Procedures for Suppressing Premature Exothermic Decomposition in Ammonium Perchlorate

S. W. Mayer,* E. K. Weinberg,† and L. Schieler‡
Aerospace Corporation, El Segundo, Calif.

In order to enhance extinguishment reliability of controllable solid-propellant motors, an investigation has been made by differential thermal analysis to search for additives or techniques that could eliminate or inhibit the normal first exotherm of propellant grade ammonium perchlorate (AP). The first exotherm was eliminated by controlled heating of the AP for several minutes at 370–390°C. This technique was effective in the presence of fluorocarbon binder or copper catalysts. It was also found that the temperature at which this first AP exotherm occurred could be raised 85°C by adding 1.5% ammonium hexafluorophosphate. The additive was also effective when fluorocarbon binder was in contact with the AP. Although the first AP exotherm was strongly catalyzed by as little as 0.04% of copper nitrate, the catalysis was suppressed by the NH_4PF_6 additive. Independent tests in a combustion-bomb and in a motor have demonstrated the increased extinguishment reliability suggested by the thermal analysis curves of AP containing 1% NH_4PF_6. The effect on AP decomposition and combustion exotherms has also been tested for a series of additives consisting of ammonium salts, flame retardants, Lewis acids, and transition-metal compounds.

I. Introduction

Tests of controllable solid-propellant motors have shown that premature reignition of the propellant can occur to cause the mission to fail. It has been postulated[1,2] that this inadvertent reignition of controllable solid-propellant rockets may be prevented by limiting the heat radiated to the propellant surface after extinguishment, or reducing the heat generated in the residual propellant through exothermic decomposition at its elevated temperature. The investigations reported herein are based on the second approach since computations using thermal models[2,3] of extinguishable motors had shown that the first exotherm characteristic of propellant grade ammonium perchlorate (AP) was a major factor in causing premature reignition. Differential thermal analysis[4] techniques were used, therefore, to search for procedures that could suppress the first exotherm of AP.

II. Experimental Procedure

Because of the explosion hazard associated with heated AP and its mixtures with other materials, the differential thermal analyses (DTA) were made on specimens contained in micro glass tubes, 1 mm i.d., 2 mm o.d., 25 mm high, and sealed at the bottom. The sample was loaded in the tube to form a layer 4 ± 1 mm thick, and the tube was placed in the standard DuPont§ micro heating-block. Micro glass beads in a similar micro glass tube were used as the reference material. Chromel-alumel thermocouples in the sample, in the glass beads, and in the heating-block were used to measure the temperature of the sample and the difference in temperature (ΔT) between the sample and the reference material. Sample temperature and ΔT (Fig. 1) were recorded on an X-Y recorder with ΔT on the Y axis at a scale of 10°C/in. (all temperatures in this paper are reported in °C).

The heating-block, cartridge heater, and block support were the standard DuPont micro DTA items. The micro block was an aluminum cylinder $\frac{7}{8}$ in. in diameter and $1\frac{1}{2}$ in. high. It contained two adjacent cylindrical cavities, 2 mm in diameter, for the sample and reference micro sample tubes. In the center of the block a cartridge heater was placed in a cylindrical cavity (axis parallel to axis of block), $\frac{3}{8}$ in. in diameter and 1 in. deep. The cartridge heater was rated at 55 w for 110 v. Heating was performed in air at ambient pressure. In order to maximize the heating rate, the heating cartridge was operated at 115 v from a variable transformer. As a result, the temperature rise of the microfurnace was 50°C/min at 350° (near the temperature of the onset of the first exotherm). This compares favorably with the 20°/min temperature rise commonly employed for the micro furnace. Since the voltage was constant at 115 v, the heating rate decreased at higher temperatures because of thermal losses from the microfurnace. The measured heating rates, in degrees celsius per min, at high temperature were: 46° per min at 375°, 41° at 400°, 36° at 425°, 30° at 450°, 25° at 485°, and 19° at 500°. Measured heating rates at temperatures lower than 350° were: 59° at 300° and 55° at 325°.

Except where otherwise specified, the AP used in these investigations was manufactured by the American Potash and Chemical Corporation, Los Angeles, Calif. The ammonium salts of complex halogen anions [e.g., NH_4PF_6, NH_4BF_4, $(NH_4)_2TiF_6$, $(NH_4)_2$ SiF_6,NH_4SO_3F] were obtained from the Ozark-Mahoning Company. Transition-metal compounds and other ammonium salts were of Reagent Grade. These additives were thoroughly mixed with the AP in glass vessels. Fluorocarbon(FC)-AP composite propellant was donated by the Wasatch Division of Thiokol Chemical Corporation. Perchloropentacyclodecane (Dechlorane) was obtained from the Hooker Chemical Co., and tricresyl phosphate (Kronitex AA grade) was donated by FMC Corp.

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* Staff Scientist, Aerodynamics and Propulsion Research Laboratory.

† Manager, Maneuvering Propulsion Section, San Bernardino Operations. Member AIAA.

‡ Head, Chemical Propulsion Department, Laboratories Operations.

§ Differential Thermal Analyzer Department. Instrument Products Division, E. I. DuPont, de Nemours and Co., Inc., Wilmington, Del.

