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TECHNICAL MEMORANDUM 1877

RESULTS OF LABORATORY STUDIES ON TRIEX-8 DEXTRINATED LEAD AZIDE

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PICATINNY ARSENAL
DOVER, NEW JERSEY

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Technical Memorandum 1877

RESULTS OF LABORATORY STUDIES ON TRIEX-8 DEXTRINATED LEAD AZIDE

by

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February 1969

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ABSTRACT

Laboratory tests including the 100°C vacuum stability test, DTA, TGA, x-ray diffraction analysis, impact sensitivity and electrostatic spark sensitivity were conducted on two different samples of dextrinated lead azide. One of the two samples was 25 years old while the other was recently manufactured. The results obtained with both materials and the values given in the literature were in close agreement.

INTRODUCTION

On 27 August 1968 an accident resulting in a fatality occurred at the Lone Star Army Ammunition Plant, Texarkana, Texas during a destruction operation in an outside sump with dextrinated lead azide. The details of the accident are described in Reference 1.

The explosive material that was being processed at that time was Triex lead azide, Type 1, Mil. Spec. L3550. In order to determine if the sensitivity of the material had changed, a 2-ounce sample from lot Triex-8 was shipped in mid-September 1968 in a water-alcohol solution to Picatinny Arsenal for analysis. Whether or not material from this particular lot was being used at the time of the accident is not known. However, the assumption was made that it was a representative sample of the dextrinated lead azide being used.

At the present time the manufacturer, the date and place of manufacture, and other pertinent data are not known. The available information indicates that this material was most likely manufactured during World War II and subsequently repackaged in 1953. It was shipped from NAD, Crane, Indiana to Lone Star AAP in July 1968 and within a month it was being processed in line loading operations.

As a result of the accident Picatinny Arsenal was requested by the U.S. Army Munitions Command to determine whether extensive changes had developed in the Triex-8 dextrinated lead azide that might affect its sensitivity and other properties and thus shed some light on the accident.

This report describes the results obtained with the laboratory studies which determined the sensitivity and other properties of the Triex-8 dextrinated lead azide. A comparison is made with the results of similar tests with an acceptable lot of dextrinated lead azide now being used in line operations at Picatinny Arsenal.

EXPERIMENTAL

The material as received consisted of 2 ounces of lot Triex-8 dextrinated lead azide in a water-alcohol solution. At the same time a sample of Du Pont 52-127 dextrinated lead azide in a water-alcohol solution was obtained for comparison. This material had been manufactured and accepted in June 1968.

Both samples of the dextrinated lead azide were washed and dried in the same manner. Each material was placed on a Büchner funnel and washed with five portions of a mixture of 1:1 triple-distilled water and 95% ethyl alcohol. Suction was applied for an hour, and then each sample was dried in a vacuum oven at 60°C for 24 hours. Upon removal from the oven each sample was placed in a rubber conductive container which was kept sealed.

Since data for reference purposes were not available for the Triex-8 dextrinated lead azide, the method selected to determine whether changes had occurred in that material was to conduct similar tests with an acceptable lot of dextrinated lead azide of recent manufacture and to compare the results obtained. As stated previously the belief is that Triex-8 material was manufactured during World War II while the date for the Du Pont 52-127 material was June 1968. This represents an age differential of about 25 years.

The following methods and tests were used to determine if any real differences could be found between the Triex-8 and Du Pont 52-127 dextrinated lead azide:

1. 100°C vacuum stability test
2. Differential thermal analysis (DTA)
3. Thermogravimetric analysis (TGA)
4. X-ray diffraction
5. Impact sensitivity test
6. Electrostatic spark test

Only the electrostatic spark test did not follow a standard method or procedure. That method used the brass cup from the impact test as the receptacle for the explosive material (25 mg) and the probe was imbedded in the lead azide when the static discharge occurred.

The Du Pont differential thermal analyzer, Model 900, with a remote cell adapter, was used to obtain the DTA thermograms. The TGA apparatus used is an attachment, Model 950, to the Du Pont DTA apparatus.

RESULTS

Photomicrographs were taken of the Triex-8 and Du Pont 52-127 dextrinated lead azide samples at magnifications of 100X, 200X, and 300X as shown in Figures 1 through 6. Comparisons were made also with the photomicrographs that came from Lone Star AAP. These were 260X magnification and included photomicrographs of dextrinated lead azide lots Triex-8, Du Pont 52-132, and OMC 68-7 batch 113 (see Figures A through D in the Appendix).

A study of the photomicrographs indicates that on an overall basis the Triex-8 material is not much larger than the Du Pont 52-127. The Du Pont material is more crystalline in appearance, having faceted surfaces, whereas the Triex-8 is more rounded and less clearly faceted in appearance. The Triex-8 material is more opaque and whitish while the Du Pont 52-127 seems to be translucent.

The large conglomerates as shown in Figures A and B were not seen in any of the photomicrographs of Lot Triex-8 taken at Picatinny Arsenal but it should be noted that a similar conglomerate is present in the Du Pont 52-127 sample (Fig 4). Military Specification MIL-L-3055A dated 28 September 1962 does not indicate any limits for particle size for Type I (dextrinated) and the only restriction relative to the form or shape is that it has to be free from needle-shaped crystals. Needle-shaped crystals are defined as those having a length/diameter of 7/1 or greater. The size and form of the large particle in Figure 4 and in Figures A and B do not give the appearance of large single crystals.

Actually these large particles seem to fall into two categories. In Figure B the conglomerate actually appears to be several small conglomerates fused together. In Figure A and Figure 4 the appearance is that of a crust or cake which consists of fused conglomerates.

The solubility of pure lead azide in water is given as 0.02% at 18°C and 0.09% at 70°C but a solubility of up to 1% of dextrinated lead azide in cold water is acceptable according to the military specification because of the solubility of the dextrin. An instance was reported which may indicate how the conglomerates are formed.[1] During a drying operation a batch of dextrinated lead azide was removed still soaking wet with water, spread onto open pans, and then put into an oven to dry at 65°C. When the batch was removed from the oven, examination revealed that a crust had formed which resembled the particles in Figures A and 4. It is believed that the incrustation was formed when evaporation of the solution of dextrinated lead azide and water occurred. This was prevented from recurring by displacing the water with alcohol and then filtering the alcohol from the lead azide before drying. A similar situation occurs when sodium azide is permitted to stand in water at room temperature for a period of time. Partial evaporation of the solution of sodium azide and water will form a crust very similar to the particle in Figure A.

In order to determine if the Triex-8 dextrinated lead azide had undergone any physical or chemical changes that would have affected its properties or sensitivity, the material was subjected to different tests and methods. A brief description of each test and the results obtained are given below.

1. 100°C Vacuum Stability Test

A 1-gram sample of Triex-8 dextrinated lead azide was subjected to the 100°C vacuum stability test for 40 hours (Ref 3). The amount of gas that evolved was 0.32 ml/g/40 hours. The same test with the Du Pont 52-127 material produced 0.26 ml/g/40 hours. Values of 0.32 ml/g/hr and 0.4 ml/g/hr have been reported for dextrinated lead azide (Ref 5 and 6). The amounts obtained are well within the values reported, attesting to the thermal stability of both dextrinated lead azides.

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[1] This incident was described by Mr. J. D. Hopper, Explosives Laboratory, Picatinny Arsenal.

2. Differential Thermal Analysis

Differential thermal analysis (DTA) is a technique in which the thermal effects associated with physical or chemical changes are recorded as a function of temperature or time as the substance is heated at a uniform rate. In this technique the sample temperature is continuously compared with an inert reference material temperature and the difference in temperature is recorded as a function of the heater temperature. Generally speaking, phase transitions, dehydration, reduction, and some decomposition reactions produce endothermic effects; crystallization, oxidation, and some decomposition reactions produce exothermic reactions (Ref 4).

DTA thermograms were obtained on the Triex-8 and Du Pont 52-127 dextrinated lead azide samples at two different heating rates (Fig 7 through 10). The data from these DTA thermograms are listed in Table 1.

TABLE 1

DTA data

Sample Description	Peak Exotherm at 20°C/min	Peak Exotherm at 10°C/min
1. Triex-8 DLA	316°C (Fig 7)	309°C (Fig 8)
2. Du Pont 52-127 DLA	319°C (Fig 9)	310°C (Fig 10)

Note: Temperatures indicate when each sample detonated.

The lack of endotherms indicates that the melting phase transition does not occur before decomposition starts, and the exotherm peak represents the decomposition. The samples were scanned in a nitrogen atmosphere in order to study the thermal changes that are not the result of oxidation. The peak temperatures can be affected by particle size, amount of sample, swelling or shrinking of the sample, thermal conductivity, heat capacity, etc.

The DTA thermograms of the two samples at the two different heating rates indicate rather close agreement--within 3°C for a heating rate of 20°C/min and 1°C for 10°C/min.

The temperatures noted indicate where the sample detonated in the decomposition phase. Considering that the samples represented different lots and manufacturers and also different particle size, plus the age differential, the close agreement in the data indicates that on an overall basis the older material has not changed over the years.

3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique used to measure the weight of a material as a function of linearly increasing temperature. The resulting weight change vs temperature curve can give information concerning the thermal stability and composition of the sample and the composition of the residue (Ref 4).

The TGA apparatus is similar to the DTA in that it heats a small sample at a constant rate. As stated previously the weight loss instead of the temperature difference is measured as a function of temperature. This detects decomposition which results in gaseous products and provides a quantitative measure of the amount and rate of decomposition at each temperature.

The TGA can be used to measure the thermal sensitivity of lead azide. It also can be used to differentiate between detonation and decomposition, as shown by Pai-Verneker and Maycock (Ref 5). To provide a basis for comparison the same heating rates were used as in the DTA tests and the temperatures were recorded at which weight loss started and subsequently where detonation occurred.

At 10°C/min, TGA thermograms of Triex-8 and Du Pont 52-127 dextrinated lead azide of sample sizes ranging from 1 to 2 milligrams showed decomposition or weight loss. Figures 11 and 13 are typical curves that were obtained. Weight loss on both samples started at ∿200°C.

At a heating rate of 20°C/min the amount of sample weight can be used to differentiate between decomposition and detonation. With a sample weight at about 1 mg for both Triex-8 and Du Pont 52-127, weight loss started at about 200°C and continued slowly up to 400°C (Figs 12 and 14). With a sample weight of about 2 mg, under the same conditions, the weight loss started in each material between 200°C-225°C. Each sample subsequently detonated--Triex-8 at 322°C and Du Pont 52-127 at 321°C (Figures 12a and 14a).

The thermal stability and/or sensitivity of the Triex-8 and Du Pont 52-127 are practically the same.

4. X-Ray Diffraction

X-ray diffraction can be used to identify a compound and to detect changes in crystal structure of a compound subjected to a particular treatment. These changes are usually indicated by a shift in the d-values or interplanar spacings and the intensity of the peak values from the values characteristic of the unaffected sample. The detection of these changes is usually dependent upon the newly formed crystalline material if it is present.

Samples of Triex-8 and Du Pont 52-127 were submitted for analysis by x-ray diffraction. Debye-Scherrer films were obtained on each sample in a 114.60 mm diameter camera using Cu K_α radiation and a nickel filter (Fig 15). The d-values and relative intensities of the reflections were determined using a Siemens densitometer (Ref 6). In addition the films were read in a standard film reader and the film shrinkage was included in the d-value calculation. The results in Table 2 show that the samples of Triex-8 and Du Pont 52-127 are identical according to the x-ray diffraction spectra.

5. Impact Sensitivity Test

Full curves were obtained using the Picatinny Arsenal impact tester (Ref 3). Twenty samples were tested at each point with a 2-kilogram and also a 1-kilogram drop weight. At least six points were obtained between the 0% and 100% "fire" heights in each test.

The results obtained with a 2-kilogram drop weight are shown in the curves in Figure 16. The 10% and 50% "fire" heights for the Triex-8 dextrinated lead azide are 5.5 and 8 inches, respectively. The heights for the same values for the Du Pont 52-127 material are 6.5 and 8.5 inches, respectively. The 10% values reported in the open literature range from 4 to 6 inches (Ref 2, 7, 8).

When the impact sensitivity test was conducted with the 1-kilogram drop weight on Triex-8 and Du Pont dextrinated lead azide, a sample of special purpose lead azide (Lot JA-4-61) was also tested. The 10% "fire" height for the Triex-8 material was 10 inches, for the Du Pont 52-127

TABLE 2

X-ray diffraction results

α-Pb(N_3)2
Dextrinated
Triex-8

d, A	Intensity, I/Ic
5.41	50
5.03	10
4.92	100
4.695	40
4.47	10
4.328	20
4.184	90
3.95	60
3.83	60
3.32	20
3.11	40
3.05	30
2.96	40
2.90	15
2.84	80
2.72	20
2.60	30
2.56	40
2.50	30
2.31	20
2.17	20
2.10	25
2.07	25
2.05	20
2.02	<10
1.968	25
1.936	30
1.910	20
1.876	10
1.845	10
1.808	10
1.663	10
1.613	<10
1.588	10
1.569	10
1.545	10
1.524	10
1.500	10
1.431	10
1.392	10

α-Pb(N_3)2
Dextrinated
Du Pont 52-127

d, A	Intensity, I/Ic
5.40	50
5.04	<10
4.90	100
4.68	35
4.46	<10
4.31	25
4.16	70
3.94	40
3.81	50
3.32	20
3.10	50
3.05	25
2.96	30
2.90	<10
2.83	80
2.72	40
2.60	35
2.56	40
2.49	35
2.30	20
2.18	20
2.09	20
2.07	20
2.04	20
2.02	<10
1.963	20
1.933	20
1.910	10
1.876	10
1.841	10
1.808	10
1.663	10
1.613	<10
1.588	10
1.569	10
1.545	10
1.524	10
1.500	10
1.431	10
1.390	10

material 11.5 inches, and for the special purpose JA-4-61 lead azide 9 inches, as shown in Figure 17. The 50% heights for the Triex-8, the Du Pont 52-127, and the special purpose JA-4-61 were 12.5, 16, and 14 inches, respectively.

The presence of large conglomerates raised the question as to whether the sensitivity of the Triex-8 material had increased. The results of the impact tests on the Triex-8 material indicate that the sensitivity of that material does not differ to any degree from the sensitivity of the Du Pont 52-127 material. The effect of crystal size on the impact sensitivity of pure lead azide is described by Bowden and Yoffe (Ref 9). For single crystals the impact energy necessary to cause explosion increases as the size of the crystal is decreased. However, for a heap of crystals of uniform size the impact energy is independent of the size of the individual crystals in the heap and remains approximately constant. The results of the impact tests clearly showed that none of the materials tested displayed any abnormal range in impact sensitivity.

6. Electrostatic Spark Sensitivity

Tests were conducted on Triex-8 and Du Pont 52-127 dextrinated lead azide to determine their sensitivity to static discharge. Since the value of .007 joule is given for pure lead azide (Ref 2) both the Triex-8 and Du Pont 52-127 dextrinated lead azide samples were tested with 1000 and 1500 volts with .01 microfarad capacitance at 75°F and 35% RH. Ten tests were performed at each voltage without any detonations occurring after each discharge. Samples of special purpose lead azide did detonate (10%-30%) in this energy range (.005 and .011 joule). Based upon these results it is evident that both Triex-8 and Du Pont 52-127 are less susceptible to electrostatic spark discharge than special purpose lead azide.

SUMMARY

Based on the results of the laboratory tests conducted on the Triex-8 and Du Pont 52-127 dextrinated lead azide samples the thermal stability and explosive sensitivity of both materials are practically the same within experimental error. In all of the methods used the data obtained did not show any significant difference from similar results reported in the literature. It may be concluded that the

Triex-8 dextrinated lead azide does not exhibit any abnormal behavior when compared to a recently manufactured sample of dextrinated lead azide using standard sensitivity tests.

ACKNOWLEDGMENTS

The assistance of A. C. Forsyth with this work is appreciated. Also the x-ray diffraction analysis by J. E. Abel and the TGA by M. S. Kirshenbaum are acknowledged.

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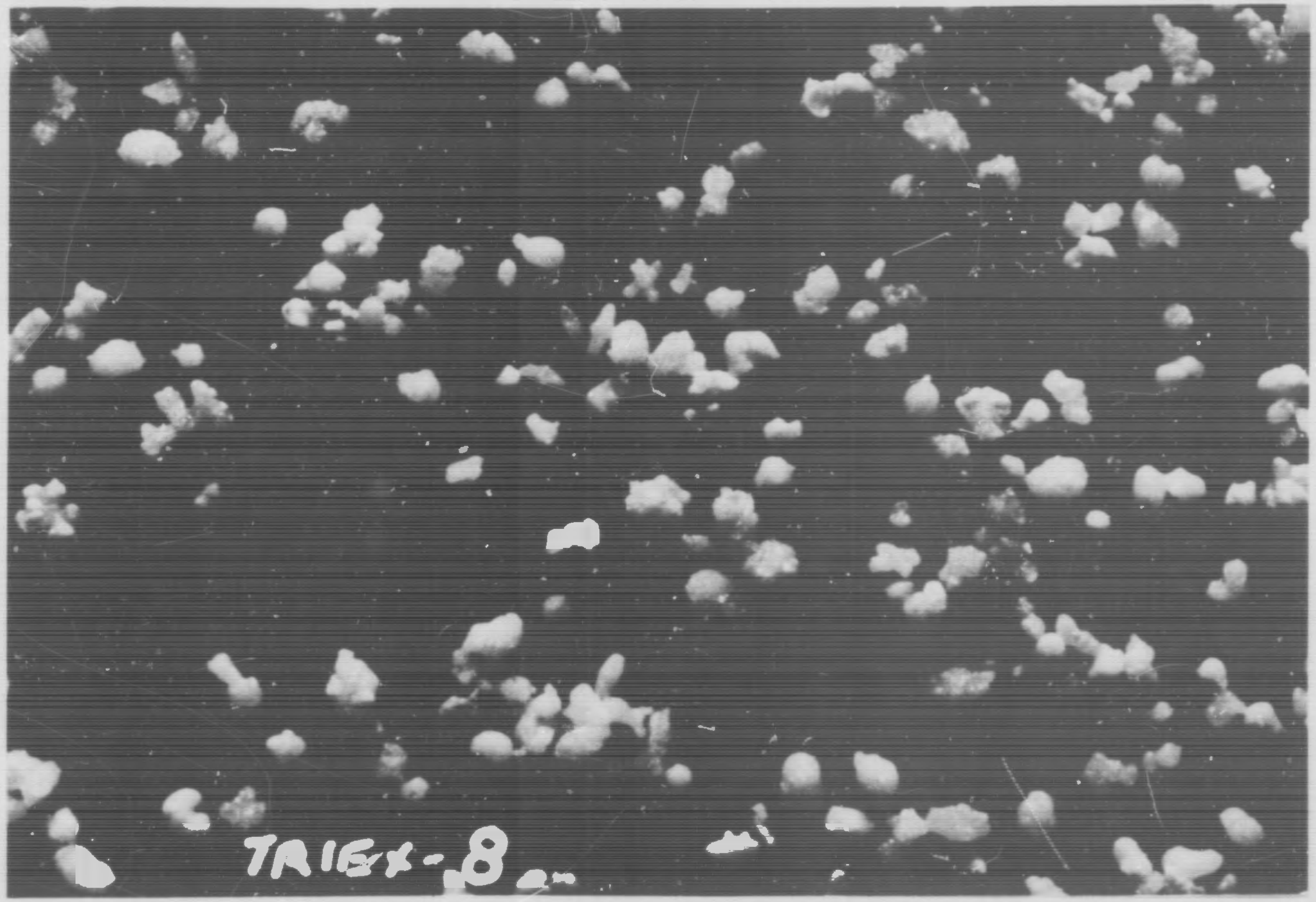


Fig 1   Photomicrograph of Triex-8 dextrinated lead azide (100X)

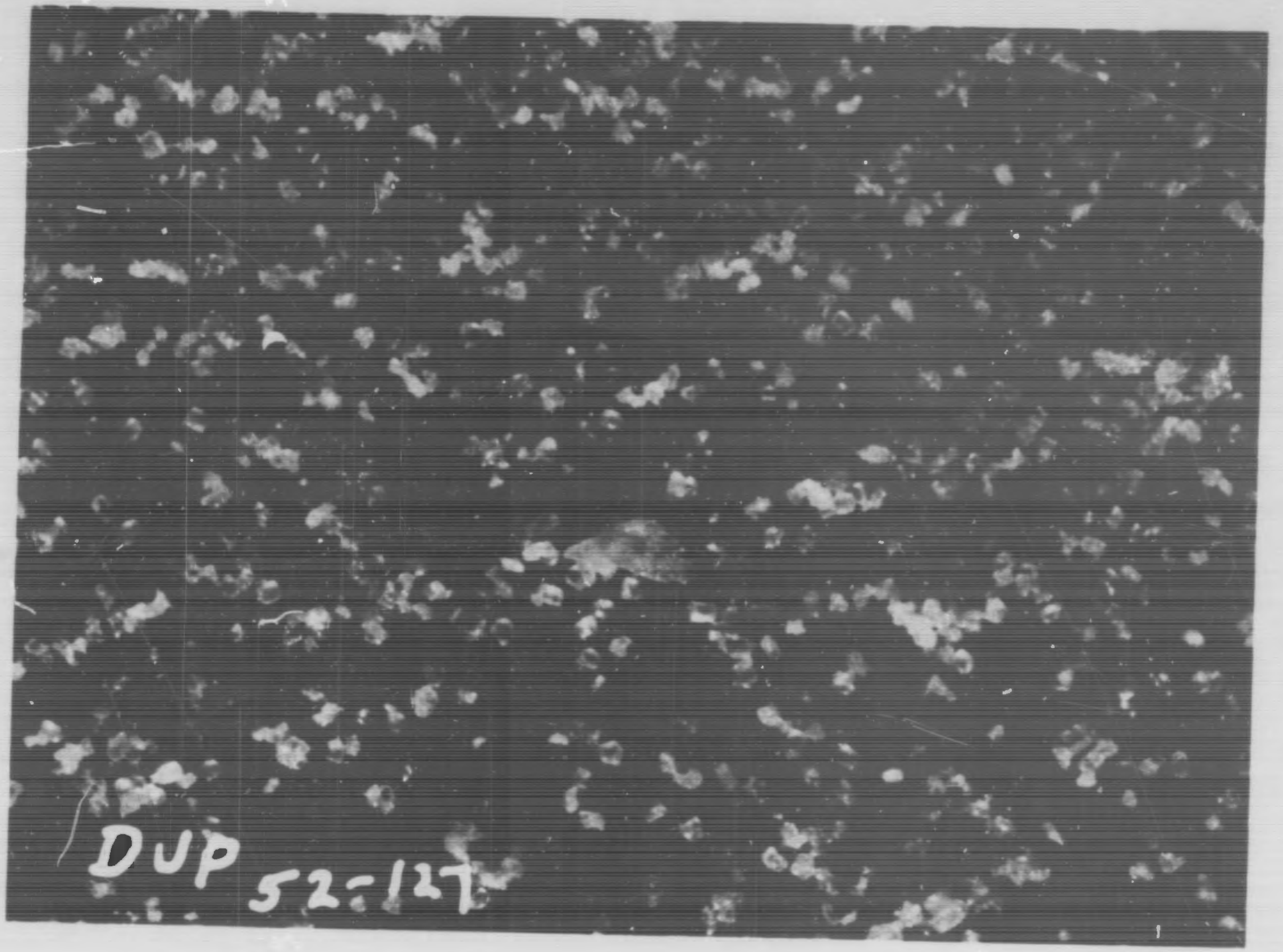


Fig 2 Photomicrograph of Du Pont 52-127 dextrinated lead azide (100X)

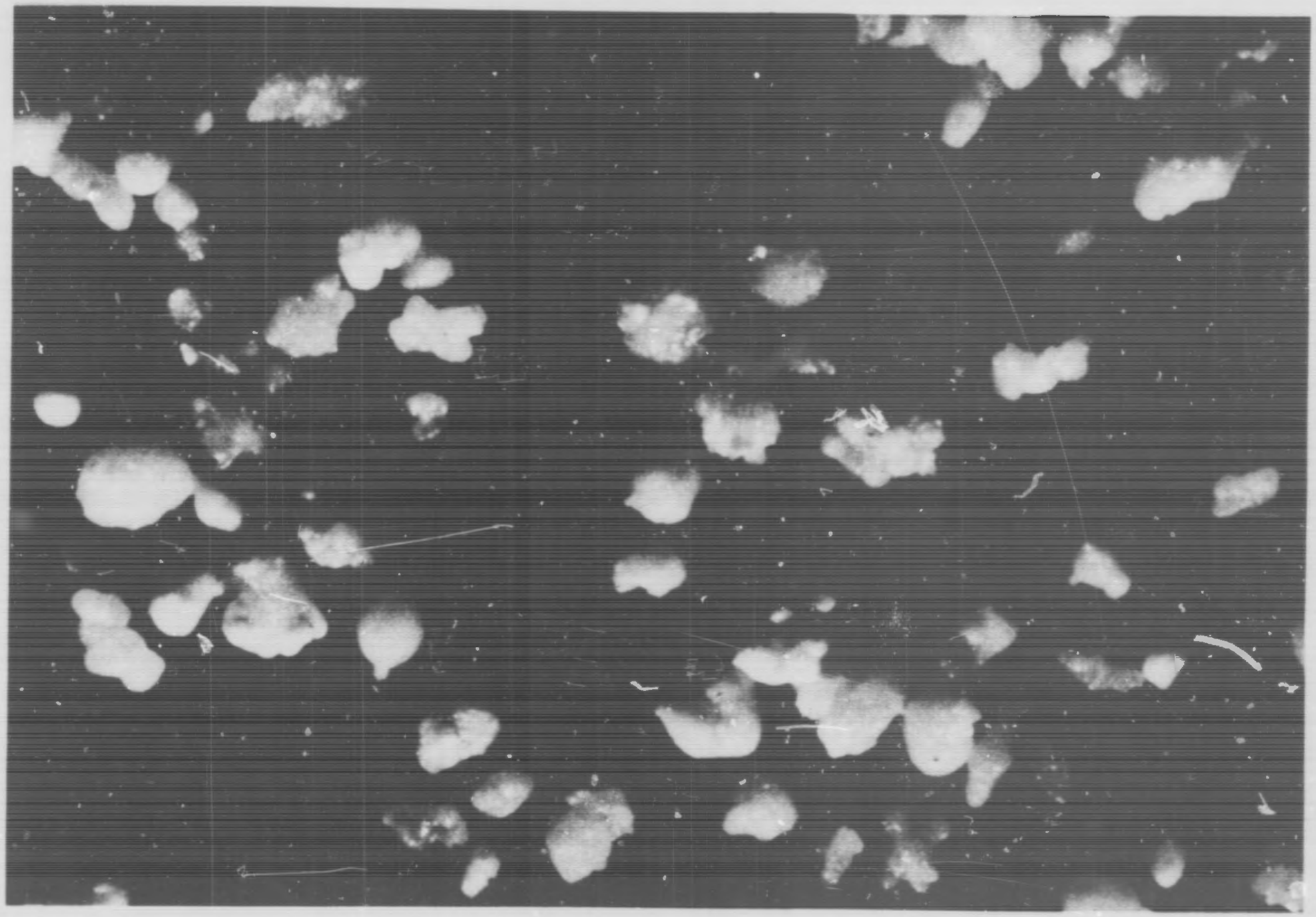


Fig 3 Photomicrograph of Triex-8 dextrinated lead azide (200X)

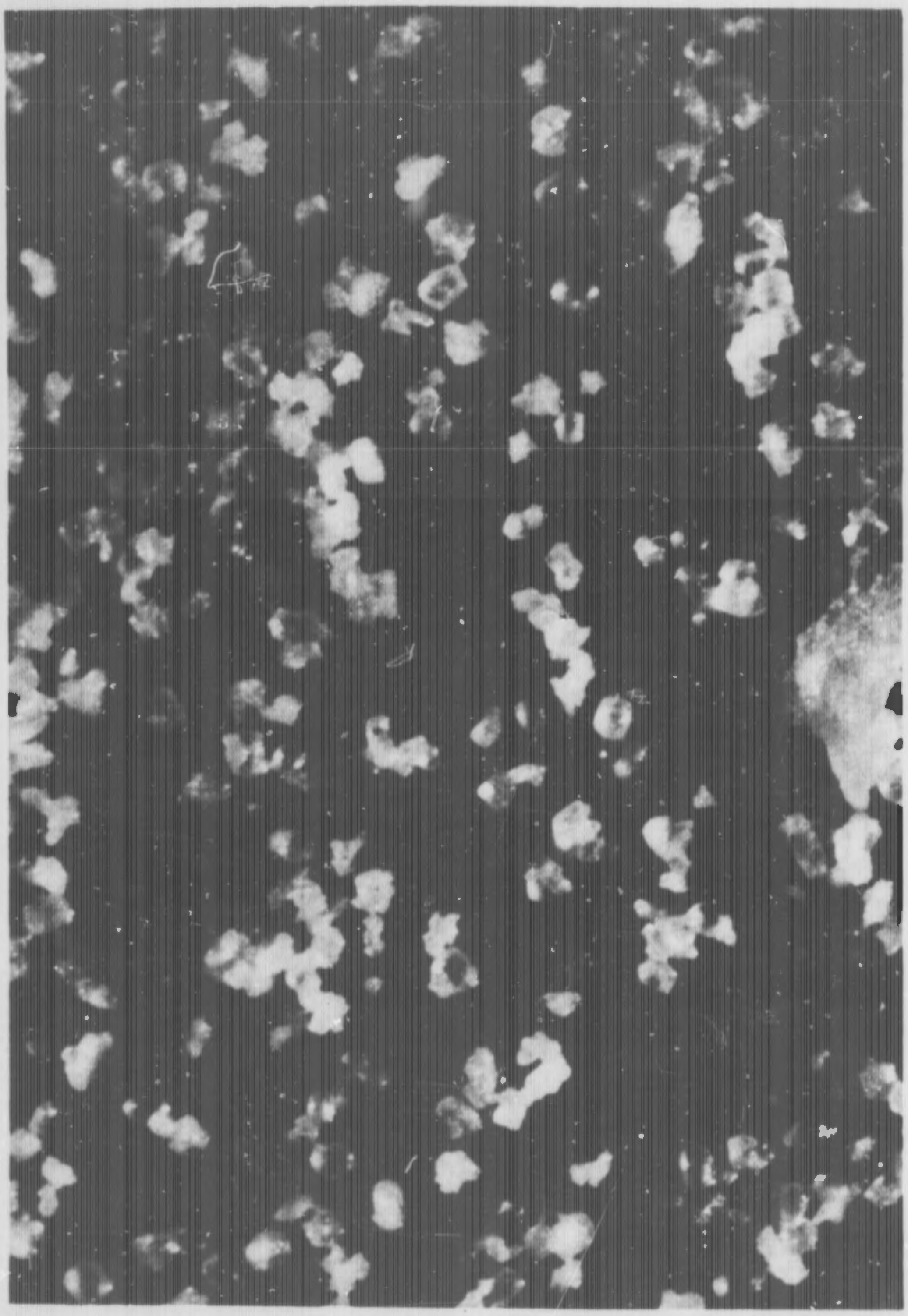


Fig 4 Photomicrograph of Du Pont 52-127 dextrinated lead azide (200X)

Fig 5 Photomicrograph of Triex-8 dextrinated lead azide (300X)

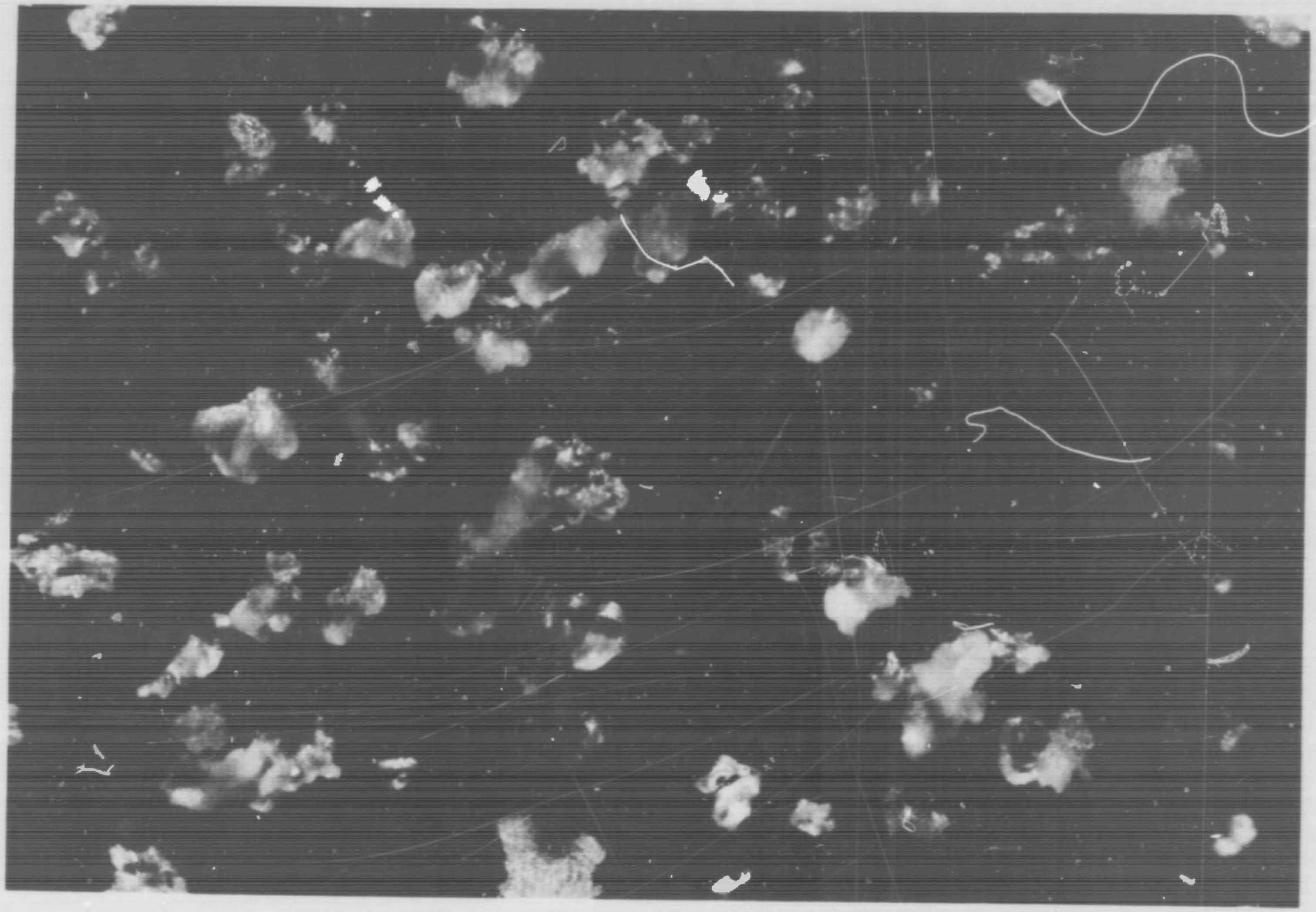


Fig 6 Photomicrograph of Du Pont 52-127 dextrinated lead azide (300X)

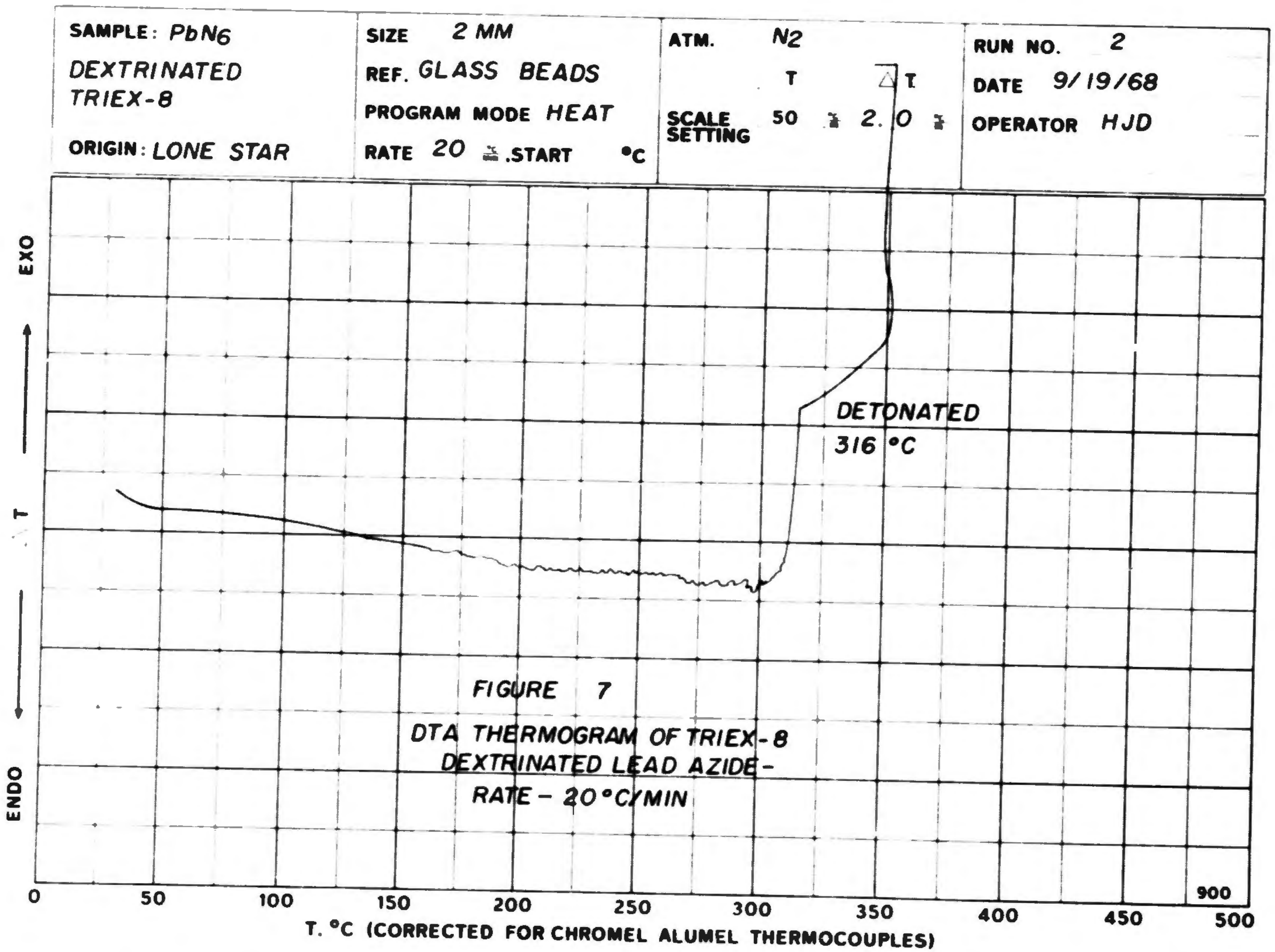


Fig 7 DTA thermogram of Triex-8 dextrinated lead azide. Rate, 20°C/min

