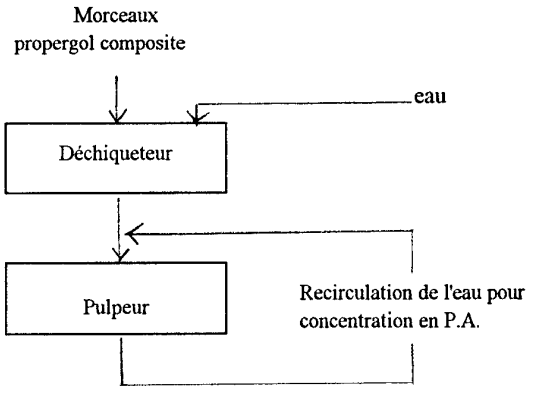
• Extraction du P.A.

La récupération du P.A. contenu dans les morceaux de propergol issus soit de la fabrication, soit de la vidange des chargements, passe par une phase de fractionnement fin des déchets en milieu aqueux. En effet, le division dans l'eau des morceaux en particules de l'ordre du $mm^3$ permet au P.A. de se dissoudre en totalité dans l'eau.

SNPE a développé une installation pilote de broyage sous eau avec un broyeur de type "pulpeur". L'installation réalisée permet la division des morceaux de propergol sous eau avec, comme pour la vidange, recirculation de l'eau pour l'amener à une concentration de l'ordre de 150 g/l (concentration choisie en adéquation avec l'atelier de vidange).

En ce qui concerne les morceaux dont la taille est supérieure à environ 100 $cm^3$ il sera sans doute nécessaire de réaliser en amont une réduction des morceaux dans un appareil de type "déchiqueteur".

Voici un schéma de l'installation :




• Séparation déchets/eau saumurée

Lorsque la dissolution du P.A. contenu dans les déchets de propergol est réalisée il convient de récupérer :

- une saumure contenant un minimum de matières solides résiduelles,
- un résidu solide essoré au maximum.

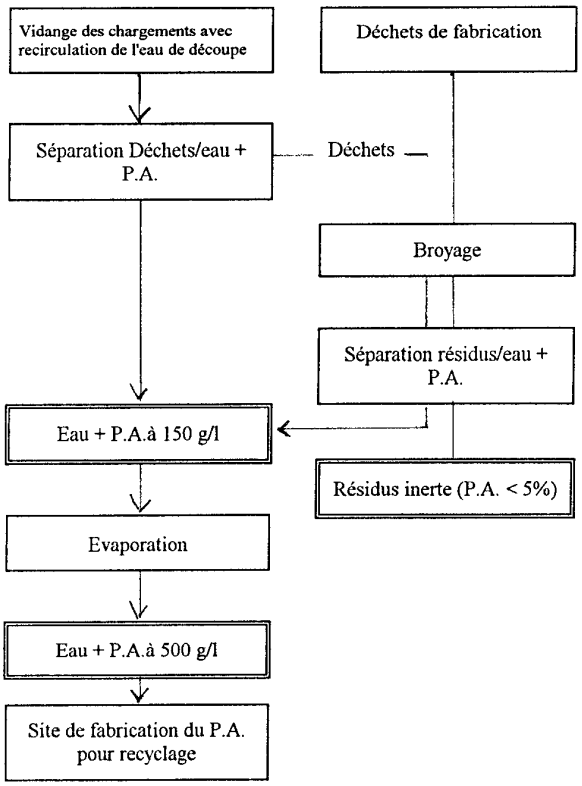
La séparation de l'eau et des résidus de broyage est réalisée sur l'installation pilote par une centrifugeuse.

La clarification de la saumure se fait quant à elle par passage dans des filtres cartouche dont le seuil de filtration est de 0,5 µm. Ce seuil a été déterminé pour pouvoir recycler le P.A. sur le site de fabrication.

• Recyclage du P.A.

Comme pour l'installation de vidange, le procédé de broyage sous eau conduit à l'obtention d'une saumure à environ 150 g/l. Cette solution est donc également concentrée par évaporation jusqu'à 500 g/l de façon à être envoyée, pour recyclage, sur le site de production du P.A..

### *c) Schéma global du procédé de récupération du P.A.*




## 2.2 - Traitement des résidus solides

La récupération du P.A. telle que nous venons de la voir conduit à l'obtention de résidus solides constitués de liant polymère et d'aluminium.Ces résidus sont considérés comme inertes même à l'état déshydraté dans la mesure où ils contiennent moins de 5 % de P.A..

Différentes voies de traitement de ces résidus ont été envisagées :

- incinération après essorage plus ou moins poussé, avec lavage des fumées
- traitement biologique
- traitement chimique :

* sur résidu séché au préalable : trans-estérification par méthylate de sodium. L'aluminium est dans ce cas séparé du liant + solvant par filtration.
* oxydation par permanganate de potassium
* dissolution dans un diester. L'aluminium peut alors être séparé et le liant + solvant peut être réutilisé en tant que carburant.

Sur l'ensemble de ces possibilités l'incinération et la dissolution dans un solvant lourd sont les voies les plus réalistes. Le choix final sera réalisé en fonction de leur intérêt économique.

## 3 - CONCLUSION

SNPE, comme de nombreuses autres organisations indusrielles, a consenti un gros effort de recherche et de développement pour un meilleur respect de l'environnement.

Cet effort a conduit au développement d'un nouveau procédé de traitement des déchets de propergol solide, en remplacement des tirs sommaires et de l'incinération à l'air libre et à la suppression des rejets de P.A. dans l'eau.

Le procédé développé permet la récupération et le recyclage du P.A. contenu d'une part dans les eaux de vidange et d'autre part dans les déchets de fabrication et résidus de découpe. Les résidus inertes alors obtenus peuvent être soit incinérés, soit dissous dans un solvant pour séparation de l'aluminium et utilisation comme carburant.

Les principales étapes du procédé proposé ont été réalisées à l'échelle du pilote et pour certaines d'entre elles en vrai grandeur.

La réalisation de l'ensemble du projet permettra à la SNPE d'être conforme aux nouvelles directives européennes concernant la protection de l'air et de l'eau, sans oublier le fait que la récupération du perchlorate d'ammonium permettra d'améliorer sensiblement le bilan économique de l'opération.

## Discussion

QUESTION BY SCHUBERT : You told us that the process of recovery of components from the composite propellants is too expensive. Regarding the fact that disposal of toxic materials will cost much more in the future, could it be that the cost balance (disposal/recycling) will change ? Could this mean that recycling will be cheaper than disposal ?

ANSWER : Aujourd'hui, aux conditions économiques qui prévalent sur le marché des matériaux énergétiques le recyclage des matières premières n'est pas rentable. Cependant si le coût de la destruction et du stockage des déchets ultimes devient suffisamment élevé (ordre de grandeur : identique au coût d'achat des matières premières non recyclées) alors le recyclage devra être préféré à la simple destruction.

QUESTION BY DR. R.H. WOODWARD WAESCHE : How do you intend to dispose of propellants with Butacene Binder ?

ANSWER : La destruction de propergol composite contenant du Butacène peut se faire avec les mêmes procédés que ceux utilisés pour les liants PBHT. Pour l'instant cependant, cela reste théorique car de telles opérations n'ont pas encore été effectuées sur le plan pratique (alors que la vidange de moteurs contenant du catocène a été réalisée à plusieurs reprises).

QUESTION BY DR. R.H. WOODWARD WAESCHE : What will happen to ferrocene moisty ?

ANSWER : La partie ferrocénique est détruite comme le reste du liant.

QUESTION BY DR. R.H. WOODWARD WAESCHE : Will ammonium perchlorate be contaminated ?

ANSWER : Le PA est contaminé par les ions Fer.

# CRITICAL FLUID DEMILITARIZATION AND INGREDIENT RECLAMATION TECHNOLOGY

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## ABSTRACT

The Department of Defense has a technical requirement to develop alternative technologies to dispose of large numbers of solid rocket motors without harming the environment. Research efforts conducted at the bench-scale have successfully demonstrated the advantages of the U.S. Army Missile Command (MICOM) critical fluid technology for safe and efficient demilitarization of solid rocket motors. This method has been successfully used to recover valuable ingredients, such as cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), ammonium perchlorate (AP), and aluminum (Al)/binder, from tactical and strategic Class 1.1 and 1.3 solid propellants. The process uses liquid ammonia for ingredient extraction and recovery. Under an Army-sponsored effort, Hercules Aerospace Company and Rust International have been awarded a contract to design and build a pilot plant test facility, and to demonstrate this demilitarization process on Class 1.1 and Class 1.3 solid rocket motors.

The report describes ongoing process development efforts to support pilot plant rocket motor demilitarization demonstrations using Multiple Launch Rocket System (MLRS) and Chaparral tactical solid rocket motors. The pilot facility is being designed to recover reusable propellant ingredients from Class 1.3 and 1.1 rocket motors at processing rates approaching 90 kg (200 lb) per hour. This report will discuss the process and design defining the pilot plant facility. Critical equipment and system components for each unit operation are identified. Process descriptions of an integrated Class 1.1/1.3 rocket motor demilitarization system involving propellant removal, ingredient extraction, binder separation, oxidizer recovery, and solvent regeneration will be described. Also included are information and test data demonstrating the ability of energetic products recovered by this process to be recycled into other products, and future work that will be performed on the program.

## INTRODUCTION

The demilitarization of obsolete, overaged, and treaty-limited solid rocket motors is a substantial and pressing problem. Safe, environmentally sound, and economical methods are required to dispose of a large number of rocket motors that exist throughout the world. A special challenge associated with this problem is the large stockpile (approximately one-third of the United States inventory by weight) of Class 1.1 rocket motors. The Joint Ordnance Commander's Group (JOCG), Demilitarization and Disposal Subgroup has identified alternative technologies to the previously acceptable disposal method of open burning/open detonation (OB/OD). These alternative technologies have been assigned to the appropriate United States military services for development and demonstration. Near-critical fluid extraction technologies for Class 1.1 and 1.3 propellant demilitarization and disposal have been demonstrated to be feasible at MICOM.

Under the Large Rocket Motor (LRM) Demilitarization/Disposal Technology Program (Contract No. DACA87-92-C-0134), Hercules and Rust International are investigating a process to demilitarize solid rocket motors and recover valuable energetic ingredients for reuse. The process, which was initially investigated by MICOM,[1] uses anhydrous liquid ammonia to wash propellant from rocket motors and dissolve the energetic compounds from propellant for subsequent recovery.

The overall objective of this program is to provide design criteria for a full-scale plant to demilitarize Class 1.3 and 1.1 solid rocket motors using high pressure liquid ammonia, and to recover ingredients with a market value. A major goal of this Army resource recovery program is to design, construct, and demonstrate a pilot plant test facility for demilitarizing all major types of solid rocket motors in the U.S. and foreign defense inventories. The facility will be of modular construction, skid-mounted, and assembled in an existing building at the Hercules Bacchus Works in

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

Magna, Utah. The ammonia-based process is designed to extract and separate rocket motor ingredients within a closed-loop system. The pilot-scale demonstrations will consist of propellant removal, processing, and component recovery using tactical Army Chaparral and MLRS rocket motors and strategic propellant from the Navy Trident ICBM system.

Data for the design criteria will be obtained through pilot-plant demonstrations of the process using tactical rocket motors for propellant washout and subsequent ingredient recovery and waste disposal operations. Ten MLRS motors containing Class 1.3 propellant, ten Chaparral motors containing Class 1.1 propellant, and 100 lb of cross-linked, double-base (XLDB) Class 1.1 propellant from a strategic rocket motor will be processed in pilot plant operations.

The unique aspect of this Army program is that it has as its foundation the recovery, recycle, and reuse of high value ingredients and components. The approach also addresses the alternate uses of lower value by-products to reduce the generation of hazardous waste and its inherent disposal problem to an absolute minimum.

Unlike traditional disposal methods where neither product or an associated value are recovered, this program is investigating the potential market uses and inherent product value of reclaimed and recycled ingredients. This program will conduct small-scale demonstration tests of products incorporating reclaimed ingredients to enhance the market demand for these cost-effective materials. Market demand and product values from the subsequent sale of recovered products will be used in the economic analysis for full-scale production facility as an offset against capital facility and recurring operating costs.

## MARKET DEMONSTRATION TESTS

Recovery of high purity RDX from solid rocket motor propellants using the liquid ammonia demilitarization process has been demonstrated at the MICOM facility. Bench-scale equipment is routinely used to process 0.5-kg quantities of nitramine (HMX and/or RDX) containing Class 1.1 propellants. These demonstration efforts have shown that the pilot plant under construction at the Hercules Bacchus Works will be fully capable of processing both HMX- and RDX-containing propellants.

The objective of these low level efforts is to screen and evaluate recovered ingredients for commercial and military reuse. The reuse of HMX and RDX is of particular interest. The high intrinsic value of these materials can provide substantial payback benefits to offset the facility and operational costs of a demilitarization production plant. Also included in these ingredient and component reuse initiatives are test evaluations for AP oxidizer, Al/binder fuel, and nitrate-ester degradation by-products. The objective is to develop and demonstrate a rocket motor demilitarization process with no waste streams (or minimal waste streams). Reuse activities are aimed at identifying reuse markets for all demilitarization recovery ingredients and by-products.

Reclaimed RDX is currently being evaluated for potential commercial and military reuses. The U.S. Army TOW-2 flight motor, from which the RDX is being generated, is a Class 1.1, cross-linked, nitrate ester-based propellant. For these recycle demonstrations, a modified experimental procedure was used to recover and separate the dissolved RDX from the liquid ammonia filtrate solution. The RDX was collected by in situ crystallization directly from cold ammonia filtrate solutions. Solution cooling was accomplished by allowing the room temperature ammonia filtrate solution to undergo liquid-to-gas expansion within the receiving vessel that was opened to the atmosphere. The solid RDX was separated by filtration from the liquid fraction. The RDX was washed in the filtration unit using ethanol. The recovered RDX was analyzed by liquid chromatography and determined to be 99.4% pure.

Approximately 3 kg of recovered RDX was provided to Austin Powder Company, Red Diamond Plant, located in McArthur, OH, and recycled into a commercially equivalent cast booster. The RDX was used without any further purification or crystallization. The recovered RDX had a mean particle size of 32 μm. For performance comparison purposes, the recycled RDX cast boosters (hereinafter referred to as "Redstone boosters") were evaluated against Austin's commercial "Orange Cap" booster in replicate tests. The Orange Cap is a Composition B, 60/40 TNT/RDX melt-cast booster with a net weight of approximately 0.45 kg.

Austin Powder conducted analytical evaluations, as well as safety, lead compression, and borehole field testing. Austin Powder provided five Redstone boosters to the U.S. Bureau of Mines, Pittsburgh Research Center, for independent detonation velocity determinations and safety test evaluations. These tests confirmed that recycled RDX would meet all the performance and transportation requirements necessary for commercial mining operations.

Analytical and hazard characterization tests performed by the Bureau of Mines and Austin Powder Company confirmed the purity, particle size, and anticipated hazard characterization properties (impact, friction, electrostatic discharge) of the recovered RDX. The Bureau of Mines determined the detonation velocity of the Redstone boosters to be essentially the same as the commercial booster. The experimental procedure (Figure 1) employed the simple technique of placing an ionization probe (twisted pair) at each end of the booster with a separation of 10.16 cm. The time for the detonation to travel between the probes on a digital oscilloscope was recorded. A standard Austin Orange Cap booster was placed ahead of the Redstone booster to ensure that a stable detonation was achieved. A time of 13.5 μsec was recorded for the detonation to travel the 10.16 cm. A detonation velocity of 7,526 m/sec was

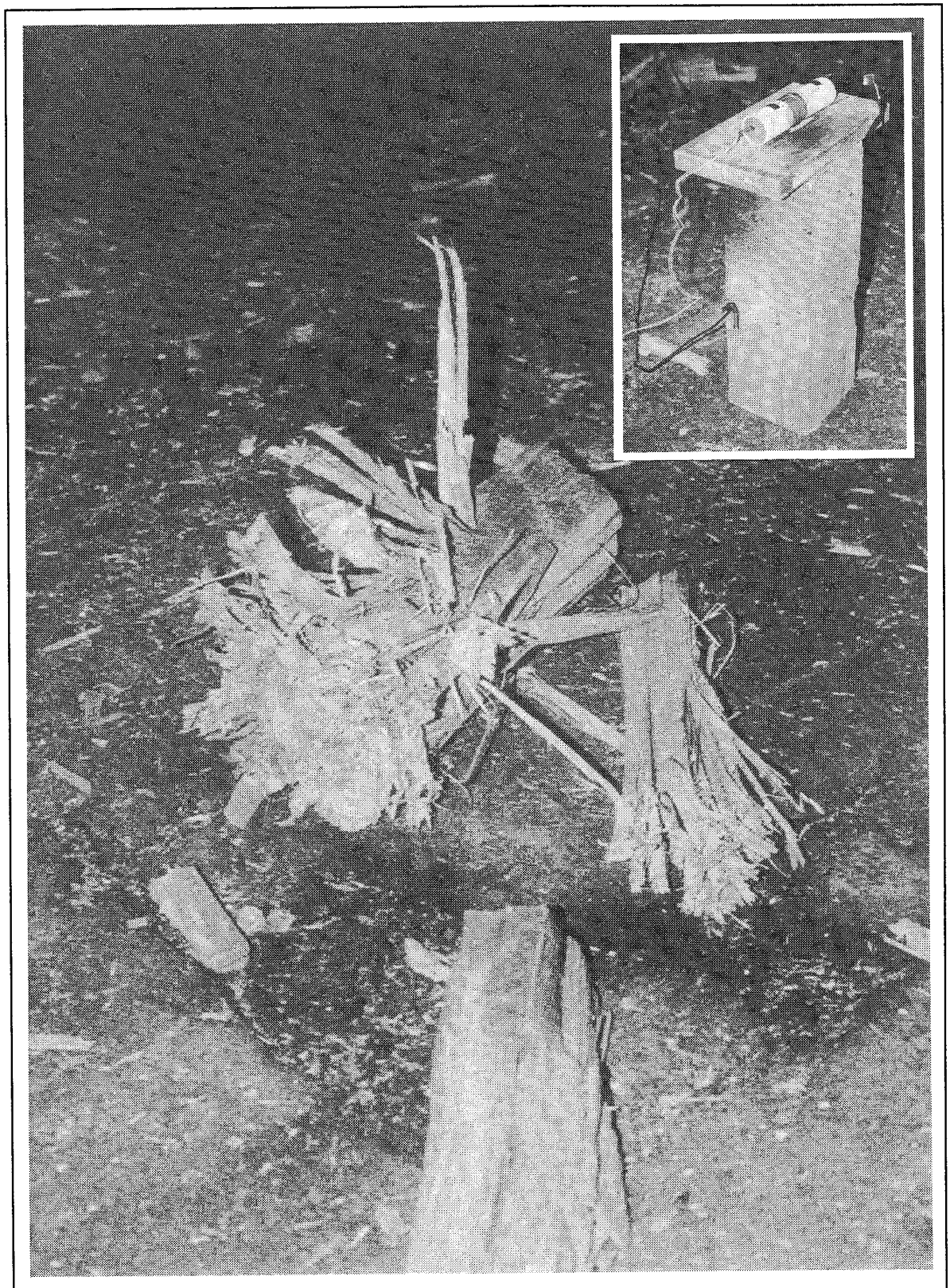


Figure 1. Redstone booster velocity measurement test setup and posttest photograph

calculated and is in excellent agreement with commercial boosters made from virgin RDX.

The lead compression test conducted by Austin Powder demonstrated that the Redstone booster was virtually identical to their commercial Orange Cap booster. This test is routinely used by the mining industry as a screening tool to evaluate the relative energy output of various booster formulations.

Austin Powder Company performed borehole tests to confirm that the Redstone boosters would initiate ANFO blasting agent and possess a performance comparable to the Orange Cap booster. In this four-hole field test demonstration, the results showed complete detonation occurred in all holes and yielded steady state detonation velocities expected for ANFO blasting agent. There was no significant measured difference between the performance of the holes primed with either the Redstone booster or the standard Composition B Orange Cap booster. The average detonation velocity recorded for the Redstone booster holes was 3.611 m/sec. The average Orange Cap detonation velocity was recorded at 3,520 m/sec. The velocity differences are insignificant because of the resolution of the system and cannot be attributed to the boosters themselves.

The conclusion from these preliminary evaluation tests is favorable for the reuse of recovered RDX. Similar verification tests will be conducted using reclaimed HMX in cast boosters and other commercial and military applications. The analytical and hazard sensitivity determinations, together with these field test results, provide credible evidence that these materials can be safely recycled into commercial products, and also show promise for military application.

## PROCESS DEVELOPMENT

The basic process concept for Class 1.3 motors at the start of the program consisted of the followings steps:

- Removal of propellant from motors by either machining or ammonia jet washout
- Separation of the solid phase and the liquid phase that contains the dissolved ingredients
- Evaporation of ammonia from the solid phase
- Evaporation of ammonia from the liquid phase, yielding dry AP (from Class 1.3 propellants) or dry HMX with combinations of NG degradation products, butanetrioltrinitrate (BTTN), and/or AP (from Class 1.1 propellants)

Studies in the laboratory examined each of these steps.[2,3,4] Equipment options were reviewed that considered: (a) acceptable size for pilot plant operations, (b) ability to be scaled to a larger operation, (c) suitability for processing the materials, and (d) suitability from the explosive hazard standpoint. In addition, each piece of equipment had to be compatible with the upstream and downstream processes.

For propellant removal, both high speed, dry propellant machining and ammonia washout worked in laboratory tests and were compatible with the remainder of the process. Ammonia washout was selected for further development and demonstration. For ammonia washout, the goal was to minimize the amount of ammonia required, because all ammonia used eventually has to be evaporated and recondensed. As a result, ultrahigh pressure (36,000 psi) ammonia washout was tested and has been designed into the process. Studies have shown removal rates of greater than 0.5 kg of propellant per kg of ammonia can be achieved. This is a significant technical breakthrough compared to state-of-the-art water washout, which is typically conducted at 10,000 psi or less and removes less then 0.05 kg propellant per kg of water.

A vessel is required to receive the slurry from propellant washout. A stirred tank was selected. This industry standard piece of equipment provides the pilot plant the flexibility needed in case the dissolution of ingredients in the propellant is not as rapid as expected from the laboratory studies. This vessel is jacketed in the event cooling or heating is necessary.

For separation of the solid and liquid phases, hydroclones, centrifuges, and various filters were considered. Hydroclones were rejected because of the problem with scaling the equipment down to handle the relatively large particles and small flows expected in the pilot plant. Pumping and pressure drops with saturated fluid were also negative for hydroclones. Centrifugation raised hazard concerns with high speed rotating components in combination with explosive ingredients. Both centrifuges and hydroclones would also require an auxiliary solids dryer in conjunction with them. The pan filter was selected because it could provide both separation and drying functions, it could be engineered to meet stringent requirements for liquid energetic materials processing, and the internal scraper would likely prevent severe agglomeration of the aluminum/binder crumb. The pan filter could easily accommodate a washing operation, which is anticipated to reduce energetic content of the crumb.

Equipment evaluated for evaporation of ammonia from the liquid phase to yield a dry product included wiped-film evaporators, circulating evaporators, and pan dryers. The wiped-film evaporator was too complex for explosive operations with many moving parts and relatively high velocities. The circulating system was determined to be too complicated and difficult to operate on a scale as small as the pilot plant. The pan dryer is simple and flexible at the expense of heat transfer. It was selected for pilot plant evaluation as it could most easily meet the criteria for explosive handling, and the flexibility would likely permit processing of materials with unknown drying characteristics.

For economic reasons in both the pilot plant and full-scale production, the Class 1.1 propellant process needed to use as much of the Class 1.3 process equipment as possible. However, additional steps are needed to separate nitroglycerin degradation products, AP, and BTTN from the HMX. It was decided that a crude HMX product (90 to 94%) would be acceptable from the pilot plant. If further refining were needed, laboratory tests showed that the product could be further or alternately processed to yield a 99%+ pure form. A process was selected where HMX-containing liquor is taken to dryness. Solvents are then added to remove ammonium salts and BTTN. After these solvents are added, the slurry is filtered in a simple bag filter, and the HMX is recovered wet (Figure 2). The only additional equipment necessary to process Class 1.1 propellant is the bag filter and solvent wash system.

A truly integrated process for demilitarizing Class 1.1 and 1.3 propellants has been developed.

## PROCESS DESCRIPTION

The following is a detailed description of the pilot plant process. It includes the various safety features present to mitigate or eliminate potential hazards.

### Propellant Removal

*Leak Check*

The rocket motor, washout discharge chute, the leacher, the pan dryer, and the pan filter will be individually leak checked using nitrogen before washout operations. The equipment will be leak checked at approximately 120 psig.

Following the leak check in the Class 1.3 process, each vessel and the rocket motor will be purged with sufficient ammonia gas to remove nitrogen from the system. For the Class 1.1 process, ammonia will be introduced when low pressure ammonia flow is started.

*Washout*

Washout begins after the rocket motor has been positioned (Figure 3), leak testing has been performed, and the air purged from the system. An isolation pinch valve between the motor and leach vessel will be opened, and the motor will then start to rotate at approximately 5 rpm. Low pressure ammonia flow (spent wash) introduced at the top of the motor and at the chute between the motor and leach vessel will be initiated. Once the position of the isolation valve and low pressure flow are verified and the leacher agitator submerged and active, the high pressure ammonia washout flow is started. The lance with jet nozzles mounted on top (Figure 4) begins rotating at approximately 1,000 rpm. The lance, following its preprogrammed path, begins traversing up the motor at approximately 2.54 cm per minute. Propellant will be eroded (washed out) using high pressure (36,000 psi) liquid anhydrous ammonia directed through four rotating jets at the propellant surface. The low pressure ammonia (spent wash) will flush interior surfaces and promote flow through the funnel into the leach vessel. The spent wash will consist of a recirculated dilute AP/ammonia solution for the Class 1.3 MLRS process and a dilute HMX/ammonia solution for the Class 1.1 Chaparral process.

Removed pieces of propellant slurried with ammonia will flow through the chute into the leach vessel until the washout has been completed. At that time, the lance will stop rotating and the high pressure flow will be stopped. The low pressure (spent wash) flow will continue for two minutes before being terminated (washing any remaining loose propellant from the washout equipment). The lance will extract from the motor, motor rotation will stop, and the isolation valve will be closed. The washout chute and motor will be vented to the atmosphere and flushed with nitrogen to remove ammonia vapors.

### Leach Vessel

After the leach vessel has been leak checked and purged with ammonia, it is given an initial charge of liquid ammonia or spent wash to submerge the agitator blades. Once the blades are submerged, the agitator turns on and the washout process (described above) begins. The leach vessel receives the propellant/ammonia slurry from the washout station through an 8-in.-diameter port located in the top section. A level sensor measures leach vessel liquid level. If a high level is detected, the washout operation begins its shutdown sequence. Otherwise, the washout operation proceeds until all the propellant has been removed from the rocket motor. When the washout is complete, the isolation valve closes, and the leaching sequence begins. When the leach sequence is complete, the vessel contents are ready to be transferred to the pan filter.

### Pan Filter (Figure 5)

*Slurry Transfer*

After the pan filter has been leak checked and purged, it is ready to receive slurry from the leach vessel. Transfer of slurry from the leacher to the pan filter is accomplished by controlling the differential pressure between the two vessels. The control system ensures that the pressure in the pan filter vessel is, at most, 20 psi less than the leach vessel, and that the crumb discharge valve of the pan filter is closed. When those conditions have been satisfied, the computer opens the leach vessel discharge valve to initiate transfer. Flow rates are monitored to determine when the transfer is complete. Upon completion of slurry transfer, the leach vessel discharge valve is closed.

For the Class 1.3 MLRS process, the constituents of the slurry transferred to the pan filter are aluminum-filled binder (crumb) and AP/ammonia solutions. The pan

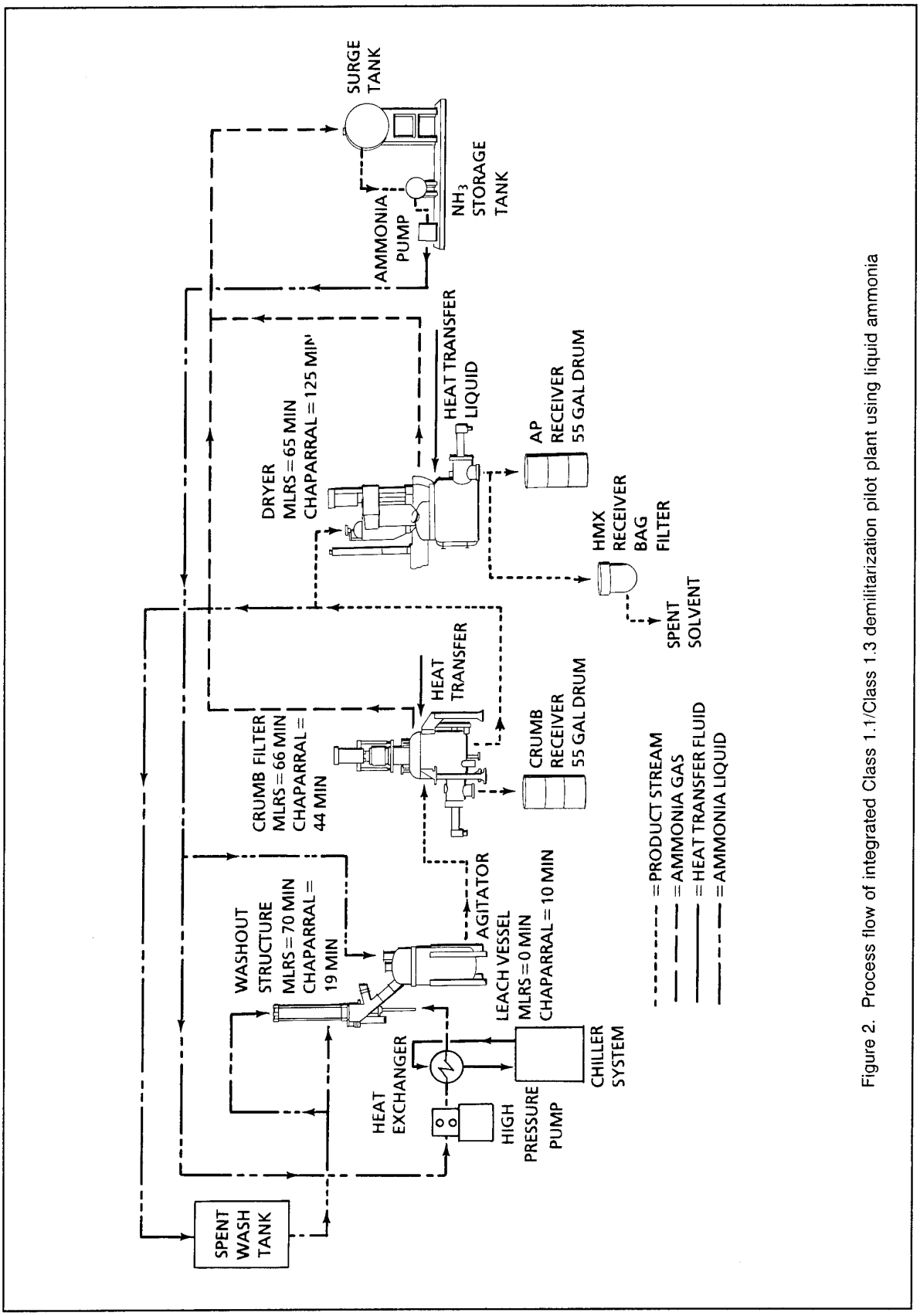



Figure 2. Process flow of integrated Class 1.1/Class 1.3 demilitarization pilot plant using liquid ammonia

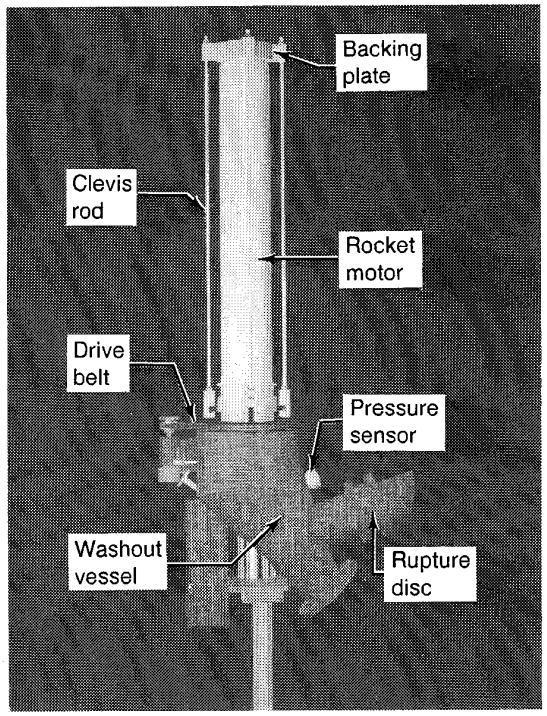



Figure 3. Rocket motor assembly into ultrahigh pressure liquid ammonia spray removal facility

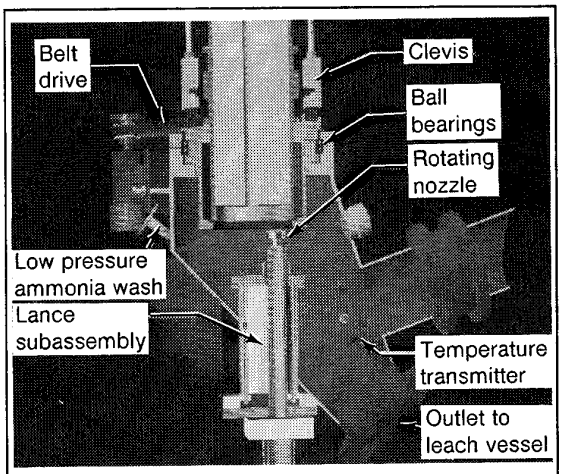



Figure 4. Mechanical and operation detail of ultrahigh pressure liquid ammonia spray removal facility

filter separates the slurry into two streams. The AP/ ammonia solution is transferred to the pan dryer, and the crumb remains on the filter media.

For the Class 1.1 Chaparral process, the constituents of the slurry transferred from the leach vessel to the pan filter are ammonia with: (a) dissolved HMX, (b) dissolved BTTN, (c) dissolved NG degradation products (ammonium nitrate, ammonium nitrite, ammonia salts of organic acids, and (d) undissolved

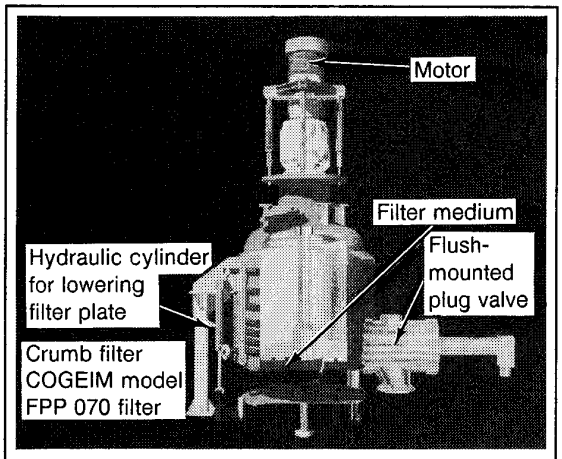



Figure 5. Pan filter for filtrate separation and aluminum/rubber crumb drying for the liquid ammonia demilitarization/ingredient recovery pilot plant

binder with trace heavy metals. The pan filter separates the slurry into two streams: the filtrate and the crumb.

*Agitation*

After the pan filter has received the slurry, the agitator in the pan filter begins rotation. The action of the agitator minimizes agglomeration and packing of the crumb. The agitator has axial translation as well as rotational capabilities. This allows the agitator paddles to be moved through the vessel top to bottom. Agitation is maintained throughout filtering, drying, and discharging operations.

*Filtration*

The filtering operation begins by opening the filtrate outlet valve on the bottom of the pan filter. The filtrate can be sent to either the pan dryer or the spent wash tank through a diverter valve. The filtrate from the initial charge is sent to the pan dyer. Subsequent washings are sent to the spent wash tank. As the filtrate leaves the pan filter, the crumb begins to accumulate on the filter. When filtrate flow to the dryer has stopped, the filtrate outlet valve is closed. The crumb remaining on the filter is washed with clean ammonia via the leach vessel. This removes trace amounts of AP or HMX remaining in the crumb. Multiple washes may be required to remove residual AP or HMX. The filtrate from washing is referred to as spent wash and is sent to the spent wash tank.

*Crumb Drying*

After the crumb has been thoroughly washed, the crumb drying operation begins. Heat is applied to the crumb by starting flow of heat transfer fluid to the jacket on the pan filter. As the temperature in the vessel begins to rise, residual ammonia is driven from the crumb. The ammonia that is driven off is recycled by the ammonia recovery system. At a predetermined value of temperature or pressure, heating of the vessel

will be discontinued. When the pressure has dropped below operating pressure of the ammonia gas recovery system, the remaining ammonia is vented to the atmosphere. The vessel will be flushed with nitrogen before discharging the crumb to the crumb receiver.

*Crumb Discharge*
The crumb is discharged through a port on the side of the pan filter and collected in the crumb receiver. The agitator provides the motive force to discharge the crumb.

**Spent Wash Tank**
The spent wash tank is the same size as the leach tank and is capable of holding approximately 200 gallons of solution. It receives spent wash from the pan filter or fresh ammonia from the ammonia supply tank. Spent wash is transferred to the washout station by using nitrogen to increase the differential pressure between the spent wash tank and the washout equipment. The total ammonia transferred is controlled using a flow meter and a control valve. An interlock will initiate a normal washout station shutdown if the spent wash tank liquid level is low, or if the spent wash tank pressure is below 125 psig.

**Pan Dryer (Figure 6)**

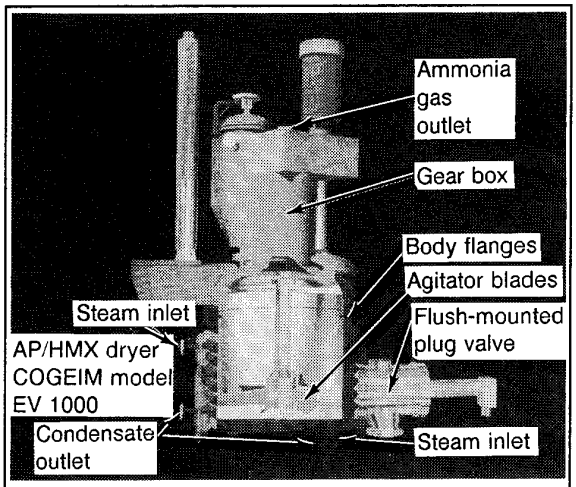



Figure 6. AP/HMX pan dryer for liquid ammonia demilitarization/ingredient recovery pilot plant

*Filtrate Transfer*
Transfer of filtrate from the pan filter to the pan dryer is accomplished by differential pressure between the two vessels. The control system will check that the initial pressure differential between the pan filter and the pan dryer is less than 20 psi, and that the solids discharge valve of the pan dryer is closed. When those conditions have been satisfied, the filtrate discharge valve on the pan filter vessel opens and the diverter valve is positioned to send filtrate to the pan dryers. The filtrate flow rates are monitored to determine when the transfer is complete. When complete, the filtrate discharge valve on the pan filter is closed.