III. Results and Discussion

Suppression of the First Exothermic Decomposition by a Heating Technique

Typical DTA curves are presented in Fig. 1 for propellant grade[5-7] AP of several mean particle sizes. The first exotherm characteristic of propellant grade AP is evident. Temperatures of the onset of this exotherm ranged, for the samples in Fig. 1, from 330° to 365°C. It has been shown analytically that the first exotherm represents a source of premature enthalpy that can cause AP propellants to reignite inadvertently after extinguishment.[2,3] A principal objective of these laboratory investigations, therefore, was to search for methods that could eliminate or suppress the first exotherm. Several views exist as to the cause of this undesirable exotherm, but there is no general agreement on which cause is the correct one.[5-7] One view is that transition metal impurities, such as copper salts, catalyze the thermal decomposition of AP to produce the exotherm that occurs before the deflagration exotherm. A second hypothesis is that the first exotherm arises from excess perchloric acid trapped with the AP crystals. A third view is that the first exotherm is caused by the presence of chlorate in the AP as a residual from the manufacturing process.

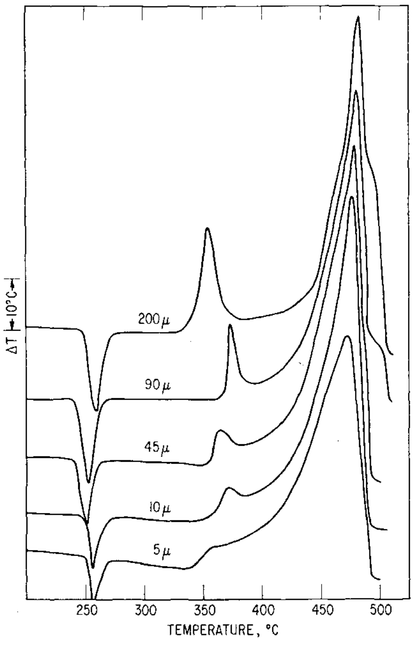

Fig. 1 DTA curves for NH_4ClO_4. Particle sizes: 5, 10, 45, 90, and 200 μ.

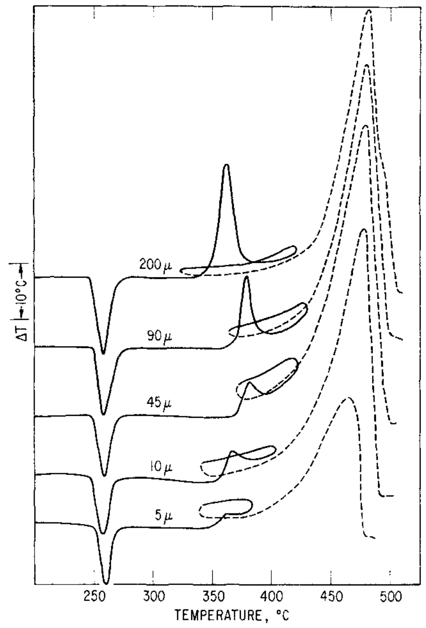

Fig. 2 Heating procedure for eliminating first AP exotherm. Dashed lines denote reheating after cooling.

Because of the thermal instability of transition metal perchlorates, chlorates, and $HClO_4$, it appeared possible to the authors that heating propellant grade AP to selected temperatures could remove these contaminants from AP. Accordingly, this idea was investigated by using the DTA furnace to heat AP specimens since the effects of a heating procedure could then be efficiently tested in the DTA apparatus. The results of tests of a heating technique are summarized in the DTA curves shown in Fig. 2. These curves demonstrate that AP in which the first exotherm has been almost completely suppressed can be produced by controlled heating, followed by cooling. The samples were heated to a temperature higher than that of the peak in the first exotherm, but not to a temperature as high as the deflagration temperature. Then the power to the microfurnace was discontinued, and the samples were allowed to cool. After the temperature had dropped well below that of the exotherm peak, the power to the microfurnace was restored and the samples were heated again, as denoted by the dashed lines in the DTA curves of Fig. 2. In every case, the DTA curve for the reheated AP showed that the first exotherm was suppressed by the controlled prior heat treatment of the propellant grade AP. This consistent suppression of the first exotherm is in disagreement with the observation of Osada and Sakamoto[8] who reported that elimination of the first exotherm did not occur at atmospheric pressure but occurred at reduced pressure. The weight loss of a 200μ sample preheated to 370° was only 9%. Differential scanning calorimetry measurements showed that the heat evolved in the second exotherm was not significantly reduced by the preheat treatment and 9% weight loss. The curves in Fig. 2 are typical of more than 50 tests of the heating technique for removal of the first exotherm. In every case, regardless of the source of the AP, the technique of heating to a temperature slightly above that of the first exotherm was successful. In Fig. 3, the bottom DTA curve is that for 90μ AP treated to remove the exotherm by the preheating technique, followed by cooling to room temperature. The treated sample had been allowed to remain in a desiccator for a week. This suggests that NH_3 trapped

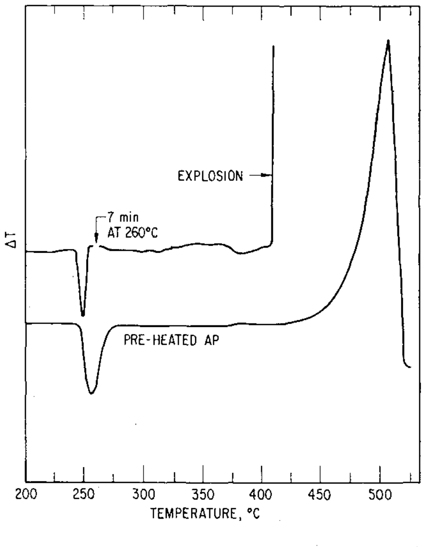

Fig. 3 DTA curves for preheating AP and 260° heating.

