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Materials for Space Cabins: The Fire Hazard and Atmosphere Contaminant Control Problems

OCTOBER 1967

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AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04695-67-C-0158.

This report, which documents research carried out from April 1966 to February 1967, was submitted on 4 October to Captain William D. Bryden, Jr., SMTRE, for review and approval.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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ABSTRACT

This report discusses the flammability and atmospheric contaminant hazards associated with the use of plastics and other nonmetallic materials in manned spacecraft cabins. Outgassing characteristics and mechanisms of typical materials are described. Flammability and combustion rates are discussed as highly important materials selection factors. An approach is presented for minimizing the hazards through judicious selection and batch control of cabin materials.

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I. INTRODUCTION

The problems of fire hazard and control of the atmosphere within the space cabin are becoming increasingly acute. Of particular concern are the accumulation of atmosphere contaminants to concentration levels harmful to the astronauts and the presence of combustible organic materials that could lead to uncontrollable fires within the space cabin.

Man himself presents one source of atmospheric contaminants; environmental control and life support (EC/LS) equipment must be provided to control this source of contamination. The major source, however, is the materials used within the cabin, especially plastics and other nonmetallic materials. These include coatings, adhesives, films, fabrics, elastomers, gaskets and seals, foams, thermoplastic sheets, thermal insulation materials, potting/encapsulations, electrical insulations, moldings, glass-reinforced plastic laminates, lubricants, greases, fluids, tubing and ducts, tapes, food containers, writing apparatus, and clothing. All of these materials are potentially combustible in the oxygen-rich cabin environment.

Improved techniques for the control of contaminant materials and the fire hazard are being established by Air Force and NASA organizations and their contractors. However, the cooperation of the plastics industry will be a vital prerequisite to any comprehensive approach to an effective space cabin materials control program.

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II. DEFINITION OF THE CONTAMINANT CONTROL PROBLEM

A manned space cabin is a pressurized compartment containing gaseous oxygen and perhaps nitrogen or helium as a diluent, at a total pressure of about 1/3 to 1 atm. The astronauts must live within this sealed compartment for practically the total duration of the mission. For the NASA Apollo lunar mission, three astronauts will be housed for approximately 14 days. Future missions will require substantially longer durations.

To illustrate the nature and severity of this problem, consider the MESA (Manned Environmental System Assessment) experiment conducted by the Aerospace Division of the Boeing Company for NASA approximately three years ago. The primary objective of that program was the experimental demonstration of an integrated human maintenance system in a closed, self-sustained environment for 150 man-days (five men for 30 days).

For MESA I, materials selection was based entirely on functional requirements with slight regard for the potential of contaminant sources. During the intended thirty-day test, contaminants built up quite rapidly, as evidenced by crew reports of increasing undesirable sweet pungent odors. The crew members developed varying degrees of nausea, cold sores, loss of appetite, and, in a few instances, vomiting. The test had to be terminated at the end of four and one-half days. The "flight" was aborted! On subsequent analysis of the atmosphere, it was found that halogenated compounds were present. These were considered to have resulted from retained cleaning solvents and subsequent degradation thereof, or from the neoprene used in the flexible ducting that carried air at temperatures as high as 350°F. Another possible source was polyvinyl chloride sleeving. Phosgene was observed to be present, probably as the result of partial oxidation of halogenated compounds. Freon-12 was surmised to result from a leak in the air-conditioning system in the chamber. Paracresol was considered to be from the degradation of tricresyl phosphate, a plasticizer used in the vinyl sleeving. Carbon monoxide was attributed to man and to the pyrolysis and oxidation of organic materials.

Another possible source of CO is carbon black, used as a reinforcement or pigment in many elastomers and plastics. Ammonia was assumed to have been produced by man. Sulfur compounds were probably due to the breakdown of vulcanizing agents and accelerators in elastomers. Various low molecular weight hydrocarbons were found; these were considered to have resulted from various resin binders in insulation materials, oils, and elastomers in seals and ducts. Methyl ethyl ketone was probably due to the evaporation of solvent in a repair adhesive. The various contaminants identified in the MESA I experiment are listed in Table 1.

With this experience as background, the Boeing Company then redesigned the entire system to eliminate all known or suspect material contaminant sources. In addition, provisions were made for the removal of contaminants as rapidly as possible, including overboard venting for critical systems. Considerable changes in materials usage were effected. The second test, MESA II, was completely successful.

These tests demonstrate that atmospheric contaminants in confined space are likely to produce ill effects unless they are prevented by careful control of the materials employed within the system. Further, it is necessary that the leakage rate be as low as possible so that makeup gas requirements (and associated hardware) can be minimized and the contaminant removal system be limited in size, weight, and power requirements.