*Pan Dryer Agitator/Scraper*
After the pan dryer has received the filtrate, the agitator in the pan dryer begins rotation. Agitator rotation is maintained throughout filtering, drying, and discharging operations. The action of the agitator minimizes agglomeration and packing of the material as the ammonia evaporates, which improves heat transfer.

*Drying*
The drying operation begins by applying heat to the ammonia solution by circulating a heated glycol solution through the exterior walls of the vessels and through channels in the agitator/scraper. The ammonia is evaporated at a constant pressure until the vessel temperature reaches a maximum of 120°F. The ammonia is recycled by the ammonia gas recovery system. At the predetermined temperature, the heat source is shut off, and the pressure is reduced to ambient. When the pressure has dropped below operating pressure of the ammonia gas recovery system, the remaining ammonia is vented to atmosphere. The vessel is purged with nitrogen and the vessel and the product allowed to cool before discharging the material to the receiver.

*AP Discharge*
The AP is discharged through a port on the side of the pan dryer and collected in the AP receiver. The agitator provides the motive force to discharge the dried AP.

*HMX Discharge*
After drying, the HMX-rich residue is slurried with a solvent. This slurry is sent to a bag filter where wet HMX is recovered. The solvent (containing BTTN and NG degradation products) would be recovered in a full-scale operation.

**Ammonia Gas Recovery**
The design of the ammonia recovery system has evolved based on vapor loading, compression ratios, and available power for the compressor. Ammonia vapor from the AP/energetics dryer and the crumb filter/dryer passes through two filters (redundant system) to the ammonia compressor. The compressed vapor is then condensed in a water-cooled condenser. If ammonia vapor is generated at a rate greater than the compressor can handle, excess vapor accumulates in a surge tank.

The liquefied ammonia flows into the liquid ammonia storage/supply tank. This tank feeds the high pressure ammonia pump, the leacher, and makeup to the spent wash tank. Because of purging and venting, ammonia is lost from this closed-loop recovery system. The level in the liquid ammonia storage/supply tank will be periodically replenished from an outside source. Noncondensable gases, such as nitrogen, will be vented from the system.

## PROPELLANT INPUT FROM OTHER TECHNOLOGIES

A beneficial aspect of the liquid ammonia technology is the ability to accept propellant feedstock supplied by other removal technologies. Propellant is required only to be size reduced (nominal $1mm^3$) and either ammonia wet (as from ammonia spray removal) or in dry form. Dry propellant compatibility allows this technology to interface with other removal technologies, such as dry high speed machining and cryogenic removal techniques. To demonstrate this capability, propellant chips from a Trident-I (C-4) rocket motor will be processed in the pilot plant. Propellant chips will be manually loaded into the pan filter, followed by the introduction of liquid ammonia. Once the propellant has been sufficiently leached, the same process as performed for the Chaparral Class 1.1 propellant operations will continue.

## HAZARDS ANALYSIS

The liquid ammonia demilitarization pilot plant design has been thoroughly reviewed for potential hazards.[6,7,8,9] Recommendations have been made and implemented to eliminate or control these hazards. With the implementation of these recommendations, the design adequately addresses and controls the identified hazards. The operational hazards analysis has been started, but will not be complete until the equipment shakedown, dry runs, and initial motors are processed thorough the pilot plant. A thorough evaluation of procedures, contingencies, process interlock effectiveness, operator training, and operator interaction with equipment will be made to ensure safe operations.

## ECONOMIC CONSIDERATIONS

To minimize costs associated with operation of a full-scale plant, washout efficiency must be maximized for the Class 1.3 process. All ammonia used for washout purposes must later be separated from the resulting products and recompressed. In the Class 1.1 process, minimizing ammonia is not as critical because larger amounts of ammonia are required as a result of low HMX solubility. Full-scale operations would also recover some energy from the compression equipment.

Because of the flexibility of the proposed designs, a full-scale plant could use either multiple small or single large processing vessels. Various removal methods could also be employed (washout, machining, etc.). Operating and capital costs will determine the approach taken. The demonstrated pilot plant could also be used for the demilitarization of tactical units.

From the Class 1.3 process, the primary recoverable ingredient with potential value is AP. From the Class 1.1 process, HMX/RDX would be the high value ingredient recovered. Crumb (Al/binder) from the Class 1.3 process may be marketable as a fuel/additive for cement kilns and mining explosives to achieve additional process cost offsets.

Preliminary economic models being developed for analysis with pilot plant operational data already support this technology as being economically viable. Assuming near-market values for high purity recovered HMX, the pilot plant can potentially be economically competitive with OB/OD. The Class 1.3 process itself is not as economically favorable; however, considering that the stockpile is a mixture of Class 1.1 and Class 1.3 rocket motors, the overall benefits of this technology appear to be real and substantial.

## FUTURE WORK

### Economic Enhancements

*HMX Purity*

Laboratory tests have verified that the current Class 1.1 pilot plant design is capable of delivering HMX/RDX at about 95% purity. This is a viable commercial product, however, with a very low market value. Preliminary literature searches and market studies have shown that HMX must be greater than 99% pure to possess high market value and have the broadest market appeal.

Studies are currently under way and will continue exploring alternative end-processing to increase HMX purity. Alternatives under consideration are:

- Alternative solvents for final wash
- Precipitating HMX directly from liquid ammonia by cooling the ammonia and taking advantage of the temperature-solubility characteristics of HMX in ammonia
- Dissolving HMX in solvent and recrystallizing analogous to HMX manufacturing

*Class 1.1 Pilot Plant Design Modifications*

Once the above studies are complete, the most cost-effective alternative will be assessed. Equipment costs, as well as supporting engineering and hazard analysis efforts, and construction modifications will be evaluated. The best approach will be implemented to achieve a 99%+ pure HMX product from the pilot plant.

### High Speed Dry Propellant Machining

In the near future, efforts will resume on high speed dry machining as a removal method to interface with the liquid ammonia extraction/recovery process. The objective of the task will be to demonstrate dry machining removal technology for large rocket motor demilitarization. This demonstration will culminate in removal of propellant from a full-scale, live motor. Additional objectives of the demonstration will be to:

- Implement safety by design in dry machining operations with live explosives
- Demonstrate propellant removal in a safe operating temperature range

- Demonstrate collection method for propellant chips
- Demonstrate tool entry into a motor port opening
- Demonstrate transportability of machining technology by conducting demonstration at remote location

**Continued Pilot Plant Operations**

Upon successful completion of the critical fluid technology, Hercules and Rust hope to convert the facility to a low level production plant for ongoing demilitarization of smaller tactical rockets, such as the MLRS, Chaparral, and Hawk.

## CONCLUSION

The proposed processes for the demilitarization of Class 1.1 and 1.3 solid rocket motors is viable. Valuable ingredients, such as HMX/RDX and AP, can be readily recovered for recycling and reuse at acceptable rates and purities. The closed-loop process will be conducted with minimal impact to the environment. The design emphasizes commercial equipment and is a skid-mounted, modular design. The design, when scaled up, shows potential to be cost-competitive with the current OB/OD disposal methods. Design and equipment selection make the pilot plant attractive for continued demilitarization of small tactical motors after the current program scope is completed.

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## Discussion

QUESTION BY V. SHELL : Is there any intent to salvage the motor case ?

ANSWER : Yes, either re-use chamber or sell for scrap.

QUESTION BY A.S. ÜCER : Have you used the reclaimed material in motors ?

ANSWER : As yet, no item program managers in the U.S. tri-services have indicated willingness to accept re-cycled materials in rocket motors. HERCULES and the Army feel the chances of re-use in motors is minimal due to strict ballistic requirements. We feel that potential markets in commercial explosives and military explosives (bomb fills or high energy projectiles) are much more appropriate since explosives have less stringent requirements, and demonstration articles are much more cost effective to prove the applicability.

# RECYCLING MILITARY ENERGETIC MATERIALS INTO PRODUCTS FOR COMMERCIAL EXPLOSIVE APPLICATIONS

by

D W BROWN
ICI EXPLOSIVES ENVIRONMENTAL
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STEVENSTON, AYRSHIRE
KA20 3LN

## SUMMARY

Technical trends in the design of explosives for mining, quarrying and construction have for the last twenty-five years been towards a reduction in the presence of chemical sensitisers. Most recent formulations for blasting have eliminated chemical or high-explosive sensitisers altogether. These developments brought benefits of lower material costs and increased safety in manufacture and use.

With the availability of huge quantities of military explosives and propellants from cold war stockpiles now a reality, the industry has to consider what commercial and technical impact these military surpluses will have on existing and new markets, and on the products which are offered for a wide range of field applications.

The paper discusses features of available surplus energetic materials which must be considered when designing into civil explosives products and the product characteristics necessary for successful field application. The processes chosen to determine the safety of manufacturing and use are explained and ICI experience in supplying to the market is described.

## RECYCLING CONSIDERATION

The concept of recycling for the conservation of resources is a cornerstone of good environmental commitment. The economics of recycling have nevertheless been the downfall of many schemes which are otherwise attractive. In the field of commercial explosives, many factors influence the economic case for recycling

- Raw material prices and continuity of supply.
- Reprocessing to appropriate forms.
- Transport and storage of new formulations.
- Methods of disposal.
- Market acceptance.
- Threat to existing production.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

Each of these factors has a relative importance and influence depending on the degree of sophistication already present in the market being analysed.

There are also significant differences in the essential characteristics of commercial explosives compared to military products. In military applications, energetic materials are normally securely contained in robust 'packaging' such as projectile cases, land mine bodies, warhead assemblies, cartridge cases, submunitions etc. The performance requirements of shock, heave, burning rate, resistance to temperature/humitidty cycling, vibration and storage life etc. are established in the course comprehensive trials during development. These features are developed to give an extended storage life and a very high reliability for functioning. The trials include the testing of packaging suitable for service in the most demanding field conditions envisaged, and storage over many years.

For commercial applications, some of these factors are important, but others are equally essential to provide safe and efficient performance in chosen applications is also dependent on such additional benefits as high borehole loading density, good water resistance, acceptable post blast fume, low flash, initiation sensitivity and suitable packaging.

The impetus now provided to ICI in the availability of much larger quantities of surplus materials which have a consistent specification. Recycling has been inhibited in the past because of lack of detailed knowledge about inventories, concerns over consistency and purity of supplies, reluctance to enter long term supply arrangements and the ease which did exist in the past for disposal of surpluses by sea dumping, open burning or open detonation.

Explosive ingedients which have the correct supply characteristics for a future in recycling are Single Base Propellant, PBX Explosives, TNT, Composition B, and Ammonium Percholate. Materials such as HMX and Sodium Azide have potential for recycling into initiating systems and automotive airbag assemblies.

## THE PROCESS AND APPLICATION

Use of materials in recycling involves four major steps:
- Characterisation
- Purification
- Processing into appropriate forms
- Incorporation into a commercial product.

ICI Explosives has been blending single base propellant as a component of commercial explosive compositions for selected applications and customers in the USA, having first established safe and cost effective processing conditions and having subjected the products
to test and evaluation.

The sequence of development is a lengthy evaluation procedure on available raw materials through to finished product.

Raw materials are subjected to
- Chemical analysis.
- Thermal stability tests.
- Impact sensitivity tests.
- Friction sensitivity tests.
- High temperature emulsion and slurry compatability tests.
- Static sensitivity tests.

Laboratory scale preparation is subjected to Hazard and Operability
studies to confirm.
- Laboratory blending procedures
- Composition specifications
- Sensitivity specifications.

The subsequent work determines
- Pilot plant blending procedures
- Material handling characteristics
- Processing specifications
- Performance characteristics
- Finished product stability.

Techniques such as parametric analysis, and particle size analysis combine with ICI proprietary computer programs to predict ideal and hydrodynamic behaviour and blasting performance of the formulations. The achievement of this objective involved in particular a detailed review of the dynamics of dropping cartridges into boreholes. Formulation had to eliminate any hazard potential from shearing of propellant particles which might cause ignition and propagation.

The compression wave generated in the explosive when coming to rest was also considered.

In the USA, Bureau of Mines and Department of Transportation approvals were obtained in after test findings at a mine in August 1992. Since then successful trials with in excess of 500 tons of packaged blasting explosive product name 'Gianite' have taken place in several States.

The high density of the product has made it particularly attractive for working conditions involving high static pressures.

In Canada, Energy Mines and Resources approval is being sought for this product. Further work is planned on cap sensitive emulsion and slurry products and bulk delivered emulsion and slurries energised with single base propellant and other explosive materials.

The recycling of TNT is a major challenge for an environmentally responsible operator. The quantities might justify investment in conversion technology for non-explosive application and there are reports of this taking place in Germany. The greatest potential lies in countries of the former Soviet Union where the mining industry is less developed. In Russia and Ukrane recycling of TNT already takes place to produce a granular TNT based blasting agent.

ICI Explosives believes that the introduction of waterproof TNT slurries and emulsion products with good hydrostatic pressure resistance will contribute greatly to the efficiency of the mining industry in these countries, as well as providing economic benefits of recycling and a satisfactory environmental alternative to disposal.

## ENVIRONMENTAL LEADERSHIP

ICI Explosives and its parent company ICI Plc is committed to rapid improvement on environmental issues, thereby placing it in the vanguard of the worldwide chemical industry on this key performance measure.

ICI Explosives Environmental focus on meeting customer needs in four main activities worldwide.

- Reusing and recycling explosive materials; and the safe, environmentally responsible disposal of unrecoverable explosive wastes.
- Demilitarisation - including the conversion of munitions into reusable materials for commercial markets.
- Remediation of sites contaminated with explosive material.
- Management and operation in the United States of the Indiana Volunteer Army Ammunition Plants, which are also developing technologies and capabilities in these activities.

## CONCLUSION

ICI Explosives is the world's leading supplier of bulk and packaged explosives and initiating systems, and also supplies energetic devices to the automotive and aerospace markets. ICI Explosives retains active development groups in Australia, Brazil, Canada, India, South Africa, UK and USA and manufactures in 18 countries. Its access to markets, willingness to undertake demilitarisation processes yielding surplus military raw materials for recycling, gives ICI Explosives Environmental a leading position in this growing activity.

D W BROWN

# Discussion

REMARKS BY H. SCHUBERT : I would like to support your statements. We now have 5 years experience in conversion and disposal of energetic materials in Germany in the context of the demilitarization of the People's Army of the former DDR, Germany has spent many millions of DM in R and D for this purpose. Also I have had many discussions with Russian colleagues in the disarmament field. All these activities lead to the following result :

1. Because of regulations, problems of reproductibility and other necessary properties it is nearly not possible to use military explosives for commercial application. If we compare the amounts of commercial - and military explosives I would say : the amounts of military explosives are peanuts !
2. Recycling and re-use of HMX - belonging to cost/benefit relation - is possible, recycling of AP and RDX depends on the quantity you have. Mercury-compounds (out of detonators or igniters) can be converted into Mercury and can be sold at a profit.
3. You would be lucky, if you are able to sell TNT for some cents. You cannot sell NC out of the propellants because of low quality compared with virgin NC.
4. All R and D projects to convert substances out of the energetic materials (except HMX and Mercury) lead to no commercial verification due to different reasons.
5. The quickest and safest way to get rid of the energetic materials is to incinerate (under environmental friendly conditions).

# *DEMILITARISATION OF LANCE ROCKET MOTORS*

*PETER SARGENT*
*ROYAL ORNANCE DIVISION*
*BRITISH AEROSPACE DEFENCE LIMITED*
*EUXTON LANE*
*CHORLEY*
*LANCASHIRE*
*UNITED KINGDOM*

## 1. Introduction

In 1992 Royal Ordnance was awarded contract by NAMSA for the demilitarisation of NATO's European stock of Lance missile rocket motors.

Lance is a liquid fuelled surface to surface guided missile designed to give general battlefield support with either a nuclear or conventional capability at ranges of up to 130km.

The NAMSA contract required Royal Ordnance to undertake the following:

(a) transportation of missiles from NATO depots In Europe to Royal Ordnance's factory at Bishopton in Scotland.

(c) establishment of a dedicated demilitarisation facility at Bishopton.

(c) Demilitarisation of live M5 and M6 training missiles by the end of 1994.

## 2. Transportation and Storage

Transportation of all the missiles was completed by February 1993 and the missile motors placed in a purpose-built secure compound adjacent to the Lance demilitarisation facility at Bishopton.

## 3. Demilitarisation Process

Royal Ordnance was contracted to demilitarise a significant quantity of Lance Main Missile Assemblage (MMA) M5 and M6.

Lance MMA M5 known as live units (see figure 1) consist of cylindrical metal container housing a rocket motor (engine) and two liquid filled propellant tanks ( one fuel and the other an oxidant), a guidance and control unit and engine and warhead initiation devices (explosive Squibs).

Lance MMA M6 known as trainer units consist of a cylindrical housing whose contents simulate those of the M5 and which are all in an inert state. This paper therefore does not address the disposal of MMA M6.

Demilitarisation of the MMA M5 is defined as being effected once the container has been destroyed (sectioned and or crushed ) and its component parts and material have been disposed of such that no part (material, explosive or liquid propellant) can/will be used for its original purpose.

The demilitarisation process (see figure 2) involves the use of trained operatives working to Authorised Control Procedures (ACPs) in a purpose built demilitarisation facility at Bishopton. Certain substances within the MMAs are dangerous to handle and some are extremely hazardous to health.

The demilitarisation process up to the point after the engine is removed is a relatively straight forward mechanical procedure therefore this paper will concentrate only on the handling and disposal of the missiles' hazardous components as follows.

### 3.1 Oxidiser

The Lance MMA M5 oxidiser tank contains 501.9 kg (320 litres) of Inhibited Red Fuming Nitric Acid (IRFNA).

IRFNA is a highly corrosive and toxic reddish brown liquid with a sharp unpeasant odour. It will react extremely violently with many organic liquids such as UDMH and Aniline and will cause seriuos burns if it contacts any part of the body. IRFNA vapours are highly toxic when when inhaled and will also irritate the skin and eyes.

The IRFNA is detanked from the MMA by displacing it with nitrogen into a temporary storage tank . The MMA oxidiser tank is then washed out with water to remove any residual acid. This operaton is carried out with the operatives wearing full protective suits with breathing apparatus.

The resulting IRFNA is disposed of by the folowing methods :

(a) once sufficient acid is available in the temporary storage tank it is transferred to a reaction vessel. To remove the Hydrogen Fluoride Inhibitor the IRFNA is

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

reacted with Silica to form Red Fuming Nitric Acid (RFNA) which is transferred to one of three storage tanks.

Fumes from this operation are vented to the IRFNA fume scrubber system located adjacent to the acid effluent pond.

At regular intervals the RFNA is transferred by tanker to RO's Nitric Acid Reconcentration Plant. Due to the residual levels of inhibitor in the RFNA the quantity of acid that can be recycled by this means is restricted to limit degradation of the glass Nitric Acid reconcentration plant.

(b) acid is transferred direct from the temporary storage tank the one of the three storage tanks. The IRFNA is transported in a PTFE lined road tanker to a licensed disposal site at which the acid is disposed by neutralisation with either limestone or calcium hydroxide and the resulting neutral solid disposed of by land fill.

### 3.2 Propellant

The Lance MMA M5 contains 170.3 kg (217 litres) of Unsymmetrical Dimethylhydrazine (UDMH).

UDMH is a clear (colourless) liquid distinguished by its ammonical or fishy odour, a general characteristic of organic amines. Its vapour in air is flammable over a wide range of concentrations.

When UDMH contacts IRFNA or some other oxidising material spontaneous combustion will occur.

The UDMH is detanked from the MMA into drums which are periodically transported to a licensed disposal site for destruction by incineration. The remnants of UDMH within the MMA are neutralised with a sodium hypochlorite solution and the tank finally washed out with water.

The neutraliser and tank water washings are treated in the UDMH effluent tank prior to discharge.

### 3.3 Solid Propellant Gas Generator (SPGG)

Once the fuel and oxidiser have been detanked the only component remaining is the SPGG which is then removed and machined to remove the propellant which is disposed of by open burning.

## 4. Demilitarisation Facility

The layout of the Lance demilitarisation facility is shown at figure 3 It was constrcted in a remote part of the Bishopton facility and contains the following buildings :

(i) 80/002 - used for the receipt inspection and unpacking of MMAs from M599 containers.

(ii) 80/003 - an air conditioned very clean building in which explosive items, guidance and control set and engine components are removed.

(iii) 80/004 - dedicated to the detanking of IRFNA.

(iv) 80/005 - dedicated to the detanking of UDMH.

(v) 80/006 - not a building but a remote area for the treatment of acids and effluents.

Also shown are the bunded MMA storage areas.

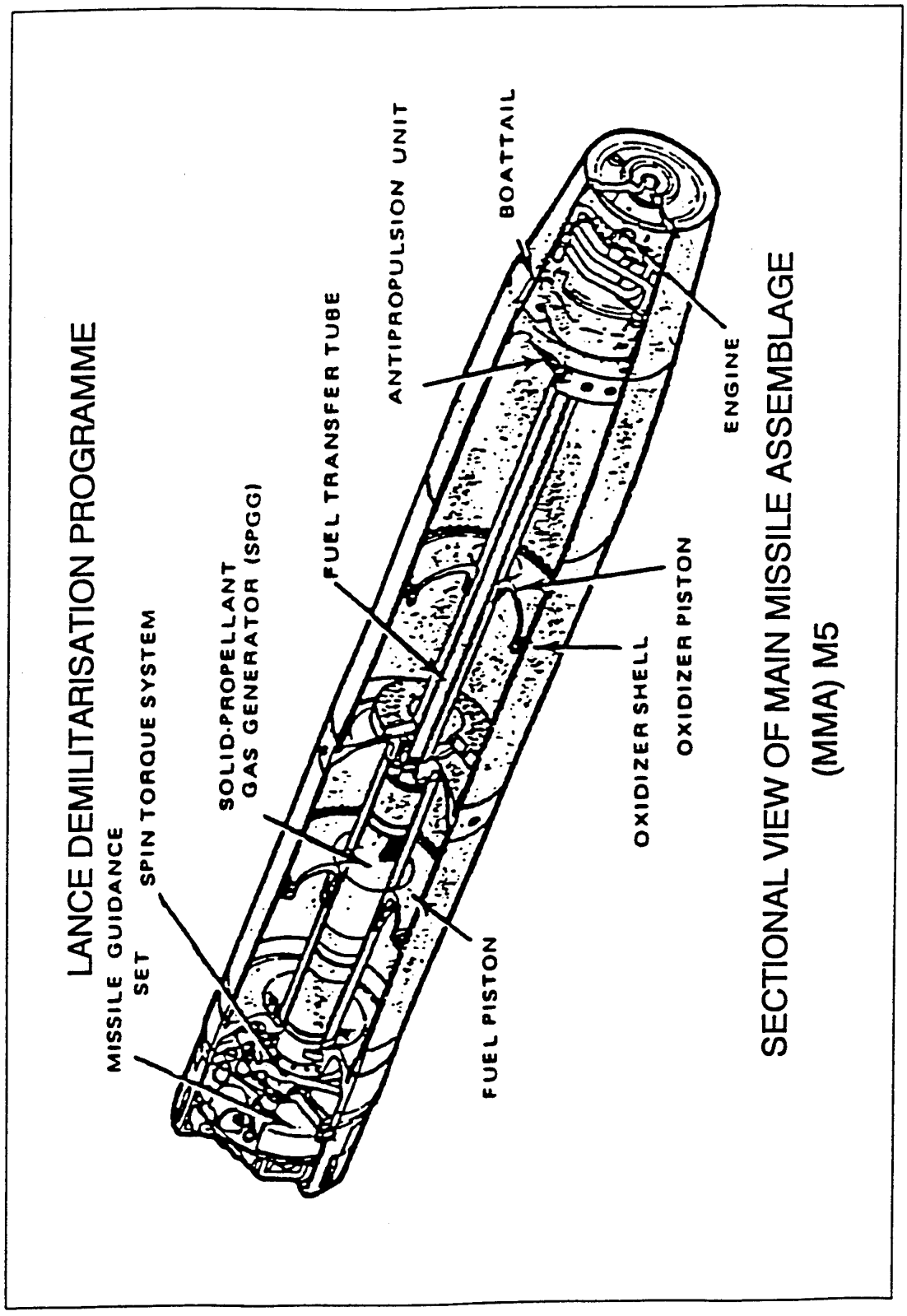

LANCE DEMILITARISATION PROGRAMME
SECTIONAL VIEW OF MAIN MISSILE ASSEMBLAGE
(MMA) M5
MISSILE GUIDANCE SET
SPIN TORQUE SYSTEM
SOLID-PROPELLANT GAS GENERATOR (SPGG)
FUEL TRANSFER TUBE
ANTIPROPULSION UNIT
BOATTAIL
ENGINE
OXIDIZER PISTON
OXIDIZER SHELL
FUEL PISTON

FIGURE 1

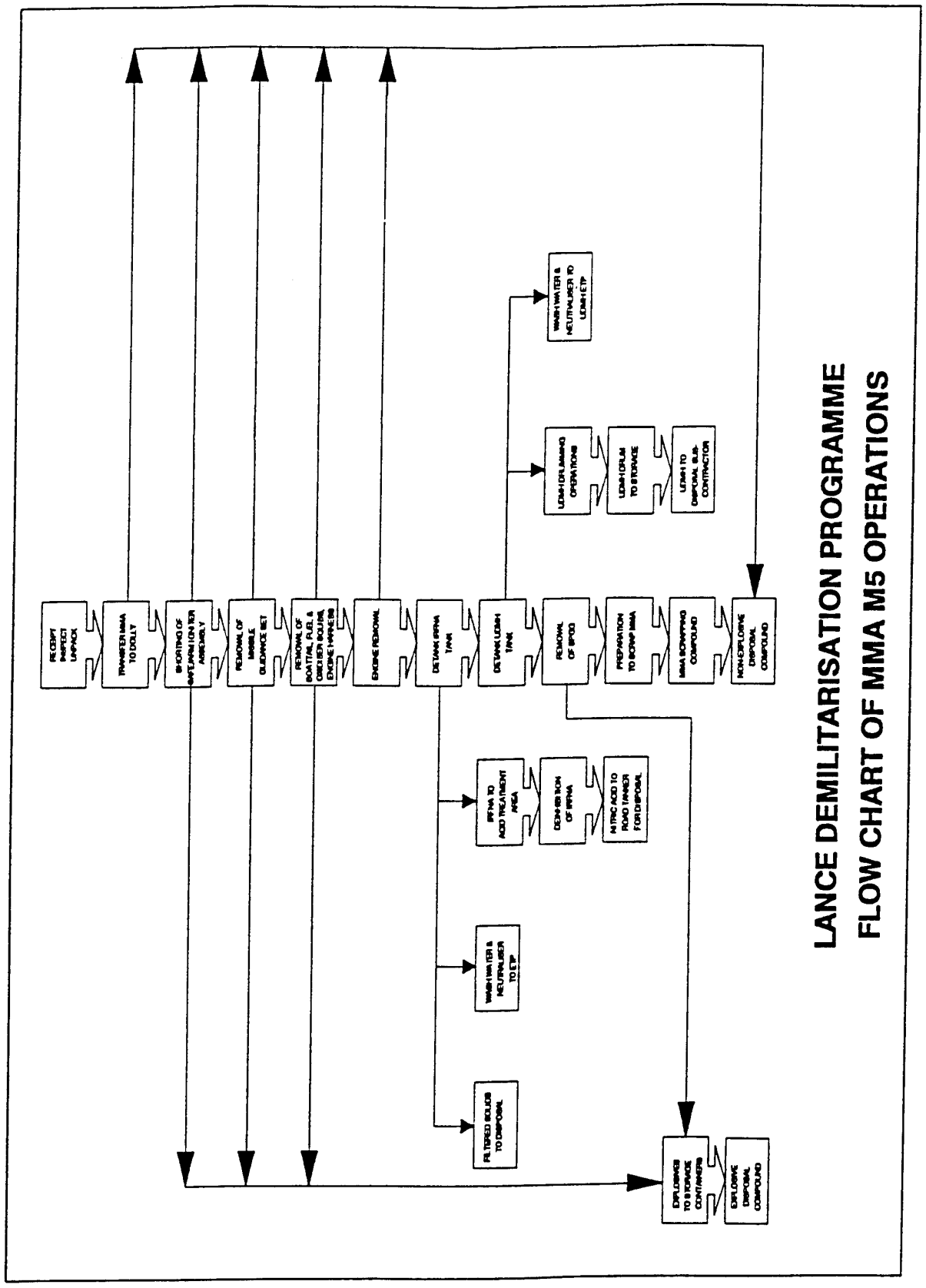

LANCE DEMILITARISATION PROGRAMME
FLOW CHART OF MMA M5 OPERATIONS
RECEIPT INSPECT UNPACK
TRANSFER MMA TO DOLLY
BOARDING OF WARHEAD/MOTOR ASSEMBLY
REMOVAL OF MISSILE GUIDANCE SET
REMOVAL OF BOOSTER, FUEL & ORDNANCE BOARD, ENGINE HARNESS
ENGINE REMOVAL
DETANK MMA TANK
DETANK UDMH TANK
REMOVAL OF SPOD
PREPARATION TO BONFIRE MMA
MMA BONFIRING COMPOUND
NON-EXPLOSIVE DISPOSAL COMPOUND
WASH WATER & NEUTRALISER TO UDMH ETP
UDMH DRUMMING OPERATIONS
UDMH DRUM TO STORAGE
UDMH TO DISPOSAL SUB-CONTRACTOR
MMA TO ACID TREATMENT AREA
DENITRATION OF MMA
NITRIC ACID TO ROAD TANKER FOR DISPOSAL
WASH WATER & NEUTRALISER TO ETP
FILTERED SOLIDS TO DISPOSAL
EXPLOSIVES TO STORAGE CONTAINERS
EXPLOSIVE DISPOSAL COMPOUND

FIGURE 2

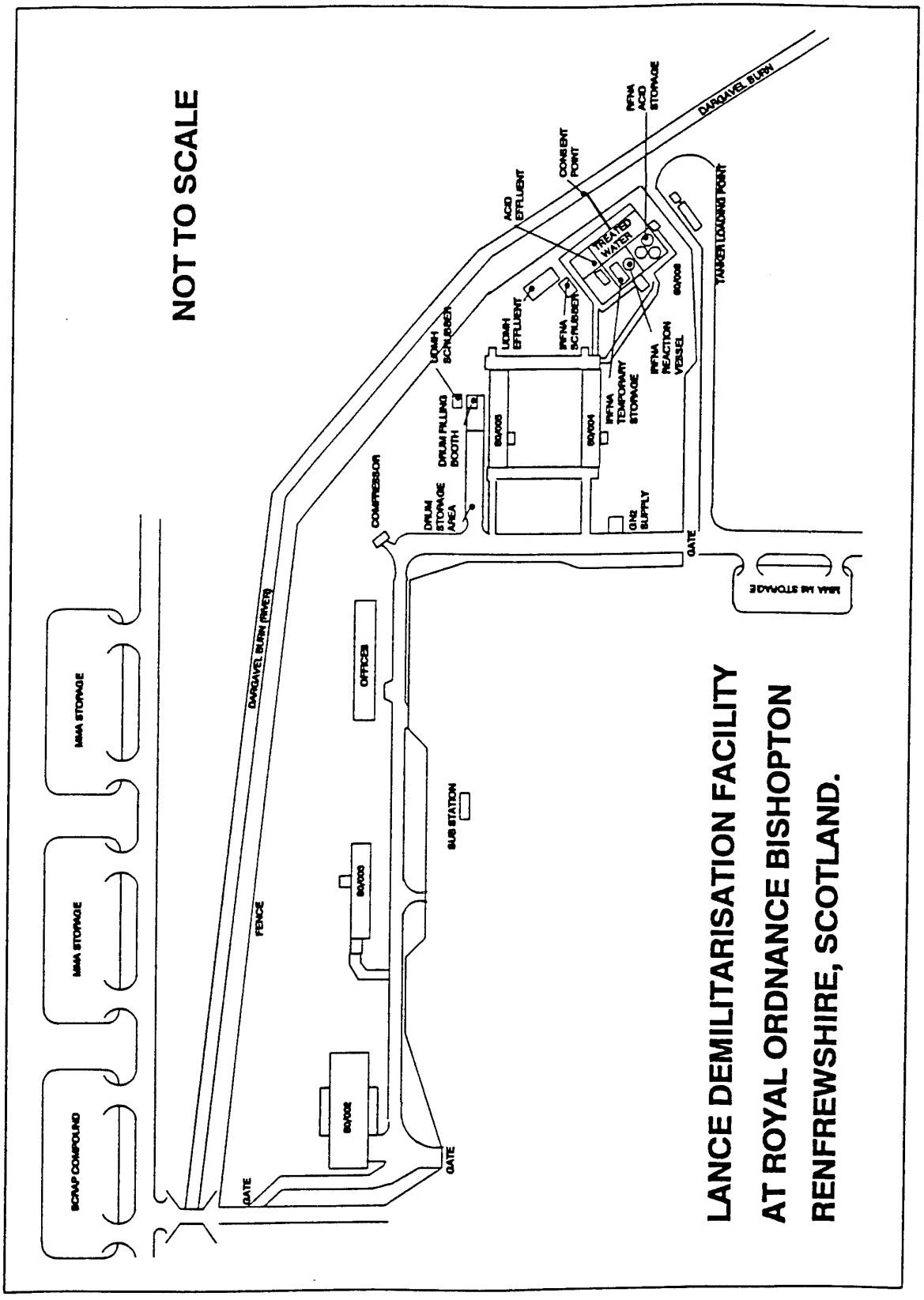

NOT TO SCALE
LANCE DEMILITARISATION FACILITY
AT ROYAL ORDNANCE BISHOPTON
RENFREWSHIRE, SCOTLAND.
SCRAP COMPOUND
MMA STORAGE
MMA STORAGE
MMA STORAGE
DARGAVEL BURN (RIVER)
FENCE
GATE
GATE
BUILDING 002
BUILDING 003
OFFICES
SUB STATION
COMPRESSOR
DRUM STORAGE AREA
DRUM FILLING BOOTH
UDMH SCRUBBER
BUILDING 005
BUILDING 004
UDMH EFFLUENT
IRFNA SCRUBBER
IRFNA TEMPORARY STORAGE
IRFNA REACTION VESSEL
GN2 SUPPLY
ACID EFFLUENT
CONSENT POINT
TREATED WATER
IRFNA ACID STORAGE
BUILDING 006
TANKER LOADING POINT
GATE
DARGAVEL BURN
IRFNA STORAGE

FIGURE 3

## Discussion

QUESTION BY R. DERR : What lessons of a generic nature can be learned from the project of demilitarizing the lance rocket motors ?

ANSWER : The lance demilitarisation programme has been very successful and Royal Ordnance now have a proven facility for processing liquid fuelled rocket motors. There are of course, with the benefit of hindsight, plan and process improvements we would have made and are now implementing.

# REDUCED HAZARD CHEMICALS FOR SOLID ROCKET MOTOR PRODUCTION

by
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## ABSTRACT

During the last three years, the NASA/Thiokol/industry team has developed and started implementation of an environmentally sound manufacturing plan for the continued production of solid rocket motors. NASA Marshall Space Flight Center (MSFC) and Thiokol Corporation have worked with other industry representatives and the U.S. Environmental Protection Agency (EPA) to prepare a comprehensive plan to eliminate all ozone–depleting chemicals from manufacturing processes and reduce the use of other hazardous materials used to produce the space shuttle reusable solid rocket motors. The team used a classical approach for problem–solving combined with a creative synthesis of new approaches to attack this challenge.

## INTRODUCTION

The manufacturing processes that were acceptable in the early 1980s are not acceptable in the '90s (Fig. 1). Forty–seven percent of the organizations that were Fortune 500 companies 10 years ago are no longer there. They were not adaptive enough to survive in the changing business environment. As budgets become smaller and competition requires us to work smarter, faster, and more efficiently, we need to make sure the processes and products we develop in the '90s serve us well into the 21st century. As our ability to gather data on the state of the Earth's environmental health increases, *environmentally sound manufacturing* must become an integral part of the business decision making process.

## BRIEF HISTORY OF ENVIRONMENTAL REGULATORY ACTIVITY

The '70s are remembered as the beginning of the legislative environmental movement with the passage of the National Environmental Policy Act (NEPA, 1969), the Clean Air and Clean Water Acts, the Toxic Substances Control Act (TSCA), and the Occupational Safety and Health Act (OSHA) (Fig. 2). The '80s concentrated on treatment, storage, disposal, and cleanup of solid and hazardous wastes, and public involvement with the passage of the Emergency Planning and Community Right–to–Know Act (EPCRA). The '90s have given us the Pollution Prevention Act, the Oil Pollution Act, additional regulations on hazardous air pollutants (HAPs), water toxins, acid rain, and the production ban of ozone depleting compounds (ODCs) scheduled to take effect January 1, 1996. The Venn diagram, shown in Fig. 3, illustrates the interrelationships of the various lists of hazardous materials that are a part of the regulatory picture.