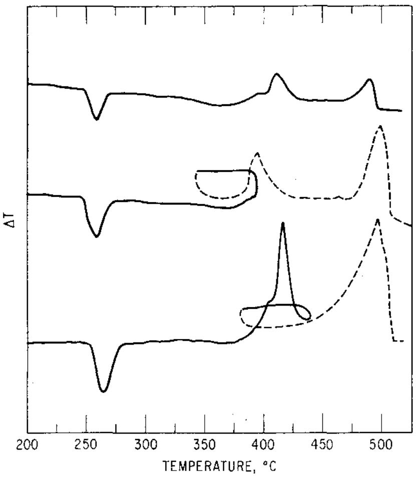

Fig. 4 DTA curves for composite fluorocarbon-AP propellant. Dashed lines denote reheating after cooling.

in the tube does not produce the inhibition of the exotherm. It can be seen that the first exotherm has been virtually eliminated. Another heat treated sample, however, was kept in a saturated water vapor atmosphere at 25°C for three days. This exposure to water vapor caused much of the first exotherm to reappear. Accordingly, it is planned to make a series of DTA tests of preheated AP that has been exposed to long time storage in air, with or without binder.

The top curve of Fig. 3 illustrates the effect of prolonged heating at a temperature just above that of the solid-state transition endotherm. In this case, 90μ AP was heated for seven minutes at 260°C. Upon further heating, the AP exploded at about 410°C, shattering the microglass sample tube. The seven minute treatment at 260°C may, therefore, have increased the specific surface area of the AP sample sufficiently so that the deflagration was rapid enough to shatter the glass sample tube. Consequently, although heating techniques promise to be of value, it is clear that treated AP merits careful testing for explosion hazards.

DTA curves are shown in Fig. 4 for an extinguishable composite propellant compounded with a fluorocarbon binder and AP (no aluminum). The top curve is the DTA curve obtained when the preheating technique was not used. The second curve of Fig. 4 shows the results of a brief test to see whether initial heating of the FC propellant could make it more susceptible to premature reignition. It can be seen in Fig. 4 that the FC propellant sample was heated to 395° (near the plateau region of the first exotherm), cooled to 345° and reheated (dashed line). This type of heating (i.e., to a temperature less than that at which the maximum of the first exotherm occurred) apparently may make the FC propellant more susceptible to premature ignition[3] since the peak of the first exotherm occurred at a lower temperature during the reheating. The bottom DTA curve of Fig. 4, however, represents a controlled heating treatment of the FC propellant similar to that applied (Fig. 2) to remove the first exotherm from AP, inasmuch as the propellant was heated to a higher temperature, 400°C, than that at which the maximum of the first exotherm occurred. Examination of the DTA curve showed that this heat treatment of FC composite propellant succeeded in removing the first exotherm, as it had when AP was tested in the absence of the fluorocarbon binder.

Additives for Suppressing the First Exotherm of AP

It was thought possible that a thermally decomposable additive such as a flame retardant would absorb enough heat during its decomposition and volatilization to delay the first exotherm to a higher temperature. The top DTA curve in Fig. 5 shows the effect of 2% Dechlorane flame retardant on the thermal decomposition of 90μ AP. The DTA curve for Dechlorane mixed in AP indicated that Dechlorane was considerably less effective than the preheating technique in inhibiting the first exotherm of AP. Since tricresyl phosphate is also widely used as a commercial flame retardant additive, a DTA test (Fig. 5) was made of its inhibiting ability at a concentration of 5% in 90μ AP. Although the DTA curve showed that 5% tricresyl phosphate raised the temperature of the onset of the first AP exotherm to about 390°, that exotherm was quite large. The relative ineffectiveness as inhibitors of the organic compounds, Dechlorane and tricresyl phosphate, may be due in part to the exothermicity generated by the ability of AP to oxidize organic groups. The exothermicity generated by even a low percent of hydrocarbon is illustrated in Fig. 5 by the DTA curve for 0.5% polyethylene powder mixed with 90μ AP. Comparison with Fig. 1 shows that this concentration of combustible hydrocarbon produced a significant enlargement of the first exotherm.