Tests have been conducted at the School of Aerospace Medicine, Brooks Air Force Base, Texas, using a simulated space cabin (Ref. 1). These tests have shown that man produces approximately 100 different atmospheric contaminants, but that only carbon monoxide and methane are produced in sufficient quantity to require active control on longer space missions. Therefore, it is the materials employed in the various parts of the space cabin that must be controlled in order to ensure an adequate and safe environment.

In submarines, for example, atmosphere contaminant problems have occurred and generally have been attributed to contaminants produced by outgassing from equipment and materials used on board. Over 200 compounds

Table 1. MESA I Contaminants Identified

Trichloroethylene
Monochloroacetylene
Dichloroacetylene
Ethyl chloride
Vinylidene chloride
Phosgene
Freon-12
Methyl chloride
p-Cresol
Hydrogen
Carbon monoxide
Ammonia
Nitrogen dioxide
Carbonyl sulfide
Carbon disulfide
Isopentane
Isobutylene
n-Butane
Propylene
n-Pentane
2 Methyl butane
Ethanol
Methanol
Acetaldehyde
Methyl ethyl ketone
Ethyl ether

have been noted in atmospheric samples from nuclear submarines; less than one third (69) of these have been identified. Of the 69 identified contaminants, 24 can be ascribed to man. Similarly, of the 40 compounds identified in Mercury spacecrafts, only 11 could be ascribed to man.

Nuclear submarines, which may remain submerged for long periods of time (perhaps as long as 60 days), have the decided advantage that extensive equipment can be carried on board to analyze and "purify" the atmosphere. Items of equipment include: air conditioning systems (remove many water-soluble contaminants), ventilation systems (dilute contaminant concentrations in pockets to nontoxic levels), inert filters, activated charcoal filters (absorb various hydrocarbons and other contaminants), catalytic burners (oxidize CO, H_2, CH_4, and other hydrocarbons), CO_2 scrubbers (remove CO_2), and electrostatic precipitators (remove ionizable materials from the atmosphere). In addition, surface ventilation or manifold breathing is available if necessary in emergencies. With all this, submarines utilize a control program to prevent excessive contaminants by elimination of possible contaminant sources and by substitution of relatively nontoxic for more toxic materials (e. g. , use of a water-based paint instead of one using a hydrocarbon solvent and use of ethyl alcohol for cleaning rather than a halogenated solvent). Basically, the differences between problems of a submarine atmosphere and those of a space cabin atmosphere are quantitative. The main differences, the necessity for a smaller volume in the space cabin and the considerably smaller amount of contaminant removal equipment that can be carried within the space cabin, relate to the size and weight limitations of the enclosure.

Thus, the problem of contaminant control has been resolved in submarines largely by use of extensive removal equipment. This luxury is not feasible for long-duration confinement in space vehicles, and contaminant control becomes increasingly critical with increasing number of mission man-days and with concomitantly increasing restrictions on the volume and weight for equipment.

Contaminant control requirements for previous manned space flights under the Mercury and Gemini programs have been much less severe than those anticipated in the future. Compared to Apollo and anticipated future missions, these earlier missions have had shorter durations and have been able to tolerate higher cabin leakage rates as well as less severe weight and size restrictions for the environmental control and life support equipment.

Even so, the Mercury and Gemini flights have had occasions when outgassing products presented operational difficulties. During early Gemini flights, clouding of the spacecraft windows consistently deteriorated visibility. At first it was thought that these contaminants were deposits either from the exhaust products of the launch vehicle engines or from dirt and moisture in the air during the boost phase. Attempts were made to solve this problem by the use of protective covers to shield the window openings during powered flight; however, this approach did not fully resolve the problem. It was then discovered that another cause of the clouding was outgassing from the silicone elastomers used to mount and seal the window glass panes. Extended postcure and vacuum treatment of the silicone elastomers prior to installation reduced the outgassing sufficiently that the problem was effectively solved, as was reported by the Gemini-12 crew members (Refs. 2 and 3).