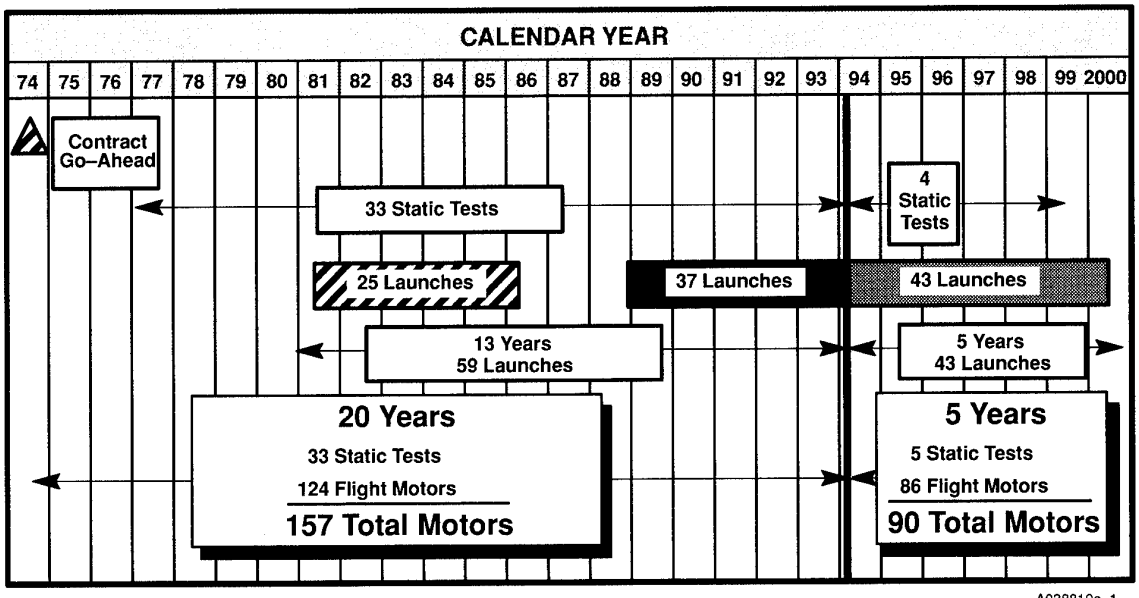



Fig. 1. Space Shuttle Program Overview

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

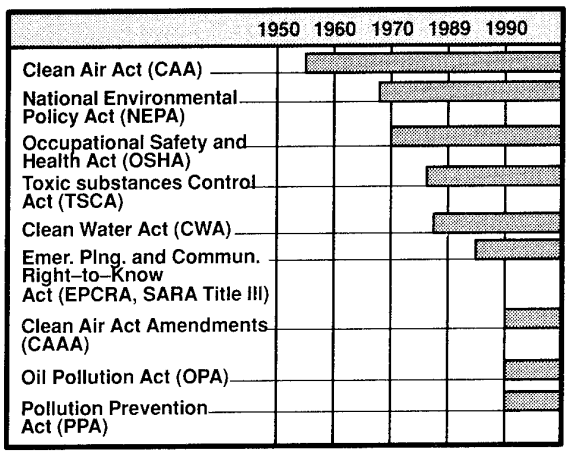


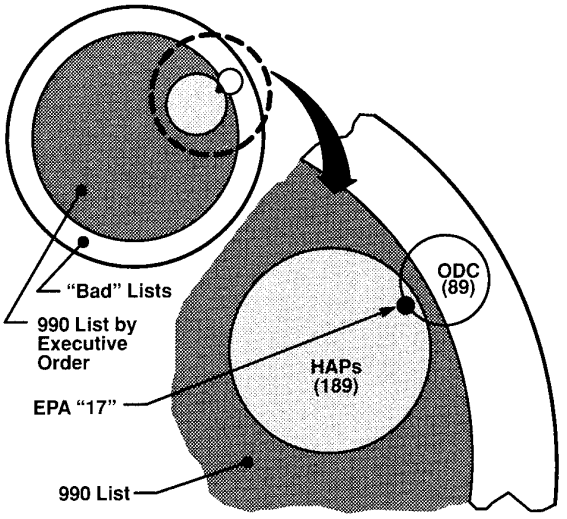

Fig. 2. Environmental Acts

**ODC: Ozone Depleting Compound (Clean Air Act, 1990)**

**HAP: Hazardous Air Pollutant (Clean Air Act, 1990)**

**EPA "17": Industrial Toxics Project, 1991**

**990 List: Executive Order of 1993 Includes EPCRA 313, 329(3), RCRA Hazardous Wastes, 189 HAPs**




**1. On EPA List and ODC List**
- Carbon Tetrachloride
- 1.1.1–Trichloroethane (Methyl Chloroform)

**2. On HAPs List and ODC List**
- Carbon Tetrachloride
- Trichloroethane (Methyl Chloroform)
- Bromomethane (Methyl Bromide)

**3. On 990 List and ODC List**
- Carbon Tetrachloride
- Trichloroethane (Methyl Chloroform)
- Bromomethane (Methyl Bromide)
- Trichlorofluoromethane (CFC–11)
- Dichlorodifluoromethane (CFC–12)
- Dichlorotetrafluoroethane (CFC–114)
- Bromochlorodifluoromethane (Halon–1211)
- Bromotrifluoromethane (Halon–1301)
- Dibromotetrafluoroethane (Halon–2402)

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Fig. 3. Sets of Bad Chemical Lists

Successful leaders must anticipate future regulations and design their products and processes to give them an advantage when new regulations are implemented. The dynamic changes in business and technology resulting from the administration's seemingly paradoxical goals of deficit reduction and infrastructure investment demand a stronger focus on the financial challenges facing the industry in the '90s.

This paper summarizes some of the plans and accomplishments made by the NASA/Thiokol/industry team. New partnerships, new technologies, and new approaches and strategies have been some of the new resources employed as part of Thiokol's plan to achieve environmentally sound manufacturing.

## TRADITIONAL APPROACH TO PROBLEM– SOLVING

Engineering problem–solving usually consists of the following steps: 1) recognize a problem exists, 2) organize to deal with the problem, 3) more clearly state the problem and establish a plan of action, 4) execute the plan, 5) analyze the data and evaluate solutions, 6) qualify solutions into the manufacturing process, and 7) report solution of the problem.

### 1. RECOGNIZE A PROBLEM EXISTS

When the Montreal Protocol members promulgated their document outlining the end of production of ODCs, the NASA/Thiokol team realized a need to start looking at changes to Thiokol materials and processes in order to be prepared for eventual elimination of ODCs. In 1992, when President Bush moved those elimination dates to 1996, the awareness of future challenges became much more acute (Fig. 4). A likely extension to the end of RSRM production added to the immediacy of the problem of ODC replacement. When a survey was completed determining the processes that used ODCs and the quantities being used by the various divisions, we recognized the magnitude of our problem.

### 2. ORGANIZE TO DEAL WITH THE PROBLEM

Thiokol's Corporate Safety and Environmental Affairs director appointed an interdivisional solvent elimination coordinator in early 1991. Each Thiokol division then selected a coordinator and was assigned a solvent replacement task based upon highest usage. Space Operations was assigned methyl chloroform—1.1.1–trichloroethane (TCA). Each division was eventually tasked with replacement of the solvents peculiar to their programs.

### 3. MORE CLEARLY STATE THE PROBLEM AND ESTABLISH A PLAN OF ACTION

An overall corporate hazardous solvent elimination plan was produced. Each division submitted a preliminary elimination plan. An overall schedule was prepared in early 1991 predicting that production phaseout would come at the end of 1995. Bonds were recognized as being critical to the reliability of the motors, therfore, no bonds would be changed without data to qualify equal or better margins of safety.

### 4. EXECUTE PLAN— ODC ELIMINATION STRATEGY

The Thiokol/NASA strategy used to eliminate all ODC from solid rocket motor production followed sound engineering principles.

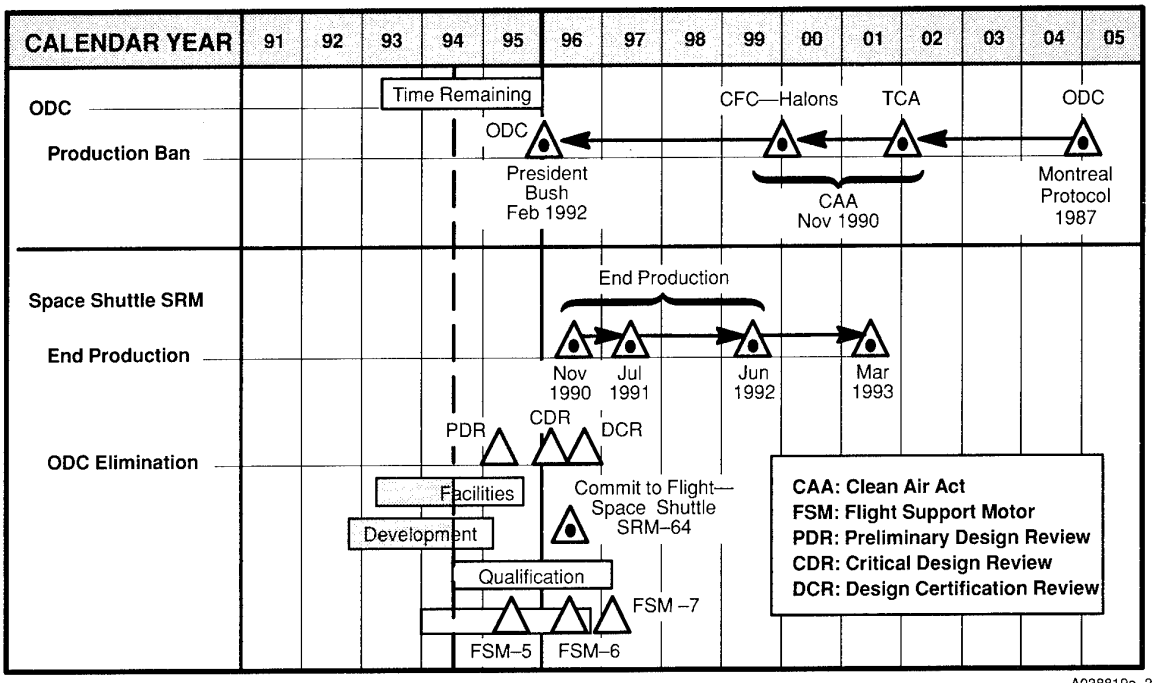



Fig. 4. Recognize Problem—Production Ban of ODCs

The issue was well defined. There would be a production ban of ODCs on January 1, 1996. Thiokol Space Operations ODC use in 1989 had been almost one million pounds in direct manufacturing operations and another 400,000 pounds in indirect use (Fig. 5). A detailed study of each ODC used identified 852 manufacturing callouts in official planning documents. Over 100 different bonds in the motor were affected (Fig. 6). The reliability of the motor depends on these bonds to prevent hot gases from reaching metal structural components. A Pareto analysis (Fig. 7) was conducted to prioritize the 32 major categories of use. The two biggest users were vapor degreasers like the one shown in Fig. 8. This analysis indicated that approximately 90 percent of the TCA use was in the top four categories, i.e., two large TCA vapor degreasers, diluent for preservative grease, and as a cleaner for propellant mix and cast tooling. Possible replacement processes for the vapor degreaser were evaluated. Requalification testing required for all of the 852 planning changes and 100 plus affected bonds were identified. An ODC team sorted through all of the possible alternate solutions to the required changes and developed a plan to eliminate all ODCs from the process.

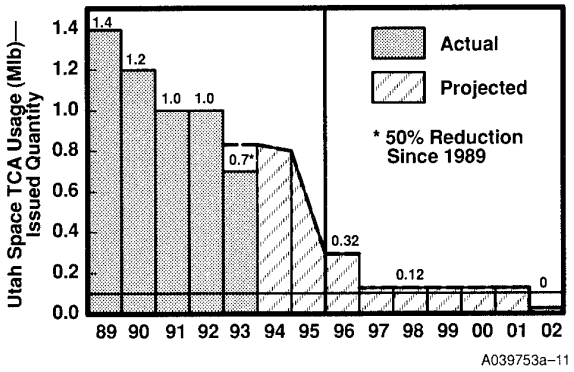



Fig. 5. Actual and Projected Reduction in TCA Usage

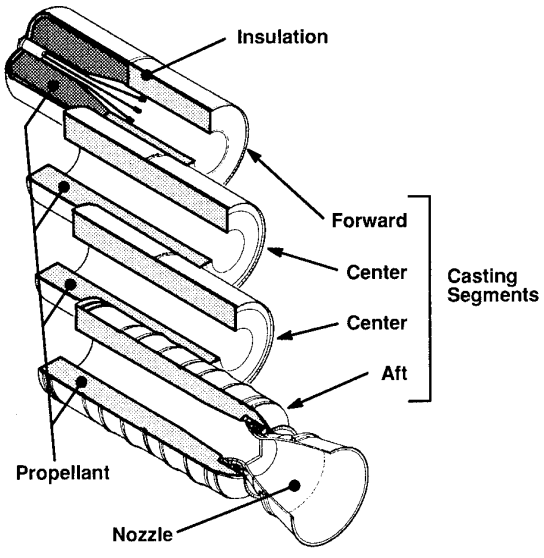



Fig. 6. Space Shuttle SRM Propellant Configuration

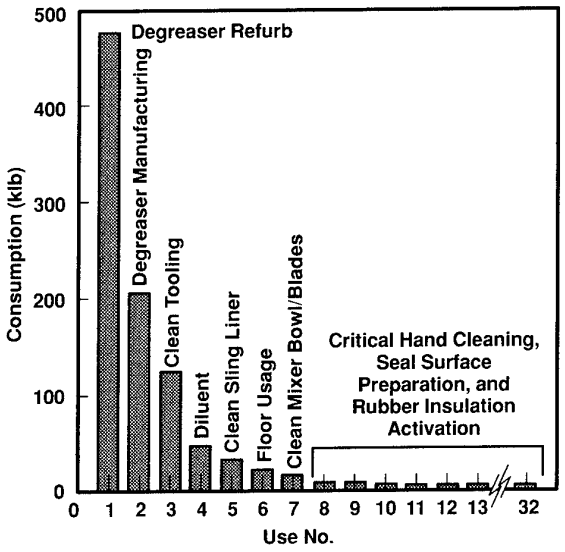
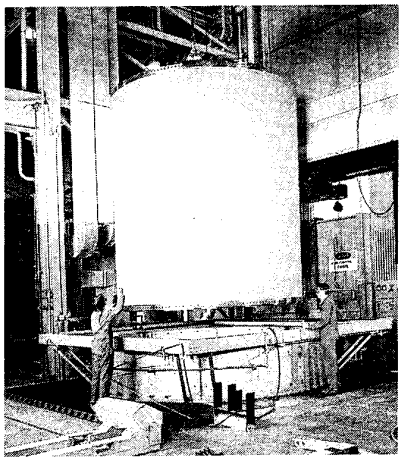



Fig. 7. RSRM Uses of TCA



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Fig. 8. Case Vapor Degreasing

**Industry Survey**

As the scope of the bonding process changes became clear, NASA and Thiokol engineers began an industry survey to identify options and alternative processes. Over a two–year period, 31 different companies were surveyed to determine how they were responding to the production phaseout of TCA. Forty–nine technical papers presented at seminars, workshops, and NASA–sponsored working groups were evaluated. Data were summarized, and a report was published in March of 1993. A matrix was prepared listing the substrates, preferred cleaners, and the person leading the project at each company. A distribution analysis was made of usage for cleaners selected by two or more organizations. From this survey, a list of factors to consider in the selection of replacement solvents and cleaners was created:

- Industrial safety considerations
  - Flammability, toxicity, allowable exposure
- Environmental release requirements
  - Ozone–depleting and global–warming potential, volatile organic compound level
- Product safety
  - Cleaning effectivity as measured by bond test results, residue on substrate, effect on metallurgical properties, material compatibility, corrosion potential, shelf–life (aging) capability
- Cleaning efficiency
  - Material and labor cost, availability, evaporation rate, soil loading capacity, stability, recyclability, disposal cost, energy cost, versatility
- Capital investment
  - Floor space required, capital expenditures, estimated life–cycle cost for equipment

*THE MAIN CONCLUSION OF THE INDUSTRY SURVEY WAS THAT WHILE MUCH CAN BE LEARNED FROM OTHER COMPANIES' EXPERIENCES AND DATA, EACH COMPANY MUST TAILOR CLEANING PROCESSES TO THE PARTICULAR SOILS, SUBSTRATES AND PERFORMANCE REQUIREMENTS OF THE PRODUCT BEING MANUFACTURED.*

**Hierarchy of Suitable Cleaning Alternatives**

Time and money are saved when permanent solutions are selected rather than short–term fixes. Dr. Katy Wolf, the executive director of the Institute for Research and Technical Assistance (IRTA), was very helpful in suggesting that companies follow her low–risk hierarchy of alternate cleaners, i.e., no clean, water, aqueous, semiaqueous, combustible solvents, and flammable solvents in decreasing order of desirability

## 5. ANALYZE DATA—PRELIMINARY TEST PROGRAM

In the early stages of selecting a replacement cleaner for TCA at Thiokol, all potential cleaners were considered. Initial screening tests favored organic cleaners because the hardware's preservative grease is soluble in organic cleaners. If all aqueous cleaners had been eliminated because the grease preservative was not soluble in them, the best cleaners would have been missed as measured by fracture energy, tensile adhesion, and residue after final rinse. Fortunately, the test program was structured to continue testing with five of the best cleaners from each group: five aqueous, five semiaqueous, and five organic—or 15 total—before a final down–selection of the two best cleaners was made. Both an aqueous and a semiaqueous cleaner produced bonds that demonstrated superior fracture toughness and tensile adhesion test data, with acceptable results in all other areas tested. A typical set of data for steel tensile adhesion strength is shown in Fig. 9.

## 6. QUALIFY SOLUTIONS INTO PROCESS—DESCRIPTION OF PHASE I—ELIMINATE 90 PERCENT OF TCA

The Phase I plan to eliminate 90 percent of the TCA was focused first on eliminating the four biggest users, i.e., the solvent in two

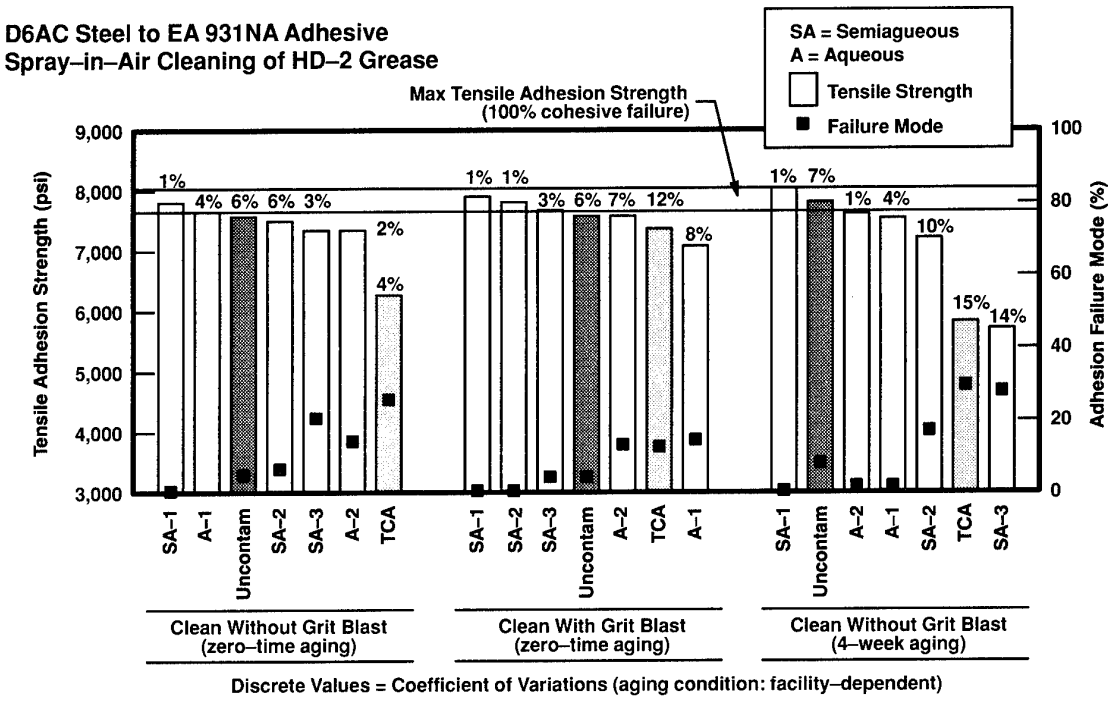
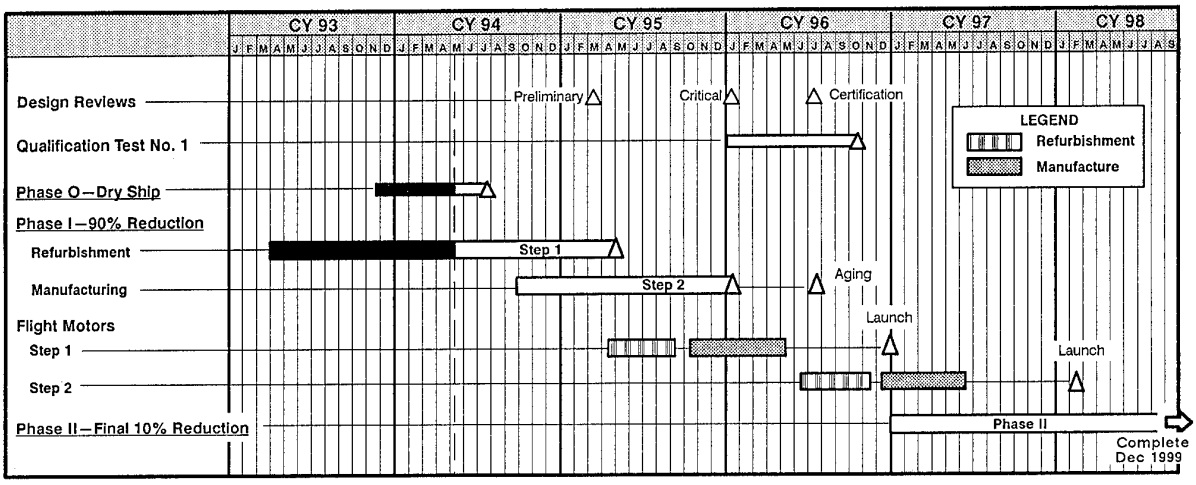



Fig. 9. Nozzle Bondline—Tensile Adhesion Test Data

large vapor degreasers, a cleaner for propellant tooling once it is out of the propellant mix and cast buildings, and diluent used to thin the preservative grease. This effort is time–phased: Step 1—replace the Refurbishment Center's vapor degreaser with a high–pressure water wash system and implement greaseless storage and shipment of hardware; Step 2—replace the Manufacturing Center's vapor degreaser with a spray–in–air precision cleaner and qualify tool cleaning process for propellant mix and cast tooling. The master schedule for this effort is shown in Fig. 10.

The Step 1 effort is 30 percent complete. Components for the high–pressure water wash system are in the procurement cycle.

The Step 2 development and qualification effort is continuing with the selection of a final cleaner to be made by mid–1994. The




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Fig. 10. Master Schedule for ODC Replacement

designing of the spray–in–air system will begin in October of 1994 and will be operational by early 1996. At that time, TCA usage will have been reduced by 90 percent from 1989 levels and TCA emissions by 95 percent.

### Phase II—Eliminate Remaining 10 Percent of TCA, Stockpile, and Obtain Essential Use Waiver

The Phase II plan eliminates the remaining 10 percent of TCA usage by the end of 1999. Critical uses of TCA associated with hand cleaning, rubber activation, and equipment cleaning that could affect critical bonds and processes essential in propellant mix and cast areas where a flash fire could be catastrophic are included in Phase II. The remaining 10 percent TCA use affects approximately 80 percent of the bonds (78 of the 101) critical to the reliability of the Space Shuttle system. An approach was established to request an Essential Use Exemption from the Solvents, Coatings, and Adhesives Technical Options Committee of the United Nations Environmental Program. This approach would allow time to address schedule and cost to ensure changes could be qualified prior to use on flight motors. Discussions were held with the Environmental Protection Agency (EPA), NASA, and Thiokol regarding the approach, and positive indications were received. The Montreal Protocol criteria for an exemption were obtained, and a final request to purchase 125,000 pounds of TCA per year was submitted to the EPA on June 24, 1993. The United Nations committee met in October of 1993 and reviewed the exemption request with final decision on the exemption to be made in the fall of 1994. If the exemption request is approved and schedules are met, we will not require stockpiling of TCA (Fig. 11).

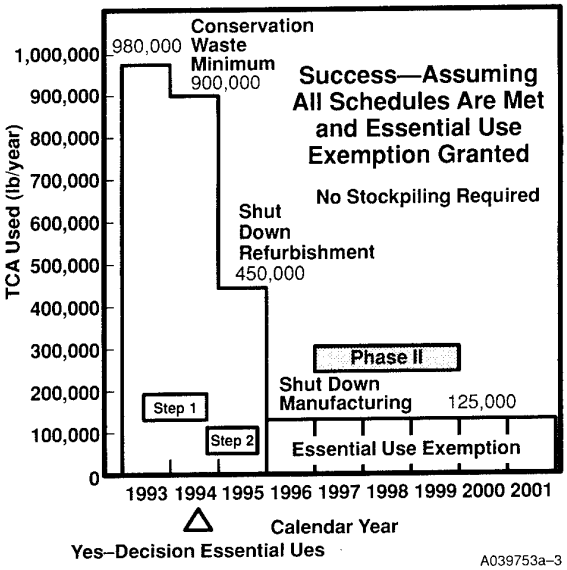



Fig. 11. ODC Program—TCA Usage

### Creative Synthesis of New Resources

The execution of our plans involved a bringing–together of a number of new resources: 1) new partnerships, 2) new technologies, and 3) new approaches and strategies.

**New Partnerships.** Our efforts benefitted greatly from the new partnerships formed with governmental organizations, professional groups, industry associations, and academia.

a. NASA Operational Environmental Team

The NASA Operational Environmental Team (NOET) was established in April 1992 to provide the entire NASA team a central resource to pursue replacement technology. The focus of this team is environmentally questionable materials and related processes involved in the design, development, test, and manufacture of NASA hardware. The two elements of the NOET, the Replacement Technology Team ($RT^2$) and the Propulsion Technology Team ($PT^2$), work through the existing program structure to emphasize resource prioritization and trade studies, to address technical issues, and to avoid redundancy. The NOET provides excellent opportunities for cooperative efforts among NASA centers, other federal agencies, subcontractors, educational institutions, and private industry. The NOET team leader is NASA's Robert (Bob) J. Schwinghamer, deputy director of Science and Engineering at MSFC.

b. NASA: Assured Shuttle Availability

In 1992, Johnson Space Center (JSC) and MSFC provided funding to allow Thiokol to conduct testing of alternate hardware preservation and shipping techniques at the refurbishment facility. The Assured Shuttle Availability (ASA) program demonstrated a process flow that eliminated the need for the three vapor degrease cycles and proved preservative grease is not required if the hardware is protected from the weather and high humidity conditions (less than 45 percent relative humidity). This program generated data to support the concept of "clean once and keep it clean," and will result in substantial cost savings and environmental benefits when qualified for production. An environmentally controlled trailer has been procured to ship segments 60 miles between plants without preservative grease diluted with TCA (Fig. 12).



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Fig. 12. RSRM Case Shipping System ODC Phase Zero

c. Environmental Protection Agency

The EPA Stratospheric Ozone Protection Division and the United Nations Solvents, Coatings, and Adhesives Technical Options Committee are providing on–going support to the aerospace industries' efforts to find acceptable alternatives for ozone–depleting chemicals. This partnership has provided access to foreign and domestic experts and has helped avoid duplication of effort while increasing confidence in the performance of selected alternate materials and processes. Dr. Stephen O. Andersen is the deputy director of the U.S. EPA Stratospheric Protection Division and chairman of the United Nations Solvents, Coatings, and Adhesives Technical Options Committee.

d. NASA Headquarters (Environmental Engineering)

The Chief Environmental Engineering Office at the Office of Space Flight (OSF), NASA Headquarters, has taken an aggressive approach to protecting the environment. This small staff has opened channels of communication between the EPA, NASA, and contractors to provide the free exchange of information. Mr. Steven Newman is OSF's chief environmental engineer.

e. Aerospace Industries Association

Thiokol Corporation, as a member of the Aerospace Industries Association (AIA), has participated on the Environmental Activities Committee. Members include the major air frame manufacturers and their suppliers, the solid rocket motor manufacturers, and other aerospace organizations. Meetings have provided valuable contacts with knowledgeable senior experts where information is exchanged in many areas of environmental concern. Mr. Glynn Rountree is the AIA chairman of this committee.

f. Academia

Brigham Young University was given a study contract to evaluate improved shipping and preservation methods. Their study supported the ASA Project conclusions which were to get the hardware clean at the refurbishment facility and provide shipping containers to keep it clean during the 60–mile transportation trip to the main plant.

The University of Alabama was contracted to develop and demonstrate a single strand fiber optic system capable of providing quantitative information on the nature of contaminants on steel, aluminum, and phenolic systems. The principal investigators on this study are Mr. Roy Marrs of Thiokol and Dr. Gary Workman of University of Alabama at Huntsville.

**New Technologies.** The team implemented plans for solving environmental problems. We benefitted from the application of new technologies and provided additional processing benefits. Some of those are described below.

a. High–Pressure Water Wash

Thiokol has used high–pressure water systems in the 10,000– to 15,000–psi range to remove insulation from metal parts since the mid–1960s. A new application of ultrahigh–pressure water up to 36,000 psi is planned as a replacement process for TCA vapor degreasing and grit blast with zirconium silicate. This environmentally superior process will eleminate TCA use, reduce process cycle times, and increase hardware life because metal removal rates with water are an order of magintude less than with grit blast media. This equipment is being demonstrated in the NASA Technology and Productivity Enhancement Laboratory at MSFC (Fig. 13). Production equipment is on order and is scheduled for installation and checkout during the first quarter of 1995. A sketch of the new equipment is shown in Fig. 14.

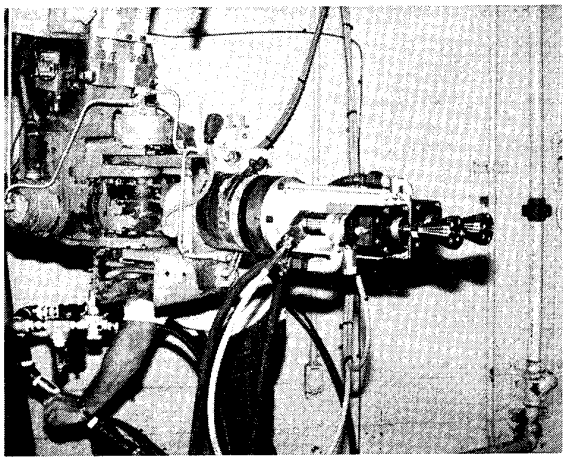
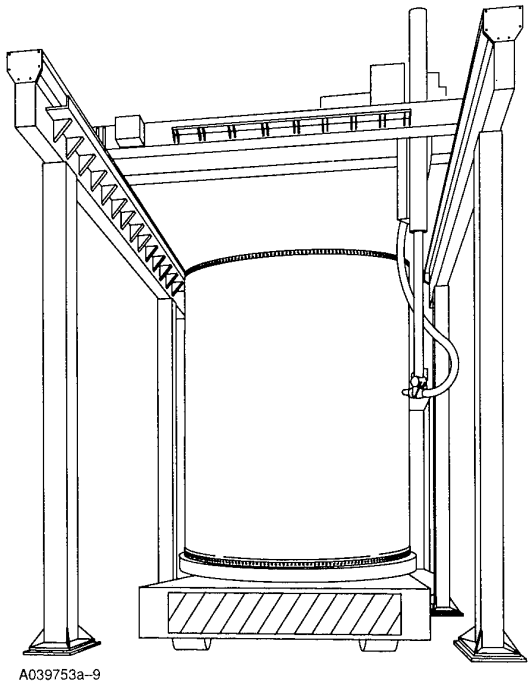


Fig. 13. Ultrahigh–Pressure Nozzle Testing at NASA Productivity Lab

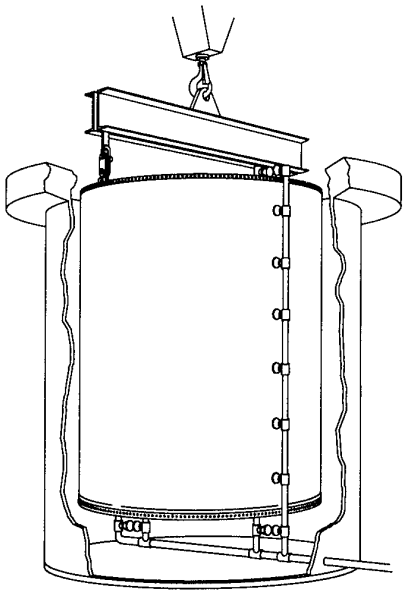


A039753a–9

Fig. 14. Ultrahigh–Pressure Water Wash System

b. Spray–in–Air With Aqueous and Semiaqueous Cleaners

Aqueous and semiaqueous cleaners had been used in dip tanks followed by a rinse and drying of the soiled part (Fig. 15). Thiokol proposed using a spray–in–air method that would be cheaper and give a cleaner part. Data gathered are shown in Fig. 9.



A039753a–10

Fig. 15. Spray–in–Air Aqueous Wash System

c. Low–Emission Vapor Degreasing

The first consideration in finding a replacement for TCA used in the vapor degreasers was to evaluate a switch to perchloro–ethylene. It does pose health risks, and, therefore, has a low (50 ppm) permissible exposure limit. An alternative to open–top vapor degreasers is an airtight system known as low–emission vapor degreasers (LEVDs). Two manufacturers were contacted and several meetings held to understand how the LEVD system works. The process was determined to be a viable alternative, but was not selected because of relatively little demonstrated use in U.S. industry on parts the size of RSRM cases. Also, the potential for future legislation on exposure and use of perchloroethylene was a concern. The two leading suppliers of this equipment are Dürr Industries, Inc., and Baron Blakeslee.

d. Surface Cleanliness Measurements

The question of "How clean is clean?" has been with us for a long time. Much has been accomplished to quantify the measure of cleanliness. NASA developed an optically stimulated electron emission (OSEE) device called ConScan that measures surface cleanliness levels and oxides and plots them for acceptance analysis. Thiokol has been using the system since 1988 to ensure acceptable surface cleanliness prior to bonding and continued reliability of motor performance (Fig. 16). The principle contact at NASA/MSFC is Mr. Billy Nerren. The Thiokol–developed SurfMap™ infrared contamination detection device uses diffuse, back–scattered light in the mid–infrared region to monitor a surface for the presence of hydrocarbons. The contact at Thiokol is Mark Walker.

e. Surface Chemistry Analysis

Thiokol has made extensive use of laboratory surface chemical analysis methods in the evaluation of replacement cleaning processes for methyl chloroform vapor degreasing of steel and aluminum bonding surfaces. Techniques include electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES), and static secondary ion mass spectrometry (static SIMs). ESCA, AES, and static SIMS are sensitive to changes in the topmost atomic layers of a surface which are directly involved in bonding. The principal investigator at Thiokol is Dr. Mike Lesley.

**New Approaches and Strategies**

a. Pollution Prevention

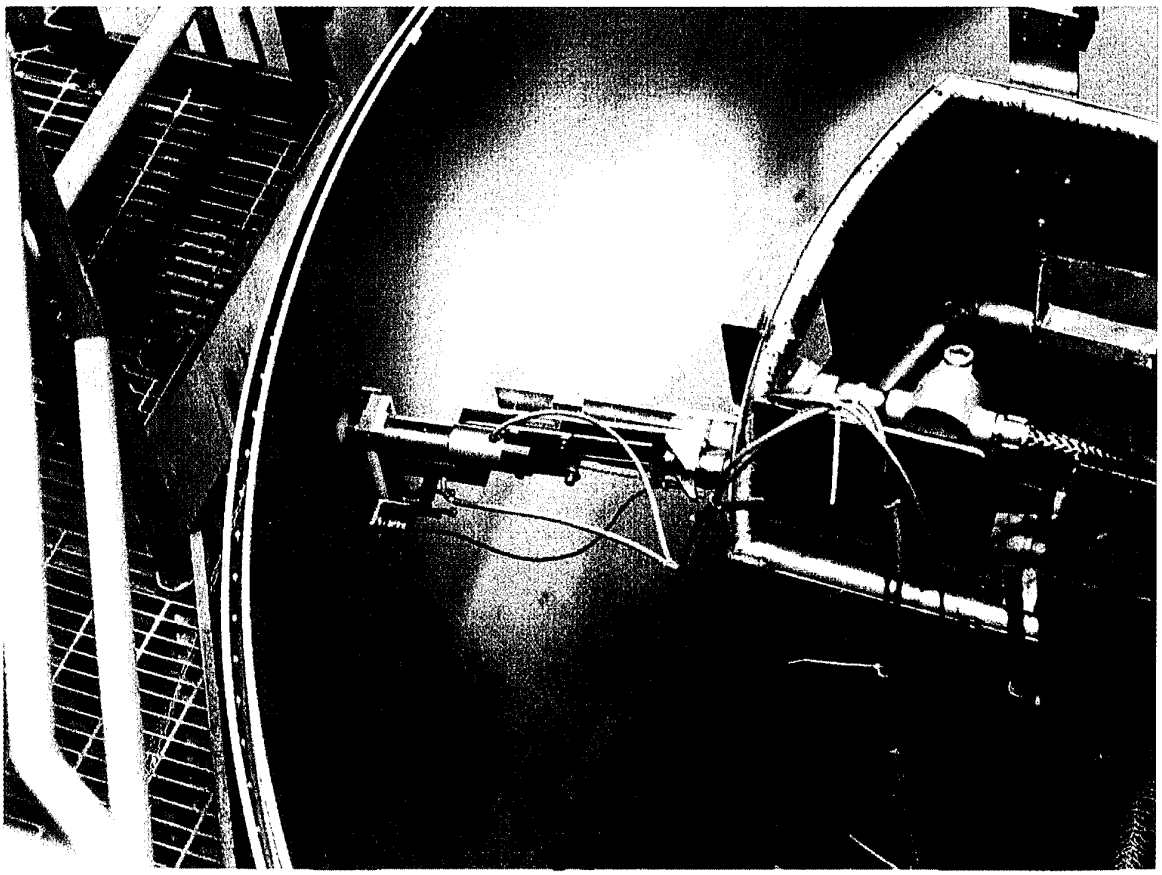
The 1990s approach to enhancing the environment is preventing pollution at the source by better, smarter planning of the product design and the manufacturing process. The EPA has published a document (*Facility Pollution Prevention Guide,* EPA/600/R–92 088, May 1992) that provides excellent instructions on how to establish and maintain a successful pollution prevention program. The document may be obtained from: **U.S. EPA, Office Research & Development, Washington, D.C. 02460.**

b. Unit–of–Issue to Match Usage

Most large organizations have a supply system that issues materials to the production line. On controlled programs, the quality of the material is assured by the seal on the container. Once it is broken, and residual material cannot be returned to Stores. If the smallest unit of issue is a gallon and the user only needs a pint, the result is scrap material, which is wasteful and expensive to dispose of. By understanding the needs of the production line, material can be issued in quantities actually used, avoiding waste and expense.

c. Listen to the User

A significant change in direction occurred in December of 1992 when Manufacturing Center directors responsible for the cleaning operations made several suggestions that completely changed the direction of the ODC replacement program. They suggested that high–pressure water be used for refurbishment operations and the final precision cleaning be reserved for use just prior to bonding operations at the Manufacturing work center. High–pressure water could remove paint and adhesive residue faster and better than the existing grit blast process. The life of the flight hardware could be extended with the high–pressure water wash because less metal would be removed than with grit blast. The change to ultra-high–pressure cleaning at the Refurbishment Center was accepted and eventually proved to be the best plan, once again demonstrating that "the user knows more about the real process than anybody else."



