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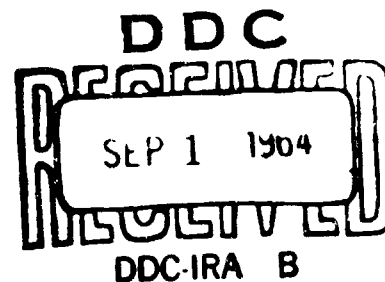
Propulsion Division
Office of Aerospace Research
Air Force Office of Scientific Research

RADIATION-INDUCED SOLID PROPELLANT DECOMPOSITION

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RADIATION APPLICATIONS INCORPORATED
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NO INVESTIGATION WAS MADE OF

1.0 INTRODUCTION

During the first year of the subject contract, we investigated the effect of ionizing radiation on the burning rates and tensile strengths of various composite ammonium perchlorate propellants. The results of these studies are shown in Table 1. ~~It is seen that~~, in many cases, drastic changes in burning rate and tensile strength occurred upon radiolysis. In order to elucidate the mechanism of these effects, a multi-pronged study of the effects of radiation on propellants and propellant components was initiated. This involved:

(1) A study of the radiation induced decomposition of ammonium perchlorate with an elucidation of the various chemical species produced upon radiolysis and their yields (G values);

(2) A study of radiation effects on burning rate by a technique in which the effect of radiation on each of the two components of a propellant, i.e., organic binder and inorganic oxidizer, is studied separately.

Table 1

Effect of Radiation on Ammonium Perchlorate Propellants

Propellant	Radiation Dose (Mrads)	Burning Rate ^a (inches/sec.)	Tensile Strength ^b (psi)
Polysulfide, Thiokol TP-L-3014	0	0.0593 ± 0.0006	249 ± 11
	10	0.0593 ± 0.0060	156 ± 9
	50	0.0549 ± 0.0025	51 ± 13
Polysulfide, Thiokol TP-L-3014a	0	0.0582 ± 0.0003	136 ± 4
	20	0.0548 ± 0.0005	138 ± 15
	50	0.0568 ± 0.0006	62 ± 6
Hydrocarbon, Thiokol TP-H-3062	0	0.0422 ± 0.0003	91 ± 4
	20	0.0428 ± 0.0004	168 ± 7
	50	0.0425 ± 0.0004	145 ± 7
Polyurethane, Thiokol TP-6-3129	0	0.0347 ± 0.0002	54 ± 3
	20	0.0355 ± 0.0002	56 ± 3
	50	0.0371 ± 0.0004	40 ± 2
Polyacrylonitrile, Hercules HES 6648	0	0.0660 ± 0.0025	190 ± 8
	10	0.0700 ± 0.0024	72 ± 2
	50	0.0860 ± 0.0027	56 ± 2
Polyethyl acrylate, Hercules HES 6420	0	0.0412 ± 0.0004	111 ± 10
	10	0.0447 ± 0.0005	67 ± 6
	50	0.0486 ± 0.0010	30 ± 4
Cellulose acetate, Hercules HES 5808	0	0.0325 ± 0.0010	541 ± 75
	10	0.0323 ± 0.0006	341 ± 34

a

Number of determinations = 10-20

b

Number of determinations = 5

2.0 RADIOLYSIS OF AMMONIUM PERCHLORATE

2.1 Background and Previous Work

The radiolysis of solid salts of oxy-acids of chlorine, in general, and of perchlorates, specifically, have received little attention. Heal has reported the production of chloride, hypochlorite, chlorite and oxygen with G values of 1.9, 0.7, 2.6 and 2.9, respectively, in the X-radiolysis of potassium chlorate.¹ In a subsequent paper, Heal also inferred the probable presence of dichlorine hexoxide and chlorine dioxide with G values of 1.4 and 0.2, respectively.² Burchill on the other hand found oxygen, chlorite, chlorine dioxide, chloride, hypochlorite and chlorate with G values of 1.95, 1.34, 0.95, 0.23, 0.21 and 0.22, respectively, in the cobalt-60 radiolysis of sodium chlorate.³ The same product spectrum was obtained for potassium and barium chlorates although yields were not reported.

Heal⁴ reported the production of chloride, chlorate and oxygen, and the probable production of hypochlorite and chlorite in the X-radiolysis of potassium perchlorate with a G value for perchlorate decomposition of approximately 5.

By far the most extensive and elegant study in this field is that by Johnson and Prince on the cobalt-60 radiolysis of the alkali and alkaline earth metal perchlorates.⁵ The results of their work are shown in Table 2.

Although the radiation chemistry of almost all of the common metal perchlorates has been studied and elucidated, that of the common propellant oxidizer ammonium perchlorate has not. Only a few qualitative reports on the radiolysis of ammonium perchlorate are to be found in the literature. Thus, Freeman and coworkers have reported the presence of chloride, chlorate, nitrite and nitrate in

the cobalt-60 radiolysis of ammonium perchlorate.⁶ Prior to the present study at RAI, quantitative work on the radiolytic chemical yields of ammonium perchlorate had not been reported.

Table 2a,b
G values of Products of Radiolysis of Alkali
and Alkaline Earth Perchlorates

Salt	G _{ClO₃⁻}	G _{ClO₂⁻}	G _{ClO₂}	G _{ClO⁻}	G _{Cl⁻}	G _{O₂}
Li	2.8	0.15	0.59	0.10	0.12	2.2
Na	3.6	0.17	0.11	0.09	0.42	3.0
K	3.0	0.18	0.12	0.09	0.45	2.7
Rb	4.1	0.20	0.12	0.14	0.75	3.8
Cs	5.3	0.22	0.10	0.17	1.1	5.3
Mg	4.3	0.14	0.07	0.03	0.15	2.6
Ca	3.4	0.00	0.51	0.08	0.12	2.0
Sr	3.9	0.19	0.14	0.11	0.19	2.6
Ba	1.8	0.84	0.42	0.12	0.06	2.2

^aG = number of ions or molecules produced per 100 e.v.

