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"COMBUSTION CHARACTERISITICS OF CRYSTALLINE OXIDIZERS"

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i. FOREWORD

This research at the University of Delaware under Grant AF-AFOSR 922-67 for the period August 1, 1968 through October 31, 1968 was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

ii. ABSTRACT

A collection of perchlorate and nitrate crystalline oxidizer DTA thermograms is presented. The effects of oxidizer purity on pres ace and location of endo and exotherms is discussed. The effects of cation modifications for both kinds of oxidizers is shown.

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I. Introduction

A fundamental understanding of the combustion characteristics of a range of physical conditions of crystalline oxidizers is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involves theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. A strandburner, window bomb and high-speed motion picture photography will be used to obtain burning rates versus pressure, and to record stability of combustion for a variety of particle sizes and pressure (density) packings of selected crystalline oxidizers (i.e., ammonium perchlorate) and analogous compounds. The study of large single crystal burning will remove particle size, shape and packing factors as complications. Data from low bulk density powder combustion studies, when compared with single crystal data, provides vital information about the characteristic surface, combustion zone thickness, ignition and conductivity contributions to the overall combustion phenomena.

In eddition, it is believed that simple combustion tests of powder oxidizer samples can serve as an efficient screening technique for determining whether chemical modifications have increased or decreased the intrinsic burning rate. Crystalline decomposition mechanisms observed during burning will be related to the oxidizer intrinsic burning rate and the basic properties of the oxidizer such as chemical neture, crystal type, and ion sizes. The validity of the models will be determined by correlation with the experimental data obtained.

II. Summary of Oxidizer DTA Thermograms

During this period, comparisons have been made of the DTA thermograms for a variety of monopropellant perchlorate and nitrate crystalline oxidizers. Nine figures are presented in this section to show the kinds of variations in endothermic and exothermic behavior we have found. Variations in the thermograms are due to purity and stability differences; and to chemical and crystal lattice structure differences. The following are summarizing statements:

1. Thermograms are excellent indices of oxidizer purity. Recrystallization and vacuum drying, for example, tend to remove endotherms and exotherms; and to move the final exotherm to higher temperatures.

2. The temperature of the final exotherm is a good measure of thermal stability.

3. Oxidizer burning rate, monopropellant performance and impact sensitivity are not reflected in thermograms in a regular manner. These attributes are a direct indication of chemical and lattice structure and the potential for energy release.

The first four figures indicate that ammonium perchlorate, and the three methyl substituted ammonium perchlorates, all have reasonable thermal stability as oxidizers. (There is a low temperature endotnerm for monomethyl not shown on Figure 2 that occurs at about 45°C.) As has been pointed out in previous reports,[1] monomethyl ammonium perchlorate has a faster burning rate and is more impact sensitive than ammonium perchlorate. These latter two attributes are traced to the near perfect balance of oxidizing and reducing species within the crystal unit cell.

In comparing figures 4 and 5, it can be seen how an impurity like water can be detected; and then can be shown to have been removed by careful drying.

Figures 6 and 7 for nitrate oxidizers show profound changes when methyl substitution is made for the ammonium hydrogens. The thermogram loses all of the well-known ammonium nitrate endotherms and the exotherm appears to split into two parts, both of which are significantly higher than for ammonium nitrate. It would be expected that the reverse would take place since we would expect that the ionic forces within the crystal would have been weakened by the substitution of methyl groups for hydrogen atoms. The interesting combustion change that takes place is that, whereas ammonium nitrate is difficult to ignite or burn, except under pressures of 50 to 100 atmospheres, tetramethyl ammonium nitrate burns readily and very smoothly at ambient conditions in the straw burning test. This combustion change is believed to be due to the better fuel-oxidizer balance in the molecule. It is important that both oxidizer and fuel species are present in a

