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Inhibitors and Catalysts for the Exothermic Decomposition of Ammonium Perchlorate

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Prepared for **SPACE AND MISSILE SYSTEMS ORGANIZATION**
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report, published by The Aerospace Corporation, El Segundo, California, under Air Force Contract F04701-69-C-0066, documents research carried out from July 1968 to June 1969.

A grateful acknowledgement is made to Vera M. Armstrong and Harry J. Sorensen for the very efficient editing of this report. The authors wish to thank Dr. A. Muraszew, San Bernardino Operations, for many valuable discussions.

This report was submitted on 19 February 1970 to Lt John F. Turk, SMTAE, 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.

John F. Turk

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ABSTRACT

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). It was 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. A series of tests was made of the catalytic effect on this exotherm of traces of impurities in 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. The burning rate was increased by adding 0.1% Cu or Zn salts. Independent tests in a combustion-bomb and in a motor have demonstrated the increased extinguishment reliability suggested by the thermal analysis curves. The effect on AP decomposition and combustion exotherms has also been tested for a series of additives consisting of other ammonium salts, flame retardants, Lewis acids, and transition metal compounds.

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I. INTRODUCTION

Tests of developmental, controllable solid-propellant motors had shown that sometimes the propellant failed to extinguish after shutdown. Furthermore, premature reignition sometimes occurred before the scheduled reignition. Such malfunctions cause mission failure. A laboratory investigation was begun, therefore, with the objective of finding additives or techniques for improving extinguishment reliability and reducing premature reignition. The achievements of the initial phases of this investigation are described in Ref. 1. Much of the initial effort was centered on the problem of inhibiting the first exotherm of AP, since suppressing the first AP exotherm inhibits premature reignition and enhances extinguishment reliability. This report summarizes a recent series of differential thermal analysis (DTA) measurements that have led to a considerable improvement in additives for inhibiting the undesirable first exotherm of AP. This new series of tests also provides some of the answers to questions raised in Ref. 1 about the possible importance of transition-metal compounds in catalyzing the formation of the troublesome first exotherm.

One discovery demonstrated in Ref. 1 was that the characteristic first exotherm of propellant-grade AP could be inhibited or almost eliminated by a preheating technique. In this technique the AP is heated to a temperature just beyond that of the first exotherm (e.g., 385°C in the case of 90-μ AP) and then cooled. Several additives of the endothermic type, such as hexachlorbenzene or NH_4Cl (Ref. 1), were tested as inhibitors of the first AP exotherm, but were unimpressive for the most part. However, 5% NH_4BF_4 additive inhibited the onset of the first AP exotherm to ∿ 407°C, although the exotherm at that temperature was quite strong. The improved inhibition obtained with other ammonium salts that contain complex halogen anions is described in this report.

It was pointed out in Ref. 1 that traces of transition-metal compounds as impurities in AP might possibly catalyze the unwanted first exotherm. Accordingly, the series of studies reported herein included DTA measurements of the catalytic effects of transition-metal compounds added intentionally to a purified specimen of AP. These measurements disclosed that very low concentrations of certain impurities can cause the undesirable first exotherm and can apparently increase burning rates. The ability of additives and the preheating technique to suppress the catalytic effects of transition-metal compounds was also tested.

II. EXPERIMENTAL PROCEDURE

The experimental procedure was similar to that used in the DTA studies of the effect of additives on the exothermic decomposition of AP (Ref. 1). The additive powders were thoroughly dry-mixed with the AP. All transition-metal compound additives were of reagent grade, unless otherwise specified. The ammonium salts of complex halogen anions (e.g., NH_4PF_6, $(NH_4)_2TiF_6$, NH_4BF_4, and NH_4SO_3F) were obtained from the Ozark-Mahoning Company, Tulsa, Oklahoma. CuO-Cr_2O_3 catalysts were donated by the Harshaw Chemical Company, Cleveland, Ohio. Purified NH_4ClO_4 (low alkali metal, low chlorate) was donated by the American Potash and Chemical Corporation, Los Angeles, California, which also manufactured the 90-μ and 200-μ AP. The fluorocarbon composite AP propellant and the Viton A were donated by the Wasatch Division of Thiokol Chemical Corporation. Dechlorane was donated by the Hooker Chemical Company, and tricresyl phosphate (Kronitex AA grade) was donated by the FMC Corporation.

Because of the explosion hazard associated with heated AP, the differential thermal analyses were made by a micro technique 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[1] micro heating block. Micro glass beads in another sample 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 temperature difference (ΔT) between the sample and the reference material. The sample temperature and the ΔT (Fig. 1) were recorded on an X-Y recorder with ΔT on the Y-axis at a scale of 10°C/in.

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[1] Differential Thermal Analyzer Dept., Instrument Products Division, E. I. duPont de Nemours and Company, Inc., Wilmington, Delaware.

The heating block, cartridge heater, and block support were the standard DuPont[2] micro DTA items. The block was a 7/8-in.-diam aluminum cylinder, 1.5 in. high. It contained two adjacent vertical cylindrical cavities, 2-mm diam and 25 mm deep, for the sample and the reference micro glass tubes. At the center of the block, a cartridge heater was placed in a cylindrical cavity (axis parallel to axis of block), 3/8-in. diam and 1 in. deep. The cartridge heater was rated at 55 W for 110 V. In order to maximize the heating rate, the heating cartridge was operated at 115 V from a variable transformer. (The rapid heating rate was considered desirable because heating rates in deflagrating solid propellants are high.) As a result, the temperature rise of the micro furnace was 50°C/min at 350°C (near the temperature of the onset of the first exotherm). This compares favorably with the 10 or 20°C/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 micro furnace. The measured heating rates, in degrees centigrade per minute, at higher temperatures were: 46°C at 375°C, 41°C at 400°C, 36°C at 425°C, 30°C at 450°C, 25°C at 475°C, and 19°C at 500°C. Measured heating rates at temperatures lower than 350°C were: 59°C at 300°C and 55°C at 325°C.

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[2] Differential Thermal Analyzer Dept., Instrument Products Division, E. I. duPont de Nemours and Company, Inc., Wilmington, Delaware.