^bData from reference 5b

2.2 Results and Discussion

The cobalt-60 gamma radiolysis of ammonium perchlorate was studied over the dose range of 0-200 megarads (ca. $0-1 \times 10^{22}$ electron volts). (The study of this radiation dose range is not yet complete; experiments at the low and high doses remain to be performed.) Procedures were developed to identify and quantitatively analyze for the following species

chlorate	ClO_3^-
chlorine dioxide	ClO_2
chlorite	ClO_2^-
hypochlorite	ClO^-
chlorine	Cl_2
chloride	Cl^-
nitrite	NO_2^-
nitrate	NO_3^-

The analytical procedures consisted of

1. Volhard titration of chloride with silver ion,
 2. Chlorine and chlorate by oxidation of ferrous to ferric ion,
 3. Chlorine, chlorine dioxide, chlorite and hypochlorite by oxidation of iodide ion to iodine in basic and acidic media, and
 4. Nitrite and/or nitrate by reduction to nitric oxide (NO).
- All of the experimental procedures were thoroughly checked out with known mixtures of the various chemical species in order to ascertain that interferences were absent. Details of the theory and procedure of these analyses are discussed in Sections 2.3 and 2.4, respectively.

The results of our work during the present contract period are tabulated in Table 3 and graphically shown in Figures 1-4.

Table 3
Radiolytic Yields of Ammonium Perchlorate

Radiation dose ^a (Mrads)	Yields ^b in micromoles per gram irradiated ammonium perchlorate				
	ClO_3^-	ClO^-	Cl_2	Cl^-	$\text{NO}_2^-/\text{NO}_3^-$
8.6	--	3.0	--	16.9	--
11.3	--	3.7	12.8	23.9	--
15.5	20.3	5.1	--	33.8	--
17.5	21.8	6.0	22.6	36.3	--
23.2	25.5	9.6	--	54.1	--
27.2	28.7	12.0	32.1	65.9	1.4
34.8	--	14.8	42.5	86.6	--
43.9	38.5	20.5	48.1	102.6	--
51.9	37.2	24.7	68.0	118.0	2.7
61.4	46.4	--	86.5	157.0	--
87.1	47.2	--	110.5	218.1	5.5
95.9	44.6	43.1	120.4	246.6	--
113.6	36.6	--	--	300.8	--
120.0	--	56.9	--	--	--

^a

All irradiations except the 11.3 Mrad one were performed at 0.36 Mrad/hr.; the 11.3 irradiation was performed at 0.17 Mrad/hr.

^b

Each reported yield is the result of 2-5 determinations. The precision of yields was $\pm 5-15\%$.