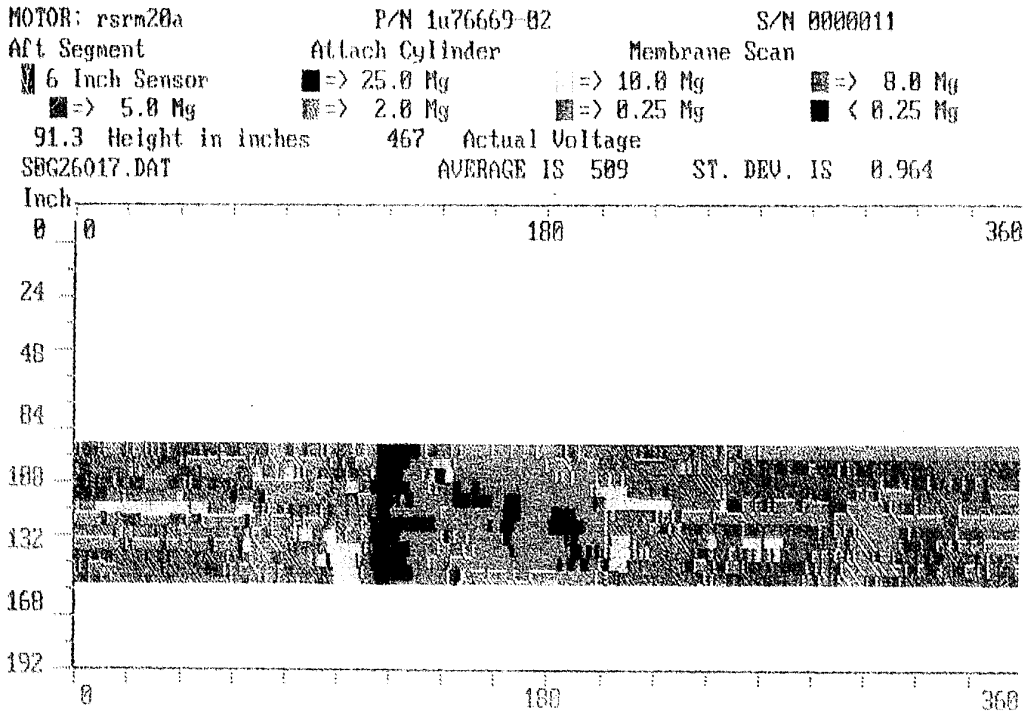



Fig. 16. Automated ConScan and Color Map of Cleanliness

### 7. REPORT SOLUTION OF PROBLEM

An engineering and environmental challenge was presented to the NASA/Thiokol/industry team when the international decision was made to stop the production of ODCs. The team used a classical approach for problem–solving combined with a creative synthesis of new approaches to attack the challenge.

**Summary of Lessons Learned**

- Establishing clear selection criteria for decisions at the beginning keeps the program on track
- Industrial safety considerations must be evaluated when selecting alternate cleaners
- Examination of current process and minor changes reduced TCA useage by 50 percent
- Bond strengths depend on cleanliness and surface chemistry
- Listening to the people who will have to implement the plan improves results
- Cost considerations are important and can be a positive competition factor
- While much information can be learned from other companies' experience, each company must tailor the cleaning process to the particular soils, substrates and performance requirements of the product being manufactured

## CONCLUSION

Since many of the processes that were acceptable in the early 1980s are no longer environmentally acceptable in the 1990s, companies need to make drastic changes to their thinking, materials, processes, and manufacturing in order to stay competitive. Companies are basically concerned with how to get the best environmental program while under tight budget constraints. Meeting environmental requirements necessitates making changes to the way products are manufactured. The requirement to make changes to processes can be an opportunity rather than a burden. Since all companies must make changes at this time, leaders can make changes in a manner that will give them a competitive edge. They have an opportunity to examine their manufacturing paradigms and incorporate better ones. New cleaning methods should make operations more economical where possible. These new environmental requirements give companies an opportunity to modernize while making the workplace safer and reducing emissions of hazardous materials.

## Discussion

QUESTION BY A. DAVENAS : In the Con Scan System you probably have to calibrate the device by using as a standard a nominal pollutant that you know may be present. How would you take care of other more "accidental" pollutants ? Do you think there are possible means to characterize the pollution of rubber or plastic hydrocarbons by an hydrocarbon pollutant ?

ANSWER : Contamination on the SRM hardware is detected with a Con Scan device using optically stimulated electron emission (OSEE). This technique was originally developed for detecting metal oxides and had applicability to the Shuttle hardware because of the extensive use of a calcium grease applied to the hardware for corrosion protection. The OSEE is not capable of determining the type of contamination, it only determines that there is some contamination present. The system is calibrated against a "clean" metal standard and various degrees of known contamination. The Conscan can be calibrated to determine the quantity of contamination in mg/sg.ft whatever the contamination may be, but it cannot determine what the contamination is. The calibration is dependent on the surface being analyzed. It gives good results for steel but is not as accurate for aluminium and is less reliable for rubber and phenolics. We are examining an infrared technique using diffuse back + scattered light in the mid infrared region to monitor the surface of rubber and phenolics. This system can be calibrated specifically for hydrocarbons. Other contaminants require a new calibration standard. The contact at Thiokol is Mr Maric WALKER for the surf Map TM IR contamination detector device. Call me at 801-863-3555 for his telephone number.

The contact for the operational Con Scan device currently being used on the Shuttle SRm's is Mr Billy Nerren at NASA/MSFC. Dr Ben Goldberg could probably provide his telephone number to you.

QUESTION BY R. DERR : Does the wet wash approach result in acceptable aging characteristics for the space Shuttle booster ?

ANSWER : Yes, providing that you dry the part sufficiently to eliminate any possible rust formation.

# Prioritization Methodology for Chemical Replacement

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## SUMMARY

This methodology serves to define a system for effective prioritization of efforts required to develop replacement technologies mandated by imposed and forecast legislation. The methodology used is a semi-quantitative approach derived from quality function deployment techniques (QFD Matrix). QFD is a conceptual map that provides a method of transforming customer wants and needs into quantitative engineering terms. This methodology aims to weight the full environmental, cost, safety, reliability, and programmatic implications of replacement technology development to allow appropriate identification of viable candidates and programmatic alternatives.

## EXPLANATION OF MATRICES

### Matrix A

Matrix A is a "chemical and use" matrix. The objective of this matrix is to define the target chemicals by the part and process in which they are used (the how and where the targeted chemicals are used). This matrix has some "bookkeeping" areas to help in tracking the particular chemical/part/process combination in other matrices. Parts of Matrix A will be used in all matrices. Each component of Matrix A may not need to be filled out. The following is an explanation of the requested information for this matrix.

• *the target chemical*

The Class I or Class II chemical which has to be eliminated due to regulation should be put in this column. Any other chemical which needs evaluation for replacement could also be put in this column. It should be noted that some materials may contain several "target" chemicals. Those materials which have several chemicals should be grouped for identification purposes. This information will be necessary for subsequent matrices.

• *a chemical registry #*

This is the standard number ( as might be found on a Material Safety Data Sheet (MSDS)) for the chemical. This is requested so that actual values necessary for evaluation can be found.

• *a chemical reference #*

This a bookkeeping number. It is assigned by the person filling out the chart. It is recommended that for every chemical the number is consistent (i.e. for all uses of TCA the number is 1, for all uses of CFC113 the number is 2, etc.). This number will be used throughout the rest of the matrices in the "chem #" column.

• *material*

This is the material that the chemical is in, identified for the specific process. This is a reference to assist defining the processes and parts. Generally this will be the manufacturing or common name. (See Figure 1)

| Chemical | Chem # (Reference #) | Material |
|---|---|---|
| Trichloroethane | 1 | TCA/Solvent |

**Figure 1**

• *the process in which the chemical is used*

This is the current process for which the chemical is being used. This process is dependent on the part, surface, etc. that will be affected. The process will be necessary for subsequent matrices.

• *a description of the part/component/subsystem which is being processed*

The part/component/ subsystem that will be processed will be completed in this part of the matrix.

| Chemical | Chem # (Reference #) | Part/Component/Subsystem |
|---|---|---|
| Trichloroethane | 1 | Large Case Segment - RSRM |
| Trichloroethane | 1 | Bolts |

**Figure 2**

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

• *a reference number for the specified part/component/subsystem*

This is a number assigned to the part/component/subsystem that will be processed. This number can be manufacturer specific as long as it can be referenced to the Failure Modes and Effects Analysis (FMEA - a tool used for risk assessment and delineation). This number will be used in Matrix C - Risk Assessment and possibly in Matrix D for specifications of surface requirements.

• *the surface being considered*

After the part has been defined, a surface on the part may need to be specified to better define the process and requirements.

• *process # (Reference)*

This is the bookkeeping number for the process. It should be defined by the chemical, the material, the part (or group of parts), and the surface. The process (reference) # should be defined such that there will be no confusion between processes. Again this reference will be used in the other matrices for tracking purposes.

**Example**: If TCA is used for a final vapor degrease of a case segment, it should be denoted by a number such as 1-1-1. If TCA is to be used for a final vapor degrease of a bolt, it should be denoted as 1-1-2. The chemical number previously defined denotes the chemical (TCA = 1 for the example), the second number denotes the process (vapor degrease = 1 for the example), and the third number denotes the part (case segment = 1, and bolt = 2)

| Chemical | Chem # (Reference #) | Process | Proc # (Reference) |
|---|---|---|---|
| Trichloroethane | 1 | Vapor Degrease (Case Segment) | 1-1-1 |
| Trichloroethane | 1 | Vapor Degrease (Bolts) | 1-1-2 |

**Figure 3**

• *a manufacturing process number*

This is another reference point for the matrix. The manufacturing process number allows a check on the stage of manufacturing in which this particular process is being done. Again this is an optional part of the matrix. It would be defined as a number (i.e. if it is the second process - it is 2).

• *the number of manufacturing processes*

This is the total number of processes a part goes through as defined by the part specifications (for a refurbished part and for a non-renewable part)

• *the pounds of chemical used in the process (for the specified part) per year*

This category is strictly for informational purposes. It provides a prospective of the amount of the targeted chemicals used.

**Matrix B**

The technical maturity of the chemicals and processes are evaluated in Matrix B. The existing chemical/process from Matrix A and the developmental chemical/process are evaluated according to the number of parts to be processed (in the program life) and the testing which has been performed on the chemical, process, and processed parts. This matrix might be sent to the environmental, research and development, or manufacturing group for completion. This matrix was designed to accommodate the existing process and the possible replacement processes, but it can also be used specifically for comparison and evaluation of possible replacement chemicals. The matrix is broken into sections which ask for the identification of the chemical and process along with the corresponding reference numbers for each.

The reference numbers for the existing chemical/process were defined in Matrix A; these same numbers should be used for the chemical/process in Matrix B. For each existing chemical/process there should be a chemical/process replacement. For each "replacement" chemical a number should be assigned to correspond with the chemical it is replacing.

**Example**: TCA = chem # 1, replacement aqueous soap = 1R1, terpene (another alternative) = 1R2 -- where the first number is the existing chemical, R denotes replacement, and the last number is the replacement chemical number. These numbers should be kept consistent while filling out the matrices.

A space is provided to identify the existing (old) technology and the possible replacement technology (new). When describing an existing chemical/process pair, check the box under the "Old" column; check the column under "New" for possible replacement chemical/processes. This is done as another bookkeeping reference while completing this matrix. However, when a "New" chemical/process is being considered, the "Old" technology information should also be included for a point of reference.

For each replacement chemical, there will be a replacement process which has some process reference number.

**Example**: From a previous example, TCA used in a final degrease for a case segment was 1-1-1, the

replacement process involves high pressure spray in air which would have a corresponding number 1R1-1-1. Another alternate solution is agitated immersion which would be designated 1R2-1-1 where the first two numbers designate the existing process, the "R" denotes a replacement technology, and the last number represents the replacement process number).

| Chemical | Chem # (Reference #) | Process | Proc # (Reference) |
|---|---|---|---|
| Trichloroethane | 1 | Vapor Degrease | 1-1-1 |
| Aqueous Soap | 1R1 | Spray in Air | 1R1-1-1 |
| Terpene | 1R2 | Vapor Degrease | 1R2-1-1 |

**Figure 4**

The process reference numbers for the processes should also remain consistent for the subsequent matrices.

The next item to be completed is "Years of Existence." This is the number of years the chemical/process has been available for commercial purchase.

Subsequent items deal with chemical, material, and process testing. In an effort to provide for every type of test, the "type tests" are very general in scope. This matrix is not necessary to complete for the analysis to be useful; it is provided to quantify the extent of testing for each chemical/material/process. Some materials and/or processes may not need a particular type (general) of test. For those areas where the test information requested is not applicable, note in the space that it was considered not necessary by placing a check in the corresponding box.

The following items are requested:

• *Toxicity Testing*

New chemicals must pass a series of toxicity tests before they are allowed to be used. By identifying the toxicity testing which has been completed, the new technology can be identified as a cost or scheduling conflict before completing the rest of the matrices.

• *Environmental Testing*

Environmental testing can be used to determine if the chemical/process is "environmentally safe." By identifying if the chemical/process has been tested, one can foresee the possibility of future environmental regulations.

• *Chemical Reactivity Testing*

By identifying the amount of chemical reactivity testing that has been done, one can see the amount of future necessary chemical reactivity testing that might possibility be needed before the chemical can be qualified for use.

• *Age Sensitivity Testing*

This category includes such areas as shelf-life, extensions of shelf life, viscosity changes over time, age sensitivity of the chemical while on the part, handling, etc. The information requested in this category is not restrictive in the nature of type of age testing; but when considering the extent of age testing for an existing chemical, the same type testing should be evaluated for the considered existing technology.

• *Misc. Testing*

This category includes any other type testing required for this chemical/process that cannot be included in one of the other categories. Again, the same consideration should be taken for testing with the existing technology and the replacement technology.

• *Parts to be Processed (Program Life)*

The program required component lifetime and the number of expected parts to be produced during that time should be entered in this space. This allows for judgment of the necessity of finding a replacement technology.

**Matrix C**

Matrix C is a risk assessment matrix which provides a valuable tool for determination of the critical safety and reliability parts and processes. This matrix is designed to allow the risk of failure of the hardware to perform its function, due to the process change, to be calculated numerically.

The existing targeted chemicals, process, and drawing numbers (from Matrix A) and the possible replacement chemicals and processes with appropriate drawing numbers should be filled in first. A space is provided to check which is "existing" technology and which is "new" technology.

The FMEA # is requested for reference purposes. The FMEA provides a ranking of criticality (Crit) of the part and process which is given a "weight" or numerical value. This number will be assigned a 1, 3, or 9 for Crit 3, 2, and 1 respectively. (A Crit 3 could result in a non-catastrophic failure with re-use ramifications, a Crit 2 failure in non-catastrophic with failure to meet mission requirements and a Crit 1 failure worst credible case would be catastrophic)

| Chemical | Process | Proc # | Criticality | Severity Value |
|---|---|---|---|---|
| TCA | Vapor Degrease | 1-1-1 | C1 | 9 |

**Figure 5**

The probability of failure value is determined by weighting the factor of safety and the type inspection(s) performed. A ssubjective scale has been established, ranging from 1 through 6, with 6 representing the least reliable inspection techniques (eg visual inspections) and 1 representing the most reliable (eg destructive evaluations such as plug pulls for bondline demonstration) The Safety Factor (a quantitative value representing the calculated amount of capability that exists in exceedence of the maximum anticipated load - typically a thermal or structural issue) should be inverted and multiplied by the Inspection value to get the Probability Value. (See Figure 6.)

| Chemical | Process | Inspections | Original S.F. | Probability Value |
|---|---|---|---|---|
| TCA | Vapor Degrease | NS | 9 | 5/9 |

**Figure 6**

The risk evaluation (weight) is determined by multiplying the probability value by the severity value. This matrix might be sent to a risk assessment group.

| Chemical | Process | Severity Value | Probability Value | Risk ( = P*S) |
|---|---|---|---|---|
| TCA | Vapor Degrease | 9 | 5/9 | 5 |

**Figure 7**

**Concerns**

The following categories are the concern categories which are listed separately in the QFD matrix. Each concern category is given a separate matrix for simplification and facilitates the use of particular parts of the entire workbook The format in specifying the chemical/process pairs is the same as Matrix B. The code following each concern is specified by three letters (such as NMH) which are defined in the legend below the evaluation matrix (None, Minimal, High). The highest score is a 9 which in this case corresponds to "None". The lowest is 1 which corresponds to "High". If the question is not applicable then place a check mark in that box noting it was recognized as unnecessary. If the criteria described in the explanation can be rewritten to better evaluate the process, then make a note of the change in the explanation and use the updated criteria for **ALL** of the chemical/process pairs that are to be evaluated.

Each new process and chemical will be "scored" for each concern listed in Matrices D through J. Each "score" will be shown as most positive, neutral, or negative (or blank for no relation). Matrices D through J will also allow the concerns to be weighted for importance. These weighted factors will need to be considered in the final prioritization calculations. Additional information such as risk factors for part failure and technical maturity of the chemical and process will be used when trade-offs become necessary. These data will be evaluated using QFD methodology.

**Matrix D**
Matrix D addresses the chemical concerns for the existing and replacement technologies. Again this can be used alone or as a part of the QFD matrix. This matrix should give the user a firm understanding of how the chemical acts or reacts during its shelf life or usage. An environmental engineering group and/or manufacturing should complete this matrix.

**Matrix E**
The process concerns deal with the way that a chemical acts or reacts during a process application. An environmental engineering group and/or manufacturing should complete this matrix.

**Matrix F**
Matrix F considers the regulatory impacts on a chemical/process. When completing this part of the matrix, one should consider the known dangers (i.e. known phase-out and reduction plans) when rating a chemical/process on meeting the laws. The regulatory concerns consider how OSHA requirements, federal, state, local environmental laws and regulations affect chemicals and processes. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

**Matrix G**
The safety concerns are worker exposure, spill response, fire response, and explosion response. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

**Matrix H**
The environmental concerns consider how chemicals impact the program environmentally. Sections of this matrix might be completed by safety, legal, and environmental management personnel.

**Matrix I**
The cost concerns evaluate how cost will deviate with the replacement of current technologies. This matrix might be completed by the project or program office (or their support personnel).

**Matrix J**
The scheduling concerns delineate how scheduling requirements will be met with respect to Environmental Regulations and NASA program schedules. This matrix might be completed by the project or program office (or their support personnel).

Appendix A includes example Matrices for use as guides in completing the prioritization process.

## QFD APPLICATION

The QFD matrix will be completed by the project office or program manager. The basic QFD format is shown in Figure 8.

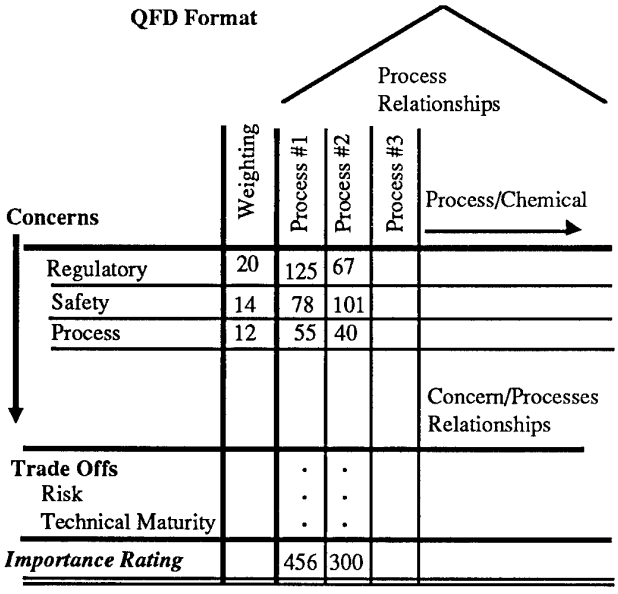



Figure 8

The QFD Matrix is quite easy to understand if it is approached one step at a time. In the case of the chemical replacement, first list the customer's (NASA or Contractor) concerns vertically on the left. Then list each chemical/process, old and new, horizontally. The relationship of each concern to each chemical/process is then rated on a scale of 1 - weak, 3 - medium, and 9 - strong. Next, a weighting factor is given to each concern. That is, on a scale of 1 to 20 in this case, assign a number rating the *importance* of each concern. To get the overall rating of each chemical/process, multiply the weighting factor times the relationship rating for each process to concern and sum the total down the page.

| | Weighting Factor | Chemical/ Process #1 | Chemical/ Process #2 | Chemical/ Process #3 |
|---|---|---|---|---|
| Concern 1 | 10 | 3 | 9 | 1 |
| Concern 2 | 15 | 1 | 9 | 3 |
| Concern 3 | 12 | 9 | 1 | 9 |
| Overall Rating | | 153 | 237 | 163 |

**Figure 9**

**Example:** Chemical/process #1 would have an overall rating of (10 * 3) + (15*1) + (12*9) = 30 + 15 + 108 = 153. Chemical/process #2 would be (10 * 9) + (15 * 9) + (12 * 1) = 90 + 135 + 12 = 237. Chemical /process #3 would be (10 * 1) + (15 * 3) + (12 * 9) = 10 + 45 + 108 = 163. This methodology would rank #2 as the "better" alternative of the three.

The "roof" at the top of the matrix simply shows how strong the chemicals/processes relate to each other. This knowledge can applied when trade-offs become necessary. In fact, the QFD Matrix can include several different entries that could be included in trade-off studies. The Chemical Replacement Prioritization Methodology applies only a limited use of the QFD capabilities.

Since this methodology is used as a guideline for comparison for replacement technology, it should be noted that there are times when a full QFD evaluation should not be performed. The times that the QFD evaluation is not recommended are:

- when another tool or system is more applicable, such as when decision, risk analysis, or analytical process models are all that are needed
- there is not enough time or resources to do it *RIGHT*
- critical elements of the process are missing (i.e. customer feedback).

In these cases, one should consider using the most relevant matrices to assist in making judgment on replacement technology.

## WEIGHTING

For each type of process, the weighting factors will vary (i.e. the weights for precision cleaning may differ from those in foam blowing). Therefore a QFD weighting application is enclosed as Matrix K. This weighting box allows the concerns to be weighted against each other. The number in the box represents the score of that concern versus each of the other concerns. The more important concerns should be represented by higher numbers. The matrix can be expanded to weight any category or all of the concerns together. For each category, the weights should be normalized by dividing the weight by the # of concerns. A blank weighting worksheet (Matrix K) is included in Appendix A.

## SCORING

Depending on the type of application, the scoring will be slightly different. If only part of the matrix packet is used then the weights should be multiplied by the number corresponding to that code. The total of these numbers is the "score" for that process. If the entire matrix packet is to be used as a QFD exercise, then for each of the concern matrices (D-J) the "score" should be determined as before by multiplying the weight by the number corresponding to the code then each concern category should be normalized by dividing by the total number of concerns in that category.

- Matrix A carries no numerical weight.
- Matrix C "scores" should be multiplied by 100 and added to the total from the concerns if using the QFD matrix as a prioritization tool or subtracted from the total if it is used as a replacement technology comparison tool.

- If the matrix packet is to be used as a comparison between alternate replacement chemicals/processes, then the percentage of testing completed as compared to the current technology (from Matrix B) should be determined for each category of tests. The total of these numbers should be added to the accumulated numbers. If the matrix packet is to be used to determine the ranking of "urgency" then this chart could be used as a reference to show the technical maturity of the existing technology. This chart does not necessarily need to be completed if it is to be used for this type of application.

## CONCLUSION

The objective of this work was the development of a quantitative procedure for determination and ranking of replacement technologies and associated technical and programmatic issues. The QFD matrices are designed to produce a numerical "importance" value. If the QFD matrix is completed, the final total will be the importance value. The higher number corresponds to the "higher priority" or "better selection" chemical/process -- depending on the application.

Several agencies have requested copies of this prioritization methodology workbook in its entirety; this includes several NASA offices, NASA contractors, Department of the Navy, Army representatives, university representatives, private consultants, and the US Environmental Protection Agency. At this point the feed back has been very positive from those that have reviewed the document. NASA contractors have actively used parts/variations of this methodology. Thiokol has used this method to determine the type of cleaner and process to be used for cleaning solid rocket motor parts. They also used parts of Matrix A and C to rank the importance (according to risk) of each use of the current cleaner. Martin Marietta has used parts of this methodology for work performed in the TPS Materials Research Laboratory at Marshall Space Flight Center. Other feedback has been less specific, however, this publication has been recommended by the Commonwealth of Virginia Department of Environmental Quality and has been made available through the technical assistance library in that area.

For additional information about the Prioritization Methodology or to receive a complete copy of this publication, contact:

Dr. Ben Goldberg (205) 544 - 2683
Wendy Cruit (205) 544 - 1130

# Appendix A

## Matrix A - Chemicals and Uses For Prioritization Methodology

| Chemical | Chem # (Registry #) | Chem # (Reference #) | Material | Process | Part/Component/Subsystem | Surface | Proc # (Reference) | Proc Step # | Total Process Steps (#) | Reference # (tracable to FMEA) | Amount Used In Process (lb/yr) |
|---|---|---|---|---|---|---|---|---|---|---|---|
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## Matrix B - Technical Maturity of Substutite For Prioritzation Methodology

| Chemical | Chem # | Process | Proc # | New | Old | Years of Existence | Toxicity Testing | | Environmental Testing | | Chemical Reactivity Testing | | | Age Sensivity Testing (shelf-life & aging) | | | | Misc.Testing | | # of parts to be processed (Program Life) -- old and new |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | # | Type | # | Type | # | Results | Type | # Samples | Shelf Life | Type | Ext. | # | Type | |
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# Appendix A
## MATRIX C - Risk of System Failure

| Chemical | Chem # | Process | Proc # | New | Old | Part/ Component/ Subsystem # | FMEA # (Ref.) | Severity (S) | | Probability (P) | | | | Risk ( = P*S) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Criticality | Severity Value | Inspections | Original S.F. | Anticipated S.F. | Probability Value | |
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| | Inspections: | | |
|---|---|---|---|
| 6 | V = Visual | 3 | W = Witness Panel |
| 5 | NS = NDE (UT, X-Ray, ect...) | 2 | WT = Witness Panel -- Tested |
| 4 | LC = LOX Cleanliness (NVR, Other) | 1 | P = Plug Test |

**NOET -- Prioritization Methodology for Chemical Replacement**

# Appendix A
## Example Matrices D and E -- Chemical and Process Concerns

Weighting Factors to be Inserted Here →
1 - Less Important 20 - More Important

* NOTE: Either Numbers, Letters, or Symbols can be used to comple the Matrices.

| | | | | | | *Chemical Concerns* | | | | | | | | | | | | | | | | | | | | | | *Process Concerns* | | | | | | | | | | | | | | | | | | |

# Appendix A

## Example of Matrices E - J -- Regulatory, Safety, Environmental, Cost, and Scheduling Concerns

Weighting Factors to be Inserted Here
1 - Less Important 20 - More Important

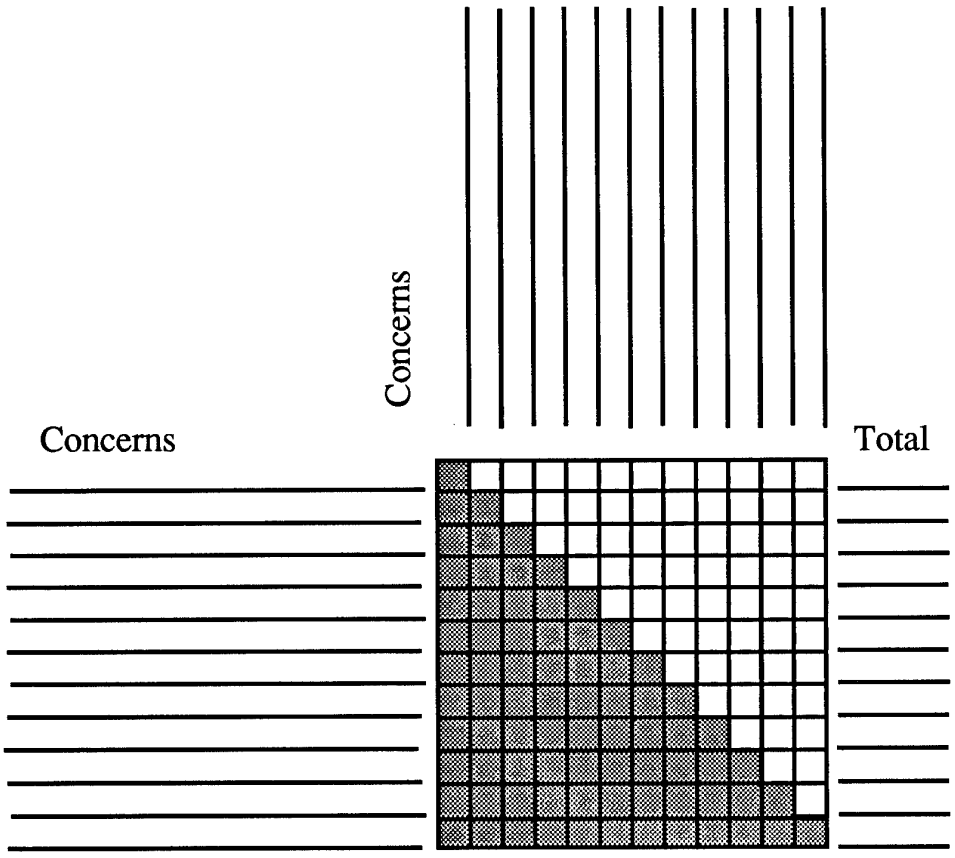
| | | | | | | *Regulatory Concerns* | | | | | | *Safety Concerns* | | | | *Environmental Concerns* | | | | | | | | | | *Cost Concerns* | | | | | | | | | | | | | | | | | | *Scheduling Concerns* | | | | | | | | | | | | | | | | | |
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| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | **Federal, State, and Local Regulations** | | | | | | | | **Present Program Schedule** | | | | | | | | | | | | | | | | | |
| Chemical | Chem # | Process | Proc # | New | Old | OSHA Requirements (EMB) | State Environmental Laws (EMB) | Local Environmental Laws (EMB) | Federal Environmental Requirements (EMB) | Future Federal Regulations (EMB) | Worker Exposure Limits (NMH) | Spill Response Plans (CPN) | Fire Response Plans (CPN) | Explosion Response Plans (CPN) | Clean Air Monitoring (EMB) | Pollution Prevention (CPN) | Toxic Emissions (NMH) | Emissions Control (GFP) | Ozone Depletor Potential (NMH) | Chemical Storage Availability (CPN) | Resource/Ingredient Recovery and Recycling (CPN) | Hazardous Waste Management (EMB) | Labor $ (DNI) | Operations $ (DNI) | Facilities $ (DNI) | Materials $ (DNI) | Chemical $ (DNI) | Other Hardware $ (DNI) | Contracts $ (DNI) | Change of Specifications $ (DNI) | Specification Verification $ (DNI) | Change of Drawings $ (DNI) | Development of Procedure $ (DNI) | Waste Management $ (DNI) | Emissions Control Testing $ (DNI) | Research (EMB) | Trade Studies (EMB) | Modification in Planning (EMB) | Specification Documentation (EMB) | Drawing/Design Changes (EMB) | Production Time (EMB) (New Equip.) | Testing (EMB) | Vendor Selection & Certification (EMB) | Research (EMB) | Trade Studies (EMB) | Modification in Planning (EMB) | Specification Documentation (EMB) | Drawing/Design Changes (EMB) | Production Time (EMB) (New Equip.) | Production Time $ (EMB) (Hardware Avail) | Testing (EMB) | Vendor Selection & Certification (EMB) |
| TCA | 1 | Vapor Degrease | 1-1-1 | | x | 3 | 1 | 1 | 1 | 1 | 3 | 3 | 3 | 9 | 1 | 9 | 9 | 1 | 1 | 9 | 9 | 3 | 3 | 2 | 1 | 3 | 2 | 3 | 2 | 3 | 3 | 3 | 2 | 3 | 3 | 9 | 9 | 9 | 3 | 9 | 3 | 3 | 3 | 9 | 9 | 9 | 3 | 9 | 9 | 9 | 1 | 9 | 9 |
| Aqueous Soap | 1R | Spray in Air | 1-1R1-1 | x | | 3 | 3 | 3 | 9 | 9 | 3 | 3 | 9 | 9 | 9 | 9 | 3 | 9 | 9 | 9 | 3 | 3 | 2 | 2 | 2 | 3 | 6 | 3 | 2 | 2 | 1 | 2 | 2 | 3 | 3 | 9 | 9 | 3 | 3 | 3 | 9 | 3 | 3 | 9 | 9 | 1 | 1 | 3 | 3 | 1 | 3 | 3 |

| | |
|---|---|
| 9 | Large Decrease (D) |
| 6 | Slight Decrease (D) |
| 3 | No Change(N) |
| 2 | Slight Increase (I) |
| 1 | Large Increase (I) |

| | | | | |
|---|---|---|---|---|
| 9 | Exceeds (E) | Good(G) | None (N) | Complete (C) |
| 3 | Meets (M) | Fair (F) | Minimal (M) | Partial(P) |
| 1 | Below (B) | Poor (P) | High (H) | None (N) |

**NOET -- Prioritization Methodology for Chemical Replacement**

# Appendix A
# Matrix K -- Weighting Worksheet




1 = Less Important
20 = More Important

## Discussion

QUESTION BY L. MEYER : How can AGARD Member nations get access to the data base/workbook, on the Chemical Selection Methodology?

ANSWER : Access is through NASA/MSFC . The contact is Beth Cook 205-544-2545 for the automated system and Wendy Cruit 205-544-1130.

# EVALUATION DE L'IMPACT SUR L'ENVIRONNEMENT DES ESSAIS STATIQUES DE PROPULSEURS A PROPERGOL SOLIDE

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**BP 2, 33165 Saint Médard en Jalles, FRANCE**

RESUME

Depuis de nombreuses années, le CAEPE réalise des essais statiques de propulseurs à propergol solide. Afin d'autoriser les créneaux de tir, il dispose de moyens prédictifs modélisant l'impact du tir sur l'environnement. Des codes de calculs de simulation dressent ainsi les zones de nuisances acoustiques et celles éventuellement sujettes à retombées acides. Ces codes qui utilisent les données météorologiques obtenues par radiosondage sur le site, ont été progressivement recalés lors d'essais d'engins de différents tonnages (jusqu'au propulseur d'appoint P230 d'ARIANE V). Dans la présentation qui en est faite l'accent a été mis sur un modèle dérivé du modèle usuel de G.A. BRIGGS pour la modélisation de l'ascension des effluents portés à hautes températures. Le réalisme des simulations de formation des pluies acides passe en effet par la bonne prise en compte de ce phénomène. Sur les autres aspects des codes, les références principales sont fournies.

## 1 – INTRODUCTION

Au sein du Ministère Français de la Défense, le CAEPE est chargé de la réalisation des essais au sol des propulseurs et sous-ensembles pyrotechniques des missiles stratégiques et tactiques. Le CAEPE exécute en particulier les essais au banc des différents propulseurs à propergol solide développés pour les besoins de la Force Nucléaire de Dissuasion, qui sont effectués sur un site soumis à des contraintes croissantes d'environnement.

Il est couramment retenu que l'impact de la propulsion à propergol solide sur l'environnement réside dans l'interaction de ses effluents avec les hautes couches de l'atmosphère (contribution à l'effet de serre et à la destruction de la couche d'ozone).

Il demeure qu'une pollution au niveau local du pas de tir peut survenir lorsque les conditions météorologiques locales sont défavorables. Dans le cas des tirs statiques, c'est essentiellement cette pollution en champ proche qui est redoutée, la dispersion des effluents s'effectuant ensuite rapidement dans des couches atmosphériques relativement basses (inférieures à 2000 m).

Avant d'autoriser tout essai, le CAEPE réalise préalablement une étude prévisionnelle d'impact sur l'environnement. Effectuée au plus près de l'heure de tir, elle a pour objet d'évaluer le risque encouru suivant la configuration de l'essai (position du propulseur sur le banc) et suivant les conditions météorologiques réelles. Cette évaluation du risque comporte deux volets, obtenus par des codes de simulations adaptés, traitant des risques de retombées acides (sous forme de pluies) et des nuisances acoustiques.

## 2 – DESCRIPTION DU PHENOMENE DES PLUIES ACIDES

Le rejet d'HCl gazeux dans de forts volumes de vapeur d'eau, tous deux issus de la combustion du propergol, peut entraîner le phénomène de pluie acide par la conjonction des deux tendances suivantes : l'abaissement du point de rosée suite à la présence de vapeurs d'HCl et la très forte capacité du gaz HCl à se dissoudre dans l'eau.

Lors d'un tir, la quantité de vapeur d'eau rejetée par le propulseur est usuellement incapable d'initier une pluie acide. Cependant, deux situations peuvent devenir redoutables:

– Forte humidité relative de l'air ambiant : l'entraînement de l'air ambiant happé par la turbulence du panache peut alors conduire à la saturation. Les gaz de combustion forment dans ce cas un nuage composé de gouttelettes très avides de chlorure d'hydrogène. Ce phénomène de formation de gouttelettes acides est d'autant plus efficace que les rejets d'un propulseur contiennent de nombreux noyaux de nucléation : particules d'alumine, imbrûlés, fragments divers arrachés au carneau du banc.

Lorsque la concentration en gouttes dépasse un seuil de quelques grammes par $m^3$, le nuage dégénère en pluie [1].

– Injection d'eau volontaire : la protection des installations du banc d'essai, notamment le carneau lorsque

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

le tir a lieu dans la configuration en ligne de vol (tuyère vers le bas), requiert une injection d'eau afin de freiner les gaz avant leur impact sur les dalles de béton, et de protéger aussi celles-ci par formation d'un film d'eau superficiel.

La masse d'eau injectée pour protéger les installations du banc participe ainsi à l'accroissement du risque de pluies acides.

Devant cette situation, le CAEPE s'est doté, avec l'aide de l'ONERA, d'un logiciel de prévision de ce type de pluie en traitant les risques naturels (taux d'humidité ambiante) et ceux générés par l'injection d'eau [2].

## 3 – MODELISATION DU RISQUE DE PLUIE ACIDES

### 3.1. – Caractéristiques générales

Le but recherché avec ce modèle est la prévision des risques générés en champ proche du point d'émission des rejets (zone de quelques kilomètres de rayon). L'utilisation opérationnelle qui en est faite (autorisation de tir) exclut tout modèle élaboré à long temps de calcul. Le modèle présenté ici ne réclame que quelques minutes de calculs et, initialisé avec un radiosondage météorologique effectué par une équipe interne au CAEPE, permet de produire une simulation réaliste en moins d'une demie heure.

Pour cela, le calcul est séparé en deux étapes successives qui modélisent d'abord l'ascension du nuage et sa stabilisation, puis sa diffusion. Cette deuxième étape, diffusion du nuage, ne sera pas exposée ici en détail (voir référence [3]) puisque l'on montre que le facteur prépondérant pour une bonne simulation concerne l'altitude de stabilisation.

En effet, la trajectoire du nuage (et donc la localisation des risques redoutés) ainsi que sa diffusion (la loi de diffusion faisant appel explicitement au vent local) sont très dépendants des vents présents dans les différentes couches atmosphériques. La connaissance de l'altitude de stabilisation est donc primordiale (Fig 1).

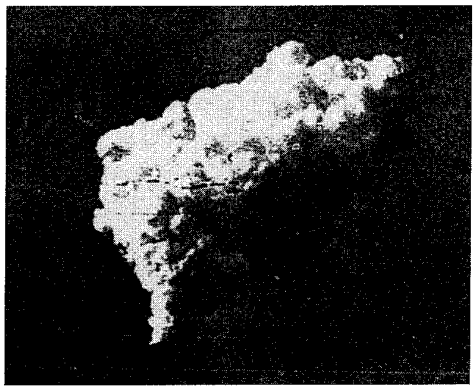


Figure 1. Ascension et début de diffusion du nuage

En conséquence les phénomènes physiques modélisés dans la phase ascensionnelle seront plus finement présentés.