III. RESULTS AND DISCUSSION

A. DTA TEST OF INHIBITORS

A series of DTA tests was made of the effectiveness of ammonium salts of complex fluoro anions for inhibiting the first AP exotherm. In this series of tests, the most effective additive was ammonium hexafluorophosphate. A typical DTA curve for 1.5% NH_4PF_6 mixed with 90-μ AP is shown in Fig. 1. Comparison with the top curve of Fig. 1 showed that 1.5% NH_4PF_6 inhibited the onset of the first exotherm by 85°C. 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 suggested (Refs. 2 and 3) that thermal radiation from the hot regions of the motor, after extinguishment, can combine with exothermicity from the residual solid propellant to raise its temperature and, thereby, produce the troublesome premature reignition. The inhibiting action of NH_4PF_6 additive on the premature exothermicity of propellant-grade AP can, therefore, suppress the tendency for premature reignition of the propellant. The superiority of NH_4PF_6 may also be seen by comparison of Fig. 1 with the DTA curves in Fig. 2, where it is evident that the heights of the first exotherms obtained with 90-μ AP mixed with 5% $(NH_4)_2TiF_6$, 5% NH_4BF_4, or 2% $(NH_4)_2HPO_4$ were much greater than the heights obtained with NH_4PF_6 additive. Furthermore, the additives shown in Fig. 2 were 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° to 57°C, compared with the 85°C inhibition achieved with 1.5% NH_4PF_6. The DTA curves obtained with 5% NH_4PF_6 in 90-μ AP were similar to those shown in Fig. 1 for 1.5% NH_4PF_6. Lowering the weight-percent of NH_4PF_6 in AP to 0.5% (Fig. 1) reduced the inhibition of the onset of the exotherm to 52°C, 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. As a rough estimate, NH_4PF_6 was at least ten times more effective than NH_4BF_4 in inhibiting the first exotherm of AP since 0.5% NH_4PF_6

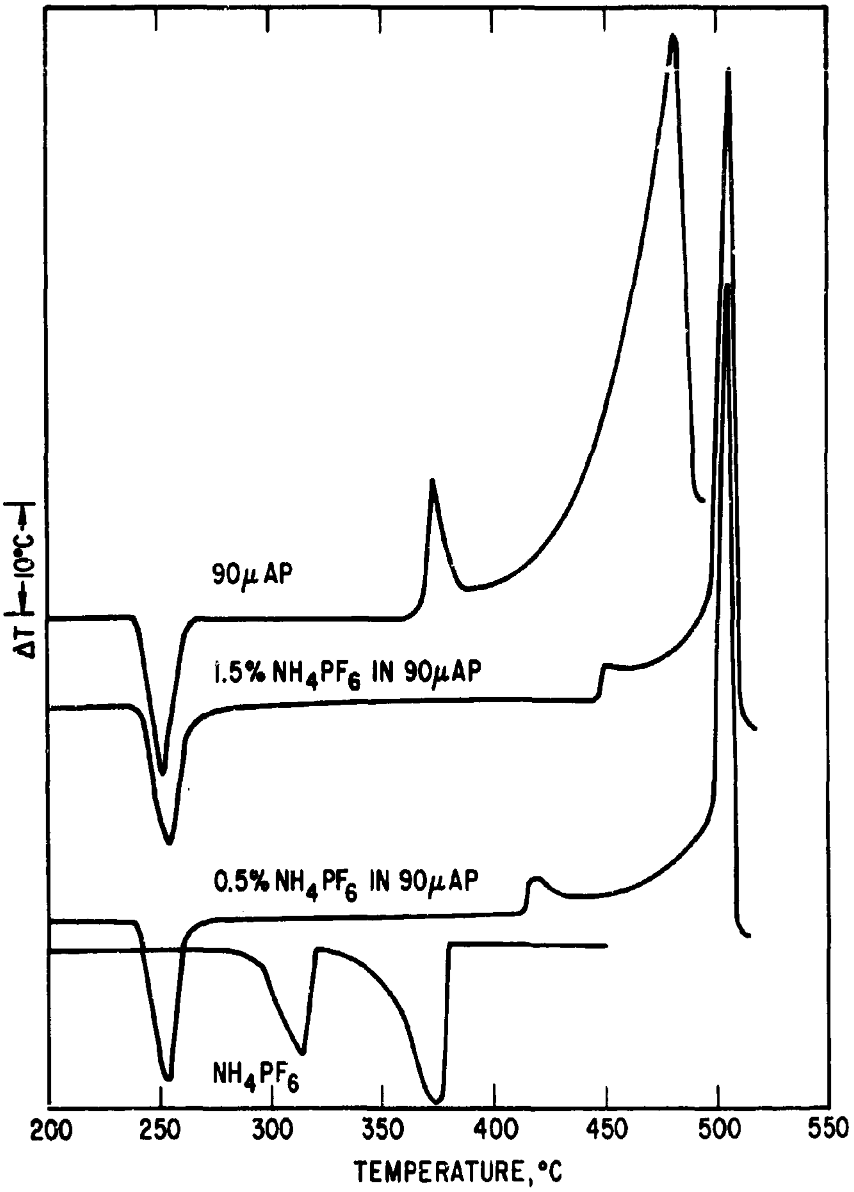

Fig. 1. DTA Curves that Demonstrate the Inhibiting Ability of Ammonium Hexafluorophosphate in AP