Figure 1 is a schematic description of the overall problem. Contaminant inputs to the space cabin are shown to arise from (1) man (the astronauts) and (2) materials. The contributions from materials are listed in three general categories: (a) the material may outgas as an inherent characteristic depending on composition, processing history, form and dimensions, and environmental conditions; (b) operation of equipment, especially electronic apparatus and other components that generate or are exposed to elevated temperatures, may produce outgassing products or levels thereof that would not occur at lower temperatures; and (c) solvents and other contaminants may be introduced by the fabrication processes and retained by the system until they are eliminated into the cabin atmosphere. As indicated previously, contaminant outputs (i.e., means for eliminating or reducing cabin atmospheric contaminants) are (1) cabin leakage (with necessary make-up gases introduced,

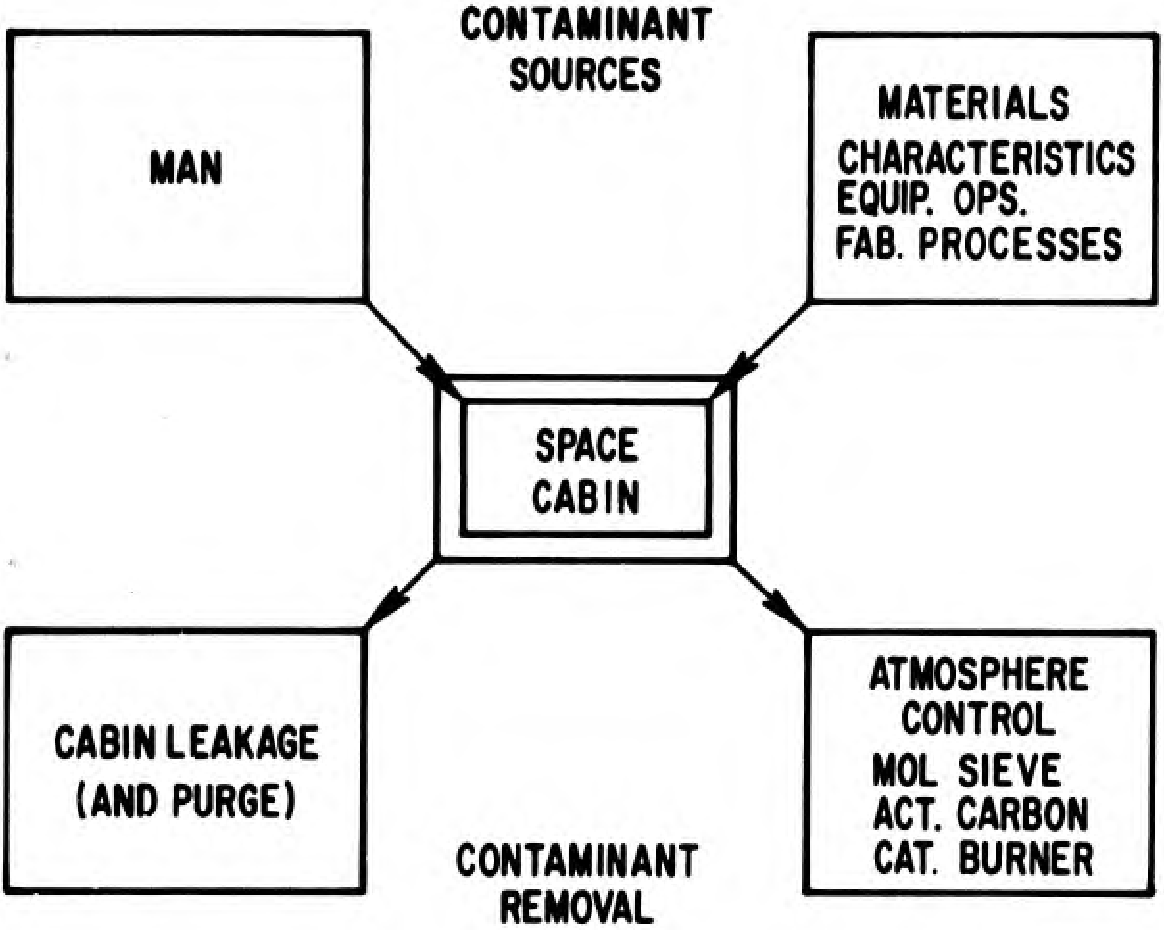

Figure 1. Contaminant Source and Control for Space Cabin Atmospheres

serving as diluents) and (2) air filtration using available contaminant absorption and removal apparatus. Purging (e. g., venting to the space atmosphere) is generally a last resort to be employed only in emergencies.

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III. MECHANISMS FOR OUTGASSING

There are four basic mechanisms by which materials can outgas to produce cabin atmosphere contaminants:

1. diffusion in solid body and vaporization of lower molecular weight species at surfaces
2. oxidation by atmospheric O_2
3. decomposition in the solid body, followed by diffusion and vaporization
4. evaporation of retained liquids and solvents

The most likely outgassing mechanism is the diffusion of low molecular weight species through the material to a surface from which they evaporate into the atmosphere. Such species include low molecular weight polymer fractions, polymerization byproducts, additives, solvents, and adsorbed or entrapped gases. Carbon black, for example, is known to adsorb carbon monoxide, which may then tend to outgas into the cabin atmosphere. Gases produced during the manufacture of foams are another such example.