FIGURE 1. DTA THERMOGRAM ULTRA HIGH PURITY GRADE AMMONIUM PERCHLORATE NH_4ClO_4

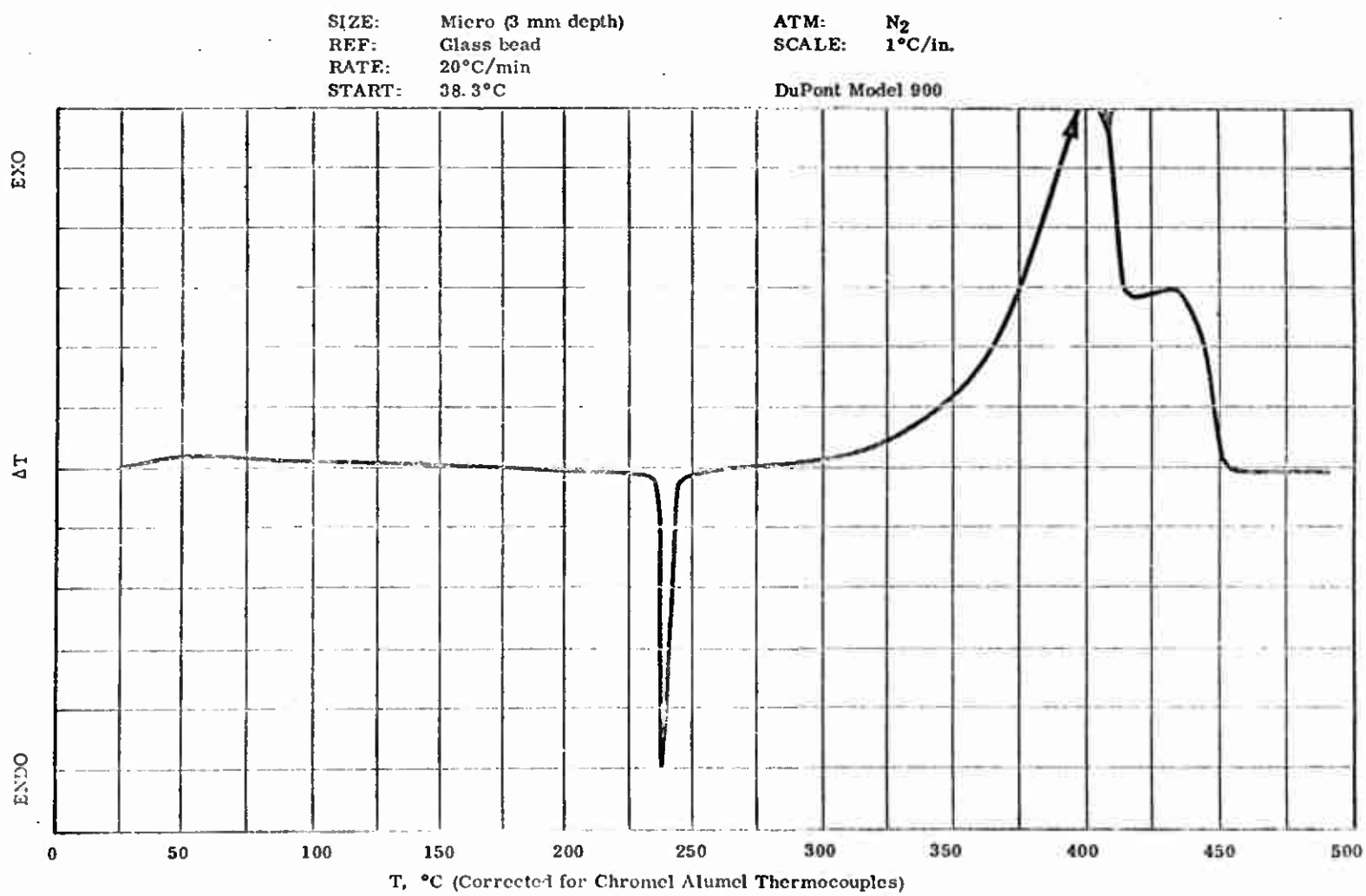


FIGURE 2. DTA THERMOGRAM MONOMETHYL AMMONIUM PERCHLORATE
$CH_3NH_3ClO_4$

SIZE:	Micro 3 mm depth	ATM.	N_2
REF:	Glass beads	SCALE SETTING:	1°C/in.
RATE:	20°C/min		
START:	39.1°C	DuPont Model 900	