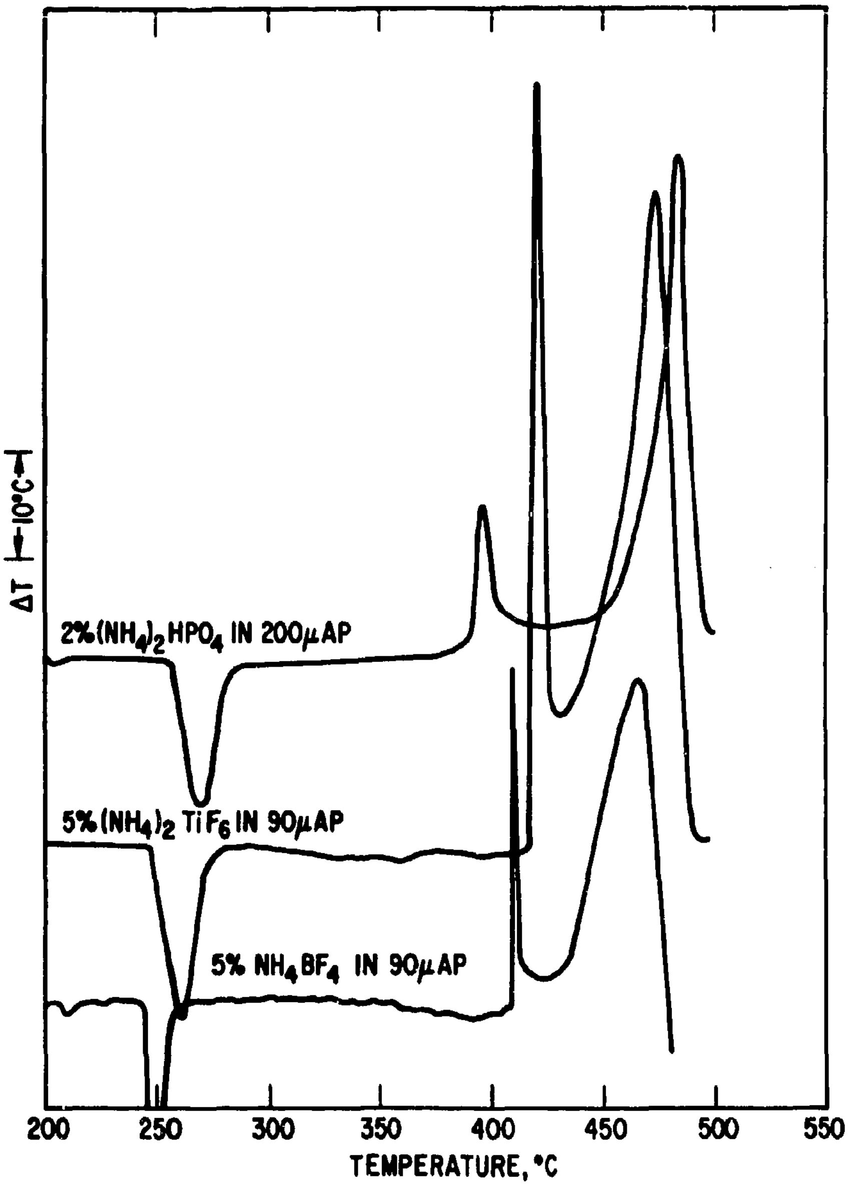

Fig. 2. DTA Curves for AP Containing Other Ammonium Salt Additives

inhibited the onset of the exotherm by 52°C compared with 47°C for 5% NH_4BF_4. Furthermore, NH_4PF_6 lowered the height of the first exotherm, reducing the likelihood of premature reignition, whereas 5% NH_4BF_4 additive increased the height of the exotherm.

The practical implications of these results (Figs. 1 and 2) are rather clear in terms of suggesting that NH_4PF_6 merits testing in motors as an additive for minimizing inadvertent reignition of extinguishable propellants. The DTA curves in these two figures, nevertheless, raise the following basic questions that, for the most part, are highly difficult to answer since the mechanism for the exothermic decomposition of AP itself has not been established (Refs. 4-7).

1. Why are the first AP exotherms observed with NH_4BF_4 or $(NH_4)_2$ TiF_6 additives higher than those observed when NH_4PF_6 additive is used?
2. Are there simpler halogen compounds that would 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 (Refs. 1 and 4), must be considered. The DTA curve for NH_4PF_6 (with no AP present) is the bottom curve in Fig. 1, and the DTA curves for NH_4BF_4, NH_4Cl, and $(NH_4)_2CO_3$ are shown in Fig. 7 of Ref. 1. The thermal decomposition of NH_4PF_6 is represented by the second endotherm of its DTA curve in Fig. 1 since the first endotherm (as in the case of AP) is apparently produced by a solid state transition (Refs. 8 and 9). The second endotherm of NH_4PF_6 begins at about 330°C and reaches its minimum (probably corresponding the maximum rate of decomposition) near 375°C. It is believed (Refs. 8 and 9) 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.

$$NH_4PF_{6_c} = NH_{3_g} + HF_g + PF_{5_g} \quad (1)$$

This equation is analogous to that used for the thermal decomposition of NH_4BF_4

$$NH_4BF_{4_c} = NH_{3_g} + HF_g + BF_{3_g} \tag{2}$$

The equation for the thermal decomposition of $(NH_4)_2TiF_6$ can be written in an analogous manner

$$(NH_4)_2\ TiF_{6_c} = 2\ NH_{3_g} + 2\ HF_g + TiF_{4_g} \tag{3}$$

Equations (1) through (3) indicate 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 the 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 micro glass tube used for the DTA measurements. Then, without mixing, the propellant-grade AP was placed over the crystals of NH_4PF_6. The micro glass tube was inserted, as usual, in the heating block of the DTA system, and the heating procedure carried out in the customary manner at 115 V. In this way, only the vapors from the heated crystals of NH_4PF_6 reached the zone of 90-μ AP (or 200-μ AP) in which the thermocouple was located. The DTA curves obtained were equivalent to the curve shown in Fig. 1 for the 1.5% mixture of NH_4PF_6 in AP. It is apparent 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 explanation for the high first exotherm produced by $(NH_4)_2\ TiF_6$ and NH_4BF_4

additives is that the 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_4 PF_6) with H_2O is endothermic. The ΔH° of the reaction of these fluorides with H_2O (at 298°K, Ref. 10) is -35 kcal/mole, -12 kcal/mole, and +22 kcal/mole, respectively, for TiF_4, BF_3, and PF_5. On this basis, NH_4PF_6 would be expected to produce a smaller first exotherm than $(NH_4)_2$ TiF_6 or NH_4BF_4, in agreement with the DTA curves of Figs. 1 and 2. The greater exothermicity of the reactions of BF_3 and TiF_4 is also indicated by the instability of fluoborates and fluosilicates in boiling water, whereas hexafluorophosphates can be boiled for a long time in a strong alkali without decomposition (Ref. 11, p. 787). The DTA curve for AP mixed with 5% $(NH_4)_2$ SiF_6 is similar to that for 5% $(NH_4)_2$ TiF_6 (Fig. 2). Although, this relative stability of PF_5 offers a possible explanation of the experimental results, the uncertainty (Refs. 4 through 7) concerning the mechanism of AP decomposition precludes accepting this explanation unequivocally.

Inasmuch as PF_5, BF_3 and TiF_4 were recognized to be Lewis acids (Refs. 8 and 9), 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. 3, the DTA curves are shown for tests of the Lewis acids $AlCl_3$ and PCl_5 mixed with 90-μ AP. It is 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 (Ref. 12) is a compound that evolves PF_5 gas when heated above 150°C; it is a chlorbenzene diazonium hexafluorophosphate. The DTA curve (Fig. 3) for 4% phosfluorogen-A added to AP indicated that the PF_5 gas evolved did not significantly inhibit the first AP exotherm. These results suggest that the NH_3 or HF gas formed concomitantly with the Lewis acid polyhalide in accordance with Eqs. (1) through (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