Inasmuch as many ammonium salts, when heated, undergo endothermic decomposition with the evolution of NH_3, it appeared desirable to test the effectiveness of such additives for suppressing or delaying the first exotherm of AP. Accordingly, a series of DTA measurements was made on ammonium salts and on their mixtures with AP. The most effective additive found to date is ammonium hexafluorophosphate. The DTA curve for the thermal decomposition of NH_4PF_6 is shown in Fig. 6, along with the DTA curve for the 0.5% and 1.5% mixtures of NH_4PF_6 in 90μ AP. Comparison with the top curve of Fig. 6 showed that 1.5% NH_4PF_6 inhibited the onset of the first exotherm by about 85°. Moreover, the apparent ability of NH_4PF_6 additive to reduce the height of the first AP exotherm, in addition to inhibiting its onset, was of particular significance in connection with the objective of minimizing premature reignition of extinguishable solid-propellant motors. It has been calculated on the basis of a thermal model[3] of motor reignition that, after extinguishment, exothermicity from the first AP exotherm can raise the temperature of the residual solid propellant to produce premature reignition. The strong inhibiting action of NH_4PF_6 additive on the first exotherm of propellant-grade AP, therefore, suppresses the tendency for premature reignition of the propellant. The superior

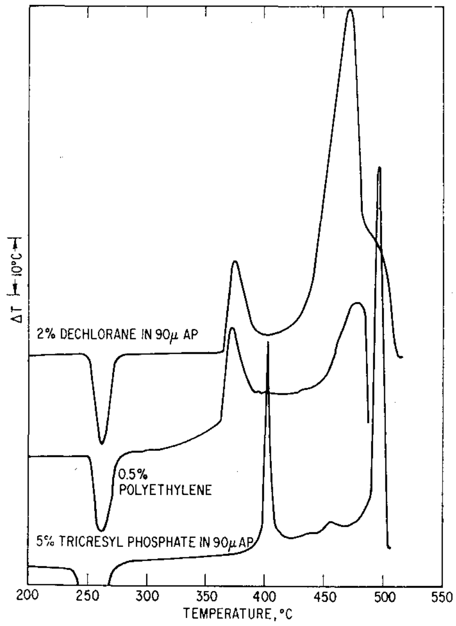

Fig. 5 Effect of flame retardants and polyethylene on AP exothermicity.

effectiveness of NH_4PH_6 can be seen from the DTA curves in Fig. 7 where it is evident that the heights of the first exotherms obtained with 90μ AP mixed with 5% $(NH_4)_2TiF_6$, 5% NH_4BF_4, or 2% $(NH_4)_2HPO_4$ were much greater than the height obtained with the NH_4PF_6 additive. (After these three DTA tests were completed, a patent[9] was discovered in which it was shown that the drop-test sensitivity of AP for explosion can be reduced by forming a solid solution of AP containing 6% or more of NH_4BF_4.) Furthermore, the additives shown in Fig. 7 are not as effective as NH_4PF_6 in inhibiting the onset of the first exotherm since they raised the temperature of its onset by 25°–57°, compared with the 85° inhibition achieved with 1.5% NH_4PF_6. The DTA curves obtained with 5% NH_4PF_6 in 90μ AP were similar to that shown in Fig. 6 for 1.5% NH_4PF_6. Lowering the weight-percent of NH_4PF_6 in AP to 0.5% (Fig. 6) reduced the inhibition of the onset of the exotherm to 52°, but the height of the first exotherm was not significantly increased compared to the DTA results for 1.5% NH_4PF_6. The DTA curve for 1.0% NH_4PF_6 was similar to that for 0.5% NH_4PF_6.

Although the practical implications of the DTA curves in Figs. 6 and 7 are rather clear in terms of suggesting that NH_4PF_6 be tested in motors as an additive for minimizing inadvertent reignition of extinguishable propellants, these curves raise the following three basic questions that, for the most part, are highly difficult to answer since the mechanisms for the exothermic decomposition of AP itself have not been definitely established.[5–7] 1) Why are the heights of the first AP exotherms observed with NH_4BF_4 or $(NH_4)_2TiF_6$ additives larger than those observed when NH_4PF_6 additive is used? 2) Are there simpler halogen compounds that could be more efficient inhibitors? 3) Why do these additives inhibit the onset of the undesirable first exotherm? In examining these questions, the behavior of the additives themselves at temperatures of 250°C and higher, where AP decomposes and deflagrates must be considered. The DTA curve for NH_4PF_6 with no AP present is the bottom curve in Fig. 6, and the DTA curves for NH_4BF_4, NH_4Cl, and $(NH_4)_2CO_3$ are presented in Fig. 7 of Ref. 10. The thermal decomposition of NH_4PF_6 is represented by the second endotherm of its DTA curve in Fig. 6 since the first endotherm (as in the case of AP) is apparently produced by a solid state transition.[4] The second endotherm of NH_4PF_6 begins at about 330° and reaches its minimum (probably corresponding the maximum rate of decomposition) near 385°. It is believed[11,12] that the thermal decomposition of solid NH_4PF_6 produces gaseous products in accordance with the following equation, which is typical for the thermal decomposition of many ammonium salts

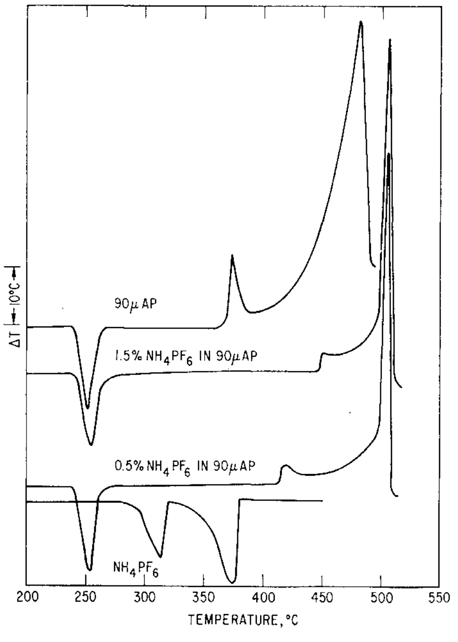

Fig. 6 DTA curves demonstrating the inhibiting ability of ammonium hexafluorophosphate in AP.