Oxidation by oxygen from the cabin atmosphere is not considered very likely to occur at the moderate temperatures (generally below 200°F) in space cabins. Oxidation might serve to change the chemical identity of a contaminant over a period of time; e. g., an alcohol might be oxidized to aldehyde and then to the corresponding acid. However, this mechanism is not regarded as a serious contaminant influence.

Similarly, thermal decomposition of nonmetallics is not likely to occur at the temperatures of interest. Activation energies for depolymerization reactions or other polymeric degradation are sufficiently large that such reactions are not likely to occur in space cabins. However, there is one exception -- "reversion" of certain polymeric materials when confined, especially if heated. For example, RTV-silicone elastomeric potting materials are known to depolymerize by a reaction that is the reverse of the original vulcanization process when a thick section is heated in a confined space.

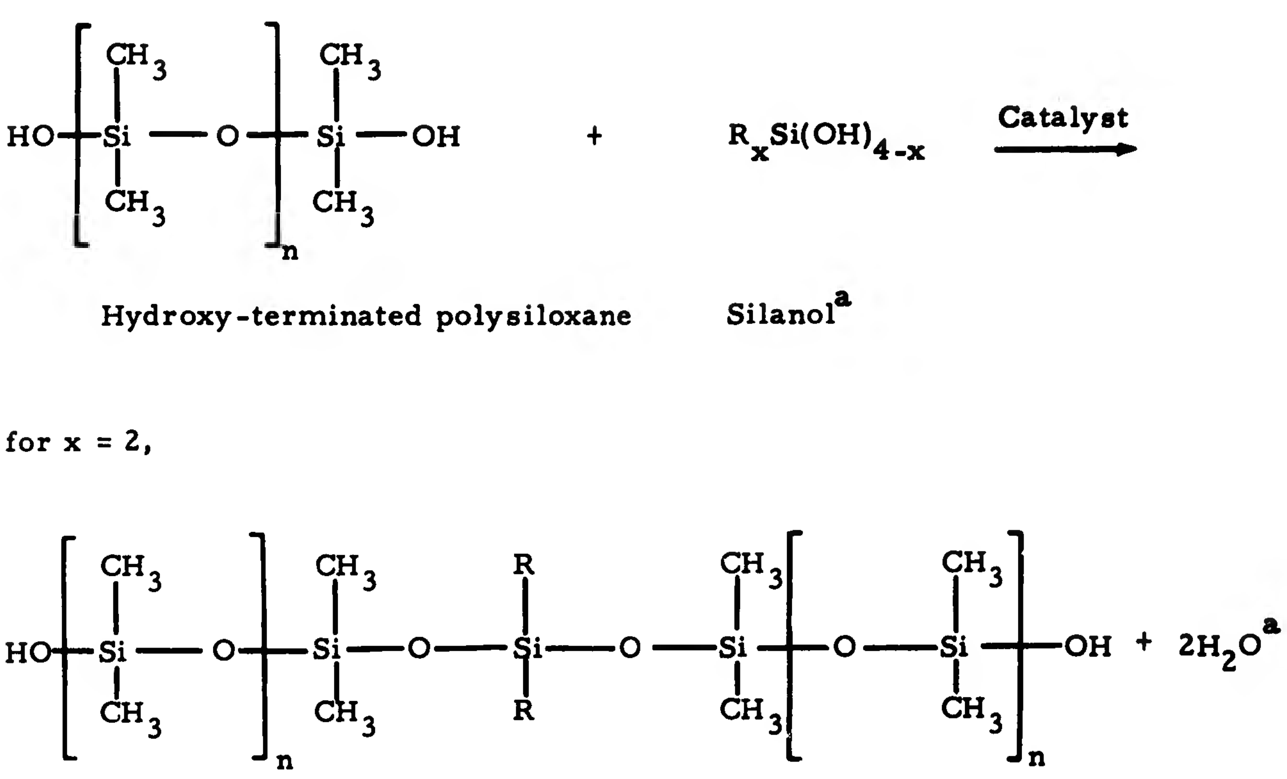
The probability of reversion can be minimized by controlling the elastomer compound mixture so that excess catalyst is not used, by subjecting the component to extended postcuring prior to installation, and, during service, by avoiding elevated temperature exposure and by venting to the surrounding atmosphere.