$$NO_2PF_{6_c} = NO_2F_g + PF_{5_g} \qquad (4)$$

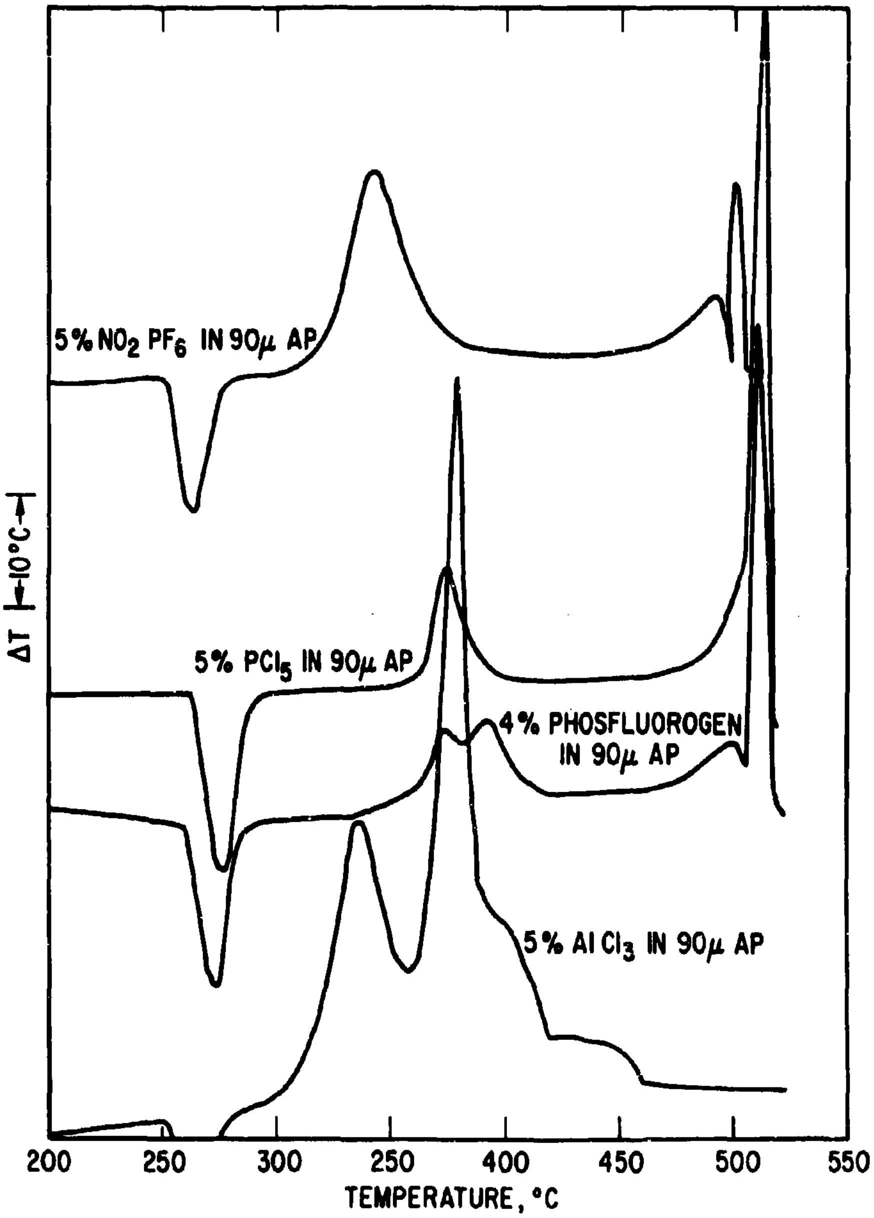

Fig. 3. DTA Curves for AP Containing Lewis Acid Additives

The DTA curve for 5% NO_2PF_6 in AP (Fig. 3) clearly shows 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 Figs. 1 or 2. This series of DTA measurements indicates that the cooperative action of a Lewis acid with NH_3 or HF is necessary in order to achieve efficient inhibition of the first AP exotherm.

Several tentative hypotheses are suggested as to the mechanisms of this inhibiting action. These hypotheses are consistent with some theories (Refs. 4 through 7) of the mechanism of the decomposition and combustion of AP and are based on the 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 (Refs. 1 and 13)
2. Lewis acids can form complexes (Ref. 8) with $HClO_4$, NH_3, and transition-metal compounds
3. A Lewis acid paired with HF is an extremely powerful proton donor (Ref. 14, p. 86).

A recent, well-received theory (Refs. 4 and 15) 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 subscript a denotes NH_3 and $HClO_4$ 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 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 that otherwise would produce the exotherm. It is also possible that the proton-donor ability of the HF-Lewis acid pair could inhibit the suggested (Ref. 7, p. 28) rate-controlling step for AP decomposition in which an electron is released from the perchlorate ion

$$ClO_4^- = ClO_4 + e \tag{6}$$

The marked ability of the HF-Lewis acid pair to transfer protons to very weak bases (Ref. 12) could inhibit reaction (6) by promoting the competing reaction

$$H^+ + ClO_4^- = HClO_4 \tag{7}$$

in which a proton is transferred to the very weak base ClO_4^-. Alternatively, this strong proton-donor ability may be consistent with the proposed NH_4ClO_4 decomposition mechanism (Ref. 5) in which the decomposition rate is correlated with electrical conductivity. The proton released by the Lewis acid-HF pair can neutralize electrons and negative charge carriers in AP to inhibit the decomposition. (Lewis acid-HF pairs produced by the thermal decomposition of salts such as NH_4PF_6 and NH_4PF_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 (Ref. 8) with transition-metal compounds would contribute to the inhibiting action since the studies described in a later section of this report clearly show that the compounds of certain transition-metals have a very powerful effect in catalyzing the first AP exotherm.

Uncertainties with regard to the mechanism of AP decomposition probably 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. In fact, the promising results obtained with NH_4PF_6 additive in DTA tests have been communicated to contractors interested in controllable solid-propellant motors. As a consequence, tests of extinguishment and burning rates have now been made[3] with 1% NH_4PF_6 added to an AP-fluorocarbon composite propellant. The results of these combustion tests support the findings of the DTA tests (Fig. 1) that indicated premature reignition could be minimized and burning rates controlled by NH_4PF_6 additive. Prior to these contractors' combustion tests, our DTA studies of NH_4PF_6 additives to AP in the presence of polymeric fluorocarbon (FC) binder had shown that the inhibiting effect of NH_4PF_6 on the first AP exotherm was not destroyed by the presence of FC binder (Fig. 4). The top two DTA curves in Fig. 4 compare the exothermic decomposition behavior of an AP-FC composite propellant before and after 2% NH_4PF_6 has been added. This additive succeeded in delaying the onset of the first exotherm to ∿455°C; the exotherm was sharper than was normally obtained (Fig. 1) with NH_4PF_6 . This may have been a result of the presence of readily oxidizable polymerizing and cross-linking organic compounds in this formulation of FC polymer. The bottom DTA curve of Fig. 4 exhibited the small, first exotherm that is characteristic of NH_4PF_6 additive. For this test, the fluorocarbon was Viton A. It can be seen, in the third DTA curve, that the first exotherm was quite prominent when 3% NH_4PF_6 was not added to the mixture of 17% Viton A in 83% AP.

The initial additive suggested as a possible suppressant for the premature exothermicity of AP was Dechlorane, a chlorinated hydrocarbon sold as a flame retardant by the Hooker Chemical Company. The DTA curve (Fig. 5) for 2% Dechlorane mixed in 90-μ AP indicated that this additive was considerably less efficient than NH_4PF_6 in inhibiting the first exotherm of AP. Dechlorane was more effective than 5% hexachlorbenzene (Ref. 1, Fig. 8). 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 90-μ AP. Although the DTA curve showed that 5% tricresyl phosphate raised the

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[3] J. Hepworth, Private Communication. Thiokol Chemical Corporation, Wasatch, Utah (January 1969).