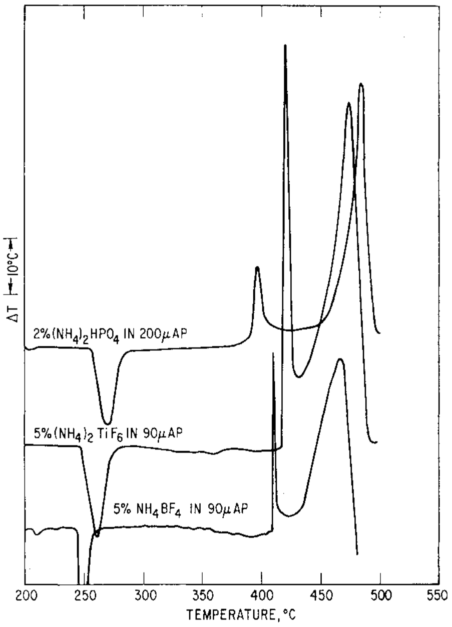

Fig. 7 DTA curves for AP containing other ammonium salt additives.

$$NH_4PF_6(c) = NH_3(g) + HF(g) + PF_5(g) \qquad (1)$$

Equation (1) is analogous to that used for the thermal decomposition of NH_4BF_4.

$$NH_4BF_4(c) = NH_3(g) + HF(g) + BF_3(g) \qquad (2)$$

Like HPF_6, HBF_4 is believed unstable and nonexistent in the gas phase.[12] The equation for the thermal decomposition of $(NH_4)_2TiF_6$ can be written in an analogous manner

$$(NH_4)_2TiF_6(c) = 2NH_3(g) + 2HF(g) + TiF_4(g) \qquad (3)$$

From Eqs. (1–3) it is clear that the decomposition of these ammonium salts of complex fluoro-anions at temperatures of interest in connection with AP is characterized by the formation of the gaseous fluoride, plus NH_3 and HF. The importance of these gaseous decomposition products in producing the observed inhibition of the first AP exotherm was tested experimentally in the following way. Instead of mixing NH_4PF_6 with AP, the desired quantity of solid NH_4PF_6 was placed at the bottom of the microglass tube used for the DTA measurements. Then, without mixing, the propellant-grade AP was placed above the crystals of NH_4PF_6. This microglass tube was inserted, as usual, in the heating block of the DTA system, and the heating procedure carried out in the customary manner at 115v. In this way only the vapors from the heated crystals of NH_4PF_6 reached the zone of AP in which the thermocouple was located. The DTA curves obtained were equivalent to the curve shown in Fig. 6 for the 1.5% mixture of NH_4PF_6 in AP. It is apparent, therefore, that the gases produced by heated NH_4PF_6 are efficient in inhibiting the first AP exotherm. Consequently, it is reasonable to consider the chemical behavior of the gaseous decomposition products in weighing the three questions raised in the previous paragraph concerning the inhibiting action of these additives on AP. One approach to explaining the higher first exotherm produced by $(NH_4)_2TiF_6$, and NH_4BF_4 additives is to note that the

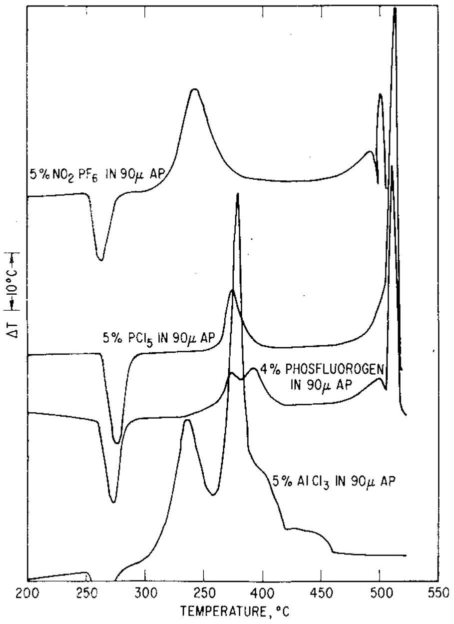

Fig. 8 DTA curves for AP containing Lewis acid additives.

TiF_4 and BF_3 gas released by decomposition of these salts can react exothermically with H_2O produced by exothermic decomposition of the NH_4ClO_4, but that the reaction of PF_5 (from NH_4PF_6) with H_2O is endothermic. The $\Delta H°$ of the reaction of one mole of these fluorides with H_2O at 298°K is −35 kcal/mole, −12 kcal/mole, and +22 kcal/mole, respectively,[13] for TiF_4, BF_3, and PF_5. On this basis, NH_4PF_6 would be expected, in agreement with the DTA curves of Fig. 6 and Fig. 7, to produce a smaller first exotherm than $(NH_4)_2$ TiF_6 or NH_4BF_4. Although this relative stability of PF_5 offers a possible explanation of the experimental results, the uncertainty[5–7] about the mechanism of AP decomposition obviously prevents accepting this explanation unequivocally.