The fourth outgassing mechanism noted above, evaporating retained liquids, relates to the probability that cleaning or other solvents or liquids employed during processing operations may have been adsorbed, absorbed, or simply entrapped in crevices on or within the material or structure. To preclude this occurrence, it is desirable to clean components prior to installation within the space cabin and to remove (by warming or ventilating or both) retained solvents. As previously noted, restriction or elimination of the use of cleaning solvents also is necessary.

Thus, diffusion of low molecular weight species is the primary mechanism for producing space cabin atmosphere contaminants. Note that for a given mass of material, the larger the surface area exposed to the atmosphere, the more rapid the outgassing rate during the early stages. After a sufficiently long period of time, depending on permeabilities and diffusion rates within the material, the contaminant concentration in the atmosphere will be independent of surface area, and a function then of the total mass of material present and, of course, of the environmental conditions.

It is of interest to explore the causes and sources of outgassing from a typical space cabin material. Consider, for example, a typical RTV-silicone elastomer. The reaction mechanism for vulcanization is shown in Figure 2. Generally an organosilicate (rather than silanol) is used as the vulcanizing agent, and therefore the byproduct is an alcohol; this, of course, is one major potential source of outgassing.

The reaction may not be completed, or the byproduct may be entrapped due to adsorption. Outgassing would then result from continued vulcanization reaction or desorption or both. In both cases, time and environment are significant factors. The primary environmental conditions are elevated temperature and reduced pressures resulting in increased diffusion, desorption, and evaporation rates.



$$HO{-}\left[Si(CH_3)_2{-}O\right]_n{-}Si(CH_3)_2{-}OH + R_xSi(OH)_{4-x} \xrightarrow{\text{Catalyst}}$$

$$HO{-}\left[Si(CH_3)_2{-}O\right]_n{-}Si(CH_3)_2{-}O{-}SiR_2{-}O{-}Si(CH_3)_2{-}\left[O{-}Si(CH_3)_2\right]_n{-}OH + 2H_2O^{a}$$

[a] A polyfunctional organosilicate may be employed in lieu of silanol. Condensation byproduct is then an alcohol.

Figure 2. Reaction Mechanism for Vulcanization of RTV Silicone Elastomer

The catalyst for the vulcanization reaction, generally a metallic "soap" in a solvent vehicle, presents another contaminant source. However, the quantities of catalyst required are sufficiently small that this need not present a major outgassing source.

Figure 3 shows actual outgassing data for a typical RTV-silicone elastomer in air at 25°C. The major product is ethanol, the vulcanization byproduct. Silicone oil and trimethyl silanol are derived from the RTV-silicone polymer as low molecular weight fractions or impurities. The hydrocarbons are believed due to retained solvents from the catalyst or perhaps to impurities in the elastomer.