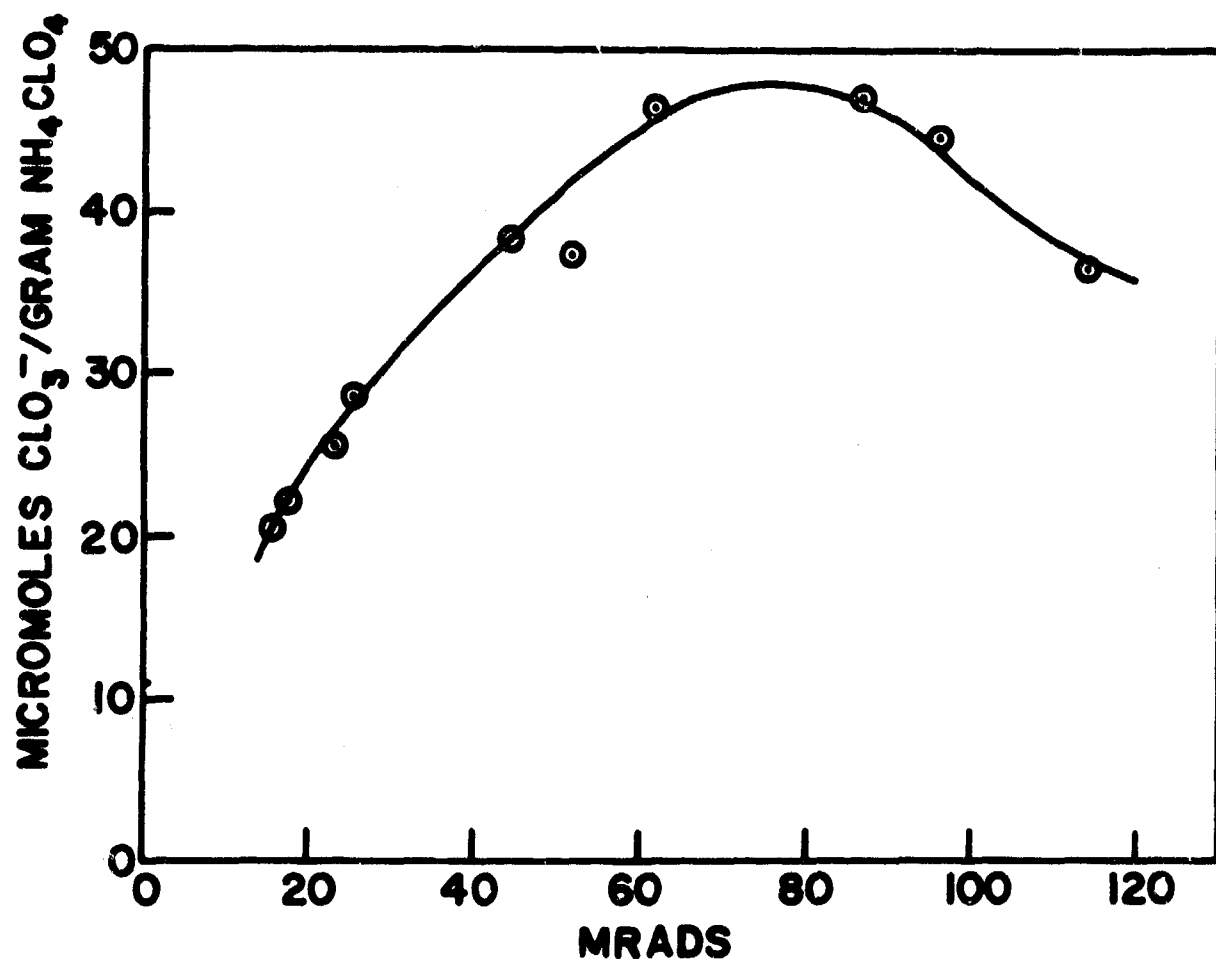


FIGURE 1. ClO_3^- YIELD IN AMMONIUM PERCHLORATE RADIOLYSIS

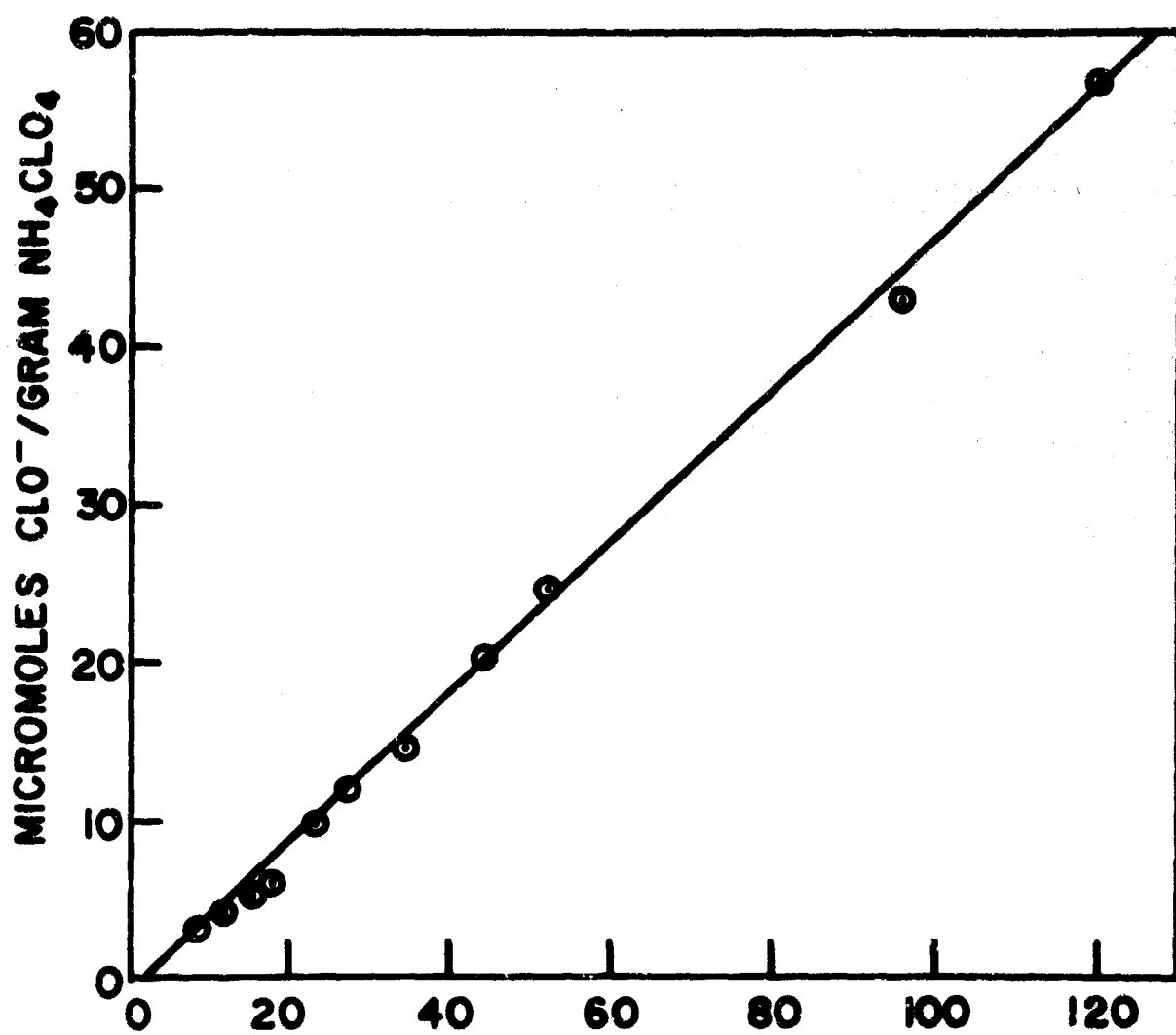


FIGURE 2. ClO^- YIELD IN AMMONIUM PERCHLORATE RADIOLYSIS

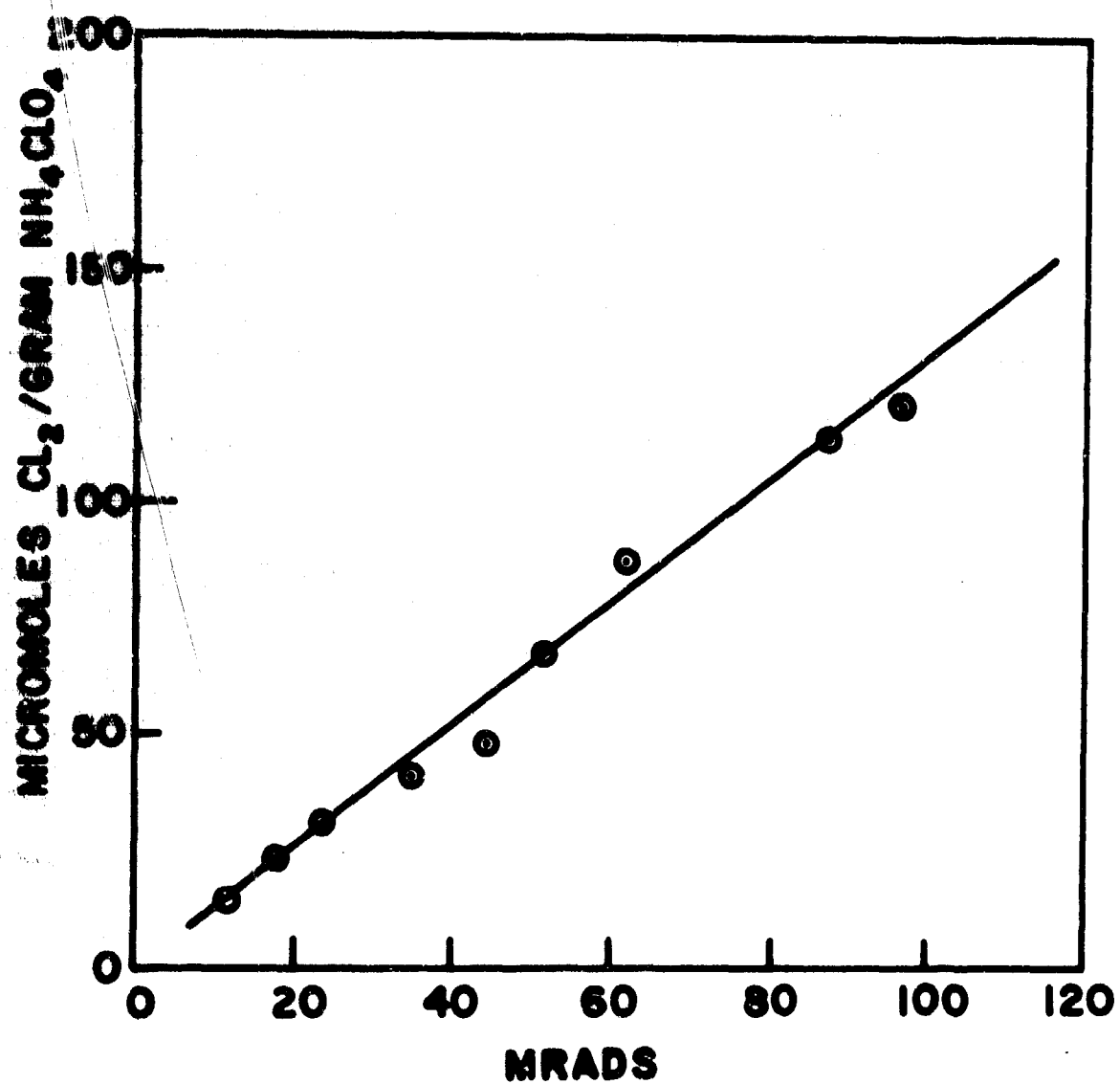


FIGURE 3. CL₂ YIELD IN AMMONIUM PERCHLORATE RADIOLYSIS

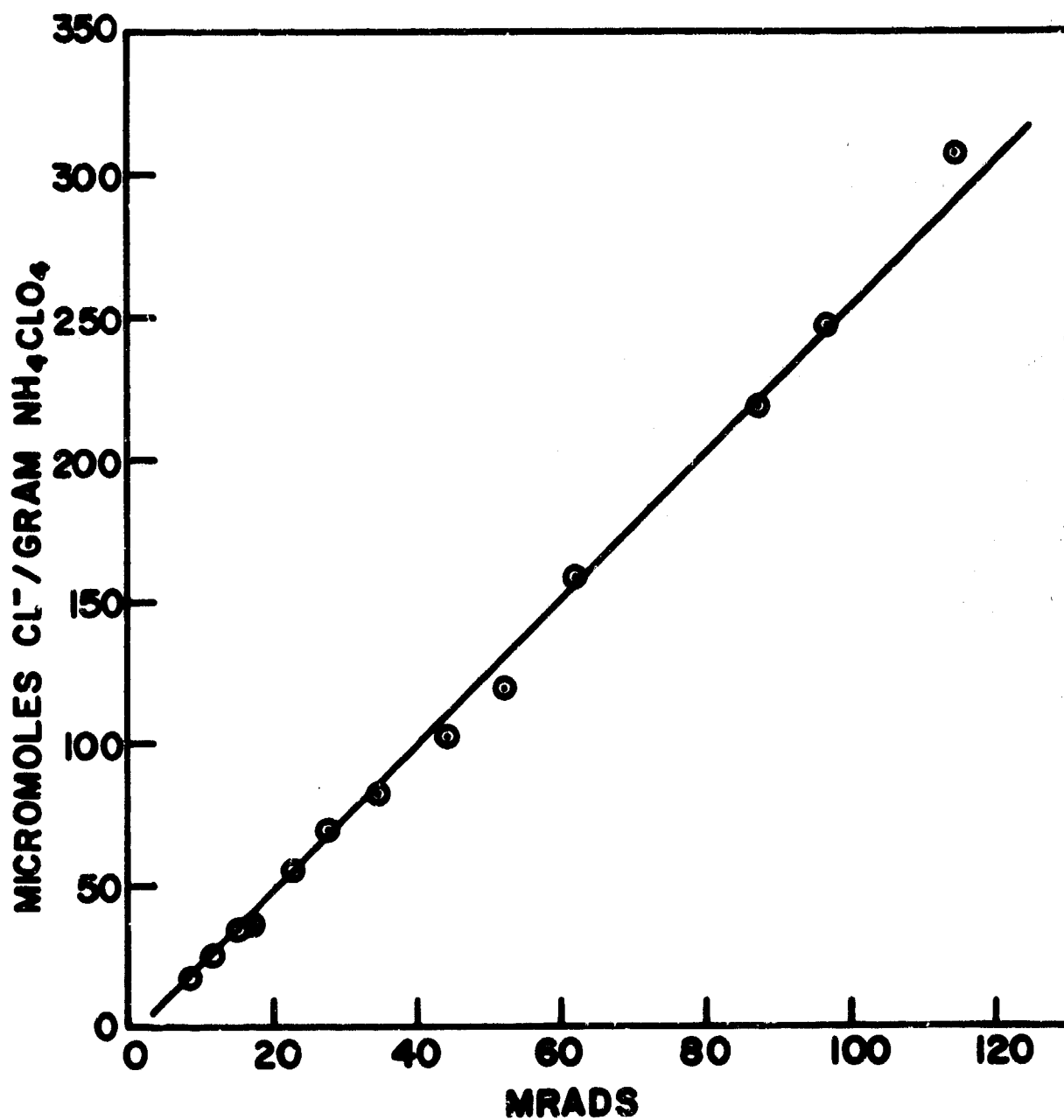


FIGURE 4. Cl^- YIELD IN AMMONIUM PERCHLORATE RADIOLYSIS

It is seen that the major products of ammonium perchlorate radiolysis are chloride, chlorine, chlorate and hypochlorite. Since the yield of nitrite plus nitrate was very small, independent analyses for nitrite or nitrate were not performed. Although we found indications that chlorine dioxide and chlorite are products of ammonium perchlorate radiolysis, their yields are extremely small and may, indeed, be within the limit of accuracy of our experimental procedures.