Inasmuch as PF_5, BF_3, and TiF_4 were recognized to be Lewis acids,[11,12] the question arose whether simply using Lewis acids as additives with AP might not be more efficient than using ammonium salts such as NH_4PF_6. In Fig. 8, the DTA curves are shown for tests of the Lewis acids $AlCl_3$ and PCl_5 as additives. It was evident from these curves that $AlCl_3$ accelerated, rather than inhibited, the exothermic decomposition, and that PCl_5 did not inhibit the first exotherm. Phosfluorogen-A is a compound that evolves PF_5 gas when it is heated above 150°; it is a chlorbenzene diazonium hexafluorophosphate.[14] The DTA curve (Fig. 8) for 5% phosfluorogen-A added to AP indicated that the PF_5 gas evolved did not significantly inhibit the first AP exotherm. These results suggested that the NH_3 or HF gas formed concommitantly with the Lewis acid in accordance with Eqs. (1–3) may be necessary for the inhibiting action. Consequently, a DTA test was made of the inhibiting ability of 5% NO_2PF_6 salt, which can be expected to thermally decompose without the formation of NH_3 or HF

$$NO_2PF_6(c) = NO_2F(g) + PF_5(g) \qquad (4)$$

The DTA curve for 5% NO_2PF_6 in AP (Fig. 8) clearly showed that the first exotherm was not inhibited, but was somewhat catalyzed by the NO_2PF_6 additive. DTA tests with 2% and 5% NH_4F additive in AP exhibited poorer suppression of the first exotherm than any of the additives in Fig. 6 or 7. The results strongly indicate, therefore, that the cooperative action of a Lewis acid, such as PF_5, with NH_3 and/or HF is necessary in order to achieve maximum inhibition of the first AP exotherm.

Several tentative hyptheses can now be suggested as to the mechanisms of this inhibiting action. These hypotheses are consistent with some theories[5–7] of the mechanism of the decomposition and combustion of AP, and are based on known chemical properties of NH_3, HF, and Lewis acids such as PF_5 and BF_3. It is known that; 1) ammonia gas, at 60 psia, can suppress the first AP exotherm,[4] 2) Lewis acids can form complexes[11] with $HClO_4$, NH_3 or transition-metal compounds, and 3) a Lewis acid paired with HF is an extremely powerful proton donor (Ref. 15, page 86). A well received theory[5] of the decomposition and combustion of AP is based on the hypothesis that the controlling step is the transfer of a proton in solid NH_4ClO_4

$$NH_4{}^+ClO_4{}^-(c) = NH_3(a) + HClO_4(a) \qquad (5)$$

where the letter a denotes that the NH_3 and $HClO_4$ are adsorbed on the AP. The endothermic step, Eq. (5), is followed by exothermic steps involving the reaction of $HClO_4$. The action of NH_3 as an inhibitor can be rationalized on the basis of this theory by noting that excess NH_3, such as that produced by the decomposition of NH_4PF_6 or $(NH_4)_2$ HPO_4 additives, could reverse the rate controlling step, Eq. (5). Furthermore, the inhibiting action of NH_3 would be supplemented by the ability of PF_5 to form a molecular complex with $HClO_4$ and thereby suppress the combustion reactions of $HClO_4$ with NH_3 and other species. It is also possible that the Lewis acid paired with the HF suppresses the combustion reactions of $HClO_4$ by donating a proton to inhibit the dissociation of $HClO_4$ into H^+ and $ClO_4{}^-$. Similarly, the proton-donor ability of the HF-Lewis acid pair could inhibit the suggested[7] rate-controlling step for AP decomposition in which an electron is released from the perchlorate ion

$$ClO_4{}^- = ClO_4 + e \qquad (6)$$

The marked ability of the HF-Lewis acid pair to transfer protons to very weak bases could inhibit reaction Eq. (6) by promoting the competing reaction

$$H^+ + ClO_4{}^- = HClO_4 \qquad (7)$$

in which a proton is transfered to the very weak base $ClO_4{}^-$. Alternatively, this strong proton-donor ability may be consistent with the proposed NH_4ClO_4 decomposition mechanism[6] in which decomposition rate is correlated with electrical conductivity. The proton released by the Lewis acid-HF pair can neutralize electrons in AP to inhibit the decomposition. (Lewis acid-HF pairs produced by the thermal decomposition of salts such as NH_4PF_6 and NH_4BF_4 could accordingly be useful as powerful trappers and quenchers of free electrons in high-temperature gases.) The ability of Lewis acids to form complexes with transition-metal compounds could contribute to the inhibiting action since the studies to be described in a later section clearly show that compounds of certain transition metals have a very powerful effect in catalyzing the first AP exotherm.

Present uncertainties[5–7] with regard to the mechanisms for AP decomposition and combustion preclude proving at this time any explanation of the inhibiting action of such compounds as NH_4PF_6. Despite the absence of a proven mechanism for the effectiveness of NH_4PF_6 additive in suppressing the first exotherm, it is nevertheless possible to attempt to apply these results to practical problems involving extinguishable propellants and controllable motors. In fact, the promising results obtained with NH_4PF_6 additive in DTA tests have been communicated to contractors interested in these areas. As a consequence, tests of extinguishment in a motor and burning rates in bombs have now been made[16] with NH_4PF_6 added to an AP-fluorocarbon composite propellant.