### 3.2. – Phase ascensionnelle

Bien que la montée du panache soit influencée par la configuration aérodynamique au niveau du sol (présence de bâtiments autour du banc, relief local constitué de merlons protecteurs...), il est fait l'hypothèse que cette influence est négligeable par rapport aux effets ascensionnels directs du panache. Ceux-ci découlent de sa vitesse verticale initiale et de sa forte température qui crée une sensible différence de densité entre le rejet et l'air ambiant.

Dans les cas de tirs en configuration horizontale (sur déflecteur) ou en configuration "tuyère vers le bas" (dans un carneau) la simulation s'affranchit de l'aérodynamique très complexe d'interaction avec le sol en positionnant la source du rejet en sortie de déflecteur ou en sortie de carneau.

Dans toutes les configurations, les données initiales se réduisent donc à une vitesse initiale purement verticale (wo), une donnée géométrique (rayon initial du nuage, ro) et une donnée thermodynamique renseignant sur le flux initial de quantité de chaleur, $Q_{H_0}$, du rejet.

Le radiosondage météorologique fournit quant à lui une description de l'atmosphère ensuite décomposée en couches au sein desquelles les variables usuelles (température, pression, humidité, vitesses et orientations des vents) évoluent linéairement.

#### 3.2.1. – Modèle

Dans le cas le plus général, les équations de conservation de la masse, de la quantité de mouvement et d'énergie (ici considéré sous sa forme enthalpique) s'écrivent :

$$\frac{\partial \rho}{\partial t} + \mathbf{div}(\rho \bar{V}) = 0 \qquad \text{(masse)} \qquad (1)$$

$$\rho \frac{D\bar{V}}{Dt} + \mathbf{div}\,\bar{\bar{\varphi}}_{D,\bar{v}} = \rho \bar{f} \qquad \text{(quantité de mvt)} \qquad (2)$$

$$\rho \frac{Dh}{Dt} + \mathbf{div}\,\bar{\varphi}_{D,ei} = \frac{Dp}{Dt} + p.\,\mathbf{div}\bar{V} - \bar{\bar{\varphi}}_{D,\bar{v}}.\,\mathbf{grad}\bar{V} \qquad \text{(enthalpie)} \qquad (3)$$

où $\rho$ représente la masse volumique locale du fluide,

$\vec{V}$, sa vitesse

$h = ei + \frac{p}{\rho}$, l'enthalpie du fluide d'énergie interne ei et à la pression p

$\overline{\overline{\varphi_{D,v}}}$, l'écriture la plus générale de la densité de flux de diffusion de la quantité de mouvement

$\vec{\varphi}_{D,ei}$, l'écriture la plus générale de la densité de flux de diffusion de l'énergie interne

$\frac{D}{Dt}$, la dérivée particulaire (dérivée totale).

On montre, en mécanique des milieux continus, que la densité de flux de diffusion de la quantité de mouvement s'identifie au tenseur $\overline{\overline{P}}$ des contraintes dans le fluide.

Enfin, la densité de flux de diffusion de l'énergie interne rend compte des flux de chaleur dans le fluide par conduction (loi de Fourier), par diffusion matérielle (loi de Fick), par rayonnement, ...

Hypothèses simplificatrices

– La seule force extérieure appliquée au fluide relève de la pesanteur :

$$\rho\vec{f} = \rho\vec{g}$$

– Le fluide est newtonien et non visqueux:

$$\mathbf{div}\,\overline{\overline{\varphi_{D,v}}} = -\overline{\mathbf{grad}\,p}$$

– Les processus sont adiabatiques:

$$\vec{\varphi}_{D,ei} = 0$$

Cette dernière hypothèse rend compte :

– de flux thermiques conductifs négligeables (ce qui est parfaitement justifié)

– de flux radiatifs faibles (ce qui est également justifiable pour des rejets essentiellement gazeux et dont la teneur en particules est faible)

– de flux convectifs nuls, ce qui est logique dans la mesure où le modèle de départ suppose un fluide non visqueux, donc incapable de produire de la turbulence.

Il est clair néanmoins que l'on constate expérimentalement un panache très fortement turbulent qui entraîne l'air extérieur pour se développer.

Pour résoudre ce problème, nous suivons le modèle de TAYLOR (d'ailleurs repris par G.A. BRIGGS) qui propose de fermer le modèle par une loi géométrique décrivant le développement ascensionnel du panache et son effet d'entraînement de l'air extérieur. Une loi simple (développement du panache en cône) modélise alors à elle seule les effets visqueux et assure une frontière adiabatique.

Le modèle se résume alors aux équations :

$$\frac{\partial\rho}{\partial t} + \mathbf{div}(\rho\vec{V}) = 0 \qquad \text{(masse)} \qquad (4)$$

$$\rho\frac{D\vec{V}}{Dt} = \rho\vec{g} - \overline{\mathbf{grad}\,p} \qquad \text{(quantité de mvt)} \qquad (5)$$

$$\rho\frac{Dh}{Dt} = \frac{Dp}{Dt} \qquad \text{(enthalpie)} \qquad (6)$$

$$r = r_0 + \gamma . z \qquad \text{(géométrie)} \qquad (7)$$

où r est le rayon du panache à l'altitude z.

En utilisant la notion de température potentielle $\theta$ qui reste constante dans une évolution adiabatique, l'équation de l'enthalpie est remplacée par (combinaison avec une équation d'état du type gaz parfait) :

$$\frac{D\theta}{Dt} = 0 \qquad (8)$$

La recherche d'une solution stationnaire conduit alors à :

$$\mathbf{div}(\rho\vec{V}) = 0 \qquad (9)$$

$$\rho(\vec{V}.\overline{\overline{\mathbf{grad}}})\vec{V} = \rho\vec{g} - \overline{\mathbf{grad}\,p} \qquad (10)$$

$$(\vec{V}.\overline{\mathbf{grad}})\theta = 0 \qquad (11)$$

$$r = r_0 + \gamma . z \qquad (12)$$

Résolution standard

La résolution proposée par BRIGGS [4][5] conduit aux équations :

$$\frac{dFm}{dt} = F \qquad (13)$$

$$\frac{dF}{dt} = -s.Fm \qquad (14)$$

$$r = r0 + \gamma.z \qquad (15)$$

avec

$$F = g.\frac{\theta - \theta ex}{\theta ex}.u.r^2 = g.\frac{Q_H}{\pi \rho ex cp Tex} \qquad (16)$$

$$Fm = uwr^2 \qquad (17)$$

$s = \frac{g}{\theta ex}\frac{\partial \theta ex}{\partial z}$, paramètre de stabilité de l'atmosphère extérieure

u = vitesse horizontale du fluide (sous l'effet du vent extérieur)

w = vitesse d'entraînement vertical

T = température du fluide

$c_p$ = capacité calorifique, à pression constante, de l'air extérieur

$Q_H$ = débit de flux de chaleur (logiquement attaché à la vitesse u d'après l'équation (16))

les indices "ex" renvoyant au fluide extérieur au nuage.

L'équation (13) provient de la conservation de la quantité de mouvement et l'équation (14) de la conservation de la température potentielle.

Cette résolution permet d'obtenir :

– dans une couche neutre :

$$z(t) = \left(\frac{3Fo}{2\gamma^2 u}t^2 + \frac{3Fmo}{\gamma^2 u}t + \left(\frac{ro}{\gamma}\right)^3\right)^{1/3} - \frac{ro}{\gamma}$$

$(s = 0)$ (18)

– dans une couche stable :

$$z(t) = \left(\frac{3Fmo}{\gamma^2\sqrt{su}}\sin(\sqrt{st}) + \frac{3Fo}{\gamma^2 su}(1 - \cos(\sqrt{st})) + \left(\frac{ro}{\gamma}\right)^3\right)^{1/3} - \frac{ro}{\gamma}$$

$(s > 0)$ (19)

Cependant ces lois sont obtenues en écrivant qu'à l'instant initial Fo et Fmo sont indépendants de u. BRIGGS réécrit donc les équations (16) et (17) en accentuant leur dépendance avec la vitesse verticale:

$$Fo = g.\frac{\theta o - \theta ex}{\theta ex}.wo.ro^2 \qquad (20)$$

$$Fmo = wo^2 ro^2 \qquad (21)$$

Dans ce cas, l'intégration des relations (13) et (14) à u = constante dans chacune des couches de l'atmosphère permet d'obtenir les relations (18) et (19) dont le mérite est de proposer une dépendance en u des expressions donnant l'altitude.

Cependant cette dépendance introduite peu naturellement présente l'inconvénient de diverger lorsque les vents de l'atmosphère extérieure sont faibles.

Autre résolution

Une autre résolution peut, semble-t-il, être tentée pour l'équation de la conservation de la quantité de mouvement (10).

En supposant les écoulements irrotationnels, l'équation (10) devient :

$$\rho.\overrightarrow{grad}\frac{V^2}{2} = \rho\vec{g} - \overrightarrow{grad}\,p \qquad (22)$$

En intégrant sur la surface $S = \pi r^2$, intersection du panache avec le plan horizontal à l'altitude z, l'équation (22) s'écrit encore :

$$\int_S \rho\frac{\partial(1/2(u^2 + w^2))}{\partial z}dS = \int_S g(\rho - \rho ex)dS \qquad (23)$$

avec u et w les composantes horizontale et verticale, respectivement, de la vitesse.

Les caractéristiques du fluide étant supposées constantes sur toute la surface S, le premier membre s'écrit encore :

$$\rho \frac{d(1/2(u^2+w^2))}{dz} \int_S dS \sim \rho \frac{d(1/2(u^2+w^2)\int_S dS)}{dz} \qquad (24)$$

le terme en $\rho \frac{d(\int_S dS)}{dz}$ étant négligeable si l'angle du cône est petit.

D'où:

$$\frac{d(1/2(u^2+w^2)r^2)}{dz} = g.\frac{\rho-\rho_{ex}}{\rho} r^2 \approx g.\frac{\rho-\rho_{ex}}{\rho_{ex}} r^2 \qquad (25)$$

(approximation également utilisée par BRIGGS)

soit :

$$\frac{d(1/2(u^2+w^2)r^2)}{dt} = g.\frac{\rho-\rho_{ex}}{\rho_{ex}} w.r^2 \qquad (26)$$

$$\Rightarrow \frac{d(1/2(u^2+w^2)r^2)}{dt} = \frac{gQ_H}{\pi\rho_{ex}c_pT_{ex}} \qquad (27)$$

où $Q_H$ est maintenant le débit du chaleur traversant la surface $\pi r^2$ à la vitesse w.

Finalement, l'équation de conservation de la quantité de mouvement s'écrit :

$$\frac{d\mathcal{J}m}{dt} = \mathcal{J} \qquad (28)$$

avec : $\mathcal{J}m = 1/2(u^2+w^2)r^2$ (29)

$$\mathcal{J} = F = \frac{gQ_H}{\pi\rho_{ex}c_pT_{ex}} \qquad (30)$$

L'équation de conservation de l'énergie trouvée par BRIGGS [5]:

$$\frac{dF}{dt} = -s.Fm \qquad (31)$$

se traduit physiquement comme un frottement qui consomme la force ascensionnelle :

$$\frac{df}{dt} = -k.\|\bar{V}\|^2 \qquad (32)$$

L'expérience montre qu'elle décrit très bien la réalité à l'échelle qui nous intéresse. Elle est reprise ici sous la forme :

$$\frac{d\mathcal{J}}{dt} = -s.\mathcal{J}m \qquad (33)$$

Résumé du modèle

Trois équations permettent d'obtenir une modélisation simple du phénomène :

$$\frac{d\mathcal{J}m}{dt} = \mathcal{J} \qquad (34)$$

$$\frac{d\mathcal{J}}{dt} = -s.\mathcal{J}m \qquad (35)$$

$$r = r0 + \gamma.z \qquad (36)$$

avec :

$$\mathcal{J}m = 1/2(u^2+w^2)r^2 \qquad (37)$$

$$\mathcal{J} = F = \frac{gQ_H}{\pi\rho_{ex}c_pT_{ex}} \qquad (38)$$

où $Q_H$ est le débit de chaleur traversant, à la vitesse verticale locale w, la surface intersection du panache avec un plan horizontal

et u représente la vitesse du fluide dans le plan horizontal et vaut pratiquement la vitesse du vent atmosphérique à l'altitude considérée.

La résolution de ce système conduit aux équations suivantes, donnant les lois d'évolution de l'altitude z en fonction du temps :

$$((\frac{dz}{dt}(t))^2 + u^2)(ro + \gamma . z(t))^2 = 2f(t)$$

où la fonction f (t) vaut :

– dans le cas d'une atmosphère neutre (s = 0) :

$$f(t) = \mathcal{F}o . t + \mathcal{F}mo \qquad (40)$$

– dans le cas d'une atmosphère stable (s > o)

$$f(t) = \mathcal{F}mo . \cos(\sqrt{s}t) + \frac{\mathcal{F}o}{\sqrt{s}} . \sin(\sqrt{s}t) \qquad (41)$$

– Le cas de l'atmosphère instable (s < o) traduit théoriquement une augmentation de la force ascensionnelle. Cependant, dans notre situation, le phénomène d'entraînement de l'air extérieur tend à contrebalancer cet effet. Il est donc traité comme une atmosphère neutre [6].

3.2.2. – Exemples de résultats

Les courbes exposées ci–dessous (Figures 2 à 5) montrent les comportements respectifs du modèle de BRIGGS et de celui du CAEPE.

Ces courbes sont obtenues pour un cas de panache usuel à notre échelle où les données initiales valent :

Fo = 20 000 $m^4 s^{-3}$
ro = 10 m
wo = 15 $ms^{-1}$

Afin de tester les deux modèles, un même coefficient d'entraînement ( $\gamma = 0,5$ ) a été utilisé.

Les courbes des Figures 2 et 3 montrent l'influence du vent décrite par les deux modèles dans le cas neutre (s = 0),

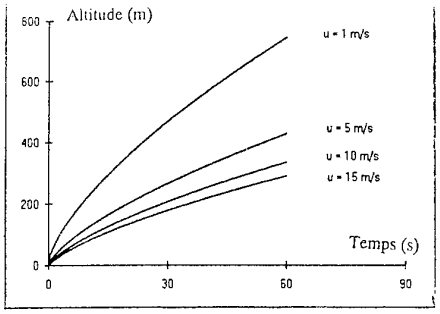



Figure 2: Calcul neutre, modèle de BRIGGS

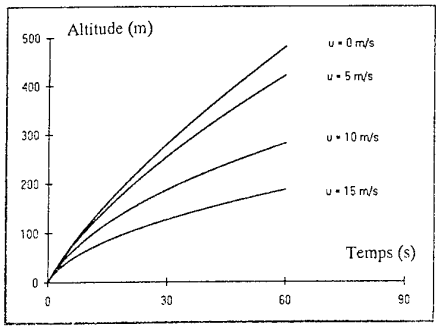



Figure 3: Calcul neutre, modèle CAEPE

et les courbes des Figures 4 et 5, la description analogue dans le cas stable (s = 0,05 $s^{-2}$).

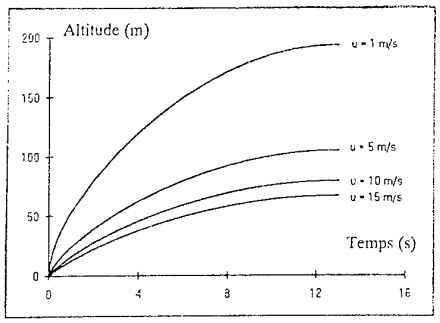



Figure 4: Calcul stable, modèle de BRIGGS

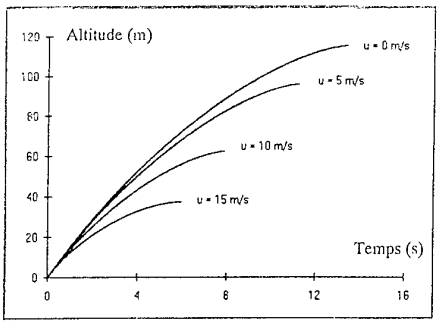



Figure 5: Calcul stable, modèle CAEPE

La comparaison met en évidence les comportements suivants :

– Pour un même cas de calcul dans une atmosphère monocouche, le modèle CAEPE donne toujours une altitude de stabilisation (pour le cas stable), ou une altitude à un instant donné (pour le cas neutre), plus faible que le modèle de BRIGGS, bien que les lois de variations soient sensiblement analogues.

– Une particularité très intéressante de notre modèle est de donner des durées de stabilisation variables suivant la vitesse du vent et toujours plus courtes que celles du modèle de BRIGGS. Ce point est d'ailleurs très bien corrélé à l'expérience (voir ci–après).

– Le cas de vent nul est normalement obtenu. La divergence connue du modèle de BRIGGS pour les faibles vitesses de vent est ici supprimée.

– Enfin, les données initiales sont naturellement dépendantes de wo et du vent au sol (l'hypothèse uo = wo de BRIGGS n'est pas nécessaire) et, quel que soit le vent au sol, la pente à l'origine de la loi de variation de l'altitude respecte la vitesse verticale initiale wo.

Une confrontation sur des observations expérimentales a également été réalisée. Elle est présentée Figure 7.

Les calculs de simulation ont été effectués avec les modèles présentés ci–dessus couplés à une décomposition de l'atmosphère en couches à s et u constants.

Il ne faut pas négliger l'influence de cette décomposition. Les modèles simples étudiés décrivent correctement les phénomènes sur des couches d'épaisseurs conséquentes et il est donc dangereux de les coupler à une décomposition trop fine de l'atmosphère (ce qui reviendrait à n'utiliser les courbes ci–dessus qu'au voisinage de t = 0). Une décomposition sur s et u par pas de 30% donne de bons résultats.

Le tableau de la Figure 7 montre la corrélation entre les résultats des deux modèles et l'expérience, pour l'évaluation de l'altitude de stabilisation ainsi que le temps nécessaire pour l'atteindre.

Les altitudes expérimentales ont été obtenues par des moyens divers (triangulations depuis le sol et mesures altimétriques par aéronefs).

Les résultats du modèle de BRIGGS ont été présentés suivant deux valeurs de $\gamma$ : la valeur habituelle ( $\gamma = 0.5$ ) et la valeur mesurée (entre 0.2 et 0.3 suivant les configurations de tir (Fig 6)).

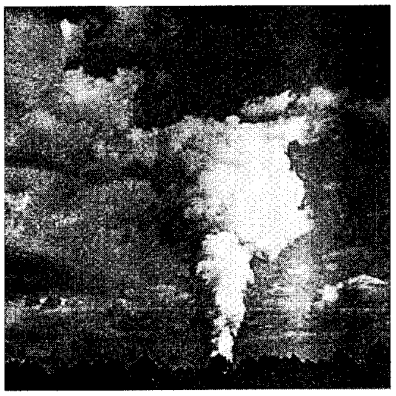


Figure 6: Panache, tir tuyère vers le haut: $\gamma = 0.2$

Des travaux antérieurs [7] avaient déjà noté cet écart et avaient opté pour un $\gamma = 0.5$, constant pour toutes les configurations, en introduisant un coefficient de pertes sur la valeur de $Q_{Ho}$ lorsque la configuration l'imposait (pertes d'ailleurs réellement justifiables par échanges thermiques avec le déflecteur ou le carneau). Nous préférons tenir compte de cet effet de pertes par son impact direct sur $\gamma$ , $\gamma$ étant d'autant plus petit que le flux de chaleur (ou, ce qui revient au même, que la force ascensionnelle) est grand(e). Les valeurs de $\gamma$ utilisées sont voisines de 0.2 en configuration tuyère vers le haut et de 0.3 sinon.

| | MODELES | | | Mesures |
|---|---|---|---|---|
| | BRIGGS * $\gamma = 0.5$ | BRIGGS $\gamma = \gamma_{exp}$ | CAEPE $\gamma = \gamma_{exp}$ | expérimentales |
| Tir N°1 TVB | 940 m 16 mn | 1 260 m 20 mn | 988 m 6 mn | 1000 m 5 mn |
| Tir N°2 TVH | 735 m 5 mn | 1 007 m 4mn | 1000 m 4mn | 1000 m 6 mn |
| Tir N°3 TVH | 851 m 6 mn | 1 455 m 9 mn | 1 530 m 6 mn | 1 500 m 4 mn |
| Tir N°4 TVH | 754 m 8 mn | 1 032 m 6 mn | 1034 m 3 mn 30 | 1 100 m 4 mn |
| Tir N°5 TVB | 724 m 4 mn 40 | 1 041 m 6 mn 30 | 1134 m 4 mn 40 | 1 200 m 5 mn |
| Tir N°6 TVB | 1 180 m 12 mn | 1 486 11 mn | 1 911 m 9 mn | X? > 1 700 m ≈ 10 mn |

* : Sans prise en compte d'un facteur de pertes

TVB : Configuration Tuyère Vers le Bas
TVH : Configuration Tuyère Vers le Haut

Figure 7: Tableau de résultats

Le tir n°1 montre un effet flagrant (dû à une importante couche de vents forts à 10 m/s, dans les données météorologiques correspondantes, qui met en évidence une trop faible pente des courbes z(t) à l'approche de la stabilisation) des écarts entre les temps de stabilisation obtenus par les deux modèles.

La modélisation proposée, bien que peu éloignée du modèle standard, permet, pour les ordres de grandeur associés aux effluents de propulseurs, de réconcilier calculs et mesures expérimentales.

### 3.3. – Phase de diffusion

Lorsque le panache a atteint son altitude de stabilisation ou que la vitesse verticale devient faible devant la vitesse horizontale, les phénomènes d'entraînement de l'air analysés au paragraphe précédent, deviennent négligeables devant ceux de diffusion turbulente et de transport.

Les phénomènes sont alors décrits par l'équation générale de diffusion :

$$\frac{dX}{dt} + \vec{u}.\,\overrightarrow{\text{grad}}\,X = \overrightarrow{\text{grad}}\,(\overline{\overline{K}}.\,\overrightarrow{\text{grad}}\,X) \qquad (42)$$

où: X est la concentration,
$\vec{u}$ , la vitesse,
$\overline{\overline{K}}$ , le tenseur de diffusion

Les travaux réalisés par l'ONERA [3] pour la modélisation de cette phase de diffusion ont conduit aux hypothèses suivantes :

– en basse atmosphère et pour les échelles de temps et d'espace considérées, le tenseur de diffusion $\overline{\overline{K}}$ est diagonalisable et ses composantes diagonales ne dépendent que des variables atmosphériques locales

– le nuage est correctement modélisé par une géométrie cylindrique

– on se ramène au problème de diffusion d'une source ponctuelle en décomposant le nuage en N sources (Fig 8):

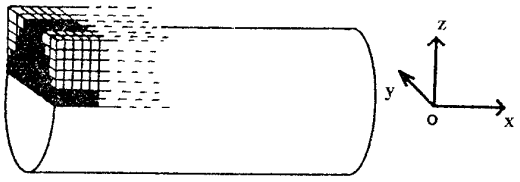



Figure 8: Décomposition en sources ponctuelles

– la répartition des concentrations sur les sources ponctuelles suit une gaussienne suivant les axes oz et oy et est constante suivant ox

– la détermination des coefficients de diffusion se fait par la méthode de Pasquill avec les valeurs numériques de Bultynck [8].

A l'aide de cette modélisation de la diffusion du nuage, et par l'intermédiaire d'un critère de pluie, il est alors possible de proposer une prévision du risque de formation d'une pluie acide.

### 3.4. – Critère de pluie

Le nuage contenant les effluents est en réalité un mélange ternaire "alumine–acide chlorhydrique–eau" dont l'évolution est extrêmement complexe.

Les travaux menés par l'ONERA [9] ont permis de construire un code de calcul élaboré modélisant la formation d'une phase liquide dans le nuage. Celle–ci est calculée à partir des quantités d'eau présentes (eau provenant de la combustion elle–même, de l'eau injectée volontairement et de l'eau de l'air atmosphérique entraîné dans le nuage) et des risques d'apparition d'une phase liquide au sein du mélange.

Les possibilités de nucléation, puis de croissance de l'aérosol formé, ont ainsi été étudiées [10]. Les équations utilisées pour le calcul de croissance, sont dérivées des équations de FUKUTA et WALTER [11].
Il s'ensuit un temps de calcul relativement long, inadapté au besoin opérationnel.

A l'aide de ce code, des observations réalisées sur des maquettes à petite échelle, et des observations lors d'essais au CAEPE, des critères d'apparition de pluie acide ont alors été mis au point.

Le risque de formation d'une pluie acide est nul lorsque les trois conditions ci–dessous sont remplies :

$RH < UC$
$E < 2$ ppm
$t > tp + 40$ s

avec : RH : humidité relative
UC : humidité critique
E : concentration en HCl vapeur
tp : dernier instant pour lequel un risque de pluie acide a été prévu

Le non respect de l'une quelconque des trois conditions entraîne la mise en évidence d'un risque.

Les paramètres RH et UC sont calculés à partir des pressions partielles d'$H_2O$ et HCl issues du modèle de diffusion.

L'humidité relative prend en compte les trois sources d'eau recensées ci-dessus (gaz de combustion, eau injectée et eau entraînée).

L'humidité critique est le rapport entre la pression de vapeur saturante de l'eau au-dessus d'une solution aqueuse d'HCl et la pression de vapeur saturante de l'eau au-dessus de sa phase liquide.

Il est facile ensuite de localiser sur un fond de carte, les zones présentant des risques.

Les Figures 9 et 10 montrent des exemples de prévision de pluies acides (matérialisées par des étoiles le long de la trajectoire).

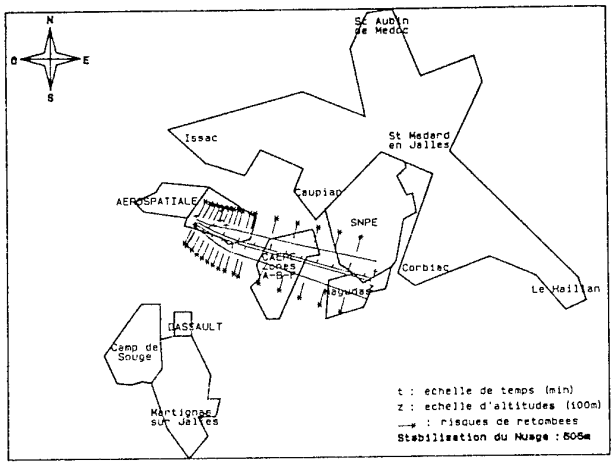



Figure 9: Prévision de retombées acides le long de la trajectoire

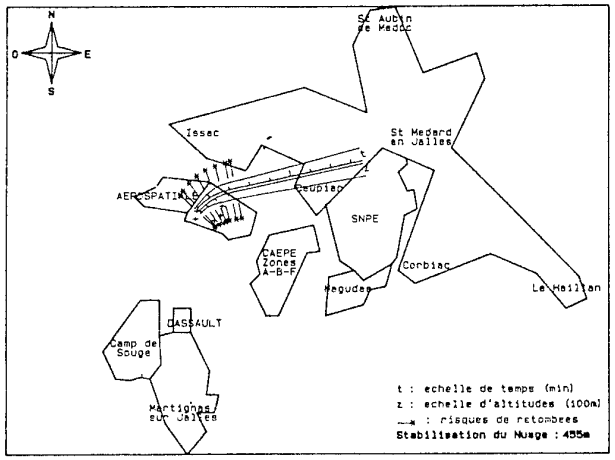



Figure 10: Prévision de retombées acides localisées

Dans le cas de la Figure 9, des pluies sont prévues le long de toute la trajectoire calculée. Pour la Figure 10, seul la zone d'essai est exposée à ce risque.

## 4 – NUISANCES SONORES

Si le risque de pluies acides constitue la préoccupation majeure du décideur de tir, il demeure qu'une nuisance sonore est générée lors d'un essai statique de propulseur. Bien que de courte durée (en général de l'ordre de la minute), cette nuisance peut s'avérer pénible.

Là encore, l'intéraction avec l'atmosphère est primordiale pour obtenir un moyen de prévision réaliste. La raison en est que certaines configurations atmosphériques (vent, température) conduisent à des zones de focalisation acoustique. Le niveau sonore atteint dans de telles zones peut approcher 160 dBa à une distance pourtant importante de la source (800 m).

Le modèle utilisé au CAEPE découle de travaux réalisés à l'Institut franco-allemand de Saint-Louis. Seules les caractéristiques principales seront présentées ici (se reporter aux références [12] à [14]).

Le calcul s'articule autour du phénomène de transport de l'énergie acoustique par les ondes sonores dont la trajectographie est obtenue par la méthode des rayons.

La Figure 11 montre le tracé de tels rayons. On identifie ainsi la présence de zones de focalisation (tel le point A).

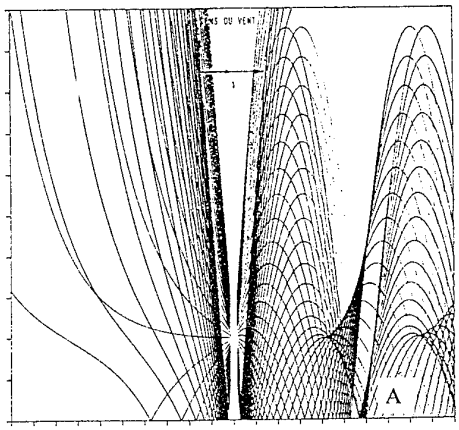



Figure 11: Propagation acoustique suivant la méthode des rayons

En de tels points, un calcul d'intensité acoustique est alors effectué. Celui-ci est déterminé en utilisant la conservation de l'énergie le long de tubes élémentaires construits sur les rayons acoustiques.

L'intensité est ensuite corrigée des phénomènes d'absorption atmosphérique (sous l'effet de l'hygrométrie) suivant les tables fournies par l'AFNOR [15].

Lors des premiers tirs du propulseur à poudre d'ARIANE V à KOUROU, le CAEPE a fourni des calculs de prévision du bruit. Les Figures 12 et 13 montrent le tracé des courbes iso-intensité (100 dBa et 80 dBa), ainsi que la corrélation mesures – niveaux calculés en quelques points remarquables.

| Azimuth | Distance | Niveau calculé | Niveau mesuré | Observations |
|---|---|---|---|---|
| 90° | 1250 m | 103 dB | 106 dB | |
| 30° | 4250 m | 79 dB | 70 dB | |
| 60° | 5300 m | 73 dB | 52 dB | Masquage par batiments |
| 225° | 7650 m | 100 dB | 70 dB | (*) |
| 115° | 9500 m | 58 dB | 60 dB | |
| 255° | 14,1 km | 76 dB | 53 dB | (*) |
| 90° | 15,2 km | Bruit de fond | 63 dB | Ville de KOUROU |
| 300° | 15,7 km | 85 dB | 53 dB | (*) |
| 300° | 29,2 km | Bruit de fond | 60 dB | Ville de SINNAMARY |
| 240° | 30,0 km | Bruit de fond | 63 dB | Usine EDF |

Les écarts (*) proviennent vraisemblablement d'un effet atténuateur de la forêt guyanaise sur les réflexions au sol

Figure 12: Tableau de résultats

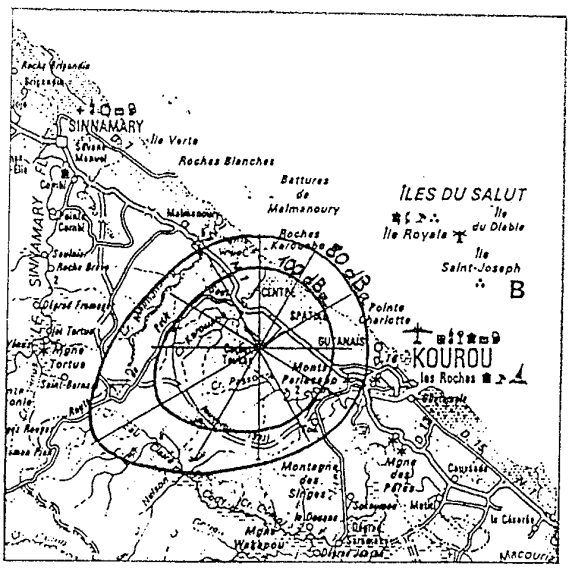



Figure 13: Exemple de cartographie des niveaux acoustiques (prévision petite saison sèche)

## 5 – CONCLUSION

Suite à la nécessité de maintenir à niveau ses codes de calculs, le CAEPE a récemment repris les travaux sur les modèles d'ascension d'effluents. Un modèle dérivé de celui de BRIGGS est proposé et semble, à ce jour, donner de très bons résultats.

D'autres essais seront nécessaires pour confirmer la validité de ce modèle dont le mérite est de pallier les insuffisances du modèle de BRIGGS dans des cas particuliers (vents faibles ou vents forts), tout en conservant des résultats globalement semblables par ailleurs.

Après plusieurs années d'utilisation, dans des configurations météorologiques très variées, les codes de simulations utilisés au CAEPE, tant du point de vue de la formation des pluies acides que dans le domaine des nuisances acoustiques, ont actuellement atteint une maturité importante, ce qui n'est pas le moindre de leurs atouts.

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# BIODEGRADATION OF ENERGETIC COMPOUNDS: APPLICATION TO SITE RESTORATION

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## SUMMARY

A multidisciplinary approach involving chemistry, microbiology, ecotoxicology and bioengineering has been undertaken in a joint effort involving the Defence Research Establishment, Valcartier of National Defence Canada (DREV/DND) and the Biotechnology Research Institute of the National Research Council of Canada (BRI/NRC). The aim of this joint collaboration is to study the bioremediation of soils contaminated with energetic compounds such as RDX, TNT, NC and GAP. Contaminated sites were sampled and analyzed for the presence of TNT, RDX and NC. Modified EPA SW 846 Method 8330 was used for the determination of RDX and TNT. As expected, the method was found accurate ($\geq$ 90 % recovery), precise (relative deviation standard $\leq$ 2 %) and sensitive (detection limit $\leq$ 0.5 mg/Kg) over a range of concentration from 0.5 to 20,000 mg/Kg of soil dry weight. Labelled -$^{14}$C energetic compounds were synthesized to monitor their biodegradation. Contaminated soils were screened for microorganism having the ability to mineralize energetic compounds. Bacteria were isolated from RDX contaminated soils based on their ability to use RDX as the sole source of nitrogen under aerobic conditions when amended with a carbon source. Using $^{14}$C- labelled RDX, the ability of these isolates to mineralize RDX in liquid medium was verified. Laboratory-scale studies using the isolates to bioremediate RDX contaminated soils indicate that bioaugmentation enhances the rate and extent of RDX biodegradation. TNT contaminated soils exhibited concentration dependent $^{14}$C-TNT mineralization activity. GAP is a relatively new energetic compound and might not yet be found as a soil contaminant. However, a soil sampled on a burning range showed some $^{14}$C-GAP mineralization activity. NC mineralization studies are planned in the near future.

## INTRODUCTION

Contamination of soils and water by energetic organonitro compounds at sites such as firing areas, destruction ranges, explosives dumping grounds and industrial production plant represents a significant worldwide environmental problem. Various solutions may be applied for the remediation of these contaminated sites. One emerging possibility is the use of biotechnological methods. These methods are innovative and inexpensive when compared to conventional methods, and tend to be publicly acceptable. *In situ* bioremediation of soil contaminated with RDX, TNT and related explosives compounds has the potential to be adaptable to specific compounds and environment (Ref. 1.)

In order to support the Canadian Armed Forces regarding their future potential environmental needs related with energetic materials, the Defence Research Establishment, Valcartier from the Department of National Defence (DREV/DND) in collaboration with the Biotechnological Research Institute from the National Research Council of Canada (BRI/NRC) have initiated a biodegradation study of some specific compounds. Of particular concern are contaminants such as 2,4,6 trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), nitrocellulose (NC), glycidyl azide polymer (GAP) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) which are derived from manufacturing of explosive munitions.

The three first energetic compounds were selected based on their extensive use in the past and thus on the high probability for their presence as soils or water contaminants. GAP was chosen to study the biodegradability potential of this new energetic product. Some limited biodegradation experiments are also planned with HMX using RDX active strains. Energetic compounds pose serious health and ecological hazards due to their mutagenicity and toxicity, and their tendency to persist in contaminated environments (Ref. 2). TNT, for example, causes liver damage and anemia in humans (Ref. 3), and concentrations above 2 µmol/ml are toxic to fish (Ref. 4). Because of the potential for groundwater contamination, and the subsequent migration of hazardous substances, treatment of the contaminated source is necessary to protect humans, crops and the environment.

An extensive literature search showed that, in general, little is known about the behaviour and biodegradation of energetic chemicals in soil and in the open environment

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(Ref. 5). Due to the xenobiotic nature and toxicity of organonitro compounds, only limited catabolic potential is found in natural microbial communities (Ref. 6). Under laboratory conditions, researchers have identified pure cultures that degrade mononitrobenzoates and mononitrophenols, but comparatively few microorganisms are known to degrade polynitroaromatics (Refs. 7 and 8). While the biodegradation and metabolic fate of TNT has been extensively studied (for a recent review see Ref. 2), comparatively little information is available concerning the metabolic fate and biodegradation potential of energetic compounds such as RDX, HMX, NC, and GAP.

In aqueous systems, RDX was mineralized by mixed populations of microorganisms under anaerobic conditions when supplemental carbon was provided (Ref. 9). Mono-, di-, and tri-nitroso compounds were identified as intermediates in the proposed biotransformation pathway. Such intermediates, however, pose a greater toxicity threat than does RDX itself. Thus, remediation of RDX-contaminated soil requires complete reduction of the toxicity of RDX and its derivatives. To our knowledge, microbial biotransformations of RDX have not been elucidated under aerobic conditions.

Fungal technologies (Refs. 3, 10) and composting (Refs. 11, 12) are suggested technologies for RDX, TNT and NC degradation. However, they have proven rather ineffective or too costly to be considered practical for large-scale application. For example, composting has the disadvantage of requiring large quantities of bulking agent with only a small fraction of the total volume composted being contaminated soil, and requiring long incubation times.

Recent studies by Spain (Refs. 13, 14) and research conducted in our laboratories suggests that aerobic bacteria may possess greater capabilities for degrading organonitro compounds than was previously thought. Identification of novel aerobic bacteria that can degrade recalcitrant energetic compounds such as RDX, TNT, GAP, and NC, and characterization of the catabolic pathways involved are imperative to developing *in situ* bioremediation strategies for these hazardous xenobiotics. Moreover, a detailed knowledge of the environmental conditions required to foster optimum rates of biodegradation may lead to the exploitation of these microorganisms for biorestoration of energetic compound-contaminated soils.

The present paper describes the collaborative work done to characterize energetic compounds in pure form and in soils and to verify their potential for biodegradation for future site bioremediation application.

## SOIL SAMPLING, EXTRACTION AND ANALYSIS

Three sites potentially contaminated with RDX, TNT and NC were selected for soil sampling: Sites A, B and C. Four samples were collected from Site A, five from Site B and six from Site C. The samples were collected at depths varying from 15 to 45 cm. Soil was collected for general use in polyethylene pails while soil samples to be used for microbiological analysis were collected in sterile tubes. Sites A and B were suspected for specific contamination by TNT, RDX or NC, while Site C was suspected for multi-contamination by various energetic compounds, since the later was previously used as an energetic material burning site.