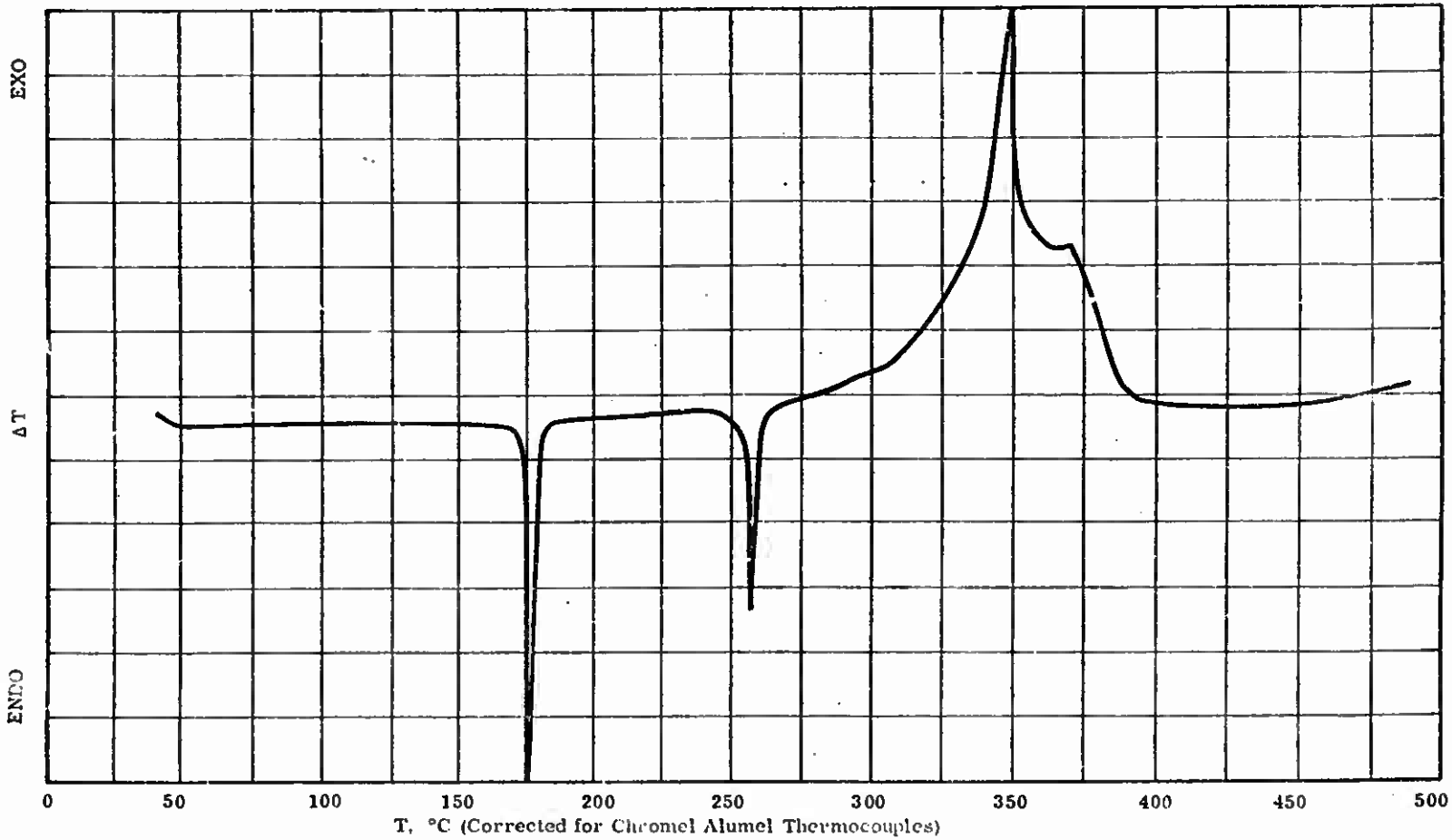


FIGURE 3. DTA THERMOGRAM DIMETHYL AMMONIUM PERCHLORATE
$(CH_3)_2NH_2ClO_4$

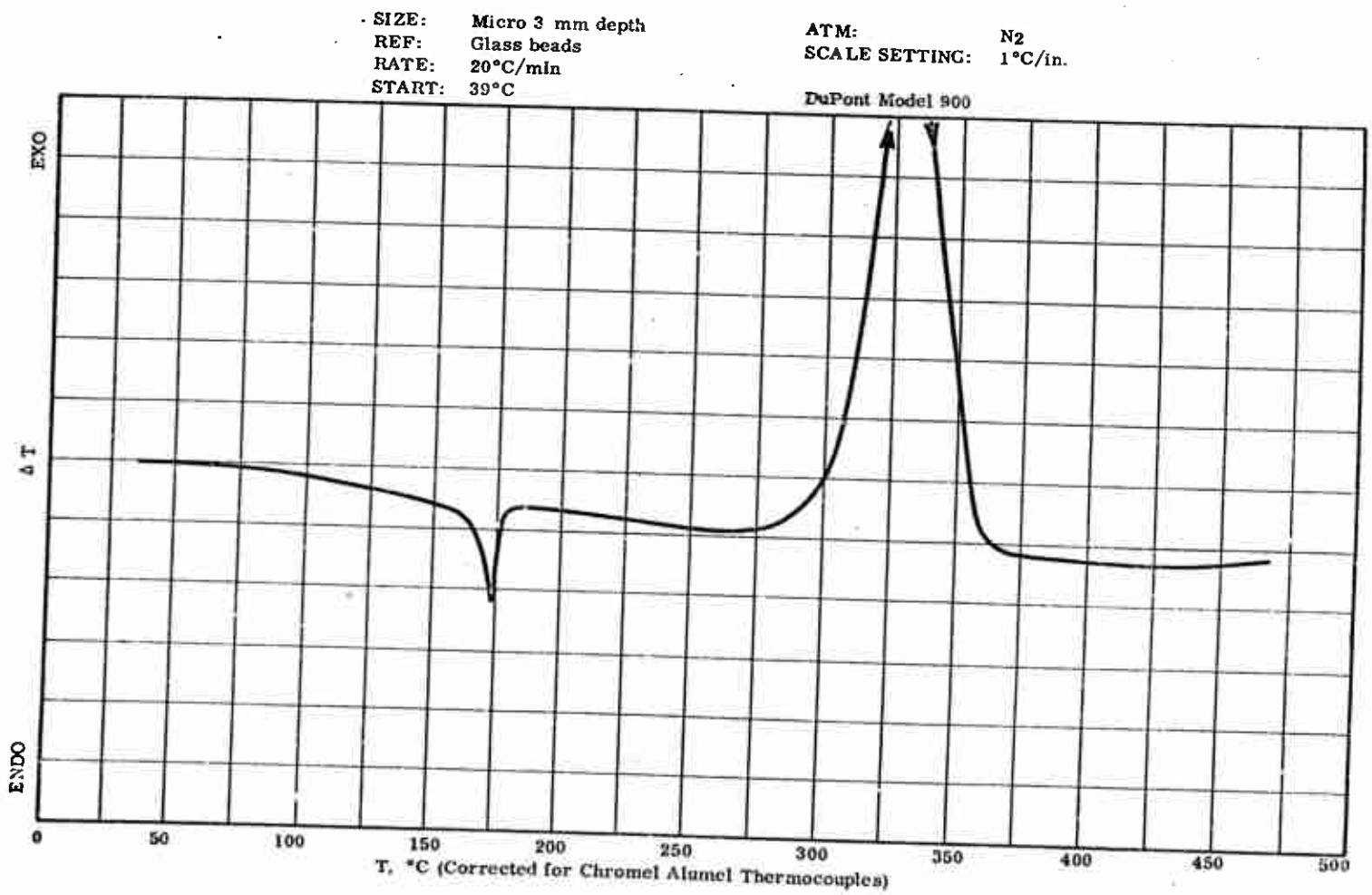


FIGURE 4. DTA THERMOGRAM TRIMETHYL AMMONIUM PERCHLORATE
(IMPURE)
$(CH_3)_3$ $NHClO_4$

SIZE: Micro 3 mm depth