The results of these combustion tests support the findings of the DTA tests (Fig. 6) that indicated premature reignition could be minimized and burning rates controlled by NH_4PF_6 additive. Prior to these contractor's combustion tests, our DTA studies of NH_4PF_6 additives in AP with polymeric FC binder present (Fig. 9) had shown that the inhibiting effect of NH_4PF_6 on the first AP exotherm was not destroyed by the presence of FC binder. The top two DTA curves in Fig. 9 compare the exothermic decomposition behavior of an AP-FC composite propellant before and after 2% NH_4PF_6 had been added. This additive succeeded in delaying the onset of the first exotherm to about 455°C. The bottom DTA curve of Fig. 9 exhibited the small first exotherm that is characteristic of NH_4PF_6 additive. For this test the fluorocarbon was present as Viton A. It can be seen, in the third DTA curve, that the first exotherm was quite prominent when NH_4PF_6 was not added to the mixture of 17% Viton A in 83% AP.

DTA Evaluation of Catalysts for AP Decomposition and Combustion

It is well known that the addition of 1% or more of certain transition-metal oxides to AP can increase the burning rate of AP propellants.[5] Accordingly, it was considered important in this investigation to test the effect on the first AP exotherm of low concentrations of transition-metal ions that could be present as traces of impurities in propellant-grade AP. The corresponding DTA tests clearly demonstrated (Fig. 10) that even low levels of copper salt contamination can have highly significant effects in terms of enlarging the undesirable first exotherm and forming the exotherm at lower temperatures. Analytical studies[3] of the reignition process show that the danger of premature reignition of extinguishable propellants is markedly increased by enlarging the first exotherm and causing it to occur at lower temperatures.

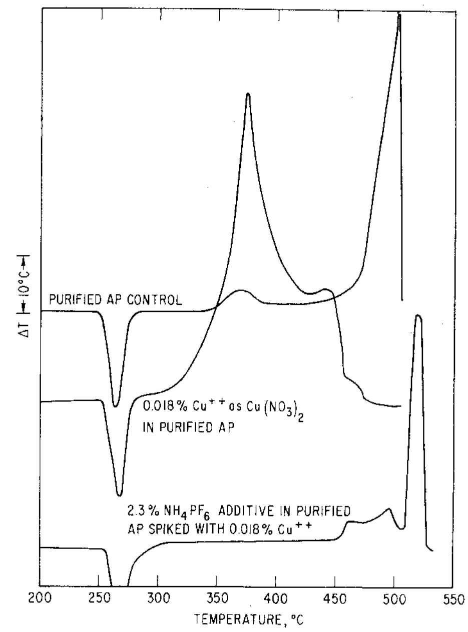

Fig. 10 Catalytic effect of traces of $Cu(NO_3)_2$.

The DTA curves of Fig. 10 are representative of the many DTA tests made with AP to which low concentrations of copper salts were added. It is evident in Fig. 10 that 0.018% of Cu^{++} (as cupric nitrate) added to AP was sufficient to catalyze the production of a first exotherm that was much larger than the important second exotherm, which normally corresponds to the combustion exotherm. Moreover, the onset of the first exotherm was lowered to about 300° compared to 345° for the first exotherm of the purified AP control specimen. Consequently,[3] even this low level of copper impurity should greatly increase the hazard of premature reignition. Adding 0.036% Cu^{++}, as copper nitrate, to the purified AP was sufficient to cause the combustion exotherm to combine with that of the first exotherm. Further DTA tests demonstrated that the addition of only 0.004% Cu^{++}, as copper nitrate, was sufficient to quadruple the area of the first exotherm relative to that of the purified AP control, and to lower the temperature of the onset of the first exotherm by 35°. Adding 0.1% Cu^{++} to the AP increased its burning rate sufficiently to shatter the microglass DTA tubes when the temperature of the heating block reached 360°.

It was shown previously in this paper that NH_4PF_6 additive is effective in inhibiting the first AP exotherm. The efficiency of NH_4PF_6 as an inhibitor is demonstrated by the

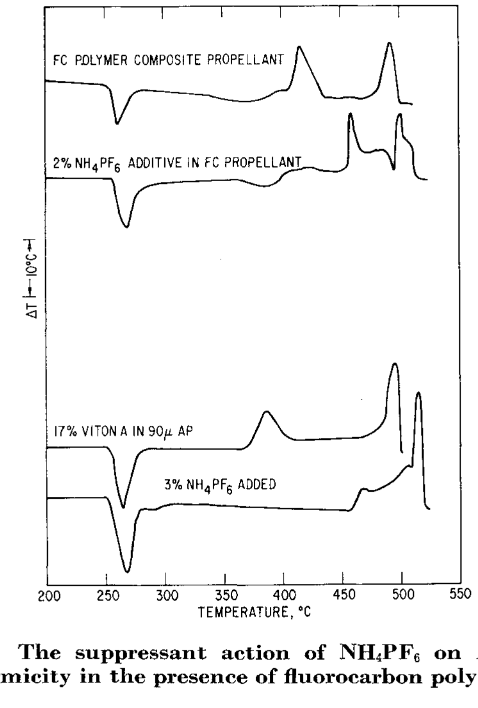

Fig. 9 The suppressant action of NH_4PF_6 on AP exothermicity in the presence of fluorocarbon polymers.