Although our studies of the radiolytic yields vs. radiation dose are not yet complete, especially the low dose range, the approximate initial G values were calculated and are shown in Table 4.

Table 4
G values of Ammonium Perchlorate
Radiolysis Products

Product	G ^a
ClO ₃ ⁻	1.3
ClO ₂	< 0.01
ClO ₂ ⁻	< 0.01
ClO ⁻	0.46
Cl ₂	1.2
Cl ⁻	2.5
NO ₂ ⁻ /NO ₃ ⁻	0.06
O ₂ (theoretical) ^b	~ 11.5

^aG = number of molecules or ions formed per 100 e.v. of radiation

^bBased on non-participation of nitrogen in the radiolysis reaction.

It is interesting to compare the ammonium perchlorate radiolytic yields (Table 4) with the alkali and alkaline earth metal perchlorate radiolytic yields obtained by Johnson and Prince (Table 2). It is seen that the relative yields of the various radiolytic products are quite dissimilar in the two cases. The following points of comparison can be made

1. The G for total yield of products from ammonium perchlorate radiolysis is larger by a factor of 2-5 than from the metal perchlorates.

2. Aside from oxygen, chlorate is the major radiolytic product of the metal perchlorates by a large factor. The other products (chlorite, chlorine dioxide, hypochlorite and chloride) are produced with much lower G values. This is not the case for ammonium perchlorate radiolysis.

3. Chlorate is a major product of ammonium perchlorate radiolysis with a G which is approximately $1/2$ - $1/3$ that for the metal perchlorates. However, chlorate is by no means the only major radiolytic product of ammonium perchlorate.

(The fall-off in chlorate yield at higher radiation doses probably means that chlorate is undergoing radiolytic decomposition and/or reaction with other radiolytic products. This is very similar to the results of Heal⁴ on the radiolysis of potassium perchlorate although Johnson and Prince⁵ did not observe such an effect. Experiments now in progress on the post-irradiation effects in ammonium perchlorates may shed light on the observed fall-off in chlorate yield in ammonium perchlorate.)

4. Chloride is a major radiolytic product of ammonium perchlorate with a G which is greater by a factor of 2-20 than in the case of the metal perchlorates.

5. Chlorine (Cl_2) is a major radiolytic product of ammonium perchlorate although it is not a product of the radiolysis of metal perchlorates.

The above points of comparison between the products of metal and ammonium perchlorate radiolysis are shown in Table 5.

Table 5
Comparison of Radiolytic Yields of Metal
and Ammonium Perchlorates

Product	G for Alkali and Alkaline Earth Perchlorates ^{a, b}	G for Ammonium Perchlorate ^c
ClO_3^-	3.6(1.8-5.3)	1.3
ClO_2	0.24(0.07-0.59)	<0.01
ClO_2^-	0.23(0.00-0.84)	<0.01
ClO^-	0.10(0.03-0.17)	0.46
Cl_2	0	1.3
Cl^-	0.37(0.06-1.1)	2.5
O_2	2.9(2.0-5.3)	~11.5 ^d

^a

Data of Johnson and Prince, reference 5

^b The value noted is the average of the G values for all of the alkali and alkaline earth perchlorates. The range of G values for these perchlorates is shown in parenthesis.

^c Data of RAI study.

^d Theoretical yield

As we have seen there are drastic differences in the radiolysis of ammonium perchlorate as compared to that of the alkali and alkaline earth metal perchlorates. One possible reason for this

may be the participation of the ammonium ion in the radiation decomposition of ammonium perchlorate. As part of our effort to search for changes in the oxidation state of nitrogen in ammonium perchlorate, we have analyzed for nitrite/nitrate. The very low yields observed for nitrite/nitrate also preclude the presence of a variety of nitrogen compounds such as NO_2 , NO , N_2O_3 , etc., since these would show up in our nitrite/nitrate analysis. Essentially the only nitrogen compounds which would not have been analyzed by our procedure for $\text{NO}_2^-/\text{NO}_3^-$ are N_2 and possible also N_2O . It is planned in the coming contract year to analyze for N_2 and N_2O in irradiated ammonium perchlorate by gas chromatographic and other means. Simultaneously during the gas chromatographic analysis we will analyze for oxygen gas as well as obtain a more positive identification of Cl_2 .

Another possibility is that the differences in the product spectrum between the metal perchlorates and ammonium perchlorate radiolyses may be due to the interaction of the various radiolytic products in the latter case. It is planned in the coming year to study this point by observing the post-irradiation effects in ammonium perchlorate.

2.3 DEVELOPMENT OF ANALYTICAL REACTIONS

2.3.1 Chloride Ion Yield

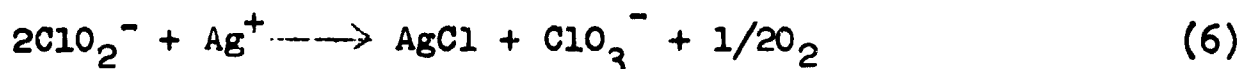
Chloride ion was determined by a modification of the Volhard procedure utilized by Burns and Muraca⁷ and by Johnson and Prince.^{5b} An excess of standard silver nitrate was added to the chloride-containing sample (eq. 1) and the excess silver ion back titrated with thiocyanate ion (eq. 2) in the presence of ferric ion which served as an indicator through the formation of the red-brown ferrithiocyanate ion (eq. 3):



Benzyl alcohol or nitrobenzene was added after the addition of silver nitrate to coat the silver chloride precipitate and prevent its equilibration with thiocyanate ion (eq. 4):



This analytical procedure was checked with known chloride solutions spiked with ClO_3^- , NH_4ClO_4 , ClO_2^- , ClO^- , Cl_2 , NO_2^- and NO_3^- and found to be free from interferences. However, corrections had to be employed to calculate the Cl^- yield because ClO^- and ClO_2^- also react with silver ion. One mole of ClO^- reacts with one mole of silver ion while one mole of ClO_2^- reacts with only one-half mole of silver ion. The probable reactions are