REF: Glass beads
RATE: 20°C/min
START: 39.1°C

ATM. N_2
SCALE SETTING: 1°C/in.
DuPont Model 900

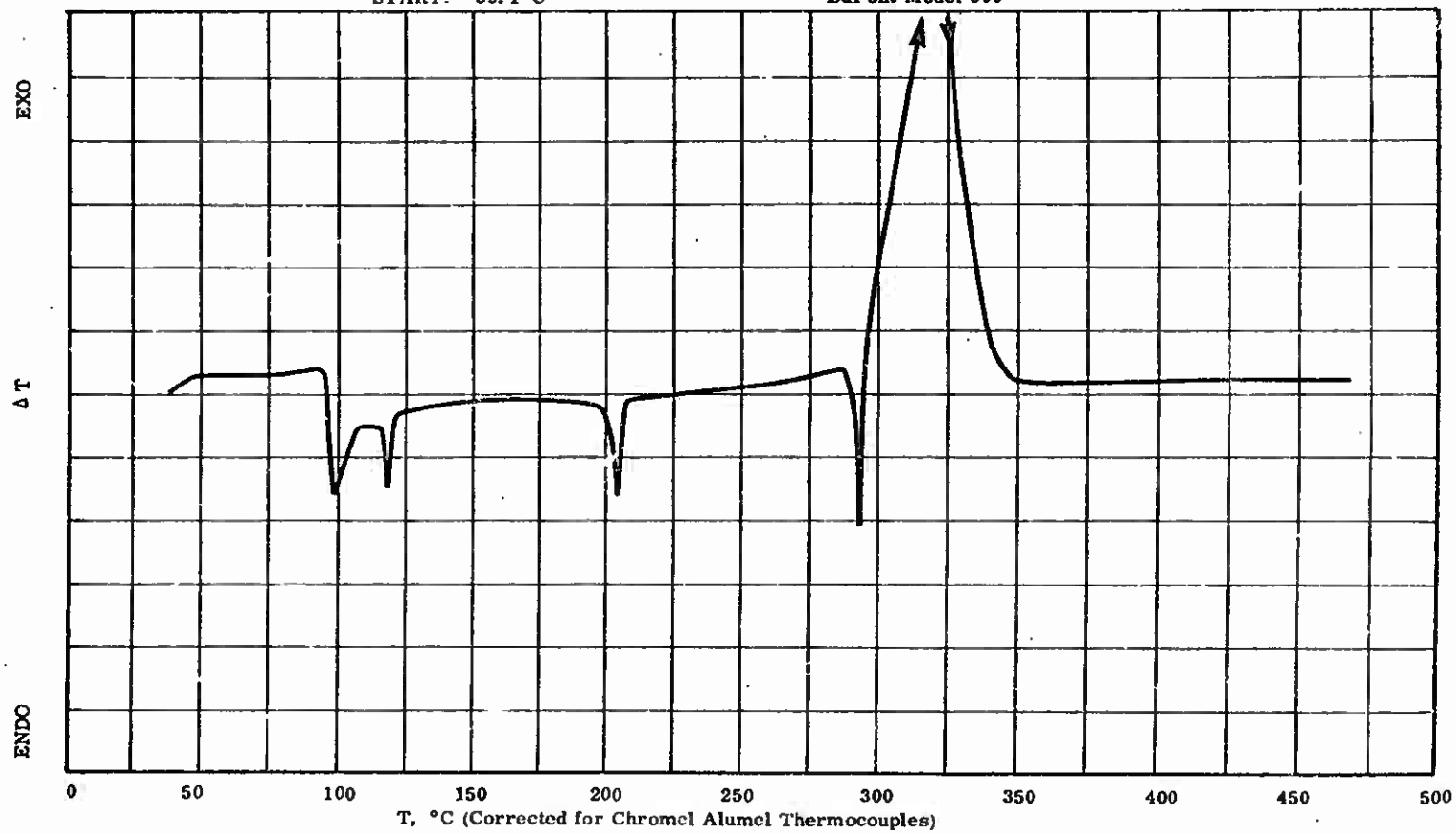


FIGURE 5. DTA THERMOGRAM TRIMETHYL AMMONIUM PERCHLORATE RECRYSTALLIZED, DRIED
$(CH_3)_3$ $NHClO_4$

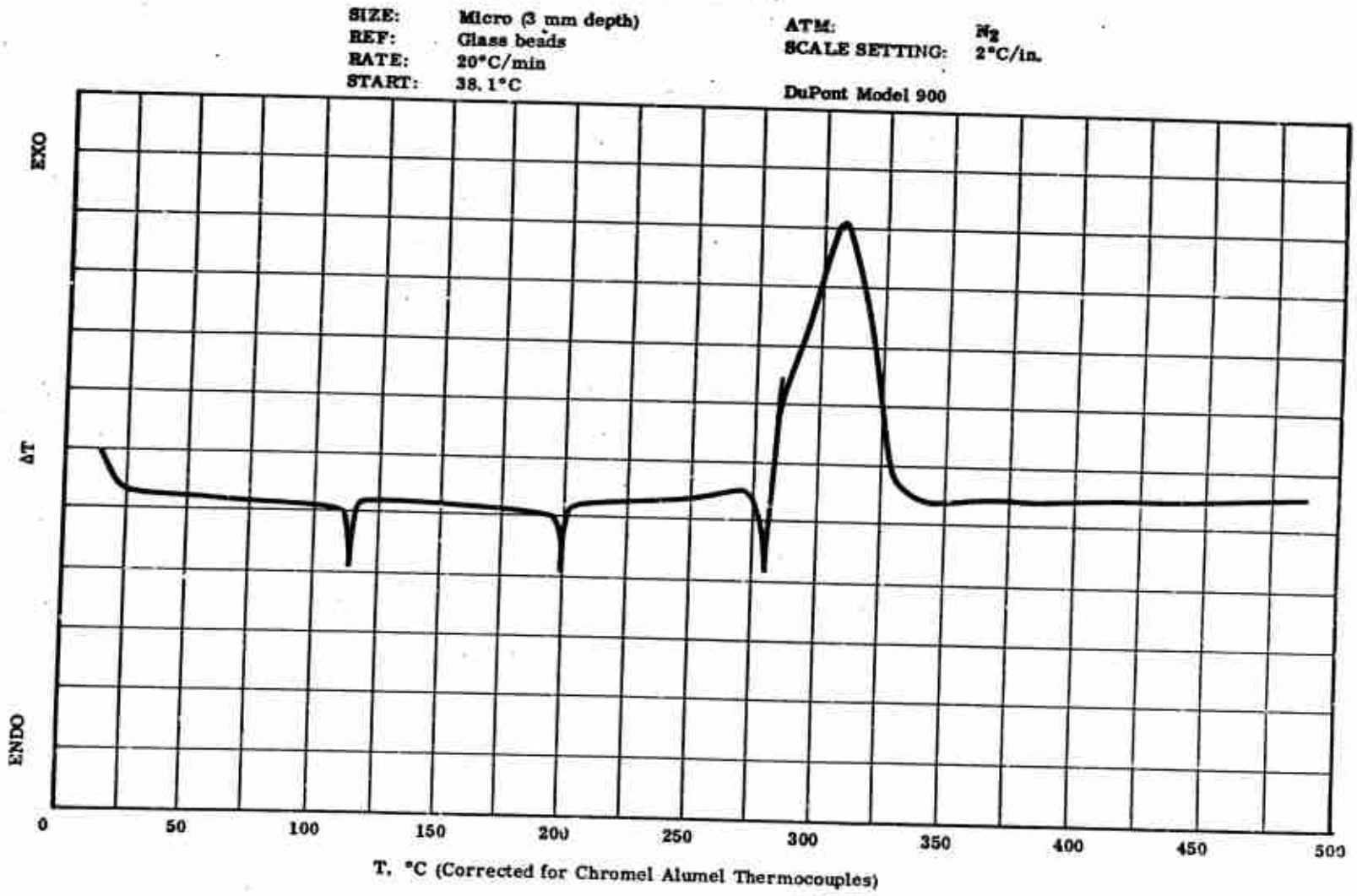