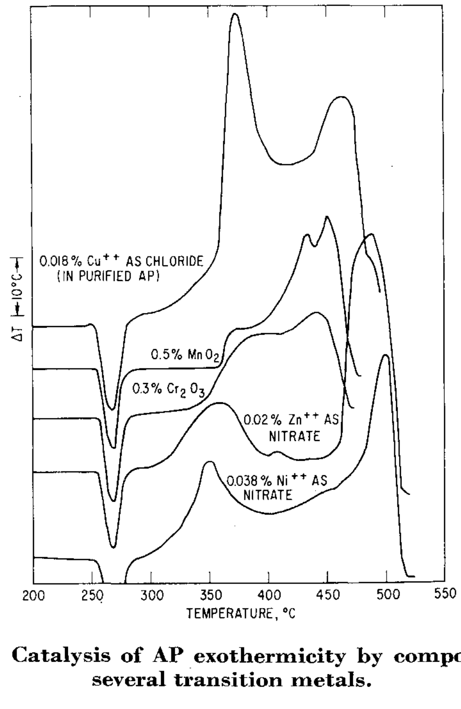

Fig. 11 Catalysis of AP exothermicity by compounds of several transition metals.

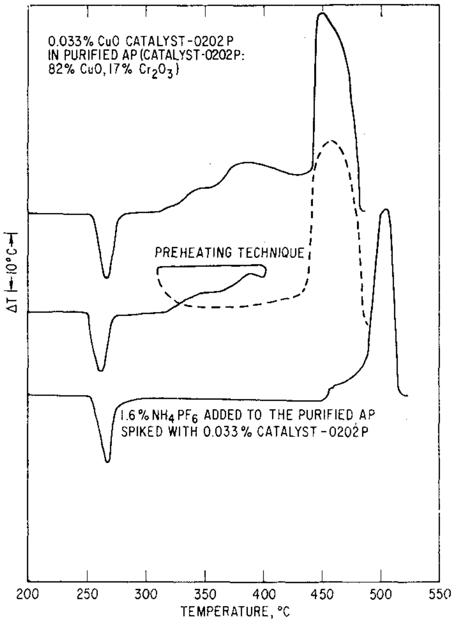

Fig. 12 Suppression of catalyst action by NH_4PF_6 additive.

bottom DTA curve in Fig. 10 where it can be seen that even the large first exotherm produced by spiking AP with 0.018% Cu^{++} was successfully inhibited by NH_4PF_6 additive. Moreover, the combustion exotherm peak was shifted back to 515° compared with 440° in the AP doped with Cu^{++}.

The very strong catalytic action exerted on the first AP exotherm by $Cu(NO_3)_2$ suggested, of course, that DTA measurements should be made of the effect of adding other transition-metal compounds to AP. Some of the results of a series of such DTA measurements are presented in Fig. 11. The top DTA curve indicated that the catalytic effect of $CuCl_2$ was somewhat similar to that of $Cu(NO_3)_2$. This suggests that the ability of traces of cupric salt impurities to enlarge the first exotherm and thereby increase the danger of premature reignition may not be particularly dependent on the anion constituent of the cupric salt. The second DTA curve in Fig. 11 indicated that traces of MnO_2 had a much smaller catalytic effect on the first exotherm. Zinc nitrate, as shown by the corresponding DTA curve in Fig. 11, was not quite as strong a catalyst as $CuCl_2$ and $Cu(NO_3)_2$, but it was stronger than MnO_2, Cr_2O_3 or $Ni(NO_3)_2$. The catalytic action of Zn^{++} is rather similar to that of Cu^{++} since increasing the Zn^{++} concentration in AP to 0.1% caused the deflagration of the AP to occur at 340°C by coalescing the first and second exotherms. The bottom curve of the figure suggested that $Ni(NO_3)_2$ was not as strong a catalyst for the first AP exotherm as $Zn(NO_3)_2$ and $Cu(NO_3)_2$ since a higher concentration of Ni^{++} was required to produce a catalytic effect equivalent to that obtained with Cu^{++} or Zn^{++} salts. Moreover when the concentration of Ni^{++}, as $Ni(NO_3)_2$, in AP was raised to 0.2% the DTA curve did not exhibit the coalescence of the first and second AP exotherm characteristic of the effect of 0.1% Cu^{++} or Zn^{++} contamination. DTA tests were made on AP containing 1% Fe_2O_3, ferrocene, or FeF_3. None of these iron compounds exhibited outstanding catalytic action; the first exotherm remained smaller than that observed (Fig. 11) with 0.038% Ni^{++} additive.

Harshaw catalyst 0202 P has been tested widely as a burning-rate catalyst for AP.[5] It, therefore, was of interest to examine its catalytic activity by our DTA techniques. The top DTA curve in Fig. 12 contained a broad first exotherm, attributable to the effect of the catalyst. The second DTA curve demonstrated that the previously developed preheating technique can suppress this catalytically enlarged first exotherm if the AP is heated to about 405°. The bottom curve illustrated the outstanding ability of NH_4PF_6 additive to inhibit the first exotherm even in the presence of $CuO\text{-}Cr_2O_3$ catalyst. Moreover, in this case the NH_4PF_6 also inhibited the second exotherm so that its peak occurred near 505° (similar to that of the AP control in Fig. 6) rather than at 450° as in the top DTA curve of Fig. 12.

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