The analytical method used for the determination of TNT and RDX in soils was based on the work of Jenkins *et al* (Refs. 15-17). The general method consists of extracting 2 g of soil by sonication in acetonitrile followed by the reverse phase HPLC analysis of the extract with methanol/water (50:50%) as the eluent. The technique was evaluated under an interlaboratory study over a wide range of concentrations from 0.5 to 20,000 mg/kg of soil, dry weight of both TNT and RDX. As expected, the technique was found to be accurate (> 90% recovery), sensitive (DL < 0.5 ppm) and precise (RDS $\leq \pm$ 2%). The method used was in fact recently adopted by the U.S. Environmental Protection Agency as the standard method for the analysis of those nitroaromatics and nitramines residues (Ref. 18). Samples contaminated with low to high level of TNT and RDX were actually identified. As expected, Site C shows both TNT and RDX contamination but at a low level.

## SYNTHESIS OF $^{14}$C-LABELLED COMPOUNDS

The $^{14}$C-substrates were all prepared using modified literature methods. RDX was prepared by the Hale process (Ref. 19). This procedure involves the condensation of $^{14}$C-formaldehyde with ammonium hydroxide to yield quantitatively $^{14}$C-hexamethylene-tetramine (HMTA) which is then nitrated under fuming nitric acid to give $^{14}$C-RDX in 60% yield. During the nitration, the opening of the HMTA by the nitrating species involves a loss of three carbons (and one nitrogen) and therefore, a loss of total radioactivity is observed. The syntheses of $^{14}$C-TNT was achieved according to the Dorey and Carper method (Ref. 20) using concentrated sulfuric acid 20% oleum instead of 15% oleum as mentioned by the authors. This method consists of nitrating toluene in three steps by increasing the power of the nitrating medium at each step. Concentrated sulfuric acid and fuming sulfuric acid were thus added to dehydrate the medium leading to a more active nitrating species. The toluene was either uniformly labelled at the ring or at the methyl group with carbon-14. There is no loss of carbon in these syntheses, and therefore the total radioactivity obtained is related to the yields.

The $^{14}$C-nitrocellulose was obtained by nitration of $^{14}$C-cellulose using the procedure of Olsen and Greene (Ref. 21). This method consists of nitrating the cellulose in a mixture of concentrated nitric acid and fuming sulfuric acid. Bacteriological $^{14}$C-cellulose was obtained by cultivating *Acetobacter xylinum* on $^{14}$C-glucose.

Glycidyl azide polymer is usually obtained by azidation of polyepichlorohydrin which is synthesized by polymerization of epichlorohydrin. $^{14}$C-epichlorohydrin was not available commercially and had to be synthesized. Hydrochlorination of $^{14}$C-glycerol as the starting material lead to 1,3-dichloro-2-propanol according to the method of Hill and Fisher (Ref. 22). The latter compound was epoxidized under basic conditions to yield $^{14}$C-epichlorohydrin which was then polymerized in

accordance with the one-step process developed by Ahad (Ref. 23). The resulting polymer is a low molecular weight $^{14}$C-GAP with a specific activity of 226 μCi/g as determined by a scintillation counter. It must be mentioned that not all monomers in the polymer are radioactive since the carbon-14 starting materials were mixed with unlabelled ones during the syntheses.

MICROBIAL ACTIVITY AND MINERALIZATION STUDIES

Total viable bacteria of each contaminated samples were determined by the spread plate technique and the population expressed as colony forming units per gram of soil. All samples showed important significant bacterial populations. Several enrichment cultures were started to isolate bacteria from contaminated soils using energetic substrates as either a carbon or a nitrogen source. In the latter case, glucose was added as a carbon source. Mineralization of $^{14}$C-labelled RDX, TNT and GAP have been attempted in microcosms to assess the ability of the indigenous microbial population in contaminated soils to biodegrade energetic compounds.

Soil mineralization studies were done either to study spontaneous mineralization or to perform bioaugmentation studies. In the first case, microcosms were prepared with contaminated soil to obtain an indication of the ability of the indigenous microbial population in contaminated soils to mineralize energetic compounds. In some experiments, agricultural soil or activated sewage sludge was used to dilute the concentration of the energetic compounds contaminated soils. On the other hand, all bioaugmentation studies have been performed in laboratory-scale soil microcosms enriched with $^{14}$C-RDX. Aqueous suspension of washed cells of actively-degrading strain was added to the surface of the soil to yield an initial inoculum density of $10^5$ or $10^8$ CFU per gram of soil. Uninoculated microcosms were included as negative controls.

RDX Mineralization

Soil from the A site (A4), containing 27 000 ppm RDX, supported a substantial indigenous bacterial population ($2.55 \times 10^7$ CFU/g). Enrichment cultures prepared from the A4 sample in a mineral salts medium with RDX as the sole nitrogen source yielded a consortium with the ability to mineralize $^{14}$C-RDX. Approximately 40% of the radioactivity was released as $^{14}CO_2$ after an incubation period of 4 days. This suggests that the use of energetic compounds, which are typically rich in nitrogen, as sole nitrogen source in enrichment cultures may favour the selection of microbial consortia capable of metabolizing these compounds by extracting the nitrogen. Two bacterial strains, designated "A" and "C", were isolated and purified from this consortium by their abilities to use RDX (100 ppm) as a sole nitrogen source under aerobic conditions when glucose was provided as a carbon source. The identification of both strain is ongoing. Most of the work accomplished to date has been focused on Strain "A". Experiments to characterize the RDX biodegradation pathway have been initiated by studying the growth of this strain in defined medium with glucose as the carbon source and RDX as the nitrogen source.

Using $^{14}$C-RDX, the ability of isolates "A" and "C" to mineralize RDX in liquid culture under aerobic conditions was verified and both organisms mineralized 34% of the RDX within 2 days of incubation. Thus, the enrichment and purification from RDX-contaminated soil of two microbial strains with the ability to mineralize $^{14}$C-RDX, when provided as the sole nitrogen source, has firmly established the biodegradation potential of RDX.

Laboratory scale bioaugmentation studies using strain "A" and "C" to bioremediate RDX-contaminated soils are currently in progress. Preliminary results indicated that bioaugmentation of RDX-contaminated soil with an RDX-degrading bacterium failed to enhance important biodegradation of RDX. Several possibilities were considered to establish the reasons for this failure. The results obtained so far suggest that in addition to its toxicity, RDX interaction with soil may influence its biodegradability. Significantly more mineralization was detected in an artificially contaminated soil amended with lower concentrations of RDX and inoculated with strain "A".

It is recognized that microorganisms can often tolerate xenobiotic compounds at low concentrations but not at higher concentrations. An understanding of the toxicity of pure RDX on RDX-degrading isolates both in liquid medium and in soil is critical. The toxicity of RDX to Strain "A" is currently being assessed in detail. Mineralization studies have been set up using increasing concentrations of pure RDX in pure cultures of Strain "A" (0-2000 ppm), and in soil microcosms (0-6000 ppm) bioaugmented with Strain "A". Once the toxicity of RDX on Strain "A" is determined, we may be able to adapt this bacterium to higher concentrations of RDX, specifically those levels likely to be encountered in the natural environment. Equally important is to have a better understanding of the fate of energetic chemicals in the soil environment. For example, the substrate may encounter various other abiotic changes normally determined by the physico-chemical properties of soil. Some of these abiotic processes include inorganic, organic, photolytic, surface-catalyzed, sorptive, and transport processes. This will be the subject of future investigation.

Having established that RDX is a biodegradable pollutant, and that bioaugmentation of RDX-contaminated soil enhances the rate and extent of biodegradation, a better understanding of the parameters (including soil/contaminant interactions) affecting RDX degradation kinetics in soil must now be developed. The fact that we observe more mineralization when the soil is artificially contaminated signifies that the soil/contaminant interactions are not as severe as in an aging soil that has been contaminated for several years. In this latter case severe adsorption becomes a problem on bioavailability.

TNT Mineralization

TNT appears to be a much more recalcitrant compound than RDX. A review of the relevant literature shows that TNT is quite resistant to biodegradation by most bacteria and fungi. Typically, biotransformations of TNT do not result in cleavage of the aromatic ring, and degradation to $CO_2$ does not occur.

Viable heterotrophic bacterial populations are lower in TNT contaminated soils than in the RDX-contaminated soil. Soil microcosms were set up with soils B4 (25 ppm), B3 (4700 ppm), and B5 (12 000 ppm) to assess [$^{14}$C] TNT mineralization by indigenous soil bacteria. Soil B4 has a slow but steady [$^{14}$C] TNT mineralization activity showing 8-10% of the radiolabel evolved as $^{14}CO_2$ after incubation for 100 days. The addition of glucose (250 ppm) as a supplementary carbon source, or yeast extract (50 ppm) as a supplementary nitrogen source did not enhance this rate of mineralization.

The effect of increasing TNT concentration on this activity has confirmed that the low level of mineralization observed in this soil is a real phenomenon as concentrations of 100 ppm TNT and higher result in complete abrogation of the mineralization activity. In light of this, soil B4 may also be inhibitory to the activity of its indigenous microbial population. When the TNT concentration in soil B4 was decreased to 2.5 and 10 ppm by diluting this soil with an agricultural soil, TNT mineralization activity was somewhat enhanced.

We therefore conclude that TNT is an extremely toxic compound with at least limited biodegradation potential. However, despite spontaneous TNT mineralization, soil B4 has as yet yielded no microbial populations with the ability to mineralize [$^{14}$C] TNT under aerobic conditions. Also the severe interactions between TNT and its intermediate metabolites with soil may limit its mineralization potential in a soil environment. An understanding of the mechanisms of transportation and transformation of TNT and its initial metabolites in the soil environment is critical in optimizing its mineralization efficiency. New enrichment cultures of soils will be set up providing TNT as sole carbon or nitrogen source at low TNT level. Finally, the biodegradation of TNT might also be evaluated under denitrifying and anaerobic conditions.

GAP Mineralization

Although it remains unknown whether any of the soils we are presently working with are contaminated with GAP, six soil samples (C1 to C6) obtained recently were all found to harbour significant numbers of viable bacteria ($10^3$-$10^6$ CFU/g). In addition, all soil samples displayed $^{14}$C-GAP mineralization activity. Soils C4 and C5 were identified as possessing the greatest potential for isolating GAP-degrading bacteria. Enrichment cultures were recently prepared using a mixture of these two soils with GAP (100 ppm) provided as either sole carbon or nitrogen source. At present, the fourth subcultures are incubating; there is significantly more microbial growth in the enrichment culture with GAP provided as carbon source. [$^{14}$C] GAP mineralization tests are in progress, but data are not available yet concerning the ability of these cultures to degrade GAP.

NC mineralization

Two soils possibly contaminated with NC were collected, but the analytical procedures are not yet in place in our laboratories to confirm this. These soils, B1 and B2, harbour significant heterotrophic bacterial populations (5.43 X $10^7$ and 5.63 X $10^6$ CFU/g, respectively). Enrichment cultures were set up using these soils where NC was supplied as either sole carbon or nitrogen source. At various stages of subculture, samples of the enrichment cultures were preserved at -80°C for subsequent analysis. $^{14}$C-NC was recently synthesized and the mineralization studies will be conducted soon.

ECOTOXICOLOGICAL STUDIES

Ecotoxicological evaluation of the four energetic compounds is essential in order to allow a future ecotoxicological follow-up of soil remediation. Therefore, different biotests were developed for analyzing pure compounds in the liquid phase. Partial results were obtained up to now and among the energetic compounds studied, TNT showed an important toxicological effect however it did not have a genotoxic effect. RDX showed an acute and a chronic toxicity but less important than TNT, and RDX did not reveal a detectable genotoxicity. According to the biotests, NC is not a potentially dangerous product for the environment since it is non genotoxic and very weakly toxic. GAP or GAP by-products were lightly genotoxic. Future work is needed to complete the ecotoxicity evaluation.

CONCLUSION AND FUTURE WORK

An interlaboratory study demonstrated that the method used to extract and analyze TNT and RDX was accurate, sensitive and precise. These two contaminants were found in soils from the three sites at concentrations ranging from low to high levels, either as the sole contaminant or as a combination. Contaminated soils, even those with high level of contamination supported substantial indigenous bacterial population. Enrichment culture techniques were employed to isolate indigenous microbes with the potential to degrade energetic compounds. Microcosm mineralization experiments were done in liquid medium with these enrichment cultures and $^{14}$C labelled energetic compounds that were expressly synthesized for that purpose. Labelled RDX, TNT and GAP were prepared with good yields starting respectively with labelled formaldehyde, toluene and glycerol. Labelled NC was prepared from the microbial polymerization of labelled glucose which was then nitrated to $^{14}$C-NC.

The present study showed that RDX was mineralized under aerobic conditions when used as a nitrogen source using isolates from RDX contaminated soil. Two RDX mineralizing pure cultures were obtained and preliminary characterization of the two strains were done. Some preliminary bioaugmentation studies using actively-degrading strains indicated mineralization of RDX when amended in agricultural soil. TNT biodegradation has been demonstrated to be highly concentration dependent and TNT toxicity appears to be a key factor. Low levels of TNT mineralization were detected in contaminated soils. Low level of mineralization of GAP were obtained by enrichment cultures from a mixture of soil contaminated with energetic compounds. Also, a multi-contaminated soil showed some microbial activity toward GAP. More work will be conducted to optimize the mineralization of the above substrates for future site decontamination. RDX small scale site decontamination is planned. Work will be conducted on quantitative

evaluation of NC in soils and on NC biodegradation with labelled $^{14}$C-NC. Future work include the ecotoxicity evaluation of explosives and their metabolites.

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## Discussion

QUESTION BY J.M. TAUZIA : Quelle relation existe-t-il entre la vitesse de dégradation de la Nitrocellulose et son taux d'Azote ?

ANSWER : On vient de commencer le travail avec la Nitrocellulose. On va déterminer "la correspondance" ou la corrélation quantitative entre le taux d'azote et le taux de neutralisation de NC. Cette étude peut servir notre projet parce que le taux d'azote de la NC explosive est d'environ 13 %.

QUESTION BY J.M. TAUZIA : Peut-on utiliser les technologies biologiques pour purifier les "eaux rouges" (Pink Water) qui proviennent de la synthèse du TNT ?

ANSWER : Nowadays our research is made on contaminated soil. Our future developments in the project may involve waste water or more specifically "pink water" treatment. We have established expertise in waste water treatment under anaerobic conditions. Several industrial products such as PCP, TCE, have been biodegraded. Further information on waste treatment may be obtained by consulting Dr S. GUIOT.

QUESTION BY T. ROSENDORFER : Cost for incineration compared to biodegradation seems too high. What is included in this price or how is this price calculated ?

ANSWER : The values shown in my presentation is what has been published by other researchers. These figures do not represent our calculations. We have not done that yet ! One source of information : Gregory D. Sayles (US EPA) and Makram T. Suidan, In : Biological Treatment of Industrial and Hazardous Wastewater, (Biotreatment of Industrial and Hazardous Waste, Ed Morris A. Levin and Michael AS. Gealt, McGraw Hill, Inc, Ch 11, 1993).

QUESTION BY T. ROSENDORFER : How do you correlate the poor migration of explosives in the soil, so that the microbes will find the explosives ?

ANSWER : Soil/contaminant interactions (adsorption/desorption) is always a problem that we have to consider when working with soil. Absorption often determines bioavailability and in turn biodegradation kinetics. We have in the past looked at the mechanisms of interactions between the contaminant (more specifically nitro PAHs and amino-PAHs, Hawari et al., Water Research 1994) and soil components so that we can understand and optimize biodegradation in soil.

QUESTION BY T. ROSENDORFER : What cosubstrates are used in addition ?

ANSWER : As explained in our paper when the explosive is used as N-source a cosubstrate is used to serve as C-source. For example, used as C-source (e. g. glucose, sucrose, succinate, etc). Some explosives were also used as C-source.

QUESTION BY H. SCHUBERT : Do you work with HMX ?

ANSWER : We have not started with HMX yet. It is a target on our agenda.

# Demilitarisation in Germany by E.S.T.

by
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**Summary:**

Munitions have only a limited live-time. At the end of their useful live they must be demilitarised into none hazardous materials. Until now the most applied technology is "open burning and open detonation" (OB/OD).

In consequence of the political situation in Germany there is the huge stockpile of the munitions of the former NVA (Nationals People Army) from the former GDR to be demilitarised.

"Open burning"/"open detonation" of this large quantities of munitions would highly affect the environment.

E.S.T., a subsidiary company of DASA Deutsche Aerospace, developed and built a plant which allows the demilitarisation of munitions and/or explosives strictly under all relevant German regulations.

## 1. Introduction:

E.S.T. is a subsidiary company of DASA Deutsche Aerospace from the Daimler Benz Group and was founded by DASA and L.U.B. (Lurgi Umwelt-Beteiligungsgesellschaft, a subsidiary company of Lurgi). E.S.T. is the acronym for Entsorgungs- und Sanierungstechnik GmbH which means demilitarisation and remediation technologies.

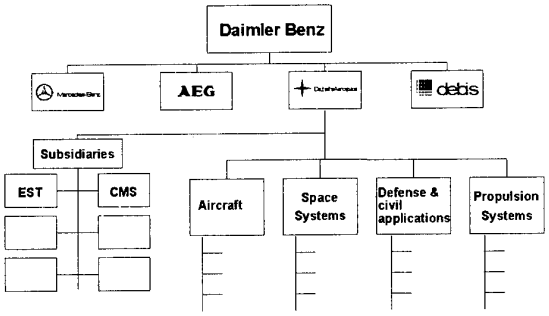



Fig. 1

E.S.T. offers its expertise in the following fields of activity.

Military site remediation, which means cleaning of battle-fields, mine-fields and also remediation of training-areas or barracks.

Removal and disposal of munitions:

Disposal of chemical agents.

Services, which means in this context basic and detailed engineering and planning of plants or facilities for the above mentioned activities and training of personnel.

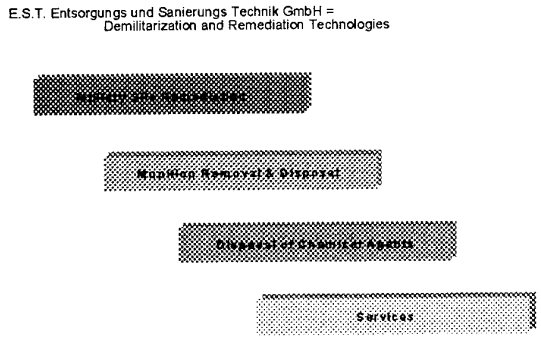



Fig.2

E.S.T. is located in Schrobenhausen, a small city in the southern part of Bavaria close to the head office of DASA, Deutsche Aerospace which is in Ottobrunn near Munich . The explosive disposal facility of E.S.T. is in Steinbach/Neusorge in Saxony, about less than 1 km from the polish boarder in the eastern part of Germany. E.S.T. also has at its disposition an intermediate munitions storage in Altenhain near Leipzig, also in Saxony with a capacity of more than 4000 tons of explosives.

## 2. Disposal technologies:

Various technologies are possibly applied to the demilitarisation of munitions and the disposal of the remaining materials.

The reuse or recycling of useful materials is the best technology for any disposal business. But this is only possible for some parts of munitions.

For the conversion of explosives into non dangerous materials it is necessary to distract all energetic characteristics. The at the present time existing technology for that is incineration (or detonation).

Also chemical and/or biological degradation of energetic materials seems possible. But concerning availability or cost such procedures do not make sense at least for now a days application.

A very promising technology for the degradation of any hazardous material seems to be the oxidation in supercritical water. Many institutes work or do research

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in supercritical water oxidation, but this technology is not ready for application.

E.S.T. together with its mother company DASA worked in all this fields, but besides of some activities in the recycling of energetic materials, only incineration is realized.

## 3. Recycling of energetic materials:

It is obvious that any recycling of material only makes sense and can be profitable, if there is a market for the recycled material, for in general recycled materials have the blemish of being down graded in quality compared with freshly produced materials. This is not the case for explosives, which after a correct recycling process are at least equal to virgin material. But explosives have a severe problem concerning a customer. All the explosives from munitions with the exception of TNT can not be used in civil explosives. So the only remaining "would be" customer is another producer of military products or ordnance. For that the explosive after the recycling must successfully pass a qualification procedure to meet the relevant DOD/MOD requirements. Such a qualification procedure in most time together with the production and testing of a pilot-lot results in very high cost so that for most of the explosives the recycling is not profitable. Only for HMX with its high price of approximately 80 DM/kg recycling is profitable.

DASA and now E.S.T. operate in Schrobenhausen since several years the to our knowledge only plant for the recycling of HMX on a production scale. This plant was built in 1986 and tailored to the needs of the shape charge warhead production at that time where HMX was used as a high performance explosive for the main charge in the MILAN and HOT warheads. The capacity of this plant is about forty tons per year depending on the requirements for the grain size distribution of the final material. The recycled HMX of our plant has successfully passed all qualification procedures for German military application. These tests were done together with the BICT (Bundesinstitut für chemisch technische Untersuchungen) of the BMVg (Bundesministerium für Verteidigung). Also the qualification for a shaped charge, i.e. the Milan warhead was successful for the recycled material.

The formulation of the starting material is 85% HMX, the rest TNT. The process starts by dissolving the TNT in Toluene, filtering and washing the HMX with water and steam and after that recristalisation of the HMX in acetone. The whole process is highly automated which helps to reduce cost. Since the material is from our own production we have strict control of the composition and of the possible impurities which seems mandatory for a successful recycling process.

If the starting material for a recycling process is from demilitarised munitions there would be no reliable control for composition, ingredients and impurities. Unknown material from demilitarised warheads could badly influence the process. And 100% surveillance of such material by analysis would increase cost to a not acceptable level.

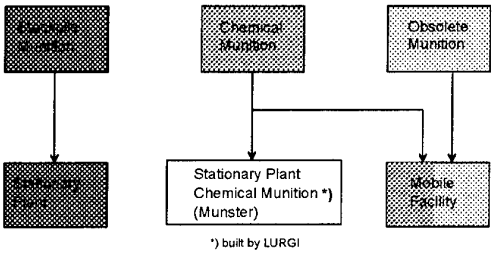
For that recycling of explosives following our experience is not applicable to the demilitarisation of munitions.

## 4. Incineration:

### 4.1 Activities.

E.S.T. uses for the disposal of explosives besides of the recycling the incineration as an effective technology. E.S.T. shares its occupation in the field of incineration in two activities which are a stationary plant for munitions in Steinbach/Saxonia and a mobile facility in Schrobenhausen, operational in the very near future.

**E.S.T. Incineration activities**




**Incineration under all relevant German regulations (i.e. BImSchV 17)**

Fig.3

E.S.T. does the demilitarisation of stockpile munitions under contract from the BMVg. E.S.T. co-operates in this field with the German company Rheinmetall, which does the disassembly and the dismantling of the munitions. The residual explosives, i. e. the main charges, the fuses and the propellants are sent to our stationary incineration plant in Steinbach, Saxony, where they are disposed. And it is E.S.T.'s policy to do the incineration strictly under all relevant German regulations, i. e. the German clean-air-act, the so-called 17. BlmschV.

E.S.T. Incineration activities

Objective:

To demilitarize the huge stockpile of munition of the former NVA (National people's army) in East Germany

under all relevant German regulations

such as

17. BImSchV ("Federal Clean Air Act")

To demilitarize the remainders of munition from second (and first) world war.

Fig.4

Obsolete munitions which are mostly found munitions from second world war are at the moment disposed by

the "Kampfmittelräumdienste", the EOD organisations in the German Bundesstaaten. They usually demilitarise the explosives by open burning and it is E.S.T.'s approach to improve this method by providing these "Kampfmittelräumdienste" with a mobile facility. It is planned that the setting to work of at least one of these facilities will be in October 1994. After positive experiences with this plant we will apply for the permission to use it also for chemical agents.

In the moment the only plant in Germany (and in Europe) to demilitarise chemical munitions is the stationary plant for chemical munitions in Munster, Lower Saxony, which is operated by the German army.

### 4.2. Regulations.

As mentioned above the incineration of hazardous or toxic materials in Germany is subject of many regulations. One is the German clean air act, the 17.BlmschV, which limits the various noxious componds in the flue-gas from incinerators, mainly from incinerators for municipal waste. This regulation is also applied to incinerators for explosives.

The following table shows an extract of the limits for the daily average value of toxic compounds in the flue-gas.

Regulated limits (17. BImSchV) for the amounts of certain toxic agents in flue gas from incinerators

| | Daily average value *) |
|---|---|
| Dust, total | ≤ 10 mg /m³ |
| Organic substances | ≤ 10 mg /m³ |
| Gaseous anorganic chloric compounds (e.g. HCl) | ≤ 10 mg /m³ |
| Sulfur dioxide / trioxide | ≤ 50 mg /m³ |
| NOx (indicated as NO2) | ≤ 200 mg /m³ |
| CO | ≤ 50 mg /m³ |
| Dioxine **) | < 0,1 ng/m³ ***) |

*) Values from 1989 draft regulations on waste material disposal facilities
**) Dioxine must not be produced in the facility (certification required) This can be achieved by e.g. flue gas temperature > 1200 °C, residence time > 2sec
***) Value still under consideration (note: nano-grams)

Fig.5

As you see this values are very low. We especially will turn your attention to the value for dioxin which is with 0,1 ng /cm$^2$ at the analytical limit.

At the beginning of our work in burning explosives we wanted to know the compounds in the flue-gas of burning explosives to evaluate the necessary installations for an effective treatment system. Until that time nobody was interested in the gases evolved by burning explosives. There were many data for the residues of detonated explosives, but not much data were available in literature for incineration. Together with the ICT in Karlsruhe we started investigation in this field and results are presented in the next two figures.

Compounds in the flue gas of burnt TNT

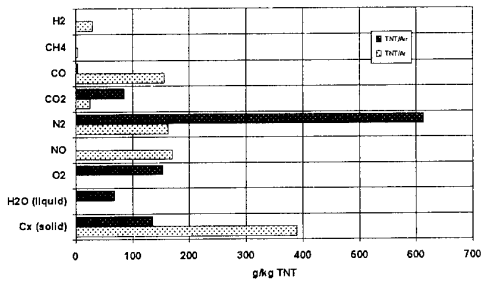



Fig.6

The first one for TNT shows two values, one for TNT burned under air and the other for TNT burned under an inert atmosphere, Argon, where only the oxygen in the TNT molecule is available for the oxidation. We thought that in open burning in a bonfire the distraction of the TNT molecule because of lack of oxygen would not be complete to the thermodynamically stable compounds. The real world during open burning as we thought would probably lay between the two experimental results.

It was very astonishing to us that according to these experiments there remains a great deal of about 15 to 30 % on unburned soot depending on the burning conditions . This $C_X$ in the plot showed in the analyses still a high content of C-N bonds which proves the incomplete distraction of TNT. Such compounds are considered verx noxious as a possible starting compound under the presence of chlorine for the resynthesis of dioxins or furanes in the flue-gas.

The second example is for a single base propellant. Burning under an inert atmosphere seemed not to be necessary concerning the oxygen balance of propellants. Also here the uncomplete burning of the propellant with about 50 % remaining solids was unexpected and astonishing.

Compounds in the flue gas of burnt single base propellant

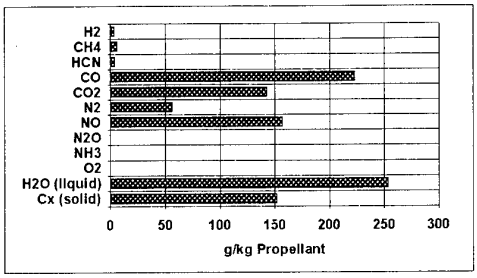



Fig.7

These results led us to the consequence that only a very effective flue-gas treatment will result in a flue-gas which can be disposed to the environment under fulfilling of the 17.BlmschV.

## 5. Thermal Disposal Plant:

The thermal disposal plant of E.S.T. with a flue-gas treatment system as indicated before was built in Steinbach/Saxony. The flue-gas treatment-system is combined from elements for this purpose according to the standard of actual technology. There was no need for any special tailoring of the installations for the treatment of flue-gases from burning explosives.

Thermal Disposal with Flue Gas Treatment

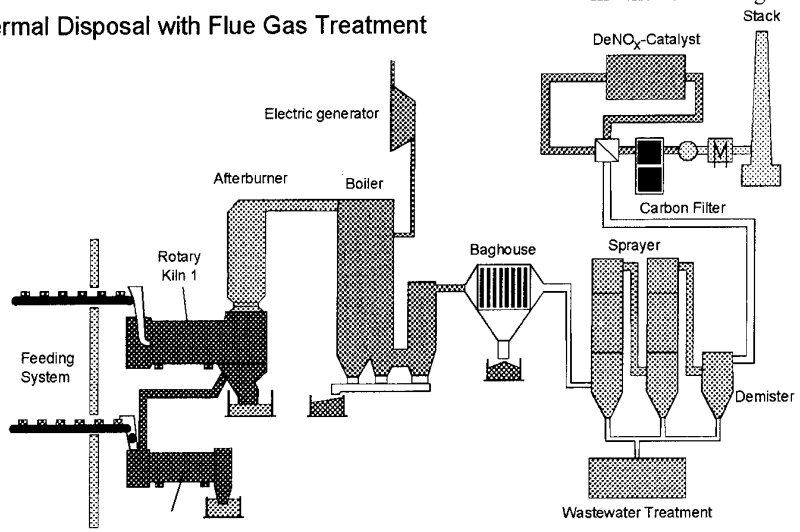



Fig.8

The rotary-kilns however were especially equipped for the incineration of explosives and parts of munitions. Two different types of rotary-kilns were installed.

One kiln is a reinforced rotary-kiln with heavy steel walls so it will withstand also fragments of shells caused by the detonation of small arms munitions. This kiln is foreseen for the demilitarisation of fuses, small calibers munitions up to 25 mm and burning out of metal parts which are contaminated with small quantities of explosive.

The second rotary-kiln is equipped with a ceramic insulation to retain the energy produced by the burning explosives inside the rotary-kiln. This reduces the amount of sustaining energy from a natural gas-burner.

Very much attention was laid on the design of the feeding system because this must protect the operators from any reverse reaction, deflagration or even detonation of the explosive materials inside the rotary-kiln.

It consists of a double sluice system which makes sure that there is always one steel wall closed between the oven and the operators. Furtheron the explosives are transported to the feeding opening in special containers on a conveyer, which assures a rather large distance between the operators and the kilns. The rotary-kilns themselves are operated under remote control.

The hot remainders of the incineration drop at the end of the rotary-kilns into a water tank where they are drowned and immediately cooled below 100°C.

All the flue gases pass an afterburner where they are burned out at a temperature of at least 1.200°C with a residence time of minimum two seconds.

The energy in the flue-gas which is not only produced by the burning explosives but also by the burned natural gas in the sustaining burners is converted into electric energy in a generator. By passing a boiler the gases are cooled to a temperature below 300°C so they don't harm the filter-system in the bag house. This filter-system filters all the dust and dusty compounds. The collected material is disposed in a hazardous disposal facility outside the plant. After the bag house the flue-gases pass a sprayer-system where the toxic and noxious ingredients i.e. hydrochloric acid or sulfurdioxid are washed out. The waste water coming from this sprayer-system is especially treated in a waste water treatment system tailored to the purpose of the plant.

The gases then pass a demister and a system where $NO_x$ is catalytically reduced under the presence of ammonia to nitrogen and water. A carbon filter is added to catch the highly toxic heavy metals like mercury or cadmium, coming from fuses or galvanically plated shells. After this the gases leave the plant through a stack.

This plant is installed as mentioned before in Steinbach at a plant-surface of 7.5 ha. About 60 employees work in a three shift operation. The plant has the capacity for an intermediate storage of fuses and explosives and also has a rather small facility for disassembly.

The material balance for the incineration plant is like that:

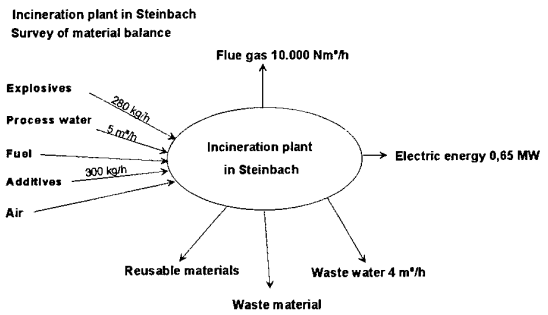



Fig.9

An average of about 280 kg of explosive can be treated per hour, depending on the type of explosive. For that about 5 $m^3$ of process water and 300 kg of additives, mostly neutralisation agents in the washers, are necessary. Fuel and air for the sustaining burners are necessary. With this incoming material a flue gas quantity of 10.000 standard $m^3$ per hour is produced and the output on electrical energy is 0,65 MW.

## 6. Transportable facility:

**Why a transportable facility?**

- many sites
- quantity varies
- transportation problem with duds and chemical munition
- obsolete munition
- OB/OD harms environment
- unearthed munition mostly unidentified (chemical munition)

Fig.10

E.S.T. developed and is now testing a transportable facility for the demilitarisation and the disposal of munitions of any kind. Such a transportable facility is mandatory if even for single items or small quantities of found munitions OB/OD is no longer tolerated or acceptable. Since this found munitions evolve on many sites and in varying quantities it is not possible to build

**Mobile disposal plant for explosives (MoDiPlEx)**

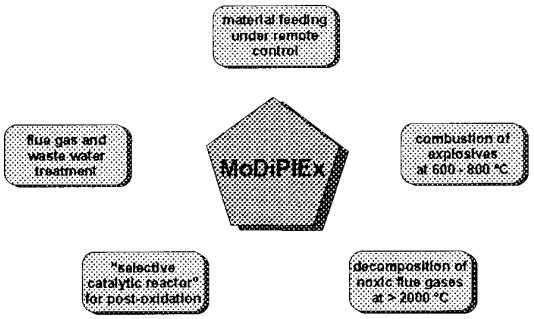



Fig.11

a stationary plant on all this sites. But the transportation of duds especially containing chemical agents is a hazardous problem and in general regulations do not allow the transportation of such items on public roads.

E.S.T. feels, that in all this cases the plant must come to the problem because the problem can not be transported to the plant.

E.S.T.'s approach to this problem is a mobile disposal plant for explosives and also munitions for which we use the acronym MoDiPlEx. The plant needs a floor-space of about 500 square-meters and has an annual capacity of approximately 350 tons of TNT or equivalent explosives.

**Mobile disposal plant for explosives (MoDiPlEx)**

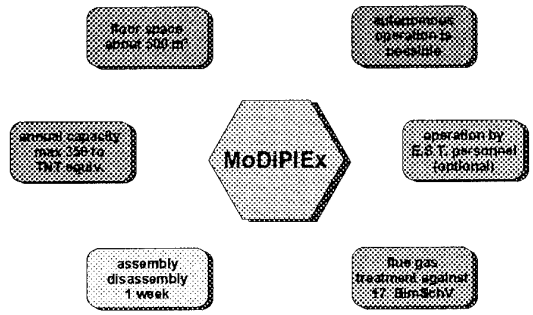



Fig.12

It can be assembled and disassembled in one week which seems short enough to call the plant transportable.

The flue-gas of the MoDiPlEx plant is treated against the 17.BImschV, which means that the flue-gases fulfil the German regulation.

In the MoDiPlEx plant the explosives are burned at about 600 to 800 C and the flue-gases are decomposed at a temperature higher than 2.000 C. The material can be fed under remote control.

The MoDiPlEx plant consists of an incineration system which includes the feeding system and optionally a batch oven or a rotary-kiln. The flue-gases go into a chemical reverser where they are converted into small molecules like HCl. This gases pass a washer where the ions are precipitated. The gases are filtered and leave the facility through a stack.

A control center is installed for all the operations. The whole equipment can be installed in about six norm containers which are transportable on truck.

MoDiPlEx Flowchart

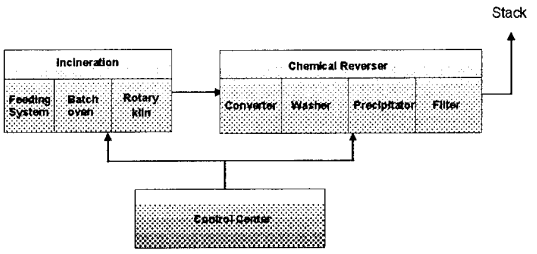



Fig.13

The flue-gas treatment-system for this small mobile plant is the so called chemical converter. It consists of a system of tubes in line. In the first tube a natural gas-burner in a ceramic tube, which is resistant against heat and corrosin, produces a very hot flame with a centre temperature of about 2.000°C. The flue-gases are directly forced into the centre of this flame and this high

temperature assures an immediate decomposition of all gases to the basic molecules. Immediately at the end of the ceramic tube the remainders of the flue gas are pushed under the surface of a basic liquid in which they are cooled and neutralised. Neutralisation is completed in several following washers according to the various compounds in the respective flue-gas. Especially tailored additives in the last tube precipitate most of the molecules which then can be concentrated or filtered so that the water either can be reused in the facility or pumped into the main drainage channel. The gases leave the facility after a demister, an already mentioned catalytic oxidation system and a carbon filter to catch heavy metals like Mercury. If in the future the plant will be used even for chemical agents Arsenic will be retained in this filter too.

## 7. Conclusion:

The demilitarisation of munitions especially in Germany includes the following scopes of work:

clearing
disassembling
disposal
decontamination

The following figure shows how for the various types of munitions, e.g. chemical munitions etc. this fields overlap.

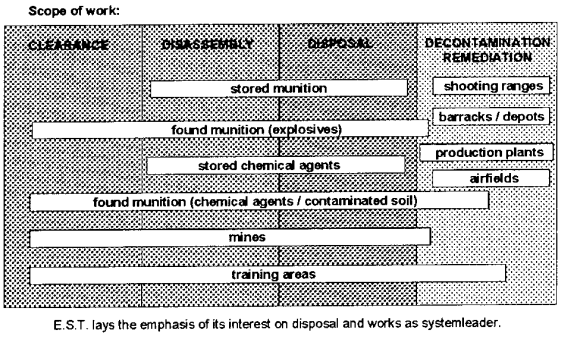



Fig.14

E.S.T. lays the emphasis of its interest on the disposal, decontamination and remediation field and works as a system-leader.

The basic technology for the demilitarisation seems for E.S.T. to be the incineration of explosives (and in future of toxic agents), because this features the following advantages:

proven safety
total capture of flue-gases
effective treatment of flue-gases
total distraction of energetic characteristics
small amount of particulate residues

E.S.T. knows how to deal with the following challenges:

demilitarisation of huge amounts of munitions
demilitarisation of single items even duds on site
demilitarisation of chemical munitions

and E.S.T. does all this under all relevant regulations.

## Discussion

QUESTION BY JM. TAUZIA : Quelle est la nature du four utilisé dans l'unité mobile de démilitarisation : rotatif ou batch ?