FIGURE 6. DTA THERMOGRAM AMMONIUM NITRATE
(Recrystallized)
NH_4NO_3

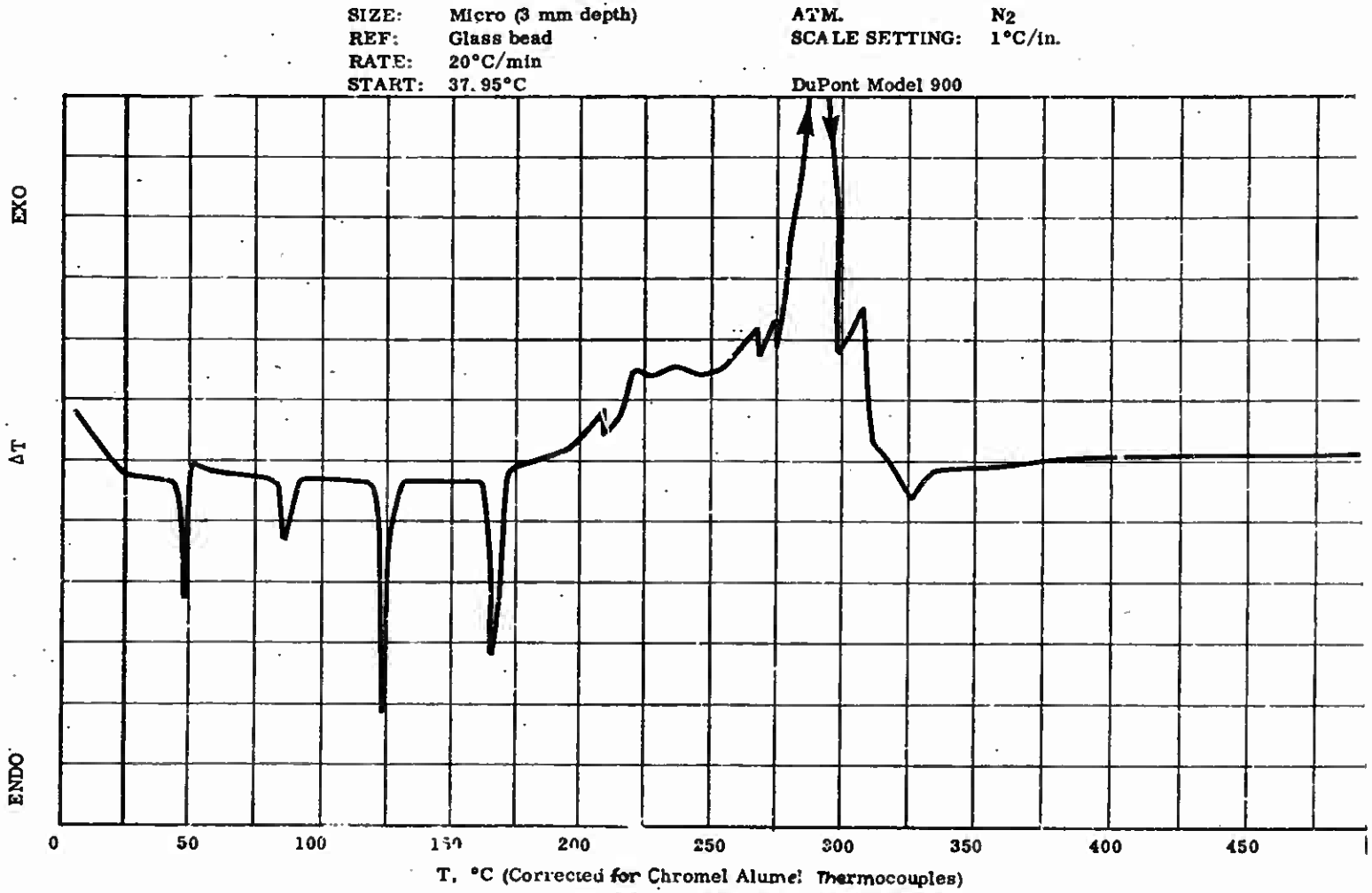
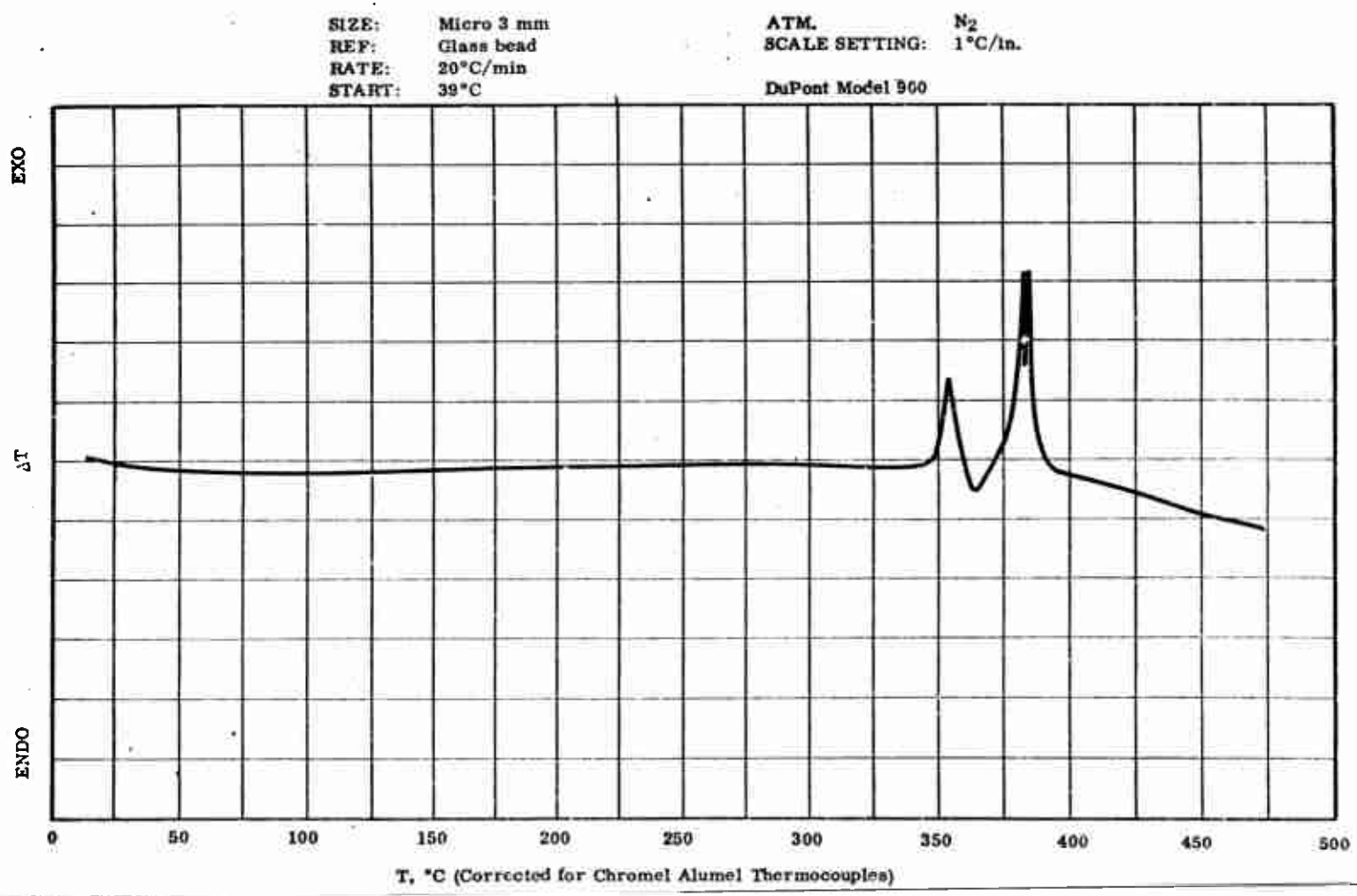


FIGURE 7. DTA THERMOGRAM TETRAMETHYL AMMONIUM NITRATE
$(CH_3)_4$ NNO_3

(Eastman Org. Chem.)



molecular level of admixture. This is pointed out because it is known that if an equivalent mixture is made of ammonium nitrate and $(CH_2)_n$ type fuel there is still considerable difficulty in achieving ignition and sustaining combustion in conditions near ambient.