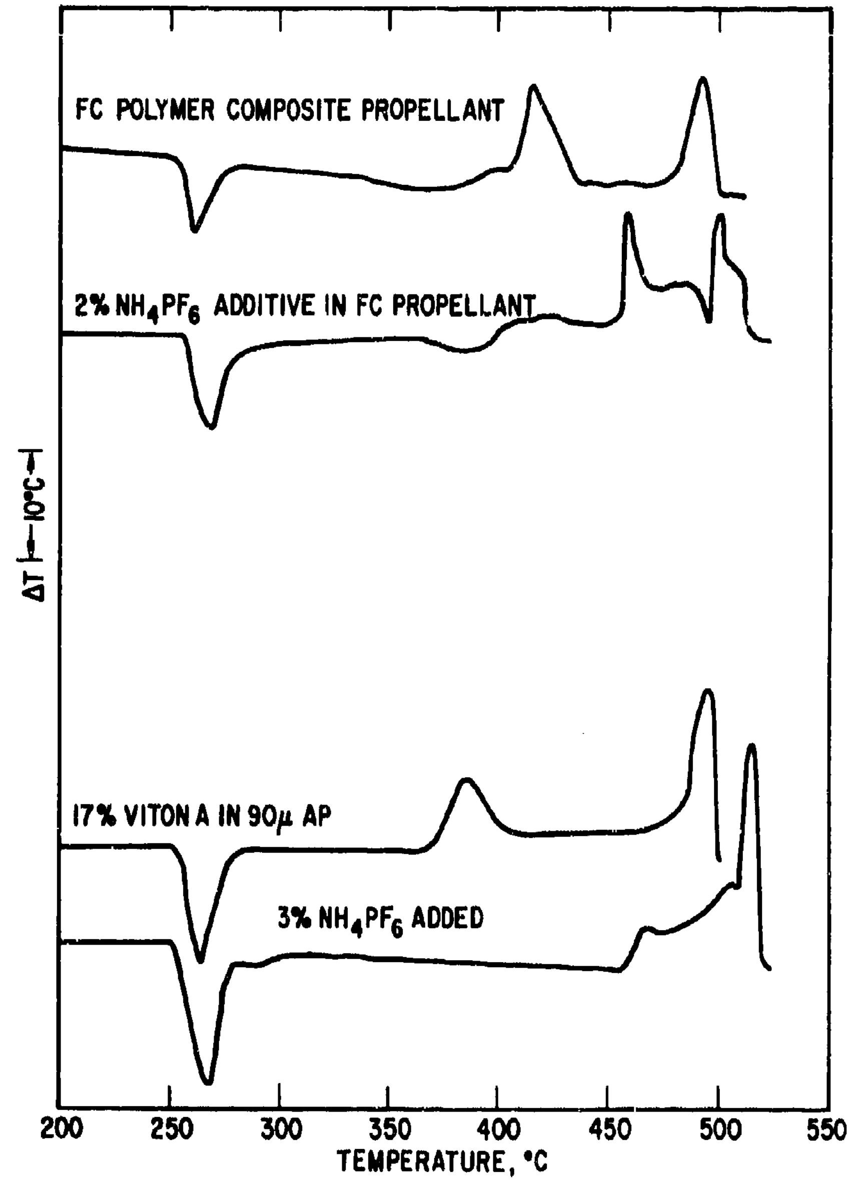

Fig. 4. The Suppressant Action of NH_4PF_6 on AP Exothermicity in the Presence of Fluorocarbon Polymers

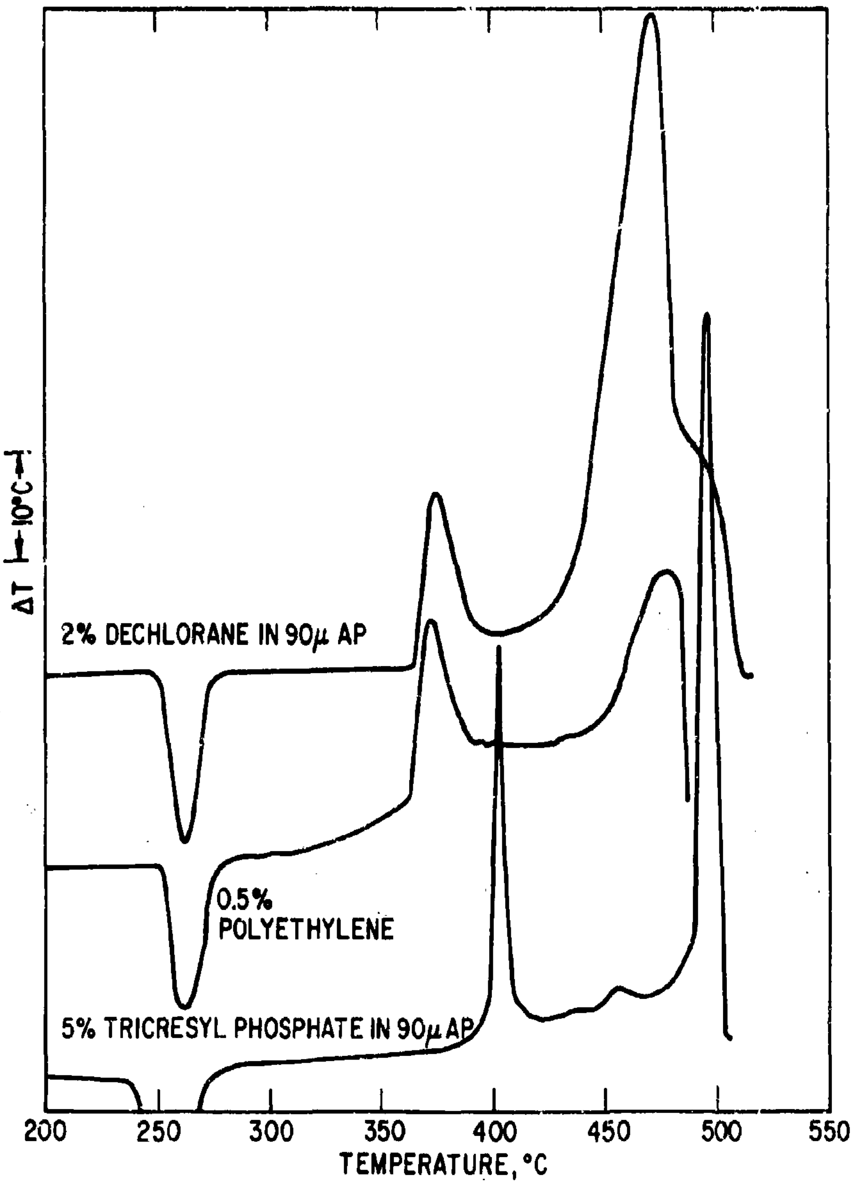

Fig. 5. The Effect of Flame Retardants and Polyethylene on AP Exothermicity

temperature of the onset of the first AP exotherm to ~390°C, this additive was apparently not as efficient as NH_4PF_6 since the first exotherm (Fig. 5) was quite high and the inhibition of the onset of this exotherm was less than that obtained with 1.5% NH_4PF_6, or even 0.5% NH_4PF_6. The relative ineffectiveness of the organic compounds, dechlorane and tricresyl phosphate, might be due in part to the exothermicity generated by the ability of AP to oxidize carbon and hydrogen groups. The exothermicity generated by even a low concentration of hydrocarbon is illustrated in Fig. 5 by the DTA curve for 0.5% polyethylene powder mixed with 90-μ AP. It can be seen that this level of combustible hydrocarbon produced a significant enlargement of the first exotherm, when compared with that of the 90-μ AP control DTA curve in Fig. 1. This augmentation of the first exotherm was small, relative to that produced by adding some transition-metal compounds to AP, as will be demonstrated by the results presented in the next section.