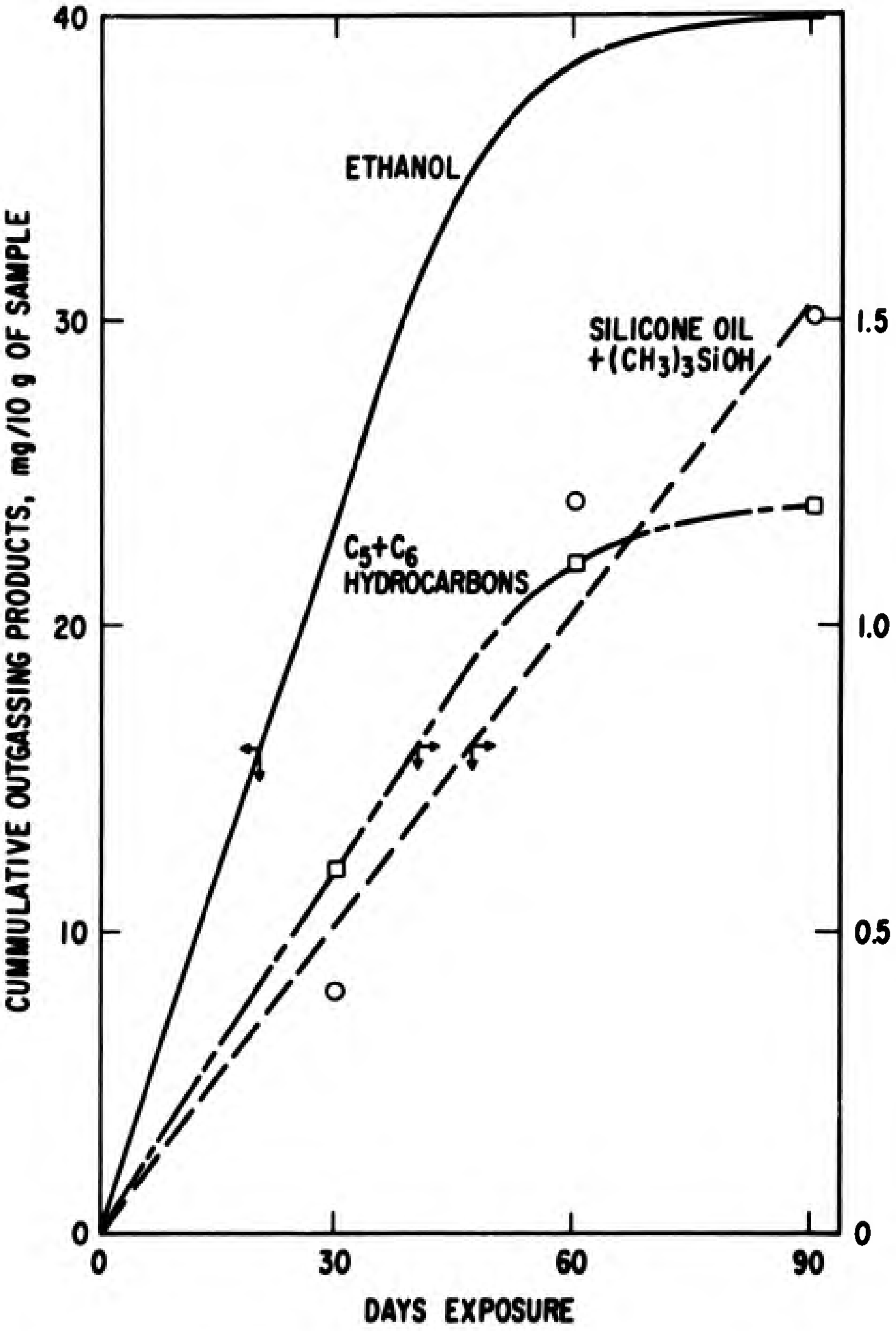


Figure 3. Outgassing of RTV-90 in Air at 25°C
(Sample cured at room temperature only.)

IV. FLAMMABILITY AND COMBUSTION RATES

The problems encountered in the recent Apollo fire have emphasized the fact that accidents are going to occur during space flight, and when they do, the limited confines and lack of flexibility in the emergency situation often bring new and ill-defined hazards into the picture. One of the most difficult hazards to predict and to protect against is a fire occurring during ground test or flight. Nonmetallic space cabin materials, which become the "fuel" for the fire, must be selected after careful consideration and test of their combustion potential in the spacecraft environment. For example, Figure 4 illustrates the influence of atmospheric composition on burning rate for a typical nonmetallic material. In the past few years, there have been a number of fire accidents occurring in the oxygen-enriched environments of space cabin simulators. Attempts by personnel to fight these fires have resulted in unexpected difficulties, many more serious than the original fire itself. The most important consideration is that a fire onboard a spacecraft cannot easily be isolated and treated as a separate problem. It can affect many systems, often disabling them or necessitating premature expenditure of storables that, in turn, can jeopardize the mission and personnel.

In a sealed cabin, the oxidation and pyrolysis products of most materials present hazards that can match those of the fire itself. These potential hazards will increase as the flights become longer and the missions and equipment more complex. For sustained periods of orbital flight, the extended operational life of the various systems will increase the probability of malfunction and the possibility of an accident. Since space and weight will be at a premium, there will be a limit on the amount of fire-fighting equipment that can be carried. Also, as spacecraft become larger, there will be an increased tendency toward compartmentation, which can complicate the problem of fire detection and assessment. However, the presence of a low-gravity field during orbital operations can be beneficial in this regard. Theoretical calculations and limited testing show that a flame may extinguish itself at low g due to the