Figures 8 and 9 are to be compared with each other and with Figure 1. When comparing with Figure 1, however, it should be noted that Figure 1 used a 1°C. per inch scale while Figures 8 and 9 use a 2°C per inch scale. In the latter figures this change kept the final exotherm on scale. It can be seen that the 235°C. to 240°C. endotherm appears unchanged. However, the final exotherm does not become really evident until 400°C. on Figures 8 and 9, whereas it was fully evident at 350°C. on Figure 1. Figure 1 was "ultra high purity" grade material as recieved from American Potash and Chemical Corporation. Figures 8 and 9 were powders prepared from single crystals we had grown from solution. As we have pointed out in previous reports, although 10% by weight strontium perchlorate and 90% ammonium perchlorate were present in the crystal growing solution; as can be seen in Figure 9, there was absolutely no stability change in the crystal that was grown. Both chemical analysis and thermal conductivity tests show that there was no detectable strontium doping in the crystal. As stated in the previous report, we are attempting to induce barium doping at the present time. However, as with the strontium doping studies, it has been found that the crystal habit is something strongly modified away from orthorhombic acid toward platelets and needles. It is also known, however, that habit modification is partly caused by temperature control and turbulence conditions within the crystal growing bath. These factors are being better controlled, and varied interests in an effort to achieve barium doping.

Thermogram studies are continuing to confirm the apparent difference between single crystal AP and the ultra high purity powder as received. It certainly appears as though the single crystal material has greater thermal stability.

III. Conclusions

1) DTA thermograms are excellent indicators of oxidizer purity. Recrystallization and vacuum drying tend to remove endo and exotherms, and to move the final exotherm to higher temperatures.