B. 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 accelerate the burning rate of AP propellants (Refs. 4 and 7). 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 demonstrate (Figs. 6 and 7) that even low levels of copper salt contamination have highly significant effects in terms of enlarging the undesirable first exotherm and causing the exotherm to occur at lower temperatures. Analytical studies (Ref. 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 appear at lower temperatures.

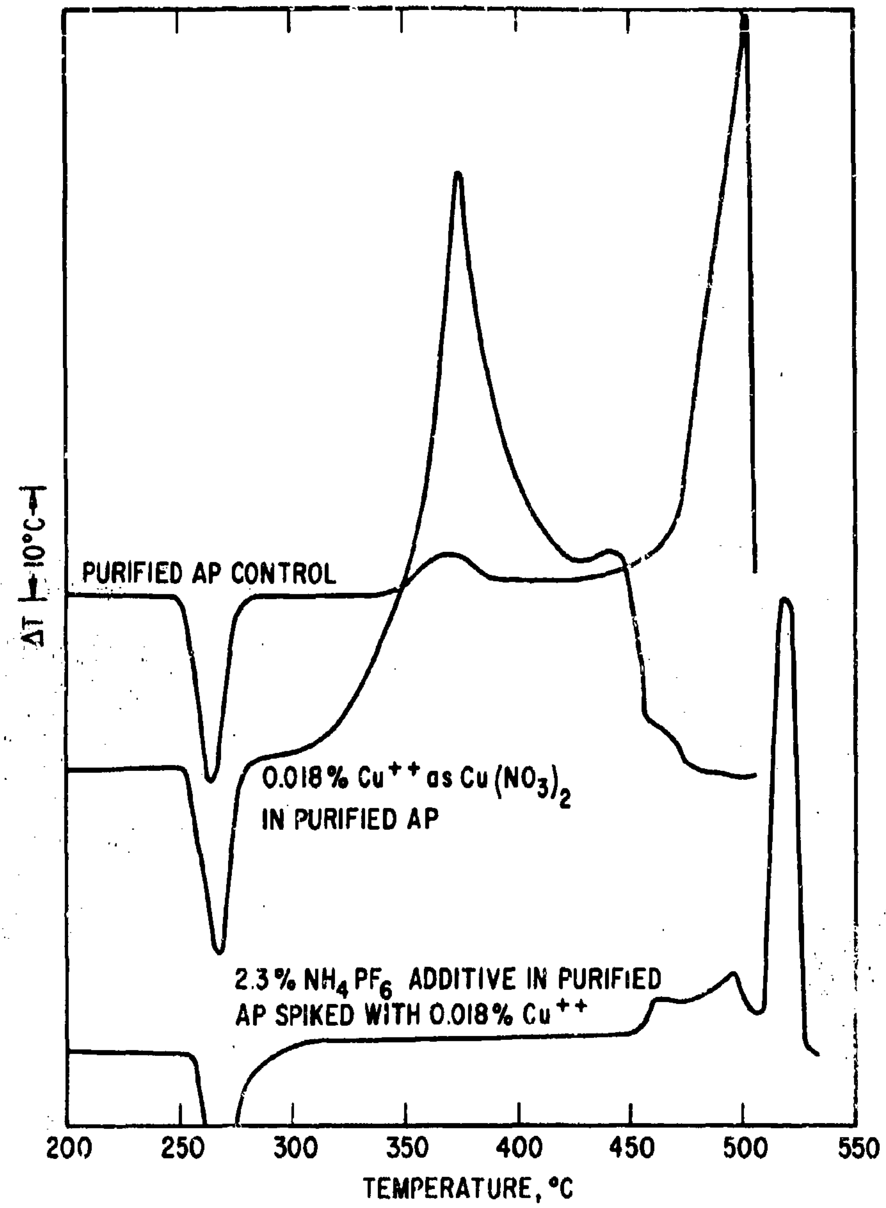

Fig. 6. The Catalytic Effect of Traces of $Cu(NO_3)_2$

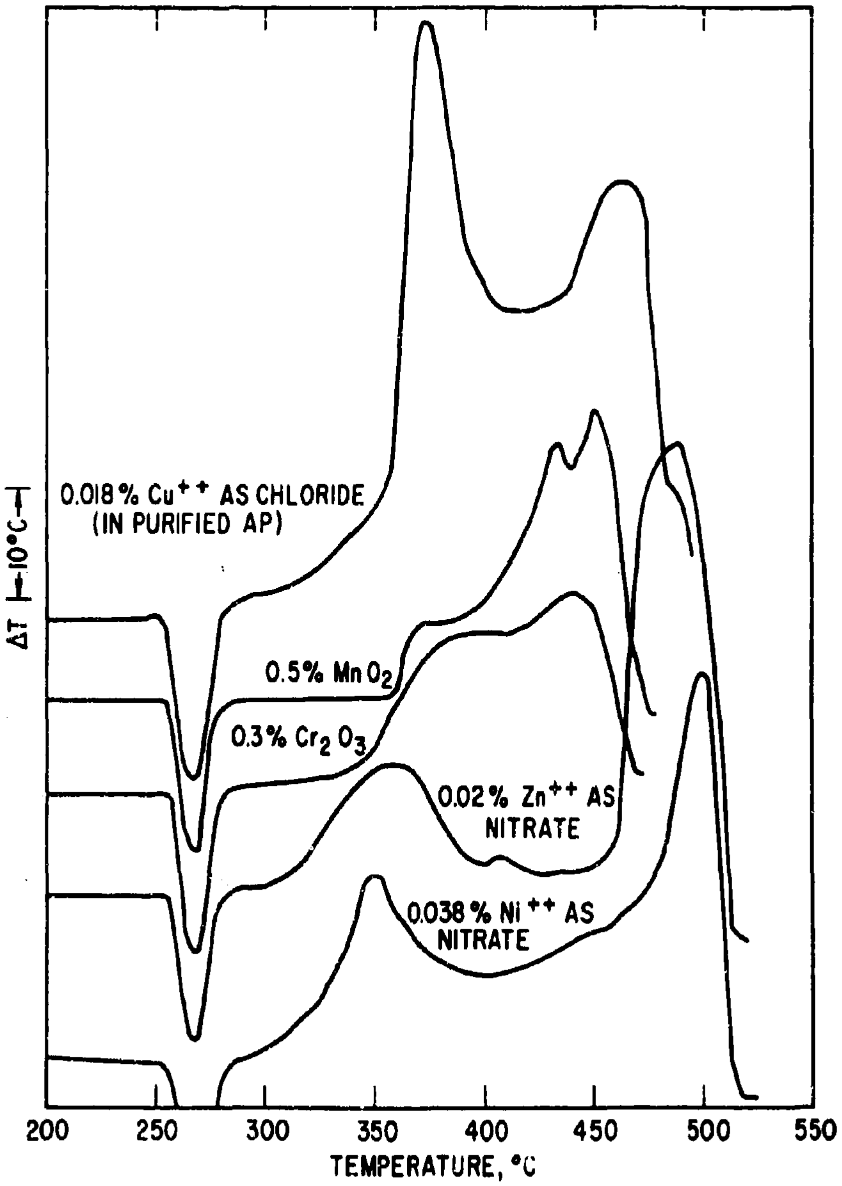

Fig. 7. Catalysis of AP Exothermicity by Compounds of Several Transition Metals

The DTA curves of Fig. 6 are representative of the many DTA tests made with AP to which low concentrations of copper salts were added. It is evident in Fig. 6 that only 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 300°C compared to 345°C for the first exotherm of the purified AP control specimen. Consequently (Ref. 2), even this low level of copper impurity should greatly increase the hazard of premature reignition. Adding 0.036% Cu^{++}, as cupric nitrate, to the purified AP was sufficient to cause the combustion exotherm to combine with 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°C. Adding 0.1% Cu^{++} to the AP increased its burning rate sufficiently to shatter the micro glass tube when the temperature of the heating block reached 360°C. Accordingly, it is probable that copper salts such as the nitrate will be efficient and economical burning-rate catalysts.

It was previously shown in this report that NH_4PF_6 additive is effective in inhibiting the first AP exotherm. The outstanding effectiveness of NH_4PF_6 as an inhibitor was demonstrated by the bottom DTA curve in Fig. 6 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°C compared with 440°C in the AP spiked with Cu^{++}. It is planned to make a related series of DTA measurements to determine the concentrations of NH_4PF_6 additive required to suppress the catalytic effects of various concentrations of copper-salt additives.

The very strong catalytic action exerted on the first AP exotherm by $Cu(NO_3)_2$ suggested 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. 7. 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. 7 indicates that MnO_2 had a much smaller catalytic effect than an equal concentration of $CuCl_2$. DTA curves for 0.5% $MnCl_2$ and 0.5% $KMnO_4$ additives in the purified AP also show a much smaller catalytic effect than that obtained with $CuCl_2$. The third DTA curve of Fig. 7 demonstrates that Cr_2O_3 was considerably weaker than $CuCl_2$ in catalyzing the first exotherm. Zinc nitrate, as shown by the corresponding DTA curve in Fig. 7, 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^{++} was 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 Fig. 7 suggests 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^{++} additive.