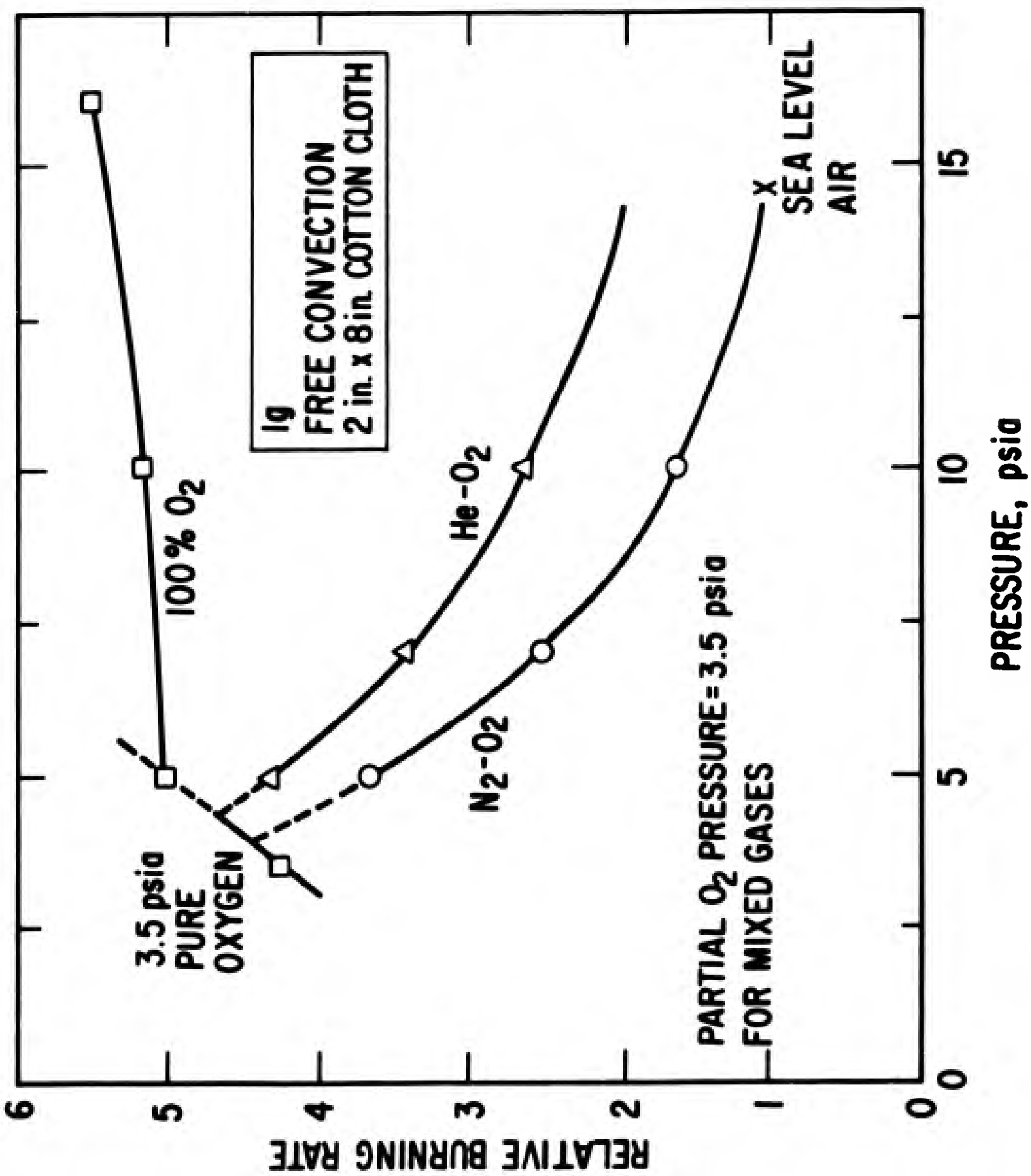


Figure 4. Comparison of Burning Rates of Cotton Cloths in Selected Atmospheres and Sea-level Air[a]

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[a] From Interim Report on Two Gas Atmosphere, NASA, OART, Washington, D. C., February 1967.

generation of combustion products and lack of free convection to clear them away. In other words, when a fire is detected, all circulating fans may need to be turned off to permit the fire to smother itself. Additional study and test are desirable in this area.

All of these facts point to one conclusion: it will be necessary to limit the quantity of combustible materials and to develop criteria related to the use of organic materials that will enable design engineers to predict the degree of fire hazard that exists in the spacecraft under all modes of operation.

V. APPROACHES FOR SOLUTION TO THE FIRE HAZARD AND ATMOSPHERE CONTAMINANT PROBLEMS

There are two general approaches to resolving the problems of fire hazard and atmosphere contaminants; short-range solution and long-range solution.

A. SHORT-RANGE SOLUTION

The first approach must be employed as an expedient to satisfy present mission requirements within a relatively short period of time. The short-range approach has been taken for all manned space programs to date. In essence, materials are selected for cabin use based on their ability to pass a series of outgassing and flammability tests. For the Mercury and Gemini programs, candidate cabin materials were heated for a period of time in a closed chamber under 5 psia oxygen and then subjected to an odor test by a panel of selected individuals. If the odor test produced a sufficiently low cumulative score, the material was acceptable for use in the space cabin. For the Apollo Program, because of its more severe demands, other test requirements were also imposed, including tests of weight loss and level of outgassing for selected species; flammability test requirements were also imposed on the candidate materials. Some of these refinements are contained within the elements of a long-range approach discussed below.