FIGURE 8. DTA THERMOGRAM PURE AMMONIUM PERCHLORATE SINGLE CRYSTAL (POWDERED)
NH_4ClO_4

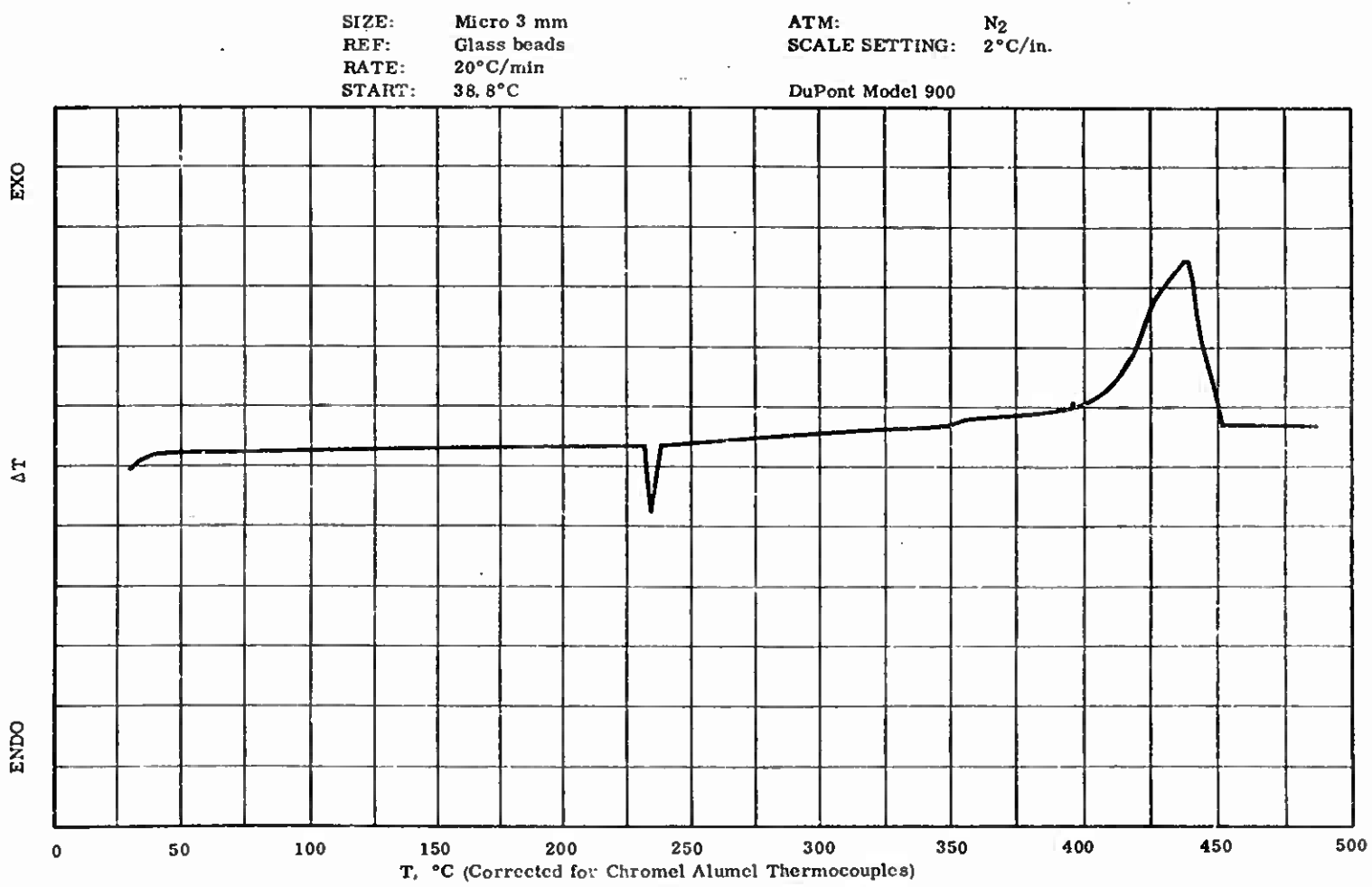
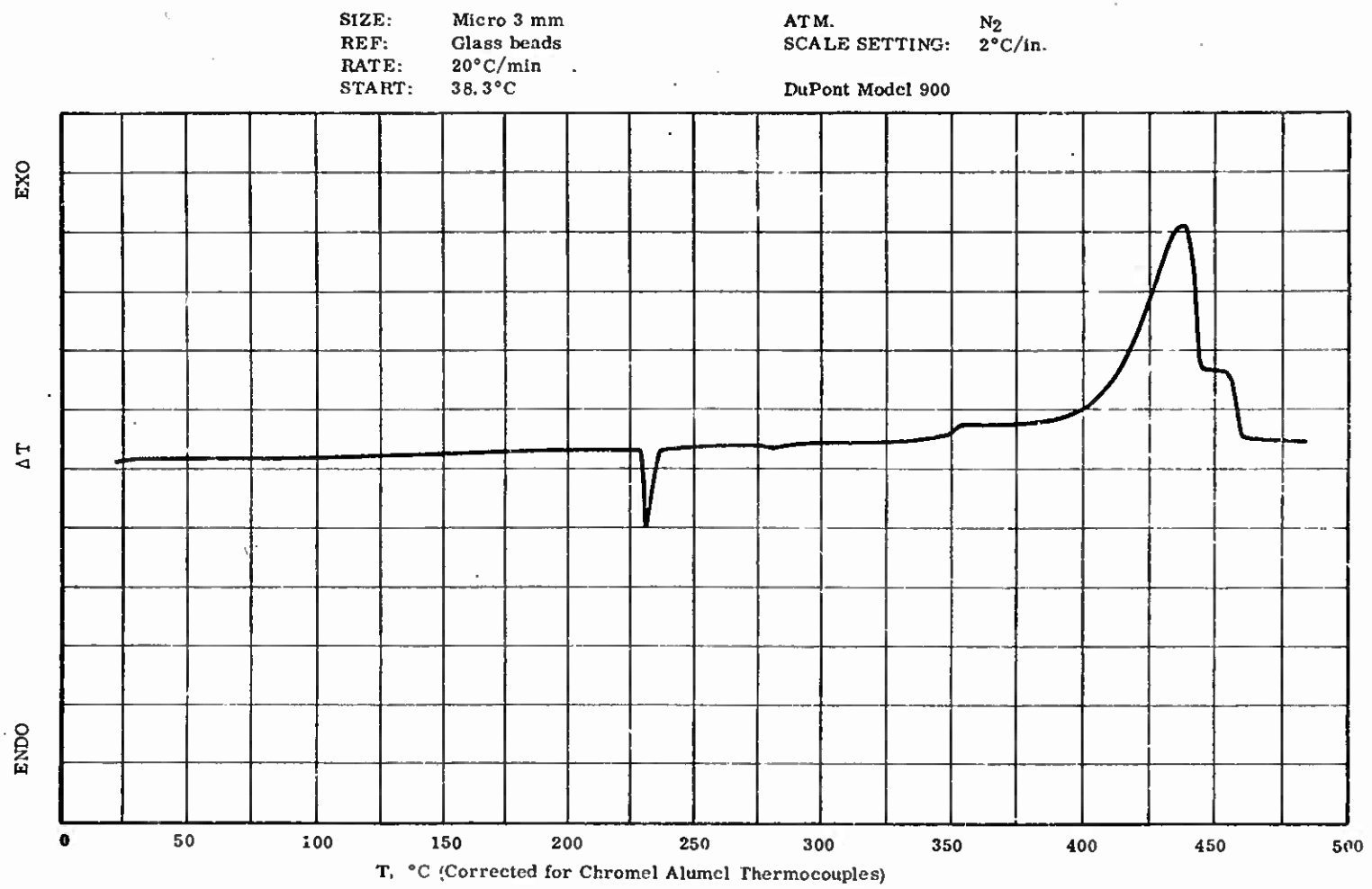


FIGURE 9. DTA THERMOGRAM SINGLE CRYSTAL GROWN FROM 10% STRONTIUM DOPED NH_4ClO_4 SOLUTION



2) The position of the final exotherm is the best measure of thermal stability.

3) Monopropellant burning rate, performance and impact sensitivity are not reflected in DTA thermograms in a regular manner.

IV. Future Work

1) Continue growth of crystals from Ba^{++} containing AP solutions.

2) Conduct burning tests at 30 to 100 atmospheres of A.P. powder/ combustion modifier mixtures.

V. References

1) H. C. Beachell, E. E. Hackman and Y. C. Kim "Combustion Characteristics of Crystalline Oxidizers" Quarterly Reports No. 3 and 4, University of Delaware, Brown Chemical Laboratory, May, 1968.

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13. ABSTRACT

A collection of perchlorate and nitrate crystalline oxidizer DTA thermograms is presented. The effects of oxidizer purity on presence and location of endo and exotherms is discussed. The effects of cation modifications for both kinds of oxidizers is shown.

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Solid Oxidizers						
Monopropellants						
Ammonium Perchlorate						
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Differential Thermal Analysis						