A possible mechanism for the catalytic effect of transition-metal compounds on the first AP exotherm depends on the tendency of these compounds to react with NH_3 to form complexes. In order to write an equation for this mechanism so as to illustrate the possible role of the transition metal compound, it is convenient to write AP structurally as $O_3ClOHNH_3$.

$$O_3\,ClOHNH_3 + CuCl_2 \rightarrow O_3ClOH\cdots NH_3\cdots CuCl_2 \rightarrow HClO_4 + H_3N\cdot CuCl_2 \qquad (8)$$

where the transition state suggests the competition between $HClO_4$ and $CuCl_2$ for the NH_3 molecule. The ability of a transition metal salt to promote this dissociation of NH_4ClO_4 would depend on the strengths of the NH_3 complex with the transition metal salt. The heats of formation (Ref. 16) of the NH_3 complex with salts of the transition metals are higher for cupric and zinc salts than they are for manganous, chromic, and nickel salts. Accordingly, the stronger catalytic effect of Cu^{++} and Zn^{++} relative to the other transition metals in Fig. 7 is consistent with this tentative mechanism. Of course, such consistency is insufficient to unequivocally establish the validity of the mechanism.

Ferric oxide and ferrocene have been considered as burning-rate catalysts for propellants based on AP (Ref. 4). The DTA curves of Fig. 8 indicate that 1% Fe_2O_3 additive has a relative small catalytic effect on the first AP exotherm, when compared with that of 0.018% Cu^{++} additive. One percent of ferrocene additive lowered the temperature of the onset of the first AP exotherm, but it was not as powerful a catalyst as compounds of copper or zinc. Anhydrous FeF_3, at a concentration of 1%, lowered the temperatures of the onset of both the first and second AP exotherm (Fig. 8).

Harshaw catalyst 0202 has been widely tested as a burning-rate catalyst for AP (Ref. 4). (The approximate composition of catalyst 0202 is 82% CuO and 17% Cr_2O_3.) It, therefore, was of interest to examine its catalytic activity by our DTA techniques. The top two DTA curves in Fig. 9 were obtained from the purified AP (used for tests of Figs. 6 through 9) to which 0.033% of catalyst 0202 was added. The bottom DTA curve was obtained from a mixture made by adding 1.6% NH_4PF_6 to the above combination of AP spiked with 0.033% of this catalyst. The top DTA curve in Fig. 9 contained a broad first exotherm, attributable to the effect of the catalyst, beginning near 315°C and extending to ∿435°C. The second DTA curve demonstrated that the previously developed (Ref. 1) preheating technique can suppress this catalytically enlarged first exotherm if the AP is heated to about 405°C, and then allowed to cool. The bottom curve illustrated the outstanding ability of NH_4PF_6 to inhibit the first exotherm even in the presence of $CuO-Cr_2O_3$ catalyst. Moreover, in this case, the NH_4PF_6 also inhibited the second exotherm so that its peak occurred near 505°C (similar to that of the AP control in Fig. 6) rather than at 450°C as in the top DTA curve of Fig. 9.