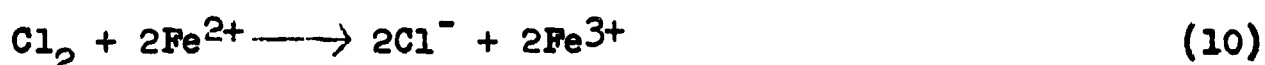
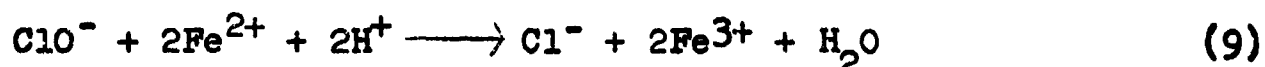
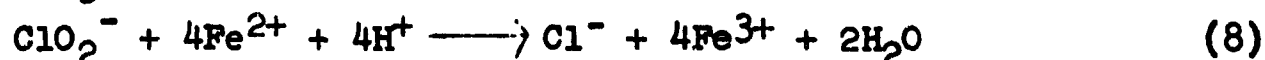
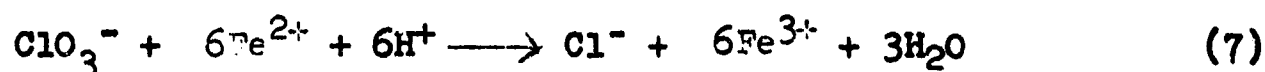


The chloride ion yield was found to be unaffected by flash boiling (See Section 2.4.1b for description of "flash

boiling" procedure) as would be anticipated since gaseous species such as Cl_2 and ClO_2 would not be expected to interfere.

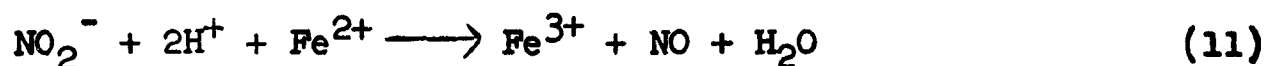
2.3.2 Oxidation of Ferrous Ion : Cl_2 and ClO_3^- Yields

Ferrous ion was oxidized to ferric ion in acidic medium by Cl_2 , ClO^- , ClO_2^- and ClO_3^- according to eqs. 7-10:



These oxidations were employed to determine the yields of Cl_2 , ClO^- , ClO_2^- and ClO_3^- in ammonium perchlorate radiolysis. The procedure was a modification of that of Johnson and Prince.^{5b} The analysis was performed by the UV spectrophotometric determination of ferric ion yield via its absorption at 305 m μ .

It was determined that NH_4ClO_4 , Cl^- , and NO_3^- did not interfere with this procedure although NO_2^- oxidizes Fe^{2+} according to eq. 11:



However, the yield of NO_2^- in ammonium perchlorate radiolysis was independently found (see Section 2.3.4) to be so small as to make a correction for eq. 11 unnecessary.

The yields of Cl_2 and ClO_3^- were obtained from eqs. 12 and 13

$$\text{Cl}_2 = 1/2 (\text{Fe}^{3+} - \text{Fe}_F^{3+}) \quad (12)$$

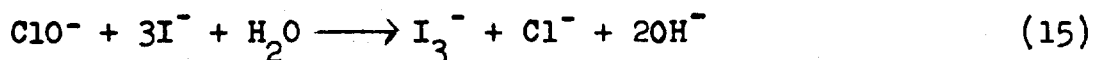
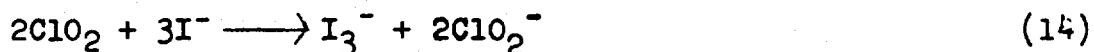
$$\text{ClO}_3^- = 1/6 \text{Fe}_F^{3+} - 1/3 \text{ClO}^- - 2/3 \text{ClO}_2^- \quad (13)$$

where Fe^{3+} , $\text{Fe}_F^{3+} = \text{Fe}^{3+}$ Yields without and with flash boiling, respectively

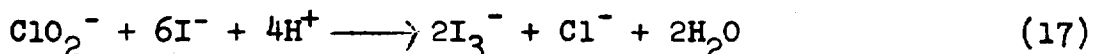
ClO^- , $\text{ClO}_2^- = \text{ClO}^-$ and ClO_2^- yields, respectively, from Section 2.3.3.

2.3.3 Oxidation of Iodide Ion Cl_2 , ClO_2 , ClO^- and ClO_2^- Yields

The oxidation of iodide ion to iodine was the basis of the analysis of ClO_2^- , ClO^- , ClO_2 , and Cl_2 . The I_2 (actually I_3^-) was determined spectrophotometrically by its absorption at 350 m μ . The analytical procedure employed was a modification of that employed by Johnson and Prince.^{5b} In basic (pH 8-9) media, ClO_2 , ClO^- and Cl_2 oxidize iodide according to eqs. 14-16 while ClO_2^- does not.



In acidic (pH 1-2) solution, ClO_2^- also oxidizes iodide (eq. 17).



It should be noted that the reaction in eq. 17 is due to ClO_2^- formed directly from ammonium perchlorate radiolysis and via the oxidation of iodide by ClO_2 (eq. 14).

Nitrite ion interferes with this analytical procedure since it will also oxidize iodide ion in acidic media but not in basic media. However, the yield of nitrite was found to be negligible as evidenced both by negligible differences observed between iodide oxidation performed in acidic and basic media and by the separate nitrate/nitrite analysis in Section 2.3.4.