ANSWER : The use of a batch oven or a rotary kiln is optional. At the moment a batch oven is being used

QUESTION BY JM. TAUZIA : Quel équivalent TNT peut-il supporter en cas d'incident (épaisseur de la paroi du four ?).

ANSWER : The batch oven withstands 1 kg of TNT, but is operated under security control.

# EVALUATION OF ENVIRONMENTALLY ACCEPTABLE CLEANERS AS REPLACEMENTS FOR METHYL ETHYL KETONE AND 1,1,1 TRICHLOROETHANE IN SOLID ROCKET MOTOR PRODUCTION AND MAINTENANCE APPLICATIONS

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PRA-SA-APP/HILL AFB 23 MAY 1994

## SUMMARY

The use of 1,1,1 trichloroethane (TCA) will be restricted and ultimately prohibited under the U. S. Clean Air Act and the Montreal Protocol. Use of methyl ethyl ketone (MEK) is currently being restricted by various state air quality districts in California and across the United States. Used widely in the production of composite, metallic, and polymeric components as cleaning solvents, TCA and MEK have long been accepted as diverse and effective solvents by many manufacturers. Therefore, evaluation of potential TCA and MEK replacements requires numerous application considerations, ranging from simple hardware and tooling cleanup to pre-bond cleaning preparation of critical bonds. This test program evaluates a wide variety of potential solvent replacements within this wide range of common applications.

## INTRODUCTION

Significant data have been gathered which suggest that many of the common cleaning solvents used in the aerospace industry contribute to the degradation of local and global environments. Two of the most commonly used cleaning solvents identified as environmentally harmful are 1,1,1 trichloroethane (TCA) and methyl ethyl ketone (MEK). TCA is specifically identified in the U. S. Clean Air Act as a known contributor to the depletion of the earth's protective ozone layer, and as such its use will be ultimately banned by United States federal and international laws.

Also restricted by the Clean Air Act are materials which emit volatile organic compounds (VOC's), which are known to contribute to low altitude pollution. The use of MEK, with its high VOC content and high vapor pressure, has already been restricted or prohibited by various state air quality management districts and is rapidly being phased out elsewhere. Methyl ethyl ketone is also classified as a hazardous air pollutant.

In response to these tightening environmental requirements, Aerojet and the Ogden Air Logistics Center teamed to evaluate replacements for TCA and MEK in all production applications used on the recent Minuteman III Stage II Motor Remanufacture Program. In addition, the various field maintenance applications were evaluated.

Remanufacture of all Minuteman III Stage II motors in the operational fleet was completed in 1993. The use of TCA and MEK in the remanufacture program was not impacted by the existing and proposed environmental restrictions. However, in that the Minuteman III weapon system is expected to remain operational beyond the year 2020, another remanufacture cycle will be required. This next production program will certainly experience severely restricted use or even prohibited use of TCA and MEK. Consequently, environmentally acceptable replacements for TCA and MEK must be qualified for use in the near future.

One of the most serious concerns regarding the qualification of solvent replacements is the potential impact that an alternative solvent may have on the service life-limiting component of the motor, the propellant-to-insulation bondline (liner). TCA is used to clean the exposed side of the internal insulation prior to liner application and subsequent propellant casting.

The potential for an alternative solvent to have an adverse effect on the liner (and the resulting service life of the motor) forced evaluation of solvent replacements. This required conducting early evaluation of solvent replacement candidates, selecting the most promising ones for qualification testing, and demonstrating them in full scale motors. The end results will included valuable functional demonstration data as well as aging and surveillance data before Minuteman begins its second remanufacture cycle.

The programs conducted at Aerojet to evaluate alternatives for MEK[1] and TCA[2], although directed specifically at qualifying replacements for use on the Minuteman second stage, should provide data applicable to a wide variety of aerospace applications.

The two test plans generated to evaluate the candidate replacements were divided into three phases. Phase I included the initial industry search and some preliminary bond testing. The two best performers were then selected for further testing with other components and materials under Phase II. Phase III tested the final replacement solvents/cleaners via full scale motor firings at simulated altitude conditions.

## APPLICATIONS

The primary use of MEK on rocket motor programs is cleaning of metal and rubber surfaces prior to bonding. It is also used to freshen the surface of elastomers prior to bonding or laminating. The use of MEK in the cleanup of hardware and tooling has generally been limited to applications requiring a very aggressive solvent. Currently, MEK is used to clean the internal insulation and chamber interior prior to bonding together.

TCA is used to a greater extent in bond line preparation because it is less toxic and non-flammable, which makes it more desirable for use in loaded motor operations. It is used in small, tactical motor operations as a vapor degreaser for new chambers. It is also used for general cleaning of large motor parts and for cleaning of tooling. TCA is also used to clean the internal insulation (V-45 rubber) of the Minuteman second stage motor prior to the application of the liner. Figure 1 shows a partial cross-section of the second stage motor and the areas of critical bonds possibly affected by alternative solvents.

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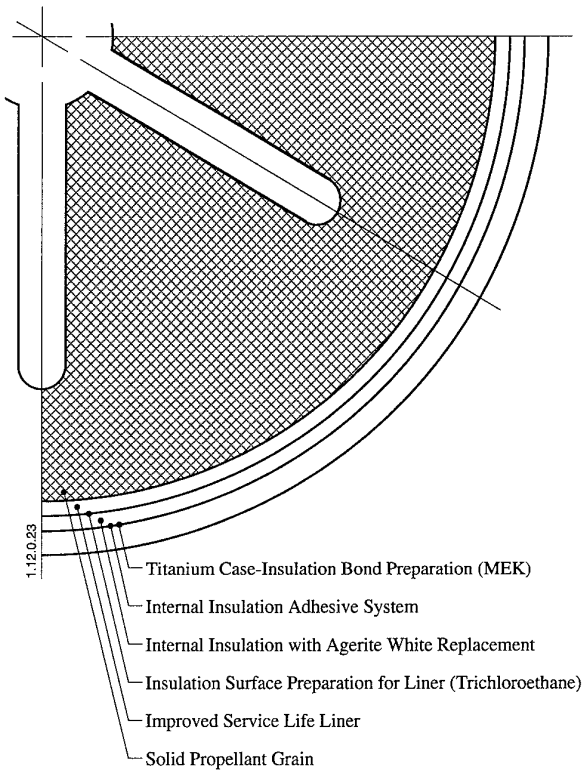



Figure 1 Partial Cross Section of Minuteman Second Stage Motor

## CANDIDATE INITIAL SCREENING

### Industry Search

The first step in the search for suitable solvent replacements was to search the solvent industry for likely candidates. This was accomplished in a number of ways. One avenue was to read trade magazine articles and advertisements for possible replacements. Many firms were aware of the growing need for replacements and were promoting their products on the basis of low toxicity, low ozone depletion potential and low or zero VOC content.

A second method employed was to ask Aerojet chemists and environmental department personnel for suggestions on likely candidates. Company chemists indicated what kind of materials would work best against the normal types of greases and oils to be cleaned. The environmental personnel were helpful in identifying which materials would be either restricted in usage or reportable under the various environmental regulations. Although a material may clean well, its use may require a great deal of reporting to various agencies, thereby making use of that material less attractive.

Another source of information was direct mail brochures from vendors. These typically were mailed to the environmental department and were passed on to the engineering department.

When a prospective candidate was identified, the vendor was called for more information (product brochure and a Material Safety Data Sheet) and a sample quantity. The MSDS would often identify the active ingredients and from that, a decision could be made as to whether or not the product should be considered for further evaluation. Some products appeared to be different formulations of the same few active ingredients.

### Selection Criteria

The primary criterion for selecting a new cleaning agent was its ability to remove greases, oils and dirt normally found in the production of solid propellant rocket motors. The advantages of TCA include its low toxicity, its non-flammability and its high volatility. These made it an almost perfect solvent for wiping on large components which could not conveniently be placed into an immersion bath or other parts cleaning apparatus. If an excessive amount of TCA was used to clean a part, the entire amount would soon evaporate and leave no significant residue behind. Similarly, MEK was very good for cleaning parts when a more aggressive solvent was needed. However, its high volatility and flammability made its use restricted to inert (no live propellant or explosives) operating areas. Other disadvantages of MEK include moderately high toxicity and an offensive odor.

One major selection criterion of the new material was the assurance of obtaining the same chemical formulation in the future. This eliminated some otherwise promising commercial products since these products can change to satisfy consumer needs. One method pursued to avoid such problems was to obtain the active ingredients (i.e., the raw chemicals) from a chemical supplier and mix them to the desired concentration within Aerojet. The exact formulation of a commercial product was never sought nor obtained.

Selection criteria were based on five basic factors:

- vapor pressure
- safety
- toxicity
- end use acceptability
- VOC content

Each candidate which was evaluated had to have sufficiently low vapor pressure that would pass the anticipated regulatory limit (less than 40 mmHg @ 20°C). Each candidate was checked for vapor pressure, safety, and toxicity data. If a candidate had a vapor pressure greater than 40 mmHg or was considered a fire hazard similar to acetone or MEK, it was dropped from consideration. Any suggested candidate that represented extraordinary safety precautions to operating personnel was also rejected. Candidates which presented toxic hazards from skin absorption and/or vapor inhalation were carefully screened. These candidates could be used if required with simple precautionary measures such as respirators and gloves. However, it was desirable to avoid the need for protective equipment.

Desirable characteristics of the replacement candidates included non-flammability and no offensive odors. If a candidate were flammable, its use could be restricted in live propellant areas. Having an offensive odor can make a material's usage unpleasant to the workers and therefore result in a reduction in productivity.

For the TCA replacement candidates, chemical similarity to TCA was not considered a requirement because use of chlorinated solvents is to be phased out. The candidates were required to either dissolve or emulsify the contaminants present on the surface being cleaned. Some candidates required a water rinse and/or dry wipe with clean cheese cloth after cleaning the surface. The end result had to be a dry, clean surface with no residue.

It became evident that some of the sales brochures were misleading and some Material Safety Data Sheets (MSDS) could be interpreted in such a way that the true toxicity was not apparent. Some vendors' sales brochures were promoting their products as being "non-toxic" yet the materials contained petroleum distillates, terpenes, and other potentially harmful ingredients. These ingredients were generally in low concentrations. Careful examination of the MSDS's for some of the ingredients indicated the products might not have been as safe as the sales brochure implied.

Some products reviewed contained terpenes, in particular, d-limonene (a citrus-based material). Some of these products and even their associated MSDS's did not list d-limonene as an ingredient because it was not considered in some literature as a dangerous substance. However, recent results of long term toxicity studies indicate terpenes are perhaps more dangerous than previously thought.[3,4]

Table 1 provides a list of the candidates selected for evaluation under Phase I along with their respective vapor pressure and measured VOC content.

**Table 1 Candidate Replacements**

| MEK Replacements | Vapor Press. mm Hg | VOC g/l |
|---|---|---|
| MEK (Control) | 71 | 806 |
| Deionized Water | 15 | 0 |
| Abrade and Dry Wipe | 0 | 0 |
| 10% 2-butoxyethanol | 15* | 39 |
| MIL-C-43616 Alkaline | Unknown | 138 |
| MIL-C-87936 Alkaline | 15.0 | 141 |
| MIAK | 4.5 | 888 |
| MIBK | 15.0 | 798 |
| Diisobutyl Ketone | 1.7 | 805 |
| Dipentene (d-limonene) | 1.0 | 838 |
| TCA Replacements | | |
| TCA (Control) | 100 | 1349 |
| Deionized Water | 15 | 0 |
| Dry Wipe | 0 | 0 |
| 10% 2-butoxyethanol | 15* | 39 |
| Axarel 52™ | <0.1 | 804 |
| N-butanol | 4.4 | 810 |
| 2-butanol | 16.0 | 808 |
| Amyl Alcohol | 2.0 | 814 |
| Hurrisafe™ (8:1 dil.) | 14.2 | 23 |
| Octowet 75™ | 15* | -- |
| M-Pyrol™ | 0.29 | 1027 |
| 0.1% Tergitol™ | 15* | 100 |
| PF Sovlent™ | <1.0 | 760 |

*Estimated as approximately equal to water.

**Preliminary Evaluation - Phase I**

The purpose of the Phase I bond tests was to determine the effects of the candidate replacement materials on the more critical bonds. In the case of MEK, the tests represented the case to internal insulation bond (titanium to V-45 nitrile rubber). Standard ASTM lap shear specimens were used for the tests. The TCA replacement candidates were tested on an aluminum-to-aluminum bond representative of an application on the motor raceway. The configuration of the ASTM lap shear specimens is shown in Fig. 2. The results of the Phase I bond tests are presented in Table 2.

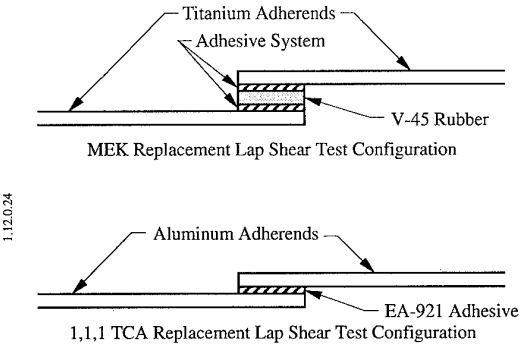



**Figure 2 Phase I Lap Shear Test Configurations**

In addition to the search for alternative solvents, other components of some critical bond areas were being changed for various reasons. The adhesive system used to bond the internal insulation into the chamber was changed because each of the three components of that system contained high levels of VOC's. The formulation of the V-45 rubber internal insulation was changed to replace an antioxidant. Also, the liner used between the propellant and the internal insulation was reformualted to extend its service life. Potentially, any one of these materials could affect the performance of one or more of the other materials. The results could be unacceptably low bond strengths.

**Table 2 Phase I Lap Shear Test Results**

| MEK Replacement | Shear Strength, psi |
|---|---|
| MEK (Control) | 767 |
| Deionized water | 623 |
| Abrade & Wipe | 739 |
| 2-butoxyethanol 10% | 549 |
| MIL-C-43616 | 1126 |
| MIL-C-87936 | 1239 |
| MIAK | 652 |
| MIBK | 593 |
| Diisobutyl Ketone | 509 |
| Dipentene (d-limonene) | 610 |
| Design Requirement: | 118 |
| TCA Replacement | |
| TCA (Control) | 778 |
| Dry Wipe | 816 |
| Deionized Water | 876 |
| 2-butoxyethanol 10% | 693 |
| Axarel 52 | 787 |
| N-butanol | 871 |
| 2-butanol | 435 |
| Amyl Alcohol | 846 |
| Hurrisafe™ | 741 |
| Octowet 75™ | 994 |
| M-Pyrol™ | 765 |
| 0.1% Tergitol™ | 834 |
| PF Solvent™ | 888 |
| Design Requirement: | 30 |

It would be a monumental effort to test the interdependency of nine MEK replacement candidates, two V-45 insulation replacement candidates, three adhesive system replacement candidates, twelve TCA replacement candidates, and two new liner formulations as well as the original materials for each. By selecting materials in Phase I based on single component changes, the program costs are greatly reduced.

During Phase I testing, only the critical bonds were represented in the laboratory. To evaluate each candidate material's effect on the bond, only one aspect of the bond was changed. In the case of the MEK replacement test plan, the bond tests included the current adhesive system and current V-45 insulation. Likewise, in the adhesive system test plan, different adhesives were used, but the adherends were cleaned with MEK and bonded to the current V-45 insulation. For each test plan, the two materials indicating the most promising performance were selected for further interdependency testing in Phase II.

Prior to cleaning and bonding, the adherends for the above tests were intentionally contaminated. Each adherend was handled so as to represent the effects of human skin oils and the dirt normally transferred by people handling and touching bond surfaces. To provide a worst case scenario, each adherend was also sprayed with WD-40™ and allowed to soak for about 24 hours. WD-40™ was used because it is a common lubricant with a release agent that would weaken the bond if not completely removed. The adherends were then cleaned with the replacement candidates and bonded per the configurations shown in Fig. 2.

Another issue associated with the replacements was the handling and toxicity of the material - this can be referred to as the "user friendliness" of the material. A worker must be protected from toxic or other harmful effects of any material he/she uses or handles. With higher toxicity, more protection is required. With more protective clothing comes less dexterity and mobility which lead to less productivity and/or possibly lower quality workmanship. By selecting a "user friendly" material, the workers need not wear as much protective clothing and can perform the assigned task with greater ease. In addition to the ease on the workers, a less toxic material is more easily disposed of and an accidental spill would not create as great an alarm as a more dangerous material. The toxicity issue was examined carefully during the initial screening process and during Phase I evaluation.

**Down Selection**

Following the Phase I evaluation and a review of the data, two MEK and two TCA replacement candidates were selected for further evaluation in Phase II. The data in Table 2 indicate that each of the candidates evaluated would provide adequate cleaning of the bond line surfaces. The down selection process then was governed more by the other aspects of the candidates - toxicity, "user friendliness," etc. Table 3 shows the candidates selected for Phase II testing.

**Table 3 Down Selected Candidates**

| |
|---|
| MEK Replacement |
| Abrade and Wipe<br>MIL-C-87936 Alkaline Cleaner |
| TCA Replacement |
| Deionized Water<br>10% 2-butoxyethanol |

The rationale for selecting these candidates was they were materials which were non-commercial (i.e., diluted solutions of raw chemicals) or which were governed by some federal or military specification. These criteria were thought to more likely ensure long term availability with a degree of control.

The "abrade and wipe" involves lightly abrading the bond surfaces (rubber or metal) with grit paper and using clean, dry cheese cloth to wipe the surfaces clean. This process would not be completely effective in all applications, particularly where heavy layers of oil and dirt are present. The abrading could also remove conversion coatings or other surface preparations which could then lead to corrosion of the metal. However, this process appeared adequate for the Minuteman III second stage internal insulation.

The MIL-C-87936 alkaline cleaner was chosen over the other alkaline cleaner, MIL-C-43616, because of the lower toxicity of the former. The Phase I bond test results indicate similar performance between the two and the highest bond strength values of all the candidates tested. Vendor literature for both materials recommends dilution to 10 percent for optimum cleaning effect. The MIL-C- cleaners were selected for evaluation primarily because they were military specification materials. In the event one supplier stops making a product which meets that specification, qualification of another supplier would be simplified.

For the TCA replacements, deionized water was found to provide adequate cleaning in many common applications. This process involved wiping the surfaces with cheese cloth soaked in deionized water followed by second wipe with clean, dry cheese cloth. A second wet wipe or water rinse was sometimes needed prior to the final dry wipe.

The choice to use a 10 percent solution of 2-butoxyethanol (aka ethylene glycol monobutyl ether or Butyl Cellosolve) was based on several factors. This chemical is the active ingredient in several common commercial cleaning products. However, in order to avoid future formulation changes by the vendor of a cleaning material, it was desirable to buy the raw chemical and dilute it in house to a prescribed concentration.

Pure 2-butoxyethanol is considered moderately toxic and has a fairly low pesonnel exposure limit (PEL). The OSHA established PEL is 25 ppm (skin). This states that at low concentrations in air the material can be harmful and it can also be absorbed through the skin. However, the vapor pressure for 2-butoxyethanol is less than 1 mmHg meaning that the fluid does not readily evaporate to the atmosphere. (By comparison, the OSHA PEL for TCA is 350 ppm, but the vapor pressure is 100 mmHg). These toxicity concerns associated with 2-butoxyethanol can be mitigated with the proper use of protective clothing. For normal industrial usage of 2-butoxyethanol, butyl, nitrile, or neoprene rubber gloves will protect the worker.

Several commercial cleaning agents have low concentrations of 2-butoxyethanol and are advertised as being non-toxic and biodegradable. The intent was to use the active ingredient in these cleaners without the other additives such as colorings, fragrances, etc. From Table 2 it can be seen that the 10 percent 2-butoxyethanol solution provided adequate bond strength. The other raw chemicals tested - n-butanol, 2-butanol, and amyl alcohol - were rejected based on their high VOC tests results.

In order to test the long term effects of the down selected TCA replacement candidates on the propellant-to-insulation bond, double plate tensile and peel tests were performed using the Minuteman second stage propellant and internal insulation. Table 4 provides the results of those tests.

**Table 4 Propellant-to-Insulation Bond Tests**

| Candidate | Peel, pli | DPT, psi |
|---|---|---|
| TCA (Control) | 17.4 | 74.9 |
| Deionized Water | 17.1 | 69.5 |
| 2-butoxyethanol | 17.1 | 66.4 |
| Design Requirement: | 10.0 | 50.0 |

## QUALIFICATION TESTING - PHASE II

Phase II testing provided test data that (1) helped in the final selection of a replacement solvent for both the MEK and TCA, and (2) led to the formal qualification of the MEK and TCA selected replacements .

### Bond Preclean Evaluation

The primary consideration of Phase II activities was the ability of each of the two down selected MEK and TCA replacement candidates to adequately clean bond surfaces in all critical applications where MEK and TCA were used. Therefore, lap shear test specimens representing all critical bond applications were prepared using each down selected candidate cleaner. These tests allowed qualitative comparisons of the cleaning effects on each bondline between each of the candidates.

### Solvent/Propellant Compatibility

One concern unique to a TCA replacement is its compatibility with the motor's solid propellant. In addition to being used during the manufacturing process, TCA is used as part of field maintenance activities in areas where accidental contact between the solvent and propellant is likely to occur. An example is when the igniter boss is cleaned prior to installation of the igniter.

To determine the effects on the propellant, compatibility tests were conducted by contaminating propellant samples with each of the TCA replacement candidates. These tests included impact, friction, and differential thermal analysis. The results of these test indicated that propellant exposed to the each of the candidates experienced a measurable decrease (greater than 16 percent) in the exothermic onset temperature. Although this was not a safety concern, this did indicate that some solvent was absorbed into the propellant. To assure further changes (which could lead to unacceptable propellant performance) do not develop over time, six month aging specimens were prepared and tested using the same test procedures as those used at zero time.

### Interdependency Testing

Both MEK and TCA were used in critical bond applications on the Minuteman second stage motor where other components in the bonds were also being replaced. These other components included the propellant liner, the internal insulation, and the chamber to insulation adhesive system. Each of the other components and their replacements were evaluated independently with down selection to two candidates each. To provide data for each of the possible component combinations, bond specimens designed to duplicate each bond line were prepared. A Taguchi matrix was employed in order to reduce the number of specimens required. Six month accelerated aging samples were also included in this evaluation.

### Final Down Selection

Based on the results of the test conducted under Phase II, the MEK and TCA replacements that demonstrated the best performance were chosen for formal qualification . If a single candidate did not prove acceptable for all applications, then multiple candidates would have been qualified for their respective applications. This, however, is a less desirable scenario as it would afford less flexibility in the manufacturing process.

## FULL-SCALE DEMONSTRATION - PHASE III

As part of the Minuteman second stage remanufacture program, one motor is chosen from each production "lot" and statically fired at simulated altitude conditions to provide assurance of sustained production quality. The Production Quality Assurance (PQA) motor provides an ideal vehicle for the demonstration of proposed process and material changes in the motor. Each of the solvents chosen for qualification was fully incorporated into the production of one PQA motor to provide full-scale performance verification prior to formal qualification.

The internal insulation bond on the motor was tested using a portable in-situ tensile test fixture. This test was performed prior to casting of the propellant. Following the tensile tests, the insulation was repaired and patched where the specimens were cut out.

Additionally, aging of the new "baseline" motor must be verified at the full-scale level. Three Aging and Surveillance (A&S) motors were built to provide vital aging stability data prior to the second motor remanufacture program. As with the PQA motor, each A&S motor included the MEK and TCA replacements as well as the other bond line components replacements

## CONCLUSIONS

Based on the data generated in this program, it is felt that environmentally compliant replacements can be found for both methyl ethyl ketone and 1,1,1 trichloroethane. Although each of these solvents may not be universally replaced by one new material for all of their respective applications, multiple cleaners exist which can provide the same end results as the old materials in all applications. Several new materials exist in the industry which provide adequate if not better cleaning than MEK and TCA while not posing threats to either the local atmosphere or to the protective ozone layer.

Bond testing on some critical bonds indicate that deionized water will provide adequate cleaning for some applications. Where possible, use of deionized water should be encouraged as it is as non-toxic and environmentally safe as one could hope for.

The use of 2-butoxyethanol in low concentrations can pose some toxicity threat to workers. Lowering the concentration of 2-butoxyethanol can reduce the toxicity but not eliminate it. Almost any cleaning agent can be considered toxic to some extent. The key to protecting the workers and the environment is responsible usage of any material. This includes informing the workers of the hazards associated with the material, specifying the proper protective clothing to wear, and proper instructions as to how the material should be used.

## REFERENCES:


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2. Aerojet Propulsion Division, 1991. Test Plan MRP-106 Revision 2, Minuteman Second Stage Remanufacture Program, Qualification of Trichloroethane Replacement. Sacramento, CA 95813

3. USEPA, 1990. U.S. Environmental Protection Agency, Office of Toxic Substances. Terpene Hazard Assessment. USEPA. Washington DC 20460

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## Discussion

QUESTION BY JM. TAUZIA : What is the nature of hazards occurring from the use of 2-butoxyethanol ?

ANSWER : In its neat form, 2-butoxyethanol can be relatively toxic and can be absorbed through the skin. It has a fairly low personnel exposure limit as established by US OSHA. In low concentrations, rubber gloves are adequate for protection - just as gloves are required for use of TCA.

QUESTION BY R. COUTURIER : You presented results on Minuteman Stage II and you have selected 2 potential candidates (ionized water and 2-butoxyethanol). Have you an experience for other motors ? More specifically for very different materials : liner/composite propellants (inert binder) ; liner/high energy propellants (energetic binder with plasticizers) ?

ANSWER : The bond systems evaluated did not involve direct contact with propellant. Propellant compatibility test were conducted to determine if a spill of the candidate on the motor propellant would cause adverse effects. No significant effects were noted.

# FINDING AN ENVIRONMENTALLY ACCEPTABLE REPLACEMENT FOR FREON 114B2 (HALON 2402) THAT MEETS MINUTEMAN LITVC PERFORMANCE CRITERIA

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## SUMMARY

Freon 114B2 (Halon 2402) is injected into the hot gas exhaust stream of the Minuteman Second Stage solid propellant rocket motor nozzle to provide thrust vector control. In response to environmental concerns, specifically ozone depletion, the United States Air Force has established a program to find and qualify a replacement for Freon 114B2. This program is currently approaching three years of age. Phase I of the program consisting of studies and analyses to identify the most promising candidates followed by laboratory testing and full scale motor tests to further screen the candidates down to a single selection (perfluorohexane) has been successfully completed. Phase II of the program consisting of qualification firings is scheduled for the latter part of this year and next year.

## INTRODUCTION

The Minuteman second stage motor, Fig. 1, has been using Freon 114B2 in its thrust vector control system since the motor's inception in the mid 1960's. Introduction of this fluid into the motor's hot gas stream results in a side force created by (1) the momentum change in the fluid as it is accelerated into the nozzle and (2) a pressure disturbance on the nozzle wall caused by the interaction of the supersonic nozzle flow and a vapor body formed by the fluid. The force from (1) is seldom more than 5% of the total. The magnitude of the side force from (2) is strongly dependent on the size of the vapor body formed which in turn depends on the amount of fluid injected, molecular weight, heat capacity, heat of vaporization, and heat release from reaction with the primary hot gas stream. An increase in injection flow provides greater side force, however, the effective $I_{sp}$ of the injectant is decreased because the reaction with the injectant and the hot gas stream is reduced. Freon 114B2 was initially chosen on the basis of its high density which allowed it to be packaged into the existing envelope, its good performance (specific impulse) when reacting with the hot gas stream, its compatibility with Liquid Injection Thrust Vector Control (LITVC) system materials and its ability to withstand temperatures from a gas generator pressurization source without rapidly decomposing. Unknown at the time of its selection was its adverse effect on the ozone layer, e.g., ozone depletion potential.* Presently Freon 114B2 is mandated for phase out by the year 1996. The Air Force has been responsive to this mandate and has directed Aerojet, the designer/manufacturer of the second stage motor, to find and qualify a replacement injectant.

The program for finding a replacement consists of two sequential phases. During Phase 1 two paths were initially

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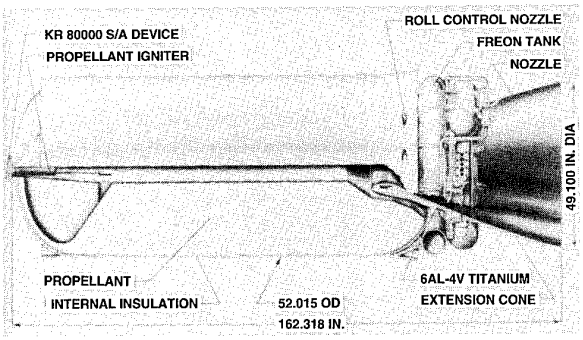



**Fig. 1. Minuteman Stage II Motor**

pursued in parallel: finding a drop-in replacement for Freon 114B2 and finding an injectant that would require a complete redesign of the thrust vector control system. This latter path was abandoned early in the program when it became apparent that a drop-in approach was feasible. The Phase I logic flow diagram covering only the drop-in paths is depicted in Fig. 2. Phase II concentrates on qualification testing of the new subsystem via motor static firings and final verification via flight test. The material presented in this paper concentrates on the Phase I analysis and trade-off studies used in identifying the initial population of candidates. The down selection of candidates via analysis and tests, and the full-scale motor tests to verify performance criteria has been completed.

## PRESENT LITVC SYSTEM

The Liquid Injection Thrust Vector Control (LITVC) system provides missile attitude control in the pitch and yaw axes in response to commands from the missile guidance control system. The LITVC system consists of a solid propellant gas generator as the pressurization source, a spring-loaded relief valve for regulating the pressure of the hot gas, a stainless steel torus shaped injectant storage tank containing a rubber bladder filled with Freon 114B2 injectant, burst disks at each of the four outlet ports, delivery manifolds, and injector valves. The injectant is expelled from the rubber bladder by the regulated hot gas applying external pressure (squeezing) to the bladder. The injectant is carried from the bladder-tank assembly to bosses on the nozzle exit cone support structure by four

* The term ozone depletion potential (ODP) refers to a factor which reflects the potential of a substance to deplete ozone in the stratosphere as compared to Chlorofluorocarbon-11 (CFC-11). Freon 114B2 has a high ODP of 6. The maximum allowable ODP value per the U.S. Clean Air Act will ultimately be 0.2.

*Paper presented at the Propulsion and Energetics Panel (PEP) 84th Symposium on "Environmental Aspects of Rocket and Gun Propulsion" held in Aalesund, Norway, 29 August - 2 September 1994.*

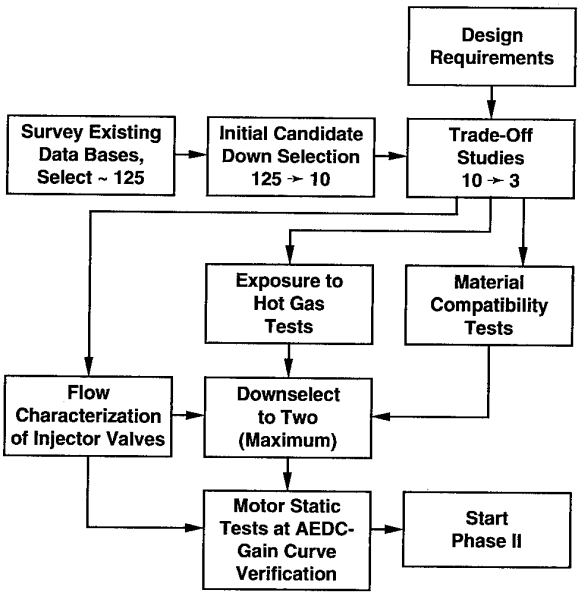



**Fig. 2.. Program to eliminate freon 114B2 as LITVC injectant - Phase I. (Drop-in path only)**

flexible hose assemblies. Injector valves mounted on the nozzle exit cone support structure control injectant flow through the exit cone wall into the nozzle exhaust stream. A schematic of the system is presented in Fig. 3. Figure 4 is an exploded view of the system hardware, excluding injector valves.

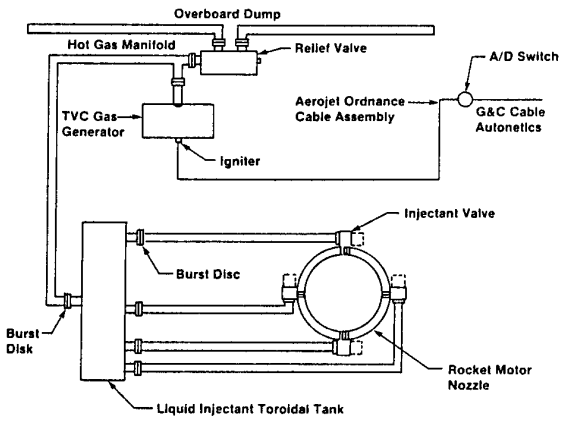



**Fig. 3. Schematic diagram of LITVC system**

## INITIAL INJECTANT CANDIDATE SELECTION*

The first step toward finding potential replacements to an existing injectant fluid is establishing realistic search criteria based on desirable injectant characteristics. Initial organic material search criteria chosen for the Minuteman second stage application were: molecular weight below 300, total atom count 3-20, and boiling point in the range 35-60°C. The compounds could include 1-6 carbon, 0-2 oxygen, 0-2 nitrogen, 0-2 sulfur, and 0-14 fluorine atoms. The presence of other types of atoms was allowed for the initial search.

The molecular weight, boiling point, and total atom count criteria were designed to yield compounds of reasonable volatility, so that a large vapor body of unreacted injectant would form quickly. For boiling point, the lower limit (35°C )

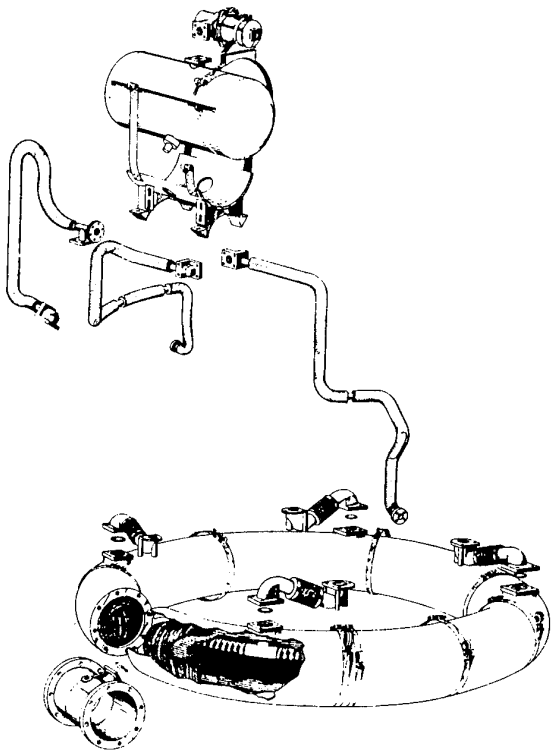


**Fig. 4. Thrust vector control system.**

corresponds to the upper limit of vapor pressure that current burst disks can withstand during storage. The upper limit (60°C) corresponds to a compound of lower volatility than Freon 114B2 (boiling point 47°C) but still able to vaporize rapidly to form a vapor body.

Selected inorganic compounds and candidates with boiling points higher than the optimum range but having other highly desirable properties (e.g., commercial availability, low toxicity, and expected high performance) were added later manually. For example, these included ethylene glycol, propylene glycol, and several high-molecular-weight amines. Inorganic compounds were selected for evaluation qualitively because it was not possible to screen by physical properties. Such tabulated properties as melting point and boiling point were not applicable screening criteria for inorganic compounds. Solubility in water was of interest, but was not tabulated in a computer-searchable form. The only major database of inorganic compounds (Gmelin's Handbook of Inorganic Chemistry) was not formatted for searching by properties. However, the extensive experience of propellant chemists at Aerojet, TRW and Hill AFB were used to develop the list of candidate inorganic compounds.

Four on-line data bases were searched using the criteria established: Design Institute for Physical Property Data (DIPPR), Thermodynamic Research Center Thermodynamic Data (TRCTHERMO), the NMERI Halocarbon Database and Beilstein's Handbook of Organic Chemistry. The DIPPR database contains extensive physical property and reactivity

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* This effort was done primarily by Dr. Jon Nimitz of The Center of Global Environmental Technologies (CGET) which is associated with the New Mexico Engineering Research Institute (NMERI) at the University of New Mexico. This agency is pursuing new products to fill the voids created by Montreal Protocol's bans on halons and Freons. Dr. Jon Nimitz has since formed his own consulting firm, Environmental Technology and Education Consultants (ETEC).

data on approximately 1000 commercial (high-volume) chemicals. The TRCTHERMO database contains data on properties of approximately 7000 widely used chemicals. The NMERI Halocarbon Database contains physical property data on approximately 650 one to eight-carbon haloalkanes, most of which have very few properties reported. Beilstein's Handbook of Organic Chemistry contains data on approximately four million organic and organometallic chemicals (the vast majority of which also have very few properties reported). The following numbers of organic or organometalic compounds met the initial search criteria:

| Source | Compounds Identified |
|---|---|
| DIPPR | 6 |
| TRCTHERMO | 5 |
| NMERI | 0 |
| Beilstein | 2,400 |

There were significant overlap among the "hits" from different databases. For example, the Beilstein hit set contained all the compounds from the other databases. The hits from DIPPR and TRCTHERMO were the most valuable because all compounds in those databases are well-studied and readily available.

Candidates identified in this initial search were screened and rejected for one or more of the following reasons: they clearly did not meet one or more of the agent requirements (even through they met the broad search criteria), they were fully halogenated CFCs or BFCs (and therefore would be ozone depleting), there was an obvious error in tabulated physical property data (e.g., the melting point of the compound had been entered in the boiling point field), or if almost no properties were reported. Chemicals with very few properties reported could not be deployed by the time frame desired, because they are not available even in research quantities and it would take several years for their synthesis and adequate testing of properties including toxicity and materials compatibility. In addition, constraints posed by the existing LITVC system for the drop-in candidates include:

- Volume - A volume of the new injectant sufficient to meet mission requirements must fit into existing toroidal tank and bladder.
- Material compatibility - The new injectant must be compatible with existing materials.
- Hot gas compatibility - The new injectant must not decompose rapidly or react when in contact with the gas generator hot gas.

Screening of the initial candidates using the above criteria yielded two lists of approximately 125 candidates each. Because the initially defined requirements for drop-in and redesign candidates were similar, there was significant overlap (approximately 75%) between the two candidate lists.

## INITIAL INJECTANT CANDIDATE DOWN SELECTION

In that numerous injectant candidates were now required to be rigorously evaluated over several criteria, a tool for providing a relative figure of merit for each was developed to accelerate the down selection process. The process proved to be an effective method of reducing to approximately 20 the overall field of candidates in a logical, traceable fashion. Supplementing this process was the integration of engineering judgment into the final decisions for down selecting from the narrowed field of approximately 20 to finally arrive at a list of 10.