B. LONG-RANGE SOLUTION

The ultimate solution to these problems, necessary for future long-duration space missions, requires an approach that combines materials, design, and biomedical disciplines, along with a sophisticated program of continuous control of the cabin materials system. The elements of such an effort are:

1. combustibility determination
2. determination of allowable contaminant concentrations
3. determination of materials outgassing characteristics
4. space cabin materials selection, utilization, and control

1. COMBUSTIBILITY DETERMINATION

The material properties that should be measured include ignition temperature, flame spread rate, heat release rate, and the evolution of smoke, flammable vapors, or toxic fumes either prior to or after ignition.

2. ALLOWABLE CONTAMINANT CONCENTRATIONS

Industry has established maximum allowable concentrations of individual atmospheric contaminants to which a worker can be safely exposed on a periodic basis corresponding to the normal work schedule. Considerable effort remains before corresponding limits can be established for continuous, long-duration exposures to contaminant mixtures. Considering the possibility of additive, synergistic, or potentiating effects, exposure to contaminant mixtures is expected to present a substantially more severe toxic hazard than does exposure to the same species individually.

3. MATERIALS OUTGASSING CHARACTERISTICS

In order to apply materials test information to long-duration spacecraft, it is necessary to ascertain the outgassing characteristics for each material to be employed within the space cabin. In particular, for each material, it is necessary to establish the outgassing products and their rates of generation. These must be determined as functions of material composition (including allowable variations), processing history, environmental conditions, form, dimensions, quantity, and time of exposure. As indicated in Figure 3, outgassing rates vary considerably for different species from the same material and also vary with time.

4. MATERIALS SELECTION, UTILIZATION AND CONTROL

Once appropriate combustibility characteristics and relationships defining outgassing products and their rates are established, it will be possible to apply this information to the design of actual systems.

Using the aforementioned maximum allowable concentrations and combustion measurements, one can select materials and determine acceptable quantities thereof for use within the space cabin. Design considerations include maximum operating temperature, access to ignition source, amount to be used (recognizing surface area exposed), area of exposed edges and corners, orientation, and proximity to other organic materials.

Material specifications (as opposed to end item specifications) are necessary to ensure the use of only those materials that will minimize the fire hazard and produce concentrations of contaminants as low as possible and still perform their functions within the system. Each batch of material procured should be sampled and tested for conformity to this specification to ensure product uniformity and reproducibility. The processing of each material in the cabin, or component thereof, likewise must be controlled by suitable processing specifications with appropriate quality control checkpoints and procedures. For example, too low a temperature for curing of a coating or adhesive might well lead to outgassing products and rates or combustion properties substantially different from those anticipated on the basis of previous laboratory measurements.

Consideration should be given to the use of prefabricated components or subassemblies. These could be subjected to a conditioning treatment (e. g. , a thermal-vacuum exposure) prior to installation within the space cabin.

An important aspect of the ideal material control program is the use of computer techniques during cabin design and construction in order to anticipate potential fire hazards and atmosphere contaminants throughout the planned mission. The computer would be fed pertinent information as to selected cabin materials and their combustibility and outgassing characteristics, as well as the maximum allowable contaminant concentrations (as noted above). During the design and subsequent construction, should any contaminant species exceed its allowable limit (considering the presence of all other species), the computer could supply information as to elimination of materials or modified usage of materials in order to return the design within the control limits. Similarly, if excessive combustible materials should be present, appropriate modifications could be effected.

VI. PLASTICS INDUSTRY CONTRIBUTIONS

There are significant opportunities for the plastics industry to contribute to the resolution of the problems of fire hazard and contaminant concentration. Several suggestions are presented below.

A. REPRODUCIBILITY AND QUALITY OF PLASTIC MATERIALS AND COMPONENTS

Efforts should be made to ensure batch-to-batch uniformity and adherence to established compounding and processing specifications. Deviations should be duly noted. Shop personnel should be educated to the necessity of exercising care to avoid introducing deviations that might produce flammability, toxicity, or other hazards.

B. DEVELOPMENT OF IMPROVED MATERIALS AND PROCESSES

It is desirable to have available materials that will provide the necessary functional characteristics, but are improved with respect to outgassing and flammability. Further, modified methods for processing currently available materials may serve to reduce outgassing and flammability without sacrificing functional properties.

Improved or new flame retardants and suppressants would also be of much interest.

C. COMMUNICATION

Industry should inform cognizant government and contractor organizations of the availability of materials, processes, and test and design information that could improve the performance of materials and components in space cabin atmospheres.

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13. ABSTRACT

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Abstract (Continued)