The separation of the total iodine yield into those attributable to the various species (i.e., Cl_2 , ClO_2 , ClO_2^- , ClO^-) was facilitated by analyzing with and without prior flash boiling. Flash boiling resulted in the expulsion of Cl_2 and ClO_2 . The yields of ClO^- , ClO_2^- , ClO_2 and Cl_2 were obtained from eqs. 18-21:

$$\text{ClO}^- = \text{I}_{2\text{B,F}} \quad (18)$$

$$\text{ClO}_2^- = 1/2(\text{I}_{2\text{A},\text{F}} - \text{I}_{2\text{B},\text{F}}) \quad (19)$$

$$\text{ClO}_2 = 1/2(\text{I}_{2\text{A}} - \text{I}_{2\text{B}}) - \text{ClO}_2^- \quad (20)$$

$$\text{Cl}_2 = \text{I}_{2\text{A}} - \text{I}_{2\text{A},\text{F}} - 2\text{ClO}_2 \text{ or } \text{I}_{2\text{B}} - \text{I}_{2\text{B},\text{F}} - 2\text{ClO}_2 \quad (21)$$

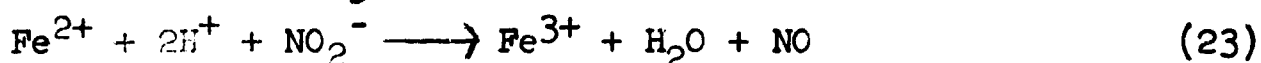
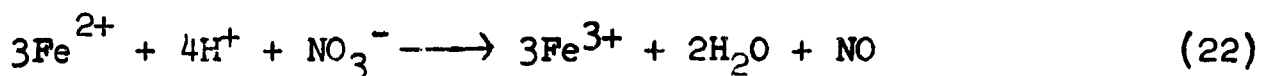
where $\text{I}_{2\text{B}}$, $\text{I}_{2\text{A}}$ = iodine yields in basic and acidic media,
respectively, without flash boiling

$\text{I}_{2\text{B},\text{F}}$, $\text{I}_{2\text{A},\text{F}}$ = iodine yields in basic and acidic media,
respectively, with flash boiling

2.3.4 $\text{NO}_2^-/\text{NO}_3^-$ Yield

a. Theory

The analysis for NO_2^- plus NO_3^- was via a modification of the procedure used by Norwitz⁸ in the analysis of nitrate ion. It was based on the reduction of both nitrate and nitrite ions to nitric oxide (eqs. 22 and 23) by ferrous ion (in concentrated sulfuric acid solution) followed (eq. 24) by the formation of the red complex ion $\text{Fe}(\text{NO})^{2+}$ whose absorption at 525 m μ was then determined.



We have determined that NH_4ClO_4 , ClO_3^- , Cl^- , ClO^- and Cl_2 do not interfere with this analytical procedure.

2.4 Experimental Procedures

2.4.1 General

a. Materials and Sample Preparation

Matheson, Coleman and Bell reagent-grade ammonium perchlorate was recrystallized twice from deionized water, dried and ground up prior to use. All other materials were reagent or analytical-grade chemicals which were dried but otherwise not further purified before use.

Samples of ammonium perchlorate were placed in ground glass test tubes, capped and then irradiated at 10-15°C. with cobalt-60 gamma radiation. (A few of the irradiations were performed at 6-10°C. with no significant differences being observed in the radiolytic yields.) Dosimetry was performed via the oxygenated Fricke ferrous sulfate dosimeter⁹ using a $G(\text{Fe}^{3+})$ of 15.6.

b. General Notes on Analytical Procedures

Many of the analyses were performed with and without prior "flash boiling." Flash boiling resulted in the expulsion of gases (Cl_2 , ClO_2) from the solution of irradiated ammonium perchlorate. It was accomplished by heating the solution in a flask with a Bunsen burner with swirling until (ca. 1/2 minute) the solution just began to boil. The flash boiling procedure was shown, via the analysis of standard solutions, not to affect the yields of the non-gaseous products (ClO_3^- , ClO_2^- , ClO^- , Cl^- , NO_2^- , NO_3^-).

All spectrophotometric determinations were performed with a Beckmann DU Spectrophotometer.

Analyses of irradiated samples were performed immediately after the completion of irradiation. In a few cases, samples were stored at dry ice-acetone temperatures overnight prior to analysis.

These two procedures yielded results which were indistinguishable from each other.

2.4.2 Analysis for Cl^-

An appropriate portion (an amount which required a back titration with approximately 1 ml. of thiocyanate) of irradiated ammonium perchlorate was added to 5-10 ml. water and 0.1 M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate) contained in an Erlenmeyer flask. (Optional: Flash boil and then cool.) One to 1-1/2 ml. of 1-1 nitric acid and then a 5 ml. aliquot of standard 0.01M silver nitrate were added followed by 10 drops of saturated ferric ammonium sulfate solution and 3 ml. of benzyl alcohol or nitrobenzene. After standing for 15 minutes the excess silver nitrate was back titrated with standard 0.01M potassium thiocyanate to the red-orange-brown end point.

2.4.3 Oxidation of Ferrous Ion

An appropriate portion (an amount which yielded an optical density of 0.2-0.5) of irradiated ammonium perchlorate was added to a 200 ml. volumetric flask containing 10 ml. water and 0.1M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate). (Optional: Flash boil and cool.) Twenty ml of 0.1M ferrous ammonium sulfate in 5% sulfuric acid, 20 ml. of 1.1-1 sulfuric acid, and then enough water to make up to volume were added. (For samples irradiated to very high doses, a 500 ml. volumetric flask was employed with appropriate adjustment of the amounts of the various reagents.) After standing for at least 4 hours, the optical density of the solution was determined at 305 m μ against a blank solution made up in the same manner as above except that the irradiated ammonium perchlorate was omitted. The molar extinction coefficient of Fe^{3+} , E, was simultaneously determined

by using standard KClO_3 solutions in place of the irradiated ammonium perchlorate in the procedure above. Our results showed an E value of 2166 as compared to the literature⁹ value of 2201.

2.4.4 Oxidation of Iodide Ion

An appropriate portion (an amount yielding an optical density of 0.2-0.5) of irradiated ammonium perchlorate was added to 10 ml. water and 0.1 M sodium hydroxide (1 ml. per 50 mg. ammonium perchlorate) in a 200 ml. volumetric flask. (Optional: Flash boil and then cool.) Twenty ml. 10% potassium iodide solution and then enough water to make up to volume were added (For samples irradiated to very high doses, a 500 ml. volumetric flask was employed with appropriate adjustment of the amounts of the various reagents.) The optical density of the resulting solution was then determined at 350 m μ against a blank solution prepared in the same manner but without irradiated ammonium perchlorate. The solution from the UV optical cell was then poured back into its volumetric flask, concentrated sulfuric acid (0.4 ml. per 50 mg. ammonium perchlorate) added and the optical density at 350 m μ redetermined. The extinction coefficient, E, of iodine at 350 m μ , was determined by using the same procedure as above with standard solutions of sodium chlorite. Our E value of 23,990 compared well with the literature^{6b} value of 24,940.