The weighted rating of attributes process (WRAP) was developed as a six step process. These steps were to (1) identify all discriminating parameters, (2) assign weights based on relative importance, (3) establish quantitative values (e.g., actual density) for each parameter, (4) transform these quantitative values to qualitative values between 0* and 10, (5) multiply these qualitative values by the appropriate weighting factor for each parameters, and (6) sum the resultant multiplication values for each candidate. The highest scores represented the most promising candidates.

Twelve parameters were identified as being important and were considered in this process. Table 1 delineates the 12 discriminating parameters, the weights assigned and the rationale for the weight assignment. Table 2 lists properties that are instrumental in developing side force predictions. Quantitative values of the parameters were acquired for each candidate injectant via literature, or in cases where such data was not available the values were estimated using established or newly developed estimation methods.

Transforming these quantitative values to qualitative values between 0-10 was accomplished by developing models. These varied from linear scales to log scales to simply poor, medium and good categories. Figure 5 provides samples of the relationships developed between quantitative and qualitative values for three of the 12 parameters.

Performance was the principal discriminator in this early down selection. Therefore, it was decided to establish WRAP scores for each candidate in all categories except performance. Down selection was based primarily on predicted performance, provided the WRAP scores did not indicate a significantly low relative ranking.

Table 3 identifies the top 20 candidates as determined by the WRAP process. The rationale or screens used to further reduce the quantity to the intermediate list of approximately 10 is stated next to those candidates eliminated.

## PERFORMANCE PREDICTIONS

Performance predictions were accomplished using several modeling techniques, each based on an approach completely independent of the others for improved confidence. In the previous down selection (WRAP), a rough order of magnitude (ROM) performance model was utilized. This ROM model was "anchored" to existing Freon 114B2, strontium perchlorate and nitrogen tetroxide experimental data. The model was tailored more for higher injectant flow rates where large amounts of unreacted injectant remain in the form of a vapor body. It assumed that only negligible amounts of injectant actually react with the exhaust. In addition, this ROM model does not account for the net change in the number of moles of gas in the exhaust stream. The ROM model proved useful in the original coarse performance screening but its use was limited in the next refinement level, especially when low injectant flow performance became an evident consideration.

The ROM model was supplemented by a thermochemical $I_{sp}$ predicted model[1] for low flow applications and an Aerojet developed computational fluid dynamic (CFD) model for both low and high flow applications. Table 4 supplemented by Fig. 6, depict predicted performance of these injectants.

### Environmental Considerations

Chlorine, bromine and nitrogen oxides are the primary contributors to atmospheric ozone depletion, with nitrogen oxides responsible for an estimated 50 to 70% of all ozone

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* A zero value for a candidate automatically eliminated that candidate from further consideration.

**Table 1. Rationale for parameter selection and weighing**

| Parameter | Weight | Rationale For Weight Assignment |
|---|---|---|
| Environment | | |
| 1. Ozone Depletion Potential (ODP) | 5 | High weight assigned in that environmental regulations specifically restrict these materials |
| 2. Global Warming Potential (GWP) | 3 | An important factor to consider although no regulations in place. |
| 3. Safety and Handling (i.e., Toxicity) | 4 | An important discriminator. However, precautions can be taken for the handling of some hazardous materials. |
| Performance | | |
| 4. Decomposition | 5 | The performance of the injectant is directly related to the volume of gas produced by the injectant when it vaporizes and/or reacts with the fuel-rich exhaust. |
| 5. Computed Side Force | 5 | A computer model is used to calculate expected side force for a given flow rate of injectant. This parameter is influenced by the properties listed in Table 2. |
| System | | |
| 6. Vapor Pressure | 1 | Vapor pressure at normal temperatures should not exceed the capability of the valves and burst disc to contain it. However, a high vapor pressure would be desirable during motor operation. |
| 7. Existing Aging Data | 1 | Extent of available data will reduce aging program, material study, and reduce risk. |
| 8. Stability in Storage | 4 | A significant discriminator in that the injectant must be stable (i.e., not drop out of solution nor decompose) over a span of approximately 25 years. |
| 9. Packaging | 1 | The system to hold the volume of material needed for the required total impulse of the system must be able to fit into the space available. |
| Cost | | |
| 10. Injectant Costs – Lab | 1 | A consideration but not a prime one. Cost of injectant for lab samples is not recurring and quantities are minimal. |
| 11. Injectant Costs – Production | 4 | A major consideration in that production quantities must be purchased. |
| 12. Availability | 4 | The injectant elected must be available in sufficient quantities to support production. |

**Table 2. Properties that influence performance**

| Parameter | Rationale For Weight Assignment |
|---|---|
| a. Exothermic Reaction With Exhaust | The performance of the injectant is directly related to the volume of gas which is a function of the temperature and number of moles produced. In general the more exothermic a reaction the more it goes to completion, forming gas products and releasing heat that aids rapid vaporization. |
| b. Surface Tension | This determines the size of the droplets in the injectant streams and subsequent vaporization rate. |
| c. Viscosity | Formation of small droplets is enhanced by low viscosity. It is a second order effect (behind surface tension and density). |
| d. Density | Important in terms of packaging – i.e., volume limited system. However, a more efficient injectant or reduction of total yaw/pitch requirements makes this a minor parameter. |
| e. Molecular Weight | The volume of gas from a given mass of liquid is maximum for a low molecular weight. |
| f. Ratio of Specific Heats | A primary gas property. A low heat capacity, Cp, (and thus a large gamma) is desired so that a large gas volume from a given heat input is produced. |
| g. Boiling Point | A low boiling point enhances the early formation of a vapor body from the injected liquid. |
| h. Heat of Vaporization | It is felt that this is relatively important in that a high heat of vaporization may actually cool rocket exhaust. |
| i. Thermal Conductivity | This will influence the heat of vaporization and will enhance the reaction (i.e., burn it into a gas). The injectant is in a very high temperature environment and thus this parameter is not considered a major discriminator. |

destruction (the overwhelming majority of these nitrogen oxides are produced naturally). Of the remaining injectant candidates, none contained chlorine or bromine (this was one of the elimination criteria), although several promising fluids were nitrate-bearing compounds. This was determined not to be contradictory, as the fuel-rich rocket motor exhaust is believed to completely react with any nitrogen oxides at the low flow rates experienced in operational conditions.

Global warming potential (GWP) is a fast-growing environmental concern, although not as well understood a phenomena as ODP. Additionally, there is no universally accepted method for calculating GWP. There are presently no regulations in place or proposed to limit GWP. Only one of the remaining fluid candidates poses a GWP concern: perfluorohexane has a long atmospheric lifetime. However, it is reported that the EPA agrees that it does not contribute significantly to global warming. On this basis perfluorohexane was retained as a viable long term candidate.

### Trade-off Studies

A series of trade-off studies were employed with emphasis placed on more in-depth refining of data and analyses in the area of performance, environmental impact, toxicity, stability and compatibility of the injectant candidates with materials that they would be in contact with. Twenty-five years was the assumed lifetime that the injectant had to be stable and not

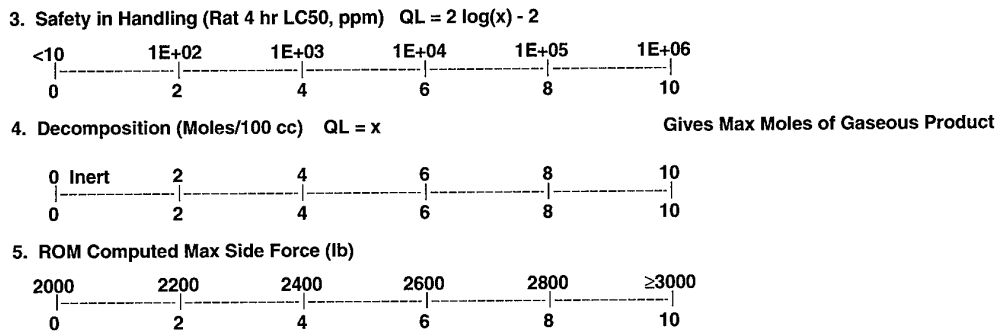



**Fig. 5. Conversion of quantitative values to qualitative values – WRAP**

**Table 3. Downselection From 20 to 10 Candidates**

| | | Drop-In | |
|---|---|---|---|
| | | Candidate Name | Rationale For Rejection/Selection |
| | 13 | 1,1 dimethylethyl methyl ether | Not best in either class |
| | 9 | Nitrogen tetroxide | Hot gas compatibility; redesign only |
| | 16 | Hexafluorobenzene | Not best in FC class |
| | 18 | Oxazole | Availability, cost, flammability |
| ☑ | 32 | 2-methoxyethanol | Common, low volatility solvent |
| | 19 | 2-methylfuran | Toxic; mutagenic |
| | 7 | 2-propanol (IPA) | Not the best performing alcohol |
| | 1 | Carbon disulfide | Very toxic; offensive odor |
| ☑ | 6 | Dimethoxymethane (Methylal) | Best of ether class |
| ☑ | 8 | Ethanol (Denatured) | Widely used; can mix w/water |
| ☑ | 12 | Ethylene glycol in water | High performance; common coolant |
| ☑ | 4 | Furan | The only aromatic studied |
| | 31 | Methyl heptafluorobutyrate | Availability, insufficient information |
| | 26 | Undecafluorpiperidine | Availability |
| ☑ | 2 | Methanol | Best of alcohol class |
| ☑ | 14 | Methyl ethanoate | Best of ester class |
| | 28 | Methyl formate | Being considered as a redesign candidate |
| | 5 | Nitromethane | Explosive danger |
| ☑ | 10 | Sodium nitrate in water (40% solution) | Top performer; the only inorganic solution |
| ☑ | 3 | Perfluorohexane | Highly inert; low toxicity; good performance |

**Table 4. Drop-in candidates**

| | Candidate Name | Walker Isp | CSD Isp | Walker | CFD | ROM | Max Flow Side Forces | |
|---|---|---|---|---|---|---|---|---|
| | | | | All at 1.0 lbm/sec | | | ROM | CFD |
| Fre | Freon 114B2 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 2 | Methanol | 1.16 | | 0.42 | | 0.31 | 0.56 | |
| 3 | Perfluorohexane | 1.24 | 1.17 | 0.98 | 0.92 | 0.73 | 0.81 | 0.68 |
| 4 | Furan | 1.17 | | 0.52 | | 0.30 | 0.47 | |
| 6 | Dimethoxymethane | 1.17 | | 0.47 | | 0.24 | 0.48 | |
| 8 | Ethanol (Denatured) | 1.10 | 1.10 | 0.40 | 0.41 | 0.26 | 0.43 | |
| 10 | Sodium Nitrate in Water | 0.95 | .89 | 0.58 | 0.54 | 1.07 | 1.14 | 0.82 |
| 12 | Propylene Glycol | 1.21 | 1.12 | 0.58 | 0.54 | 0.34 | 0.44 | 0.67 |
| 14 | Methyl Ethanoate | 1.05 | 1.08 | 0.46 | 0.47 | 0.26 | 0.42 | |
| 32 | 2-Methoxyethanol | 1.19 | | 0.53 | | 0.27 | 0.43 | |

Note: All valves are relative to Freon 114B2

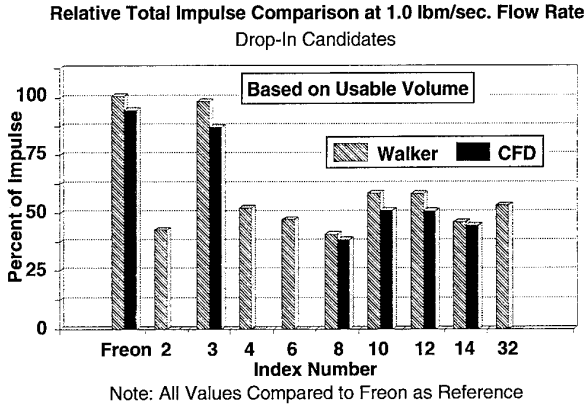



**Fig. 6. Freon 114B2 replacement candidates**

have adverse compatibility effects. The objective of these trade-offs was to reduce to three drop-in injectant candidates.

### Performance Requirements

The current performance specification delineates a minimum side force capability early in the stage 2 operation to offset staging effects and a lesser capability thereafter to maintain missile stability.

Based upon predicted injectant performance the candidate will not meet the existing specification requirements. In anticipation of this finding, at the start of this program a re-evaluation of Stage II LITVC system requirements was initiated in order to develop technically justifiable performance requirements while affording the greatest possible chance of accommodating a drop-in injectant. Rockwell Autonetics and TRW, with support from Aerojet were tasked to derive new requirements. Both teams developed computer models to simulate missile flight behavior. (These models were similar but not identical). The models were validated using data from two dissimilar flights out of Vandenberg AFB.

A Monte Carlo simulation approach was then employed using the validated models under conservatively established operational conditions. Computer trials, consisting of 1000 runs each were performed for each condition until an unacceptable failure rate of more than three failures out of 1000 was achieved. Each of the computer iterations (1000 runs) held certain boundary conditions as fixed; other parameters were allowed to vary. The results of these efforts yielded a mean side force requirement which was approximately 79% of the original requirement.

### Toxicity

As would be expected, most of the best performing fluids (highest specific impulse) were significantly volatile and posed substantial handling concerns. Although hydrazines and other compounds of similar toxicity are handled regularly in the industry, their toxicity caused them to be eliminated as candidates for this application. The perfluorocarbons are good examples of adequate performance combined with minimal toxicity.

### Stability

The environmental storage requirements for the Minuteman second stage prevent all but brief excursions into what are otherwise very benign conditions. As a conservative limit, however, all solutions considered were limited to concentrations dilute enough to prevent solute precipitation to temperatures as low as 0°C.

### Compatibility

Initial considerations for injectant compatibility addressed prior exposure experience with metallic and nonmetallic materials similar to those found in the current LITVC system.

### Down Selection

The selected candidates were:

- 40% sodium nitrate/water
- Perfluorohexane
- Propylene glycol

Three separate chemical families exist for the drop-in category.

### Testing Leading to 3-1 Downselection

Hot gas compatibility, material compatibility, flow testing and injectant side force demonstration tests were employed in the further downselecting from three candidates to a single candidate. Early in the testing sodium nitrate solution and propylene glycol were determined to be inadequate during the injector flow testing resulting in barium perchlorate being added to the candidates under consideration.

### Hot Gas Compatibility Tests*

In the hot gas compatibility tests the candidate injectant was placed in a small pressure vessels connected to a LITVC gas generator. Pressure at the vessel was regulated to approximately 610 psig to simulate LITVC system operational pressure. The firing of the gas generator introduced hot gas into the pressure vessel for the same duration at the same pressure, temperature and gas composition as an actual LITVC system firing. All three original candidates, plus barium perchlorate, reacted satisfactorily to the hot gas environment.

### Material Compatibility

Material compatibility tests were designed to verify the resistance of the LITVC system materials to the liquid injectant candidates and included immersion and accelerated aging tests. After 1, 2 and 6 months of immersion at 25°C, materials were tested for physical and mechanical properties. Degradation of material properties would indicate the liquid injectant(s) are unsuitable for further evaluation.

The accelerated aging specimens were identical to the above material compatibility specimens (25°C storage) in configuration but were stored at 43°C and 57°C. Both ambient and elevated temperature storage specimens were tested concurrently. Accelerated aging samples used material compatibility zero time data as a baseline. Specimens were encapsulated with candidate injectants similar to previous Minuteman Stage II aging programs. Test types and data collection were identical to that of the original Stage II Aging and Surveillance Program to allow for direct comparison to original program results.

Perfluorohexane was the best choice of the four candidates for compatibility with the current LITVC materials. It was stable with all LITVC materials. Propylene glycol was compatible with all material with the exception of an adhesive. Sodium nitrate and barium perchlorate were found to be non compatible with one or more significant materials (bladder or tank).

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* The hot gas compatibility tests were required based on results of a 1960's experiement in which a LITVC system test was conducted in which strontium perchlorate was substituted for Freon 114B2. An explosion occurred.

### Flow Testing and Injectant Side Force Demonstration

The injectant side force demonstration involved motor static test firings at simulated altitude in which side forces were measured. In preparation for these tests an auxiliary feed system was fabricated which allowed storage and delivery of two injectant candidates for each motor firing. This auxiliary feed system was used in flow characterization of each injector valve (four per motor) used for each test. During the flow characterization tests it was discovered that sodium nitrate and propylene glycol did not flow well at very small valve openings. During missile operation the majority of the valve openings are at small openings. Consequently this led to their being eliminated as viable and barium perchlorate was added as a candidate. Both barium perchlorate and perfluorohexane flowed satisfactorily through the valves. The characterization tests allowed Aerojet to quantify the variability in the valves. This variability related directly to the variability seen over the years for the maximum measurement side force using Freon 114B2.

Three static motor tests have been conducted to date.

Maximum side force delivered at time of staging, total impulse were the two areas being closely monitored. The results are summarized in Table 5 and shown in Fig. 7

**Table 5. Motor Static Firing LITVC Results**

| | Measured Side Force * | Total Impulse |
|---|---|---|
| Perfluorohexane Test #1 | 1.13 | Satisfactory |
| Barium Perchlorate Test #1 | 1.25 | Satisfactory |
| Perfluorohexane Test #2 | 1.16 | Satisfactory |
| Perfluorohexane Test #3 | 1.19 | Satisfactory |

* Ratio of Revised Requirement

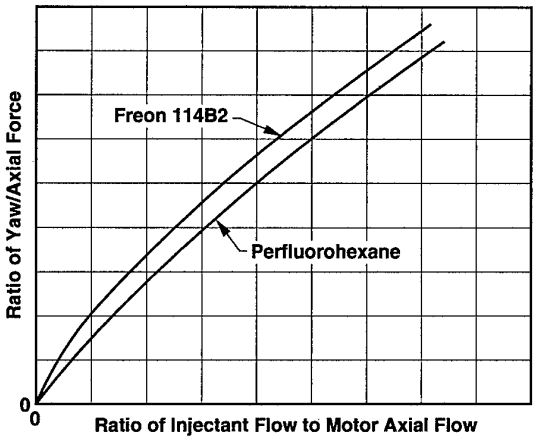



**Fig. 7. LITVC liquid injection grain curve for Minuteman Stage II Freon 114B2 and perfluorohexane**

### Selected Candidate For Phase II

Based on static firing, flow testing, material compatibility, and hot gas compatibility test results, perfluorohexane was chosen as the injectant to be qualified during Phase II of the program.

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# Discussion

QUESTION BY R. COUTURIER : Perfluorohexane is the selected candidate to replace Freon (or Halon). At this level of characterization do you think this candidate can be extended to other motors ?

ANSWER : Liquid injection thrust vector control was the state of the art in the 1960s. Nearly all 1990s systems employ some form of nozzle movement. Minutem Stage III uses strontium perchlorate in their LITVC system and will continue to use it. Polaris uses Halon 2402 but polaris is being decommissioned.
No--perfluorohexane will probably not be used in other thrust vector control systems.

# PROPELLANT HANDLING PROVISIONS AT A TEST FACILITY FOR HYPERGOLIC BIPROPELLANT ROCKET ENGINES

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## SUMMARY

Ground testing of bipropellant rocket engines with storable propellants demands for adequate test facility concepts to fulfill the needs with respect to health hazards and safety aspects. The general properties and handling instructions for the todays most important hypergolic propellants are reviewed.

For a 20 - 30 kN engine [1, 2] to be tested at sea level conditions with the hypergolic propellant type Monomethyl Hydrazine (MMH) and Nitrogen Tetroxid ($N_2O_4$) test facility lay-out criteria are presented for two test positions.
Design concepts and test facility handling during propellant loading/deloading and hot run phase are described for an engine and a full flight like stage test position.

After 4 years of operation a first positive resumée can be drawn.

## LIST OF SYMBOLS

| | |
|---|---|
| MMH | Monomethyl Hydrazine |
| $N_2O_4$ | Nitrogen Tetroxid |
| UDMH | Unsymmetrical Dimithyl Hydrazine |
| $HNO_3$ | Nitric Acid |
| He | Helium |
| $CO_2$ | Carbon Dioxide |
| TGSE | Tanking Ground Support Equipment |

## INTRODUCTION

The operation of test facilities with hypergolic propellants is experienced at Deutsche Aerospace for more than 30 years. A typical test facility established 30 years ago is characterized today by many additional set-ups which were created during numerous development steps and 'lessons learned' loops. Therefore to design and to built-up a complete new test facility with skilled, experienced people gives a challenge to create an efficient facility which is easy to handle and safe in operation. Due to the high toxicity of hypergolic propellants suitable measures for personnel protection are mandatory. Safety requirements and minimizing of environmental pollution (atmosphere, ground, water) are therefore the driver for general test facility lay-out.

This paper has been written from the view point of a test facility designer and is limited, therefore, to safety and system requirements that affects typically development and qualification ground testing of earth-storable liquid propulsion systems. Safety during flight operations is not discussed.

## GENERAL PROPERTIES AND HANDLING INSTRUCTIONS FOR HYPERGOLIC PROPELLANTS

The majority of earth-storable bipropellant systems being designed today use NTO as oxidizer and MMH or UDMH as fuel [3]. Some applications for missiles use $HNO_3$ due to the lower freezing point and lower vapour pressure. Hypergolic propellant ignite spontaneously when they are get in contact to each other, so no special ignition devices are necessary and full reignition capability is given. The basic physical properties of the most important fuels and oxidizers for liquid hypergolic bipropellant engines are given in *Table 1.*

The general characterization of the two groups with respect to health hazards, safety measures and transfer and storage procedures can be given for each group despite small individual differences.

### Fuels

Hydrazines are clear, water-white liquids with an odor similar to that of ammonia. They are strong reducing agents, weakly alkaline and very hygroscopic. Exposure to air may result in spontaneous ignition. They are mixible with water and freeze at very low temperatures (-52 °C) but due to contraction there is no damage to storage vessels or closed feed-lines.

Hydrazines are highly toxic and can cause local damages in contact with skin or eyes and systemic effects. Due to its acute toxicity thereshold limit value below 0,1 ppm is recommended. If hydrazines are splashed on skin or clothes first aid and self aid is given by flushing with large amount of water. Also air-supported fires are most effectively combated by water sprays.

For all operations involving the handling of hydrazines safety precautions have to be applied as regular education of personnel and personal protection clothing.

Hydrazines may be stored in containers or shipping drums and should always be handled and stored under a nitrogen atmosphere. Main storage sites shall have a concrete pad with an adequate drainage system and a roof to protect the containers or drums from direct rays of the sun. The preferred

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materials for hydrazines are stainless steel metals and gaskets may be made of Teflon or Kalrez compounds.

**Oxidizers**

Nitrogen tetroxide ($N_2O_4$) is the todays most important storable oxidizer in use for rocket engines and has some advantages compared to nitric acid like higher performance and better corrosion properties. Red Fuming Nitric Acid (RFNA) as a mixture of $N_2O_4$ and nitric acid is a compromise and well-known for missile application. Another potential measure to reduce the freezing point of $N_2O_4$ is the addition of nitrogen monoxide (NO) which is called in the literature MON (Mixed Oxides of Nitrogen).

At room temperatures, nitrogen tetroxide is a heavy brown liquid giving off yellowish to reddish-brown fumes. Its color coming from the $NO_2$ content which is a temperature depending-function of the equilibrium shift of $NO_2$ to $N_2O_4$. Nitrogen tetroxide is a corrosive oxidizing agent and is not sensitive to mechanical shock, heat or detonation and non-flammable with air. Nitrogen tetroxide in water reacts to form nitric and nitrous acids.

The inhalation of toxic nitrogen tetroxide vapours is normally the most serious health hazard. The recommended maximum allowed threshold limit value is in the range of 2,5 ppm. The main danger from acute poisoning is the development of pulmonary edema, in which the long spaces fill with fluid, with the result that their ability to transport oxygen is reduced.

As first aid and self aid when liquid nitrogen tetroxide is spilled on skin or in eyes flushing with large amount of water should be applied.

The suppositions for handling of liquid oxides like nitrogen tetroxide are well educated and trained personnel and adequate personnel protection measures (hand and foot protection, respiratory protection clothes).

Liquid nitrogen tetroxide can be stored or transported safely in moderate-pressure cylinders with capacities up to 1 ton or in large tank containers. All buildings in the main storage area shall be constructed of materials not readily affected by nitrogen tetroxide or its fumes. The strucural frame work shall be steel, the floors shall be made of concrete with an approved protecting coating and an adequate recovery volume. Although dry nitrogen tetroxide at ordinary temperatures and pressure is not corrosive to most common metals, the selection of metals is governed by the oxidizer moisture content (standard water equivalent value $\leq 0.1$ weight percent) and the maximum allowed iron content. This complex chemical correlation has been subject of different investigations [4, 5, 6]. Recommodations for gaskets and "0" rings materials are Teflon compounds.

In general, the precautions taken in handling liquid nitrogen tetroxide are very similar to those for fuming nitric acid.

| | | Density 20 °C [g/cm³] | Freezing Point [°C] | Boiling Point, 1 bar [°C] | Vapour Pressure, 20 °C [bar] |
|---|---|---|---|---|---|
| FUEL | MMH Monomethylhydrazin $CH_3NHNH_2$ | 0,879 | -52,4 | 87,6 | 0,050 |
| | UDMH Unsymm. Dimithylhydrazine $(CH_3)_2NNH2$ | 0,790 | -57,2 | 62,3 | 0,119 |
| OXIDIZER | $N_2O_4$ Nitrogen Tetroxide | 1,447 | -11,2 | 21,5 | 0,950 |
| | $HNO_3$ Nitric Acid | 1,570 | -41,6 | 84,1 | 0,063 |

*Table 1:* Physical properties of typical hypergolic propellants

## TEST FACILITY LAY-OUT CRITERIA

In this chapter the general requirements on the test facility for a 20 - 30 kN class hypergolic bi-propellant engine will be outlined. Two test positions in this programme are requested. One for engine development and qualification testing and the other one for a full flight like stage test. Both test positions are under sea-level conditions therefore no special set-ups for altitude simulation are necessary for this test facility.

General requirements:

- short duration testing (≤ 60 s)
- long duration testing (≤ 1400 s)
- short-duration reloading capability of run-tanks
- storage tank loading capability with given transport tanks
- minimum propellant contamination of atmosphere
- optimization of minimum necessary operation team size
- implementation of all propellant safety provisions for stage testing

More requirements with respect to the automatic control and computer system of the facility are defined of course but are not subject of this presentation.

## TEST FACILITY SET-UP: ENGINE TEST POSITION

The schematic of engine test position is given in *Figure 1.* The engine can be supplied either by the short duration or by the long duration run tanks. It is a pressure feed system therefore the different operation points have to be adjusted by different pressure levels in the tanks typically the tank pressure range varies in between 16 - 24 bar. Going from one operation point to the other the tanks have to be depressurized. The amount of propellant vapour is proportional to the ullage volume of the tanks, therefore the smaller tanks are used for the majority of the tests to minimize the amount of propellant vapours which have to be recondensated or decontaminated. The larger tanks are only be used for long duration testing. At the end of a long duration run the tanks are filled with propellant vapours and pressurant. Corresponding to the propellant vapour pressure typically 25 kg of $N_2O_4$ and 0.5 kg of MMH have to be recondensated. The condensation system is connected to the storage tanks, so the recondensated propellants can be reloaded in a closed loop to the storage tanks. The pressurization gas is led through the condensation system to the washing column. Here only small amounts of non-recondensated propellant vapours will be combined to water and collected in the facility catch area before they are released to the common local site neutralisation system.

The run tanks can be reloaded in a closed loop via pumps out of the storage tanks during the tanks are connected on the gas side. With the help of liquid level gauges the amount of run tank filling can be controlled. Tests with increased propellant temperatures can be performed by pumping the propellants for some minutes in a closed loop between storage and run tank before final loading of the run tank.

Due to the set-up of storage-tanks, condensation system, engine position and run tanks at different levels all liquid residuals can be transferred back in the storage tanks by gravity flow. The feed-line system between run-tanks and engine is designed in such way that the deepest point is at engine inlet so that in case of engine dismounting the liquid propellant can be drained and retransferred to the storage tanks. Propellant vapours will be sucked with gas jet pumps and led via the condensation system back in the storage tanks. Loading of storage tanks can be performed again by gravity flow in a closed loop.

So all propellant transfer operations from and into storage tanks and run tanks can be done in such a manner that air connot enter the transfer and storage system. This is of prime importance to avoid the possibility of introducing moisture or oxigen into the system and to minimize the contamination of the surroundings and the atmosphere.

For emergency safety reasons the run-tanks and storage tanks are equipped with pressure relief valves set to vent at maximum allowed tank pressure. These relief valves are connected to adequate sized vent lines which discharge into the atmosphere above the highest point of the facility.

Between engine and run-tanks two shut-off valves in each feedline are implemented to have maximum safety in case of an engine failure.

The operations of valves, pumps and all other systems can be controlled locally in the facility and in a remote controlled way out of the control room located 100 m away from the facility.

During hot run phase the test facility housing can be opened by large moving doors and movable roof segments whereas during non-operation phase the test facility will be closed and air conditioned.

A communication system between test position, control room and safety center of the test site supports the personnel safety.

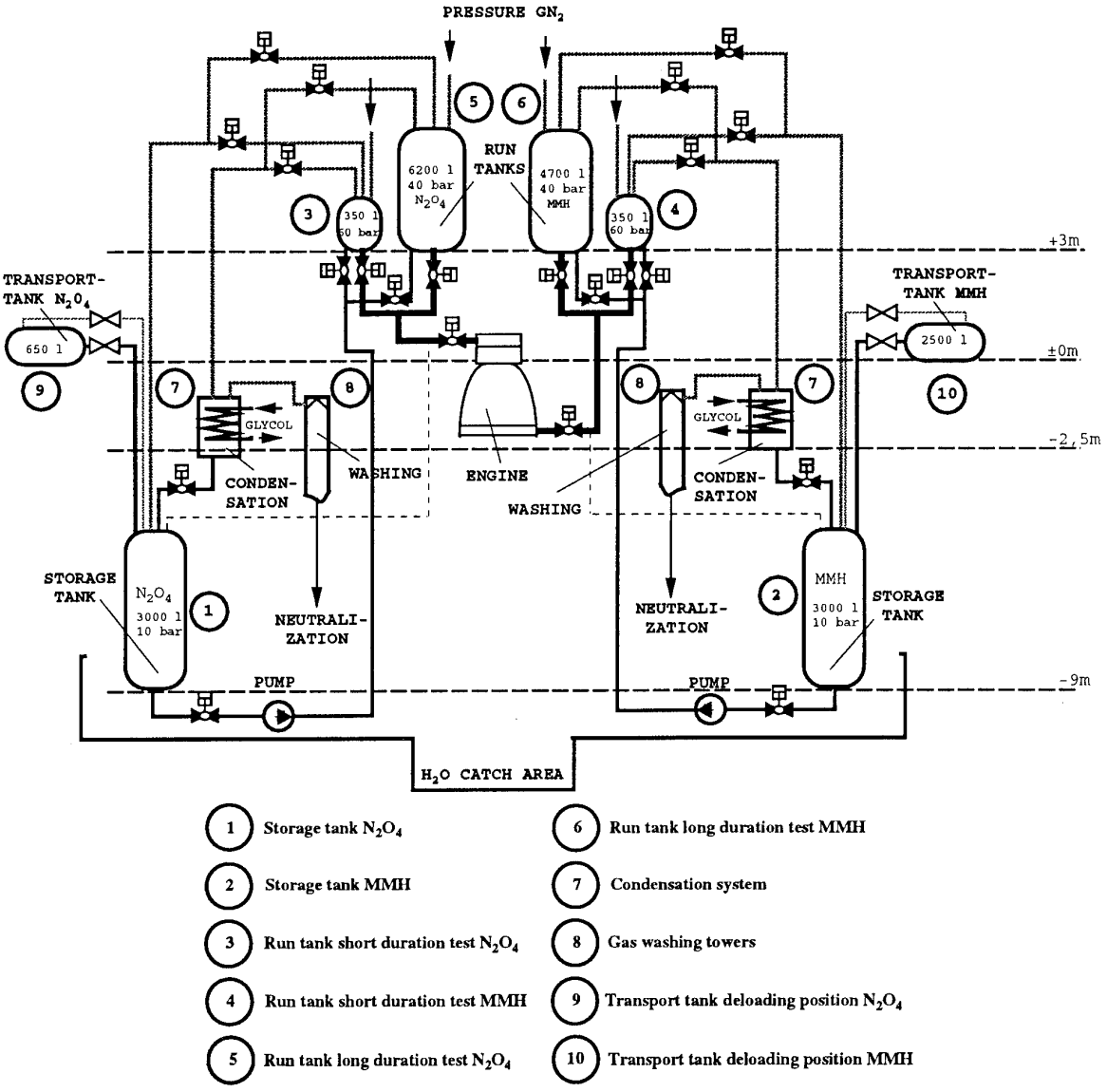



*Figure 1:* Schematic of test facility for engine test position

## TEST FACILITY SET-UP: STAGE TEST POSITION

The stage is placed on a second test position and is fixed on a test facility thrust rig. The stage once prepared for hot run with its own He high pressure bottles and loaded tanks is an autonomous unit. The hydraulic and pneumatic connections to the test facility infrastructure are described in the schematic of *Figure 2.* All these connections and set-ups are typical ground test provisions necessary due to different safety aspects.

Stage tank depressurization or purging of liquid propellant lines can be performed via the test facility condensation system and back in the storage tanks. In case of emergency when larger amounts of propellant will be escape caused by a broken line or a larger leak a liquid $CO_2$ spraying system will be initiated to recondensate fuel or oxidizer vapour and at the same time a foam generator system will fill the bottom of the catch area with a foam layer in a couple of minutes to avoid the evaporation and the contact with the atmoshere. The liquid fuel or oxidizer collected beneath the foam layer can be pumped in an emergency catch tank.

Standard stage loading and deloading will be performed by an autonomous Tanking Ground Support Equipment (TGSE). But during the hot firing phase the TGSE's are disconnected from the test position. Therefore emergency deloading is realised by fixed stage-test facility connection. In this way the complete deloading process can be performed remote controlled and without any environmental pollution.

Test facility and the test item are of course automatically and visually surveyed by state of the art techniques like single or multiple red-line logic, process visualization and several modern video systems.

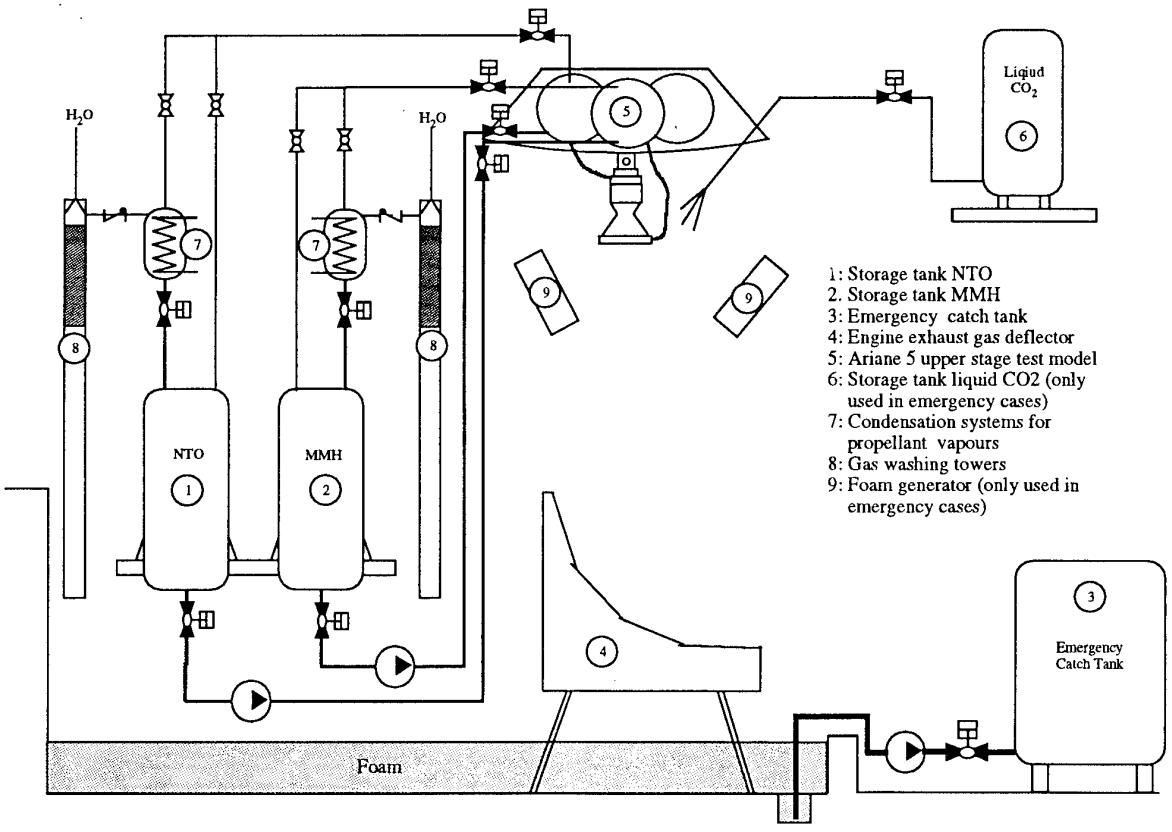



***Figure 2:*** Schematic of test facility for stage test

## CONCLUSION

Respecting the toxicity of hypergolic propellants and their safety requirements the application of general set-up rules can simplify the operation procedures. Closed loop loading and deloading between transfer containers and facility storage tank by using gravity flow and pumps do avoid contamination of atmosphere and prevent penetration of moisture and air oxygen into the propellant system. Run tanks with different volumes adaptable to short and long duration tests optimize the necessary work load and minimize the amounts of propellant vapours to be decontaminated. Dismounting of facility feed lines and test items efforts intensive decontamination which can be performed by evacuating the system with gas jet pumps and a subsequent condensation system which reload the propellants in the closed loop set-up.

Experience with the operation of the test facility in the last 4 years over 950 engine burns and handling of more than 100 tons of MMH and $N_2O_4$ underline the high flexibility, relatively small manpower need and very low contamination level of surroundings.

Due to the higher risk of the flight like stage tests special safety measures are realized. A combination of a $CO_2$ condensation spray with a generated foam layer will minimize the atmospheric contamination and catch most of the excaped propellant during an emergency failure.

Despite numerous technical improvements and the consequent application of automatique control systems skilled, reliable personnel trained to working with detailed procedures are key elements for successful rocket testing.

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## Discussion

QUESTION BY R. COUTURIER : In your conclusion you say there is a very low contamination of environment. Could you give us more quantitative details ?

ANSWER : No systematic measurements are available, but checks with simple methods ("Dragest") showed that required threshold limits can be met.

# REPORT DOCUMENTATION PAGE

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**14. Abstract**

The Conference Proceedings contains 36 papers presented at the Propulsion and Energetics Panel 84th Symposium on Environmental Aspects of Rocket and Gun Propulsion which was held from 29 August – 2 September 1994, in Aalesund, Norway. The Technical Evaluation Report and the Keynote Address are included at the beginning and discussions follow most papers.

The Symposium was arranged in the following Sessions: Clean Propellants (7); Propellant Development (6); Measurements (7); Disposal (3); Material Recovery and Re-Use (8); Contamination (5).