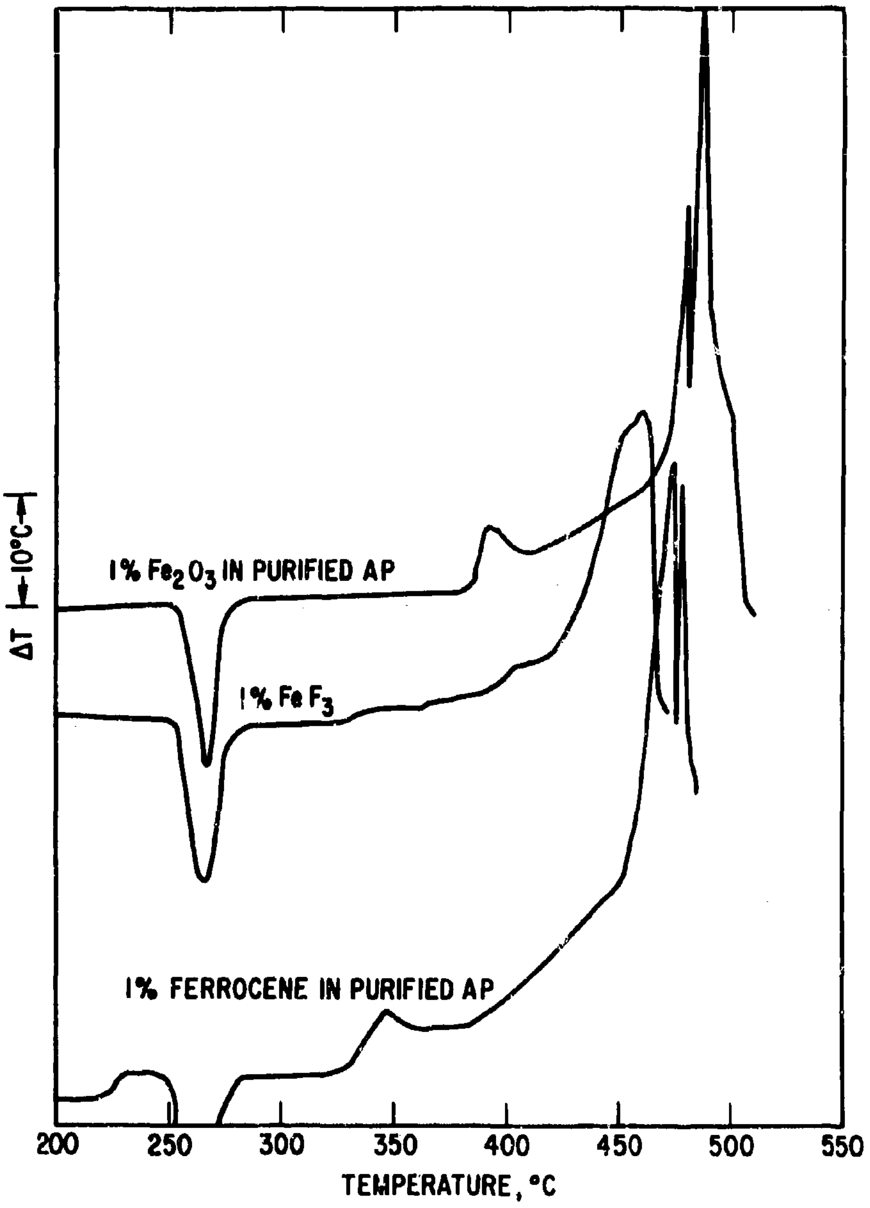

Fig. 8. Catalytic Effects of Three Compounds of Iron

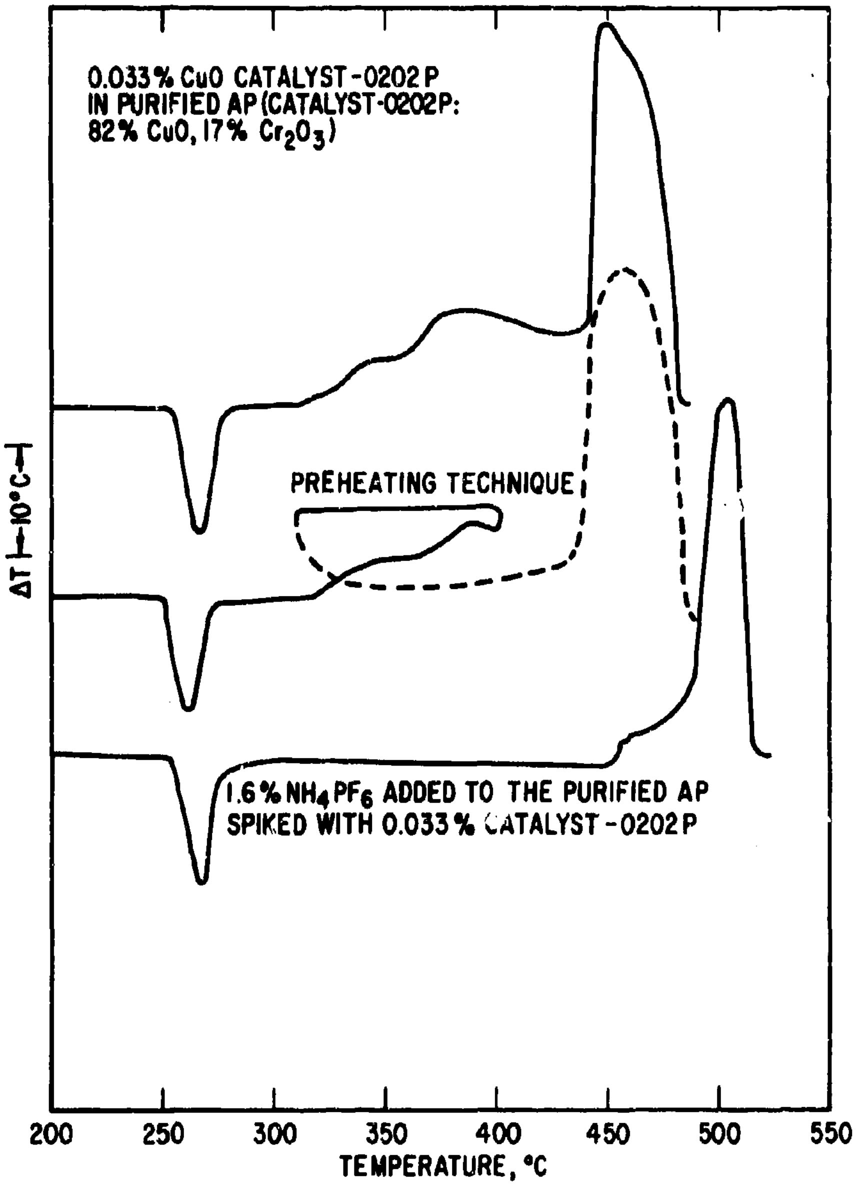

Fig. 9. Suppression of Catalyst Action by NH_4PF_6 Additive

The results of the DTA tests described in this report indicate that it is now feasible, by the use of inhibiting or catalytic additives, to exercise a wide range of control over the burning rates and ignition temperatures of solid propellants based on AP. It is planned to investigate the applicability to other oxidizers of the inhibiting (and catalytic) techniques suggested by these DTA tests with AP.

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13. ABSTRACT

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). It was 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. A series of tests was made of the catalytic effect on this exotherm of traces of impurities in 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. The burning rate was increased by adding 0.1% Cu or Zn salts. Independent tests in a combustion-bomb and in a motor have demonstrated the increased extinguishment reliability suggested by the thermal analysis curves. The effect on AP decomposition and combustion exotherms has also been tested for a series of additives consisting of other ammonium salts, flame retardants, Lewis acids, and transition metal compounds.

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