2.4.5 Analysis for $\text{NO}_2^-/\text{NO}_3^-$

To a 5 gram portion of irradiated ammonium perchlorate in a 10 ml. volumetric flask, was added sufficient ferrous sulfate solution (2.5 g. ferrous sulfate heptahydrate in 3:1 by volume of concentrated sulfuric acid and water) to make up to volume.

After standing for one hour, the optical density at 525 m μ was determined vs. a blank of the ferrous sulfate solution. The extinction coefficient was determined to be 237 by using the above procedure with standard nitrate solutions.

3.0 BALLISTIC STUDIES OF IRRADIATED PROPELLANT SYSTEMS

The deflagration rate of ammonium perchlorate composite solid propellants is altered by exposure to radiation. For some propellants the rate is increased, while for others it is decreased - the direction of change apparently controlled by the nature of the fuel and the magnitude by the dose level (RAI Report 314). During the coming year, the mechanism by which exposure to radiation effects the combustion dynamics of these propellants will be investigated.

Experiments to be performed are designed to isolate the effect of radiation on both the deflagration rate of the ammonium perchlorate and on the fuel. This can be done simply by burning ammonium perchlorate specimens, both irradiated and non-irradiated, in environments of fuel that have experienced no exposure and measuring their deflagration rate as a function of dose level; and by burning fuel specimens, both irradiated and non-irradiated, in environments of oxidizer that have experienced no exposure and measuring their deflagration rate as a function of dose level. However, these combustion experiments must be performed with specimens in a configuration that simulates the actual propellant combustion flame in order that the results can be related to the deflagration process of an actual propellant. Recently, a novel laboratory burner technique has been developed that permits ready execution of such experiments.¹⁰

The burner is an experimental analogue of the composite solid propellant process that models all of its essential elements, including a detailed simulation of the complex structure of the propellant burning surface, while still permitting ready experimental control of sensitive parameters over a much broader range than is possible with actual propellants. Composite propellant burning surface structure is a complicated function of combustion pressure level, ammonium perchlorate crystal size, mixture ratio, etc., e.g., the crystals project from the fuel surface for some conditions and are recessed within it for others. Therefore, two types of burners are required: a fuel pellet burner, through which oxidizer gases are passed, and an oxidizer pellet burner, through which fuel gases are passed. Point-of-contact bonding between pellets, and between the tube that contains the pellets and adjacent layers of pellets prevents fluidization and elutriation by the throughput gas, and produces structural integrity. Bonding is produced by exposure to a weak concentration of a pellet solvent, followed by thorough drying. During fabrication, three fuze wires are inserted at precisely located 1 in. axial intervals near the middle of the 9 in. long x 0.402 inch i.d. stainless steel tubes, as well as a resistance wire at the top, before exposure to the pellet solvent. An electrical current passed through the resistance wire produces ignition, and the plug is consumed by the flame it supports by reaction with the throughput gas. Deflagration rate is obtained by measuring the intervals between successive burnouts of the three fuze wires. A critical orifice technique is employed to measure the gas throughput rate. A burner housing, with appropriate attachments, permits combustion pressure to be controlled.

Employing this burner technique, the effect of radiation dosage on ammonium perchlorate deflagration rate will be obtained for a series of pellet sizes, pressure levels, gaseous fuel chemistry, fuel-to-oxidizer ratio, etc.; then, the effect of radiation dosage on the deflagration rate of several solid fuels typical of those employed in actual propellants will be obtained for a series of pellet sizes, pressure levels, gaseous oxidizer chemistry, oxidizer-to-fuel ratio, etc. Interpretation of this data should reveal the detailed mechanism by which the individual composite propellant components respond to radiation exposure.

One interesting practical result of this work might be the control of composite deflagration rate by irradiating one component or the other before formulation.

4.0 FUTURE PROGRAM

The program for the coming contract year will, in general, consist of the following:

1. A continuation of the ammonium perchlorate radiolysis study (Section 2.0). Emphasis will be placed on the analyses of the gaseous products via gas chromatography for O_2 , N_2 , Cl_2 , etc.

Studies will also be performed to determine the post-irradiation changes which occur in irradiated ammonium perchlorate. Preliminary results indicate that appreciable changes occur in the concentrations of the various radiolytic products on standing after the termination of irradiation.

2. The ballistic studies outlined in Section 3.0 have only been recently initiated. These will comprise a large portion of our effort in the coming year.

5.0 REFERENCES

1. H.G. Heal, Can. J. Chem. 31, 91 (1953).
2. H.G. Heal, ibid. 37, 979 (1959).
3. C.E. Burchill, Nature 194 (1962).
4. H.G. Heal, Can. J. Chem. 31, 91 (1952).
5. a. E.R. Johnson, Paper presented at A.S.T.M. Meeting, Atlantic City, New Jersey (June, 1963).
b. L.A. Prince, Ph.D. Thesis, Stevens Institute of Technology (1963).
6. a. E.S. Freeman and D.A. Anderson, J. Phys. Chem. 63, 1344 (1959) and 65 1662 (1961).
b. J.S. Hyde and E.S. Freeman, ibid. 65, 1636 (1961).
c. E.S. Freeman, D.A. Anderson and J.J. Campisi, ibid. 64, 1727 (1960).
7. E.A. Burns and R.F. Muraca, Anal. Chem. Acta. 23, 136 (1960).
8. G. Norwitz, Anal. Chem. 34, 227 (1962).
9. A.O. Allen "Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., Princeton, N.J. pp. 20-23 (1961).
10. R.F. McAlevy, III and S.Y. Lee, "A Porous Plug Burner Technique for the Study of Composite Solid Propellant Deflagration on a Fundamental Level and its Application to Hybrid Rocket Propulsion," Paper presented at the AIAA Heterogeneous Combustion Conference, Palm Beach, Florida, 12 December 1963.

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