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# Techniques for Controlling Exothermic Decomposition of Ammonium Perchlorate

Prepared by S. W. MAYER, Laboratory Operations
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Laboratory Operations
AEROSPACE CORPORATION

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 is published by the Aerospace Corporation, El Segundo, California under Air Force Contract No. F04701-68-C-0200.

This report, which documents research carried out from April 1968 through July 1968, was submitted for review and approval on 22 November 1968 to Lieutenant Harold D. Gibbs, SMTTP.

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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.

Harold D. Gibbs, 2d Lt, USAF
Project Officer

## ABSTRACT

In order to prevent or reduce premature reignition of extinguishable solid propellant motors, a laboratory investigation has been made to search for methods that could eliminate or reduce the exothermicity of propellant grade ammonium perchlorate exposed to temperatures of 350-390°C. It was found that ammonium perchlorate (AP) in which this first exothermic peak was eliminated could be prepared by heating the propellant grade AP to 365-390°C for several minutes and allowing it to cool. Furthermore, this exothermic peak was eliminated by the pre-heating technique even when fluorocarbon polymer binder was in contact with the AP. This technique for preventing the first exotherm was successful in all samples of AP tested; the samples were from several sources and in several particle sizes.

It was found that the temperature at which the first exotherm occurred could be raised as much as 45°C by adding several percent of an ammonium salt (e.g., ammonium fluoborate) to the AP. The delayed exotherm was stronger than that found in AP to which no ammonium salt was added. This technique also was effective when fluorocarbon binder was in contact with the AP. Neither technique appeared to reduce the heat liberated by the deflagration of AP at 470-500°C. Co-crystallized ammonium salts were also tested as AP additives.

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# I. INTRODUCTION

Tests of extinguishable solid propellant motors had demonstrated that premature reignition of the propellant could occur after apparent extinguishment. Recent developments in the technology of controllable solid propellants have prompted an investigation of the thermal decomposition phenomena associated with this problem.

The purpose of the research being performed is to enhance the thermal stability of primary formulation constituents in order to increase extinguishment reliability and to decrease the probability of inadvertent reignition of on-off rocket motors.

The propellants of interest in this case are those likely to be considered for postboost propulsion. Efforts thus far have been centered upon fluorocarbon/ammonium perchlorate (AP).

It has been postulated that reignition of controllable solid rockets can be prevented by limiting the rate of thermal heating (Refs. 1 and 2) of the propellant surfaces, by controlling the exothermic decomposition of propellant ingredients, or both. The work reported herein is based upon the second approach. The technique of differential thermal analysis (Ref. 3) has been used in the experiments to evaluate means whereby the initial exotherm of AP and AP/binder mixtures could be modified.

Although investigations are being continued, results obtained to the present merit reporting.

## II. EXPERIMENTAL PROCEDURE

Because of the explosion hazard associated with heated $NH_4ClO_4$ (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 Du Pont[1] micro heating block. Micro glass beads in a similar micro 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 difference in temperature ($\Delta T$) between the sample and the reference material. Sample temperature and $\Delta T$ (Fig. 1) were recorded on an X-Y recorder with $\Delta T$ on the Y-axis at a scale of 10°C[2] per inch.

The heating block, cartridge heater, and block support were the standard Du Pont[1] micro DTA items. The micro block was an aluminum cylinder 7/8 inch in diameter and 1-1/2 inch 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), 3/8 inch in diameter and 1 inch deep. The cartridge heater was rated at 55 watts for 110 volts. In order to maximize the heating rate, the heating cartridge was operated at 115 volts from a variable transformer. (The rapid heating rate was considered desirable because propellant heating rates in deflagrating solid propellant motors are, of course, very rapid.) As a result, the temperature rise of the micro furnace was 50° per minute at 350° (near the temperature of the onset of the first exotherm). This compares favorably with the

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

[2] All temperatures in this report are given in °C.

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20° per minute temperature rise commonly employed for the micro furnace.[3] Since the voltage was constant at 115 volts, 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° per minute 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, California. The other ammonium salts were reagent grade materials, except for the ammonium fluoborate. The latter was a technical grade obtained from the Ozark-Mahoning Company, Tulsa, Oklahoma. Fluorocarbon AP propellant was donated by the Wasatch Division, Thiokol Chemical Corporation.

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

## III. RESULTS AND DISCUSSION

### A. ELIMINATION OF FIRST EXOTHERMIC DECOMPOSITION BY HEATING TECHNIQUE

Typical DTA curves are presented in Fig. 1 for propellant grade (Ref. 4) AP of several mean particle sizes: 200μ, 90μ, 45μ, 10μ, and 5μ. The characteristic endotherm was found to occur in the vicinity of 260° in all cases. The endotherm arises from the solid state transition (Ref. 3) of orthorhombic to cubic AP. In Fig. 1, the first exotherm characteristic of propellant grade AP is also evident. The temperature of the occurrence of the first exotherm can vary fairly widely from sample to sample, depending on impurities and particle size. For the samples in Fig. 1, the temperatures of the onset of this exotherm ranged from 330 to 365°. The temperatures at which the maxima of the first exotherms occurred ranged from about 355 to 375°, although the height of the exotherm progressively diminished as the particle size decreased. No clear maximum was evident for this exotherm in the 5μ AP; the first exotherm of the 5μ AP coalesced into the large exotherm corresponding to AP deflagration (Ref. 3). The maxima of the second exotherms in Fig. 1 occurred within a 5° range for the 10μ through 200μ AP samples, and the maximum for the 5μ AP occurred only 5° lower than that of the 10μ sample.

It is the exothermicity of the deflagration step, of course, that provides most of the enthalpy generated by AP in extinguishable propellants formulated with a fluorocarbon binder and no aluminum (Ref. 2). The first exotherm, however, is considered to represent a source of premature enthalpy (Refs. 2 and 5) that can cause such propellants to reignite inadvertently after extinguishment. A principal objective of these laboratory investigations, therefore, was to search for methods that could eliminate or reduce (or postpone to a higher temperature) 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 (Refs. 5, 6, and 7). It is not unlikely, of

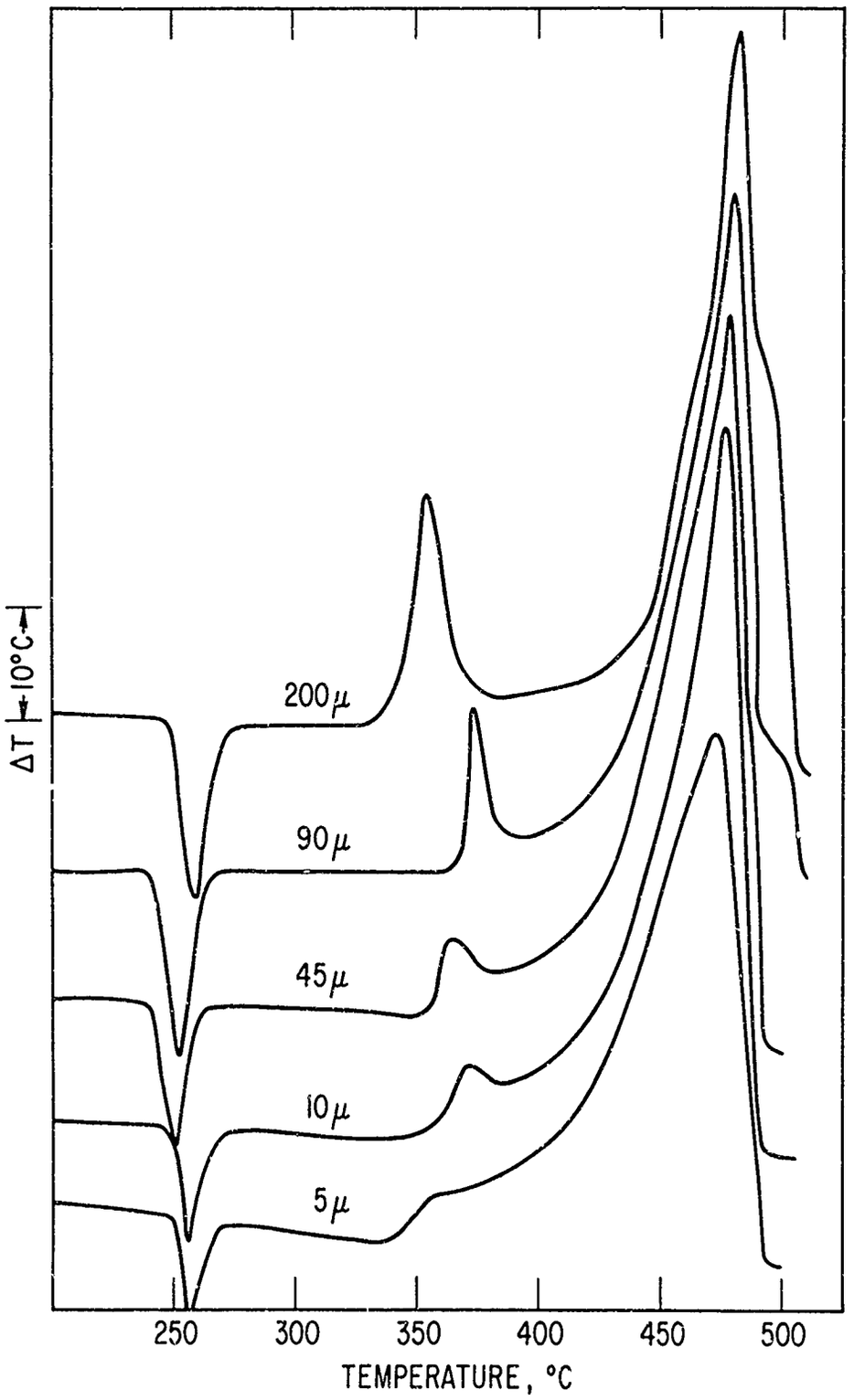


Fig. 1. Typical DTA Curves for Propellant Grade $NH_4ClO_4$
Particle Sizes: 5, 10, 45, 90, and 200 μ

course, that several factors can produce the exotherm. One view is that the first exotherm is caused by the presence of chlorate in the AP as a residual from the manufacturing process. Since ammonium chlorate is less stable than AP, the chlorate could thermally decompose at a lower temperature than the deflagration temperature of pure AP and produce decomposition products that react individually or with perchlorate to produce the first exotherm. A second view (Refs. 5 and 6) is that the first exotherm is caused by excess perchloric acid trapped with the AP crystals during the manufacturing process. The $HClO_4$ is presumed to be less thermally stable than $NH_4ClO_4$ since it is believed (Ref. 6) that AP requires an activation energy to transform it to $HClO_4$ and $NH_3$ as part of the mechanism for thermal decomposition and deflagration. Consequently, the presence of free $HClO_4$ in AP could lead to premature thermal decomposition that causes the first exotherm. A third view (Refs. 5 and 6) 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.

Because of the volatility or thermal instability of chlorates, perchloric acid, and transition metal perchlorates, 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 merits of a heating procedure could then be efficiently determined in the DTA apparatus. Without removing the sample from the micro furnace, the effectiveness of a heating procedure could be evaluated by examining the DTA curve of the heated and cooled AP. A major achievement of this investigation is evident in the DTA curves shown in Fig. 2. These curves demonstrate that AP in which the first exotherm has been practically eliminated 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 micro furnace 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 micro furnace

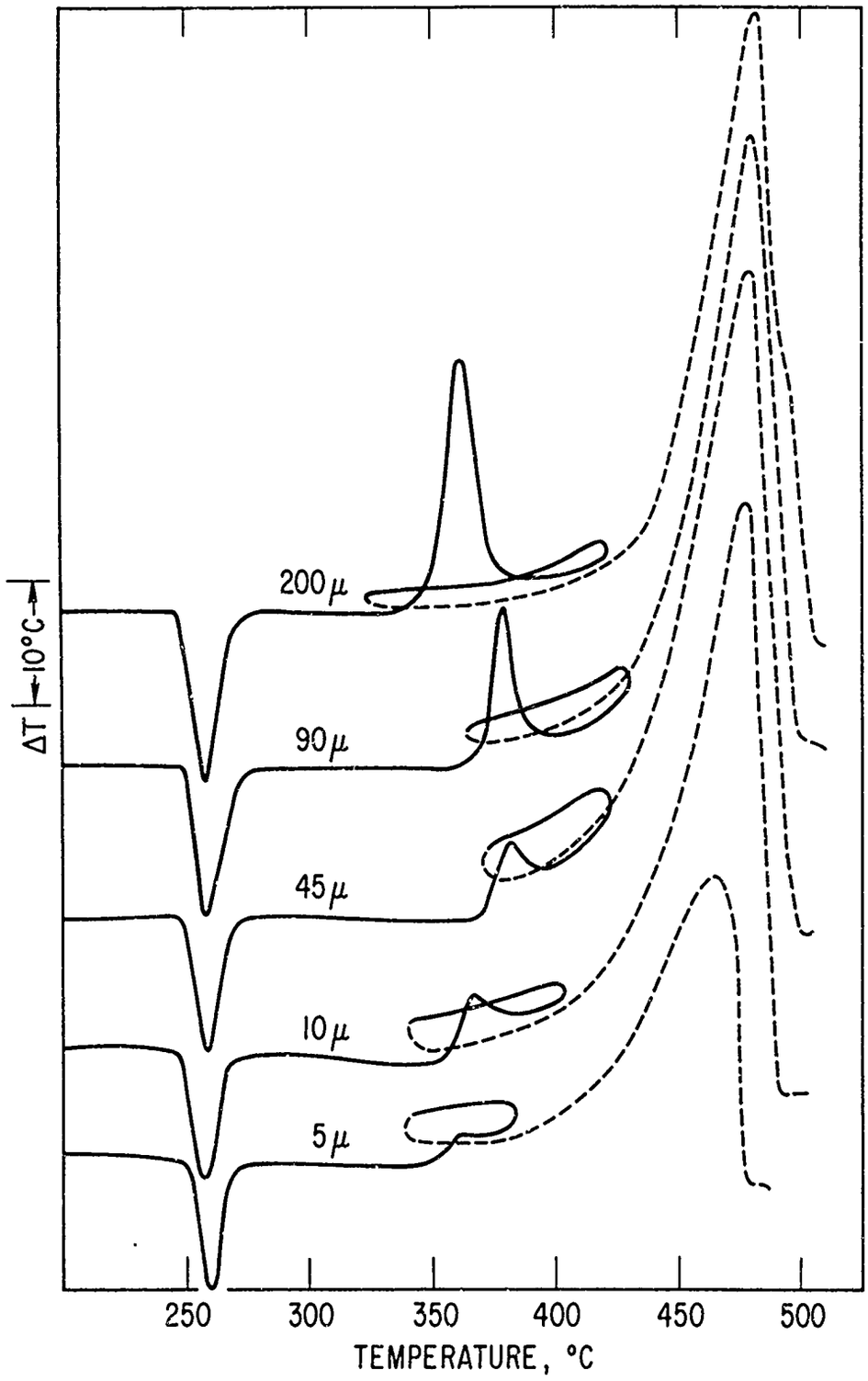


Fig. 2. Heating Procedure for Eliminating First AP Exotherm
Dashed Lines Denote Re-heating After Cooling

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 re-heated AP showed that the first exotherm was eliminated by the controlled prior heat treatment of the propellant grade AP. Also, the deflagration exotherms of the heat-treated AP in Fig. 2 were about as large as the exotherms of the untreated AP samples in Fig. 1. 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.

The DTA curves (for 90μ AP) in Fig. 3 indicate that the extent of cooling is not critical. The top curve shows that cooling the heated AP to a temperature below that of the solid state transition does not cause the first exotherm to appear again on re-heating (dashed line). In a test run similar to that of the top curve, the temperature was maintained at 400° for seven minutes before the sample was allowed to cool. Although re-heating demonstrated that the first exotherm had been eliminated by the seven minute heating, the deflagration exotherm was significantly smaller than that in the top curve of Fig. 3, because some of the AP had sublimed from the sample tube during the prolonged heating. A subsequent test showed that all the AP could be volatilized without deflagrating by heating the sample tube at 425° for twenty minutes. These observations suggest, of course, that prolonged heating above the temperature of the first exotherm should be minimized if it is necessary to avoid loss via volatilization of the AP.

The second curve of Fig. 3 indicates that cooling the heated AP to a temperature just above that of the solid state transition does not cause the first exotherm to appear again. In Fig. 3, the bottom DTA curve is that for AP (90μ) treated to remove the exotherm by the heating technique, followed by cooling to room temperature. This treated sample had been allowed to remain in a desiccator for a week. It can be seen that the first exotherm has been virtually eliminated, although there is a slight rise in the curve at 375°. Another heat treated sample, however, was kept in a saturated water vapor

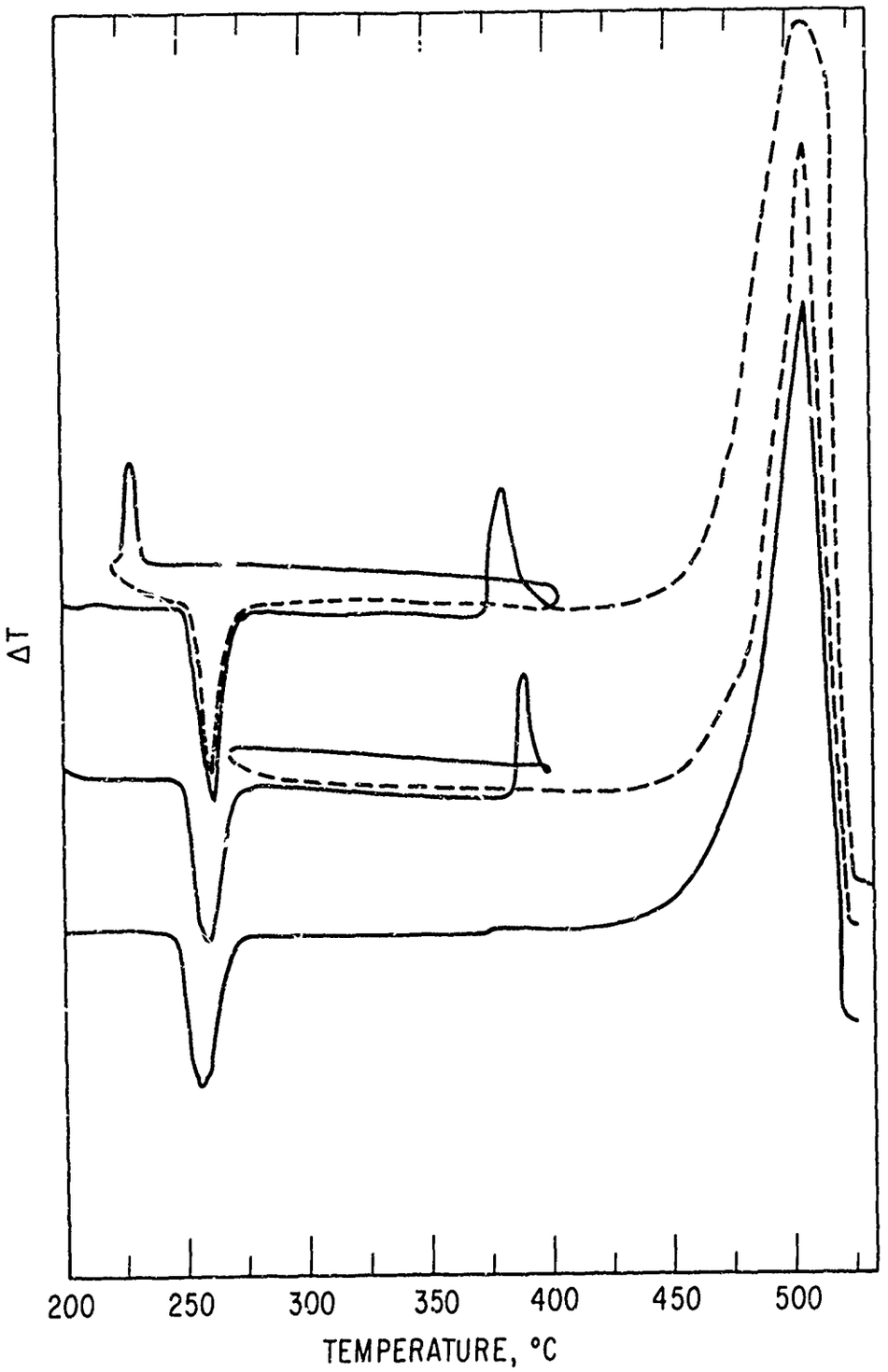


Fig. 3. DTA Curves for Varied Heating and Cooling of AP
Dashed Lines Denote Re-heating After Cooling

atmosphere at 25° for three days. This exposure to water vapor caused much of the first exotherm to reappear. It is possible that high humidity can cause hydrolysis of the $NH_4ClO_4$ to $HClO_4$ (with the $NH_3$ volatilizing). In any event, it appears desirable to minimize exposure of AP to water vapor. The polymeric binders used in solid propellants are typically hydrophobic and, therefore, may act effectively as encapsulating agents to protect the AP from water vapor.

In Fig. 4, the top curve 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 7 minutes at 260°. Upon further heating, the AP exploded at about 410°, shattering the glass capillary sample tube. It has been pointed out (Ref. 8) that it is possible to prepare a porous AP under prolonged heating conditions. However, the 7 minute treatment at 260° may 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.

The bottom DTA curve of Fig. 4 is for purified AP, a reagent grade purchased from the Matheson, Coleman and Bell Division of Matheson Company, Inc. It is apparent that purified AP can have a much smaller first exotherm than technical, propellant grade AP. Purified AP supplied by the American Potash and Chemical Company, Inc., also had a relatively small first exotherm. Although purified (or heat-treated) AP is more expensive than technical AP, the additional cost would be warranted if the improved AP prevents inadvertent reignition of extinguishable propellant motors.

DTA curves are shown in Fig. 5 for a solid, extinguishable propellant compounded with a fluorocarbon binder and AP (no aluminum powder). The top curve is the DTA curve obtained when a heating-cooling technique is not used. The endotherm characteristic of the solid state transition was obtained, but the first exotherm had two segments. The first segment began near 375° and then formed a plateau that was followed at about 405° by the second segment, which had a relatively high peak. The height of this peak was

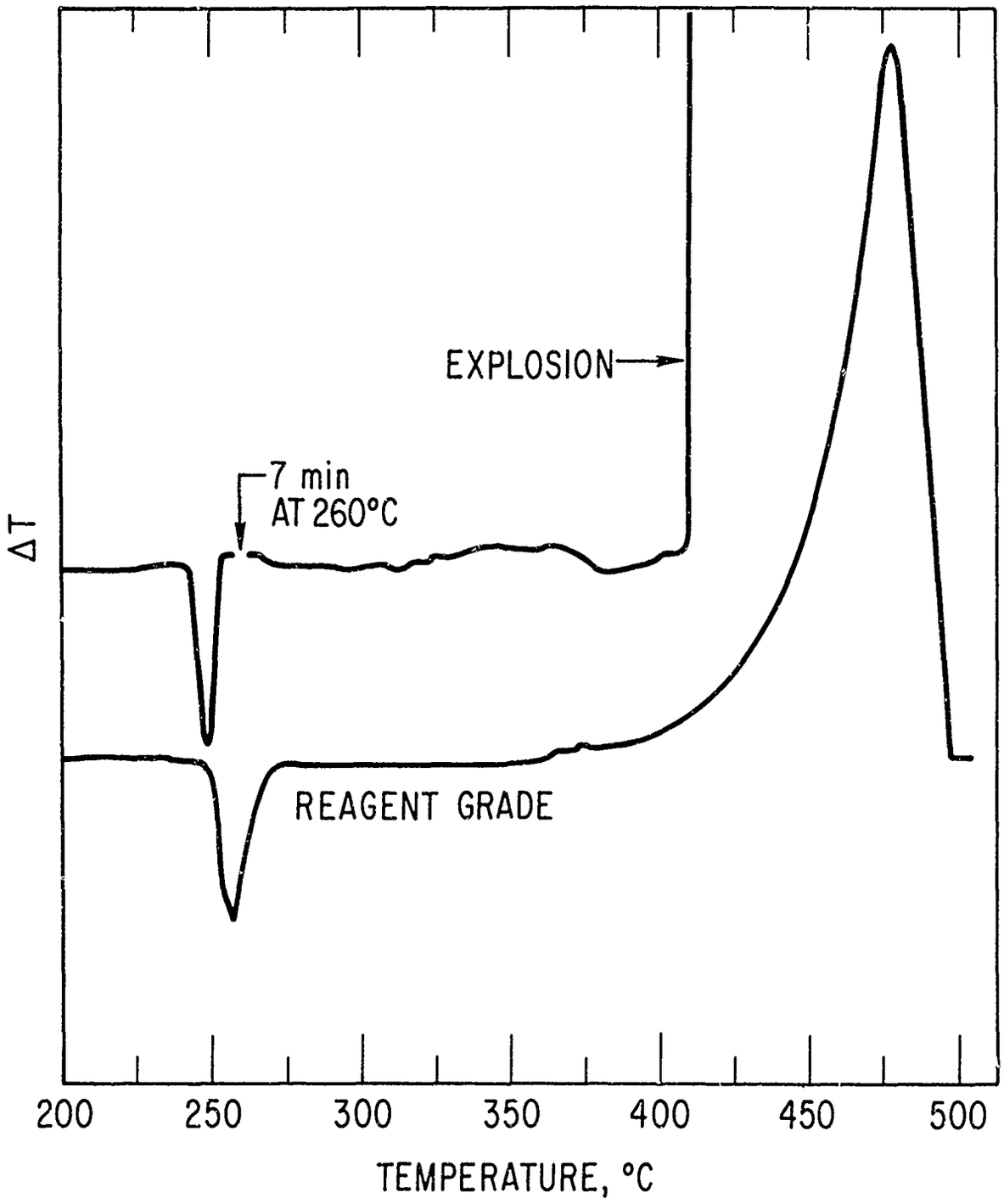


Fig. 4. DTA Curves for Reagent Grade AP and 260°C Heating

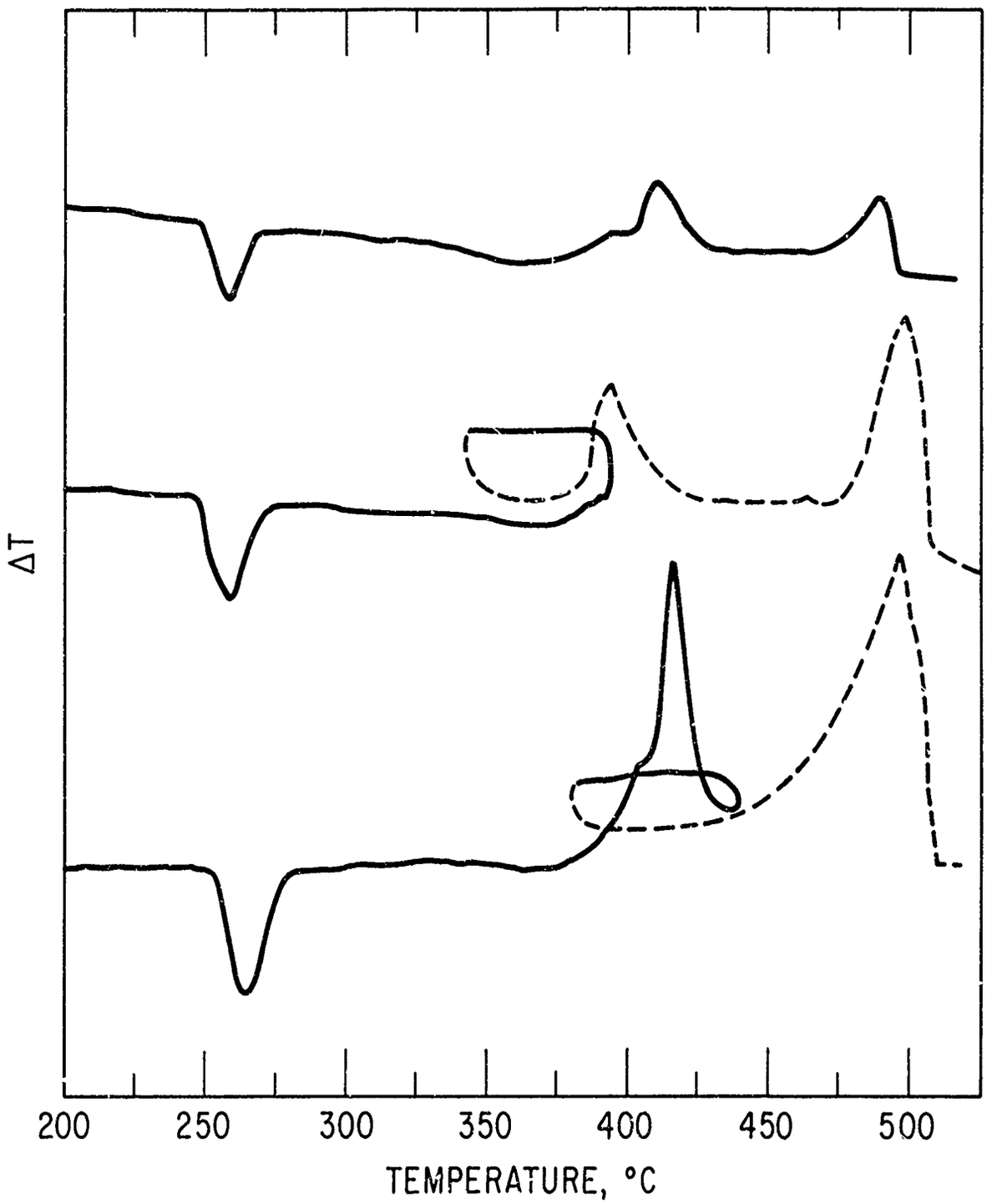


Fig. 5. DTA Curves for Composite Fluorocarbon – AP Propellant
Dashed Lines Denote Re-heating After Cooling

similar to that of the final deflagration exotherm at 490°. The similarity of heights between the final exotherm and the first exotherm in this composite fluorocarbon (FC) propellant was in marked contrast with the DTA curve for AP (Figs. 1, 2, and 3) where the second exotherm was considerably higher and larger than the first exotherm.

Motor tests of extinguishable solid propellants indicate that the surface of the residual propellant has been heated to an elevated temperature before the extinguishment (Ref. 7). The second curve of Fig. 5 shows the results of a brief test to see whether such initial heating of the FC propellant could make it more susceptible to premature reignition. It can be seen in Fig. 5 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 reignition, since the peak of the first exotherm occurred at a lower temperature during the reheating. The bottom DTA curve of Fig. 5, however, represents a controlled heating treatment of the FC propellant similar to that applied (Figs. 2 and 3) to remove the first exotherm from AP, inasmuch as the propellant was heated to a higher temperature (440°) 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. Consequently, it appears feasible to remove the first exotherm from FC propellant that already had been compounded, if that should become desirable. However, this practice would not be recommended for large rocket motors.

The DTA results of Fig. 6 show that the removal of the first AP exotherm in the presence of FC binder (Fig. 5) was not limited to this one case. The curves for Fig. 6 were obtained with 90μ AP mixed with the fluorocarbon elastomer Viton A[4] and a fluorocarbon plasticizer. The mixture

[4]Elastomer Chemicals Department, E. I. duPont de Nemours and Co., Inc., Wilmington, Delaware.

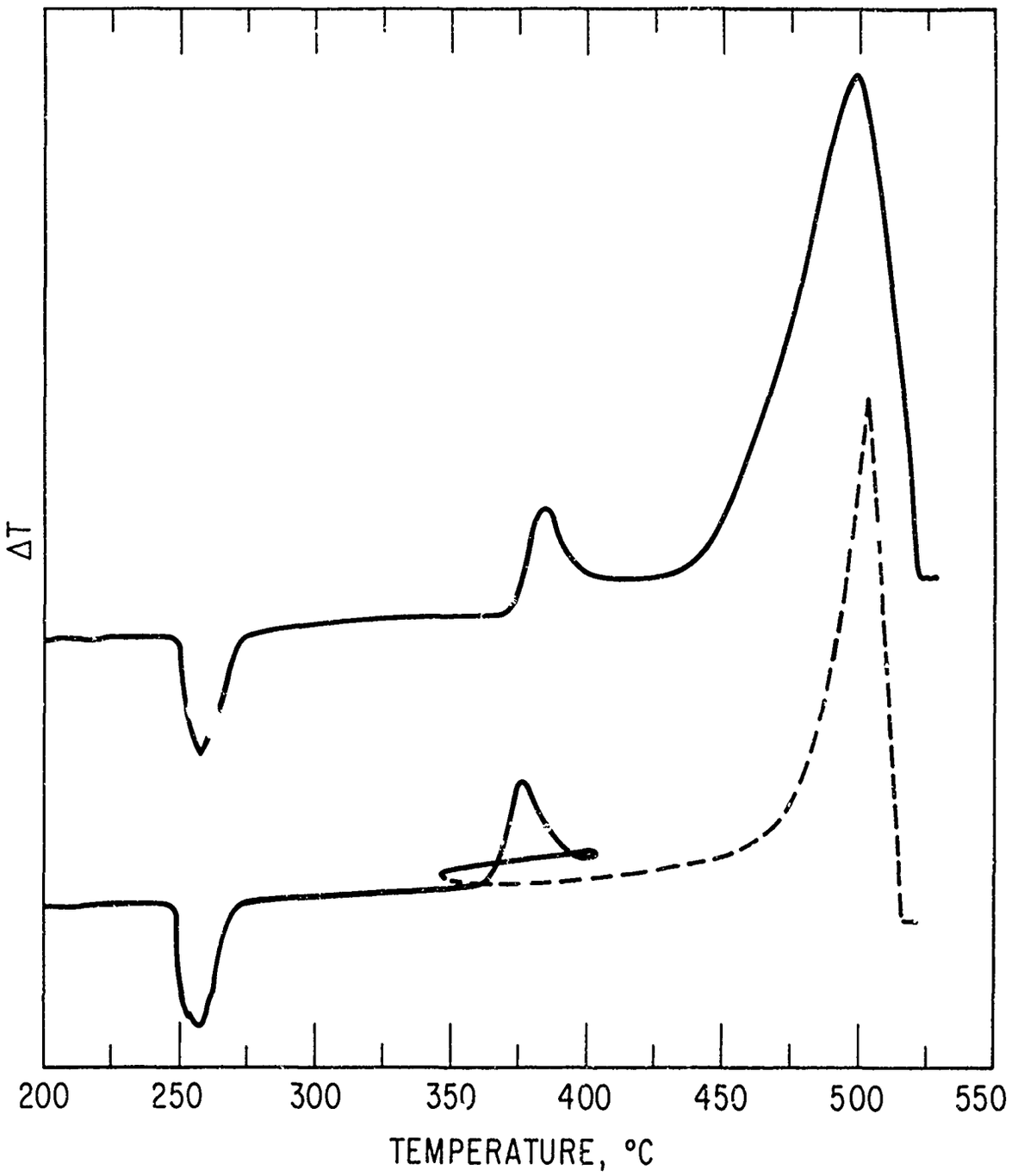


Fig. 6. DTA Curves for AP-Viton A Mix. Dashed Lines Denote Re-heating After Cooling

contained 80% AP. A typical DTA run is shown in the top curve. The effectiveness of the heating technique, even when fluorocarbons are mixed with the Al powder, is demonstrated by the bottom DTA curve of Fig. 6. Heating to just beyond the exotherm was apparently about as effective in the presence of fluorocarbon elastomers as it was for AP alone (Fig. 2).

The mechanism whereby the heating technique removes the first exotherm has not yet been determined, but it is planned to make some relatively brief studies of this question in the near future. The observation that exposure to water vapor can regenerate a first exotherm in the heat-treated AP suggests that free perchloric acid can produce the exotherm since water vapor apparently cannot introduce transition metal salts or chlorate into AP. However, chlorate or metal impurities may also produce this exotherm. Therefore, it is planned to test the effect of added chlorate, metals, and/or perchloric acid on the formation of the first exotherm. It is also planned to analyze gas generated by the AP during the decomposition occurring at the first exotherm. Nevertheless, despite the absence of an understanding of the mechanism, the controlled heating technique apparently is a useful method of controlling the exothermic decomposition and reactivity of AP.

## B. THERMALLY DECOMPOSABLE ADDITIVES FOR DELAYING FIRST EXOTHERM OF AP

Before the heating technique described above was discovered, a series of tests was made to investigate the possibility of controlling premature reignition by mixing an additive with the AP. It was hoped that a thermally decomposable additive would absorb enough heat during its decomposition and volatilization to delay the first exotherm to a higher temperature. Then the thermal radiation from the walls of the combustion chamber and other hardware of the heated rocket motor after extinguishment (Ref. 2) might not be sufficient to raise the temperature of the residual propellant to this higher temperature.

One class of thermally decomposable additives consists of flame retardants, used on buildings and their contents. A common type of flame

retardant is composed of chlorinated hydrocarbons such as hexachlorbenzene. The top DTA curve in Fig. 7 shows the endothermic characteristics of hexachlorbenzene as a function of temperature. The first deep endotherm arose from the fusion of this substance at about 225-230°. The second large endotherm arose from boiling accompanied by some decomposition of the compound. The top DTA curve in Fig. 8 shows the effect of 5% hexachlorbenzene on the thermal decomposition of 90μ AP. This curve can be compared with the one for 90μ AP in Fig. 1 and with the top curve in Fig. 7. The minimum at 230° in the small, first endotherm of the top curve of Fig. 8 corresponds to the minimum in the melting point endotherm of Fig. 7. Because there was only 5% hexachlorbenzene in the AP, this melting endotherm was considerably smaller than the one in Fig. 7. The deep endotherm near 250° in Fig. 8 is generated, of course, by the solid state transition characteristic of AP (Fig. 1). The shallow endotherm between 320 and 350° in the top curve of Fig. 8 corresponds to boiling of the hexachlorbenzene. The first exotherm in the top curve of Fig. 8 is much larger than in the 90μ curve of Fig. 1. This increased exothermicity suggests that the oxidizer, AP, reacted exothermically with the carbon atoms of the benzene ring of hexachlorbenzene. Furthermore, the additive did not delay the first exotherm, which began near 350° compared to 365° for 90μ AP in Fig. 1. The deflagration exotherm of the top curve of Fig. 8 is not larger than the first exotherm. The near equality of these two exotherms in the presence of a chlorocarbon compound is reminiscent of the exotherms for the fluorocarbon propellant in Fig. 5. Although the results with hexachlorbenzene were not promising, other flame retardants will be investigated. Higher priority was given to investigations of techniques for controlling the first exotherm by pre-heating and by the ammonium salt additives (described below) because of the favorable results with these two techniques in comparison with the apparent ineffectiveness of hexachlorbenzene.

It is known (Ref. 9) that the first exotherm of $NH_4ClO_4$ can be suppressed if the thermal decomposition takes place in an atmosphere containing $NH_3$ at 60 psia. Inasmuch as many ammonium salts, when heated, undergo

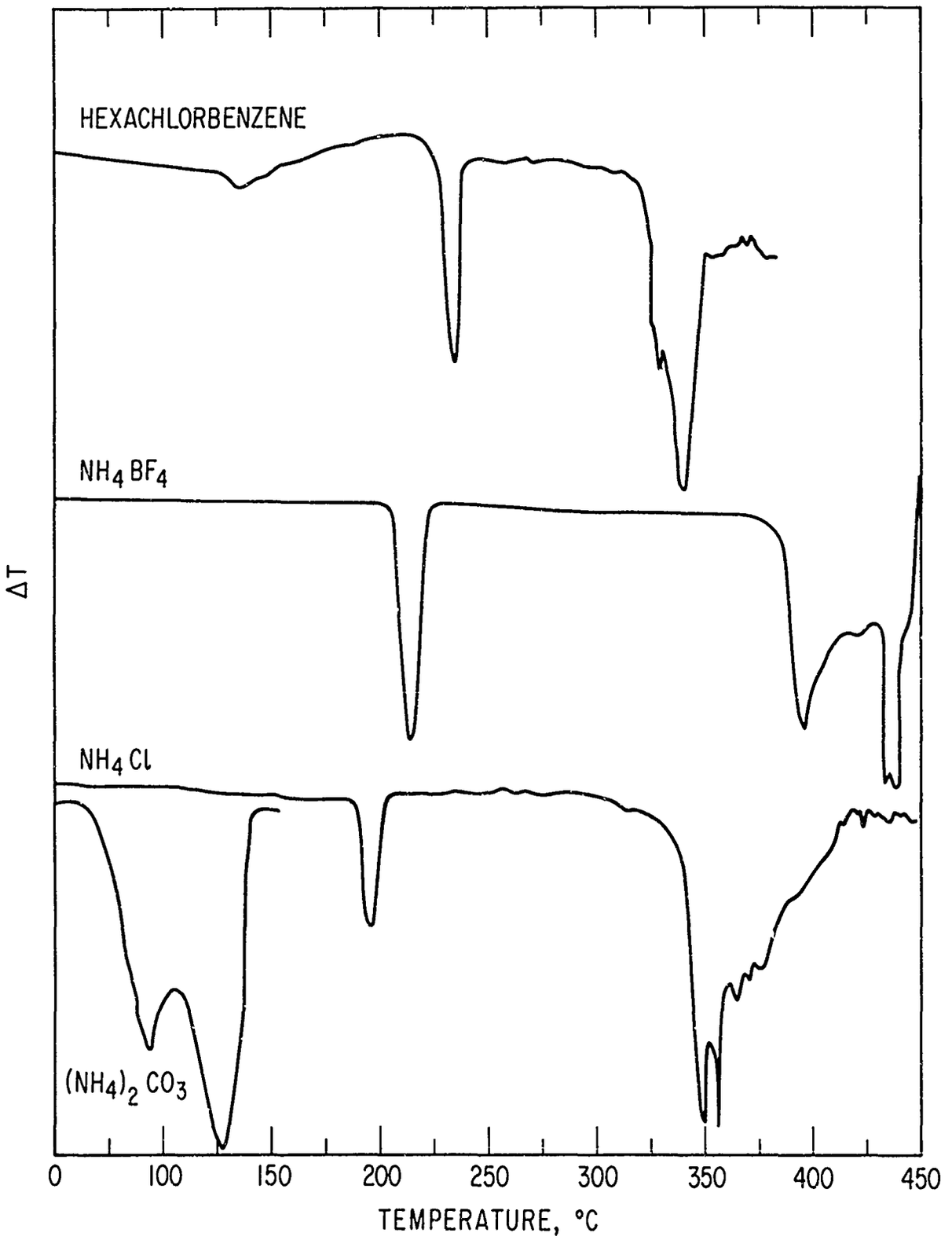


Fig. 7. DTA Curves for Hexachlorbenzene and Ammonium Salts

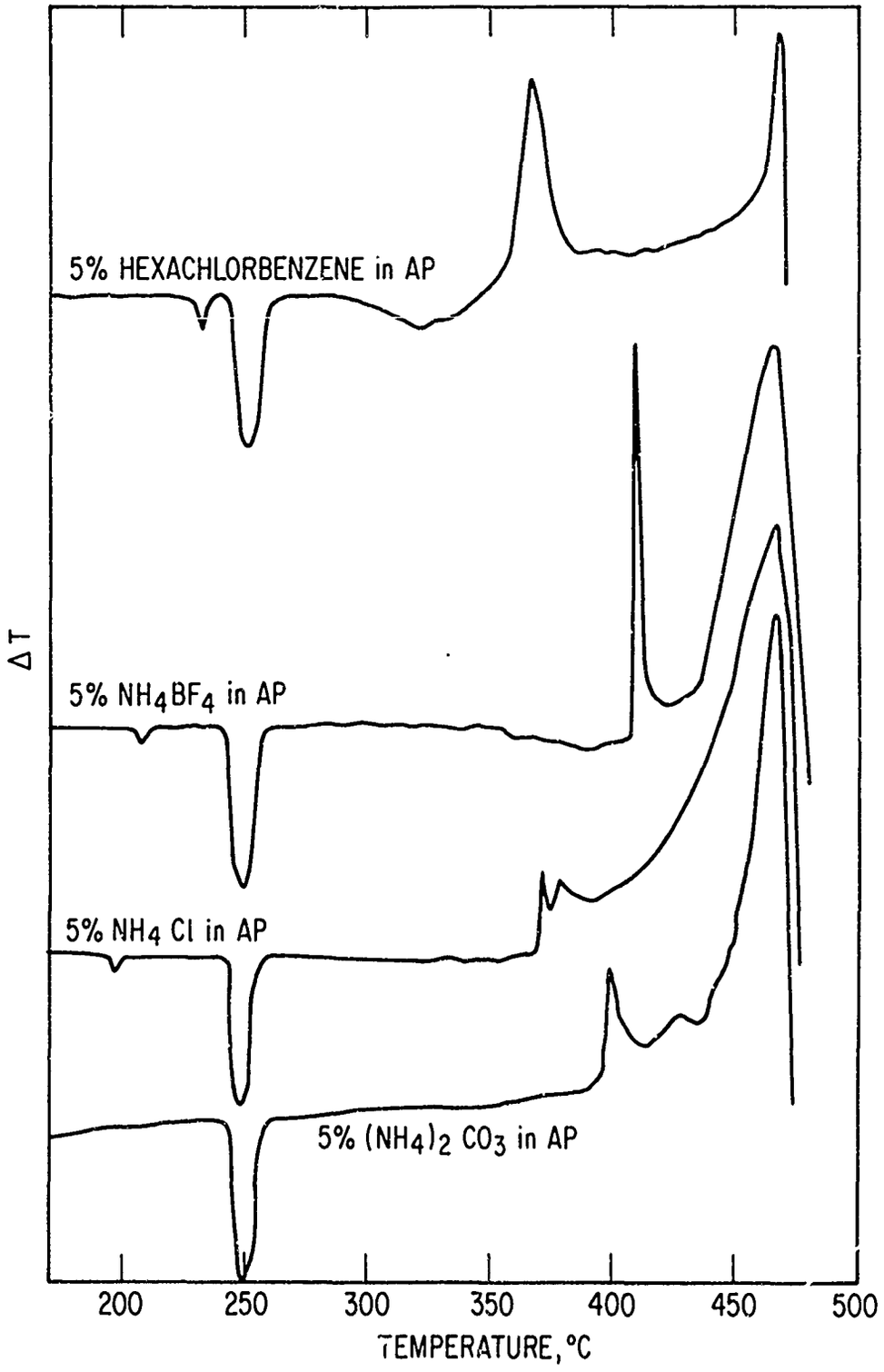


Fig. 8. DTA Curves for AP Containing 5% Additive

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. The anion in such salts may also affect the first exotherm. 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 fluoborate; it is not improbable, however, that a better additive will be found as the investigation progresses. The DTA curve for the thermal decomposition of $NH_4BF_4$ is shown in Fig. 7, and the DTA curve for a 5% mixture of $NH_4BF_4$ in 90μ AP is presented in Fig. 8. The first endotherm (Fig. 7) of $NH_4BF_4$ arises from a transition near 210°. This endotherm is also evident in the curve for the 5% $NH_4BF_4$ mixture (Fig. 8). The large endotherm beginning near 380° (Fig. 7) apparently can be attributed to sublimation and thermal decomposition of the $NH_4BF_4$, probably in accordance with the equation

$$NH_4BF_{4(c)} \rightarrow NH_{3(g)} + HF_{(g)} + BF_{3(g)} \qquad (1)$$

No solid products or smoke would be formed if this equation is followed. $HBF_4$ is presumed (Ref. 10) to be nonexistent or very unstable in the gas phase because such a structure would require pentavalent boron, which is not known. The DTA curve in Fig. 8 shows that 5% $NH_4BF_4$ additive delayed the onset of the first exotherm from 365 (Fig. 1) to 410°. This delay can help prevent premature reignition caused by radiation (Ref. 2) from the hot portions of a rocket motor. It can be seen in Fig. 8 that the first exotherm was steeper and higher as a result of the 5% $NH_4BF_4$ additive; the advantages or disadvantages of the steeper first exotherm could be established by tests with rocket motors. Mathematical thermal modelling of reignition is not yet able to assess these effects quantitatively.

The DTA curves for $NH_4Cl$ and its 5% mixture in AP are shown in Fig. 7 and 8. Like $NH_4BF_4$, $NH_4Cl$ does not melt at a pressure of one atmosphere, and the endotherm at 190° probably corresponded to a solid state transition. $NH_4Cl$ evidently (Fig. 8) was not as effective as $NH_4BF_4$ in

delaying the onset of the first exotherm. A possible explanation is that HCl, since it is a stronger acid than HF, can bind $NH_3$ more strongly in the gas phase so that the $NH_3$ is not as available for suppressing the first AP exotherm. Alternatively the $BF_3$ produced in the endothermic decomposition of $NH_4BF_4$ may act as a Lewis acid (Ref. 10) that can react with $HClO_4$, $H_2O$, or transition metals to help suppress the first exotherm. Consequently, ammonium salts of acids that are not stable in the gas phase may be more effective additives than salts of acids relatively stable in the gas phase. The DTA tests conducted to date tended to support this view since ammonium carbonate and ammonium oxalate were more effective than $NH_4Cl$ and $(NH_4)_2SO_4$. The DTA curves for $(NH_4)_2CO_3$ and its 5% mixture in 90μ AP are presented in Fig. 7 and Fig. 8, for comparison with $NH_4Cl$.

Figure 9 shows the effect of reducing the quantity of $NH_4BF_4$ in AP to 2%. The onset of the first exotherm was lowered to 395° compared to 410° for the 5% $NH_4BF_4$ mixture in AP. The objective of decreasing the percent of $NH_4BF_4$ was to maintain the specific impulse of AP, rather than to reduce the cost. $NH_4BF_4$ is not expensive; its cost is similar to that of $NH_4ClO_4$. Reducing the quantity of $NH_4BF_4$ in AP to 1% produced a DTA curve that did not differ significantly from that of 90μ AP (Fig. 1). The $NH_3$ group in AP can serve as a fuel, but the HF and $BF_3$ groups cannot be expected to augment the specific impulse by reacting very exothermically with the oxygen from $NH_4ClO_4$ inasmuch as the BF and HF bonds are strong relative to the FO, BO, and NH single bonds.

Since crystals of $KClO_4$ are isomorphous with $KBF_4$, it is not unlikely that $NH_4ClO_4$ is isomorphous with $NH_4BF_4$ because the ionic radius of potassium ion is similar to that of ammonium ion (Ref. 11). Isomorphous crystals form solid solutions in which the percent of each component can be varied continuously from 0 to 100. It was, therefore, decided to co-crystallize 5% $NH_4BF_4$ in $NH_4ClO_4$ and examine the thermal decomposition properties of the resultant crystals. The DTA curve is shown in Fig. 9. It can be seen that the onset of the first exotherm was only slightly retarded, to 375° compared with 410° for the 5% mixture and 365° for 90μ AP. Moreover, the

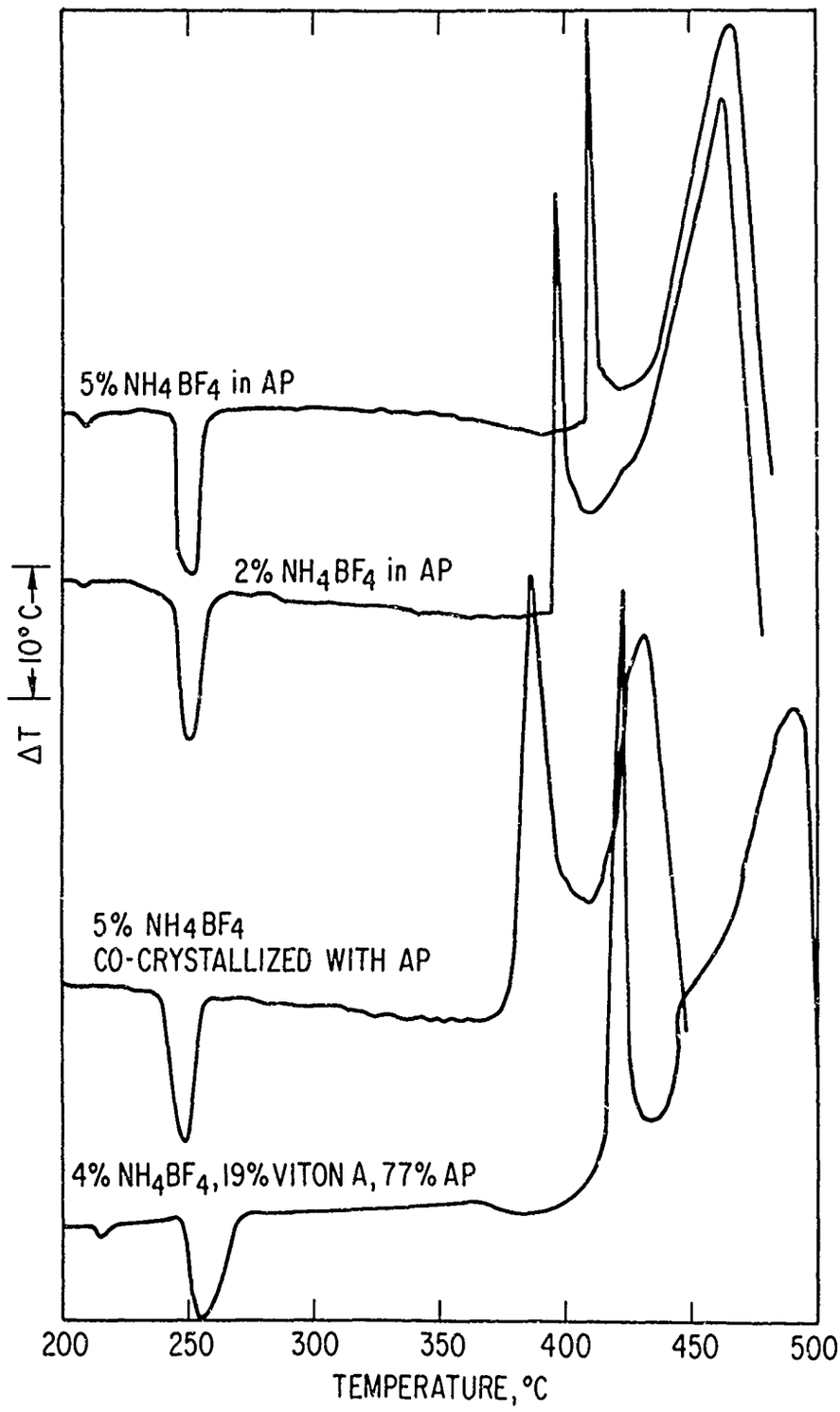


Fig. 9. DTA Curves for AP with Ammonium Fluoborate Additive

first exotherm of the co-crystallized material was larger than the normal AP first exotherm. It could be hypothesized that the suppressant $NH_3$ was less easily liberated from $NH_4BF_4$ in solid solution than it was from the "free" $NH_4BF_4$ characteristic of powder mixtures, and that the $NH_3$ group of the $NH_4BF_4$ in solid AP solution more readily acted as a fuel to enlarge the first peak. Another minor point of interest is that the small endotherm near 210° in the 5% mix has disappeared in the co-crystallized material, as it should in a solid solution since $NH_4BF_4$ would be no longer be present as a separate solid phase. Also, the 5% $NH_4BF_4$ in solid solution could lower the temperature of the onset of the AP solid state transition, as it apparently did in Fig. 9.

The bottom curve of Fig. 9 shows that $NH_4BF_4$ additive is effective in retarding the onset of the first exotherm even when the fluorocarbon elastomer Viton A[5] was mixed with AP. The mixture contained 4% $NH_4BF_4$, 19% Viton A, and 77% AP (90μ). The first exotherm was delayed to 415°. Note that the $NH_4BF_4$ solid state endotherm appears again (at 205°) in this mixture.

Additional tests are planned to search for somewhat more effective additives, and to examine the effect of additives and binders on AP that has been heat treated to remove the first exotherm.

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## REFERENCES


1. L. W. Carlson and J. D. Seader, AIAA J. 5, 1272 (1967).

2. G. M. Lehmann and G. R. Schneiter, "Analytical Investigation of the Reignition of a Solid Propellant", TOR-0158(53801-04)-4, Aerospace Corporation, San Bernardino Operations, San Bernardino, California (Apr. 1968).

3. P. D. Garn, Thermoanalytical Methods of Investigation (Academic Press, New York, 1965).

4. R. F. McAlevy, et al., Investigation of the Ammonium Perchlorate Composite Propellant Deflagration Mechanism by Means of Experimental Analog Techniques, ME-RT67006, Stevens Institute of Technology, Hoboken, New Jersey (Sept. 1967).

5. G. D. Sammons, ICRPG Third Combustion Conference, CPIA Publication No. 138, Vol. 1, p. 75 (Applied Physics Laboratory, Silver Spring, Maryland, Feb. 1967).

6. P. W. M. Jacobs, ICRPG Third Combustion Conference, CPIA Publication No. 138, Vol. 1, p. 19 (Applied Physics Laboratory, Silver Spring, Maryland, Feb. 1967).

7. P. L. Micheli, A Stop-Start Study of Solid Propellants, Report 1090-81F, Aerojet-General Corporation, Sacramento, California (Nov. 1967).

8. R. K. Manfred, P. L. O'Neil, and E. L. Lista, Third ICRPG/AIAA Solid Propulsion Conference, CPIA Publication No. 167, Vol. II (Applied Physics Laboratory, Silver Spring, Maryland, June, 1968).

9. R. L. Bohan, Anal. Chem. 33, 1451 (1961).

10. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (Interscience Publishers, Inc., New York, 1962).

11. J. R. Partington, An Advanced Treatise on Physical Chemistry, Vol. III (Longmans, Green and Company, New York, 1957).


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13 ABSTRACT


In order to prevent or reduce premature reignition of extinguishable solid propellant motors, a laboratory investigation has been made to search for methods that could eliminate or reduce the exothermicity of propellant grade ammonium perchlorate exposed to temperatures of 350-390°C. It was found that ammonium perchlorate (AP) in which this first exothermic peak was eliminated could be prepared by heating the propellant grade AP to 365-390°C for several minutes and allowing it to cool. Furthermore, this exothermic peak was eliminated by the pre-heating technique even when fluorocarbon polymer binder was in contact with the AP. This technique for preventing the first exotherm was successful in all samples of AP tested; the samples were from several sources and in several particle sizes.

It was found that the temperature at which the first exotherm occurred could be raised as much as 45°C by adding several percent of an ammonium salt (e.g., ammonium fluoborate) to the AP. The delayed exotherm was stronger than that found in AP to which no ammonium salt was added. This technique also was effective when fluorocarbon binder was in contact with the AP. Neither technique appeared to reduce the heat liberated by the deflagration of AP at 470-500°C. Co-crystallized ammonium salts were also tested as AP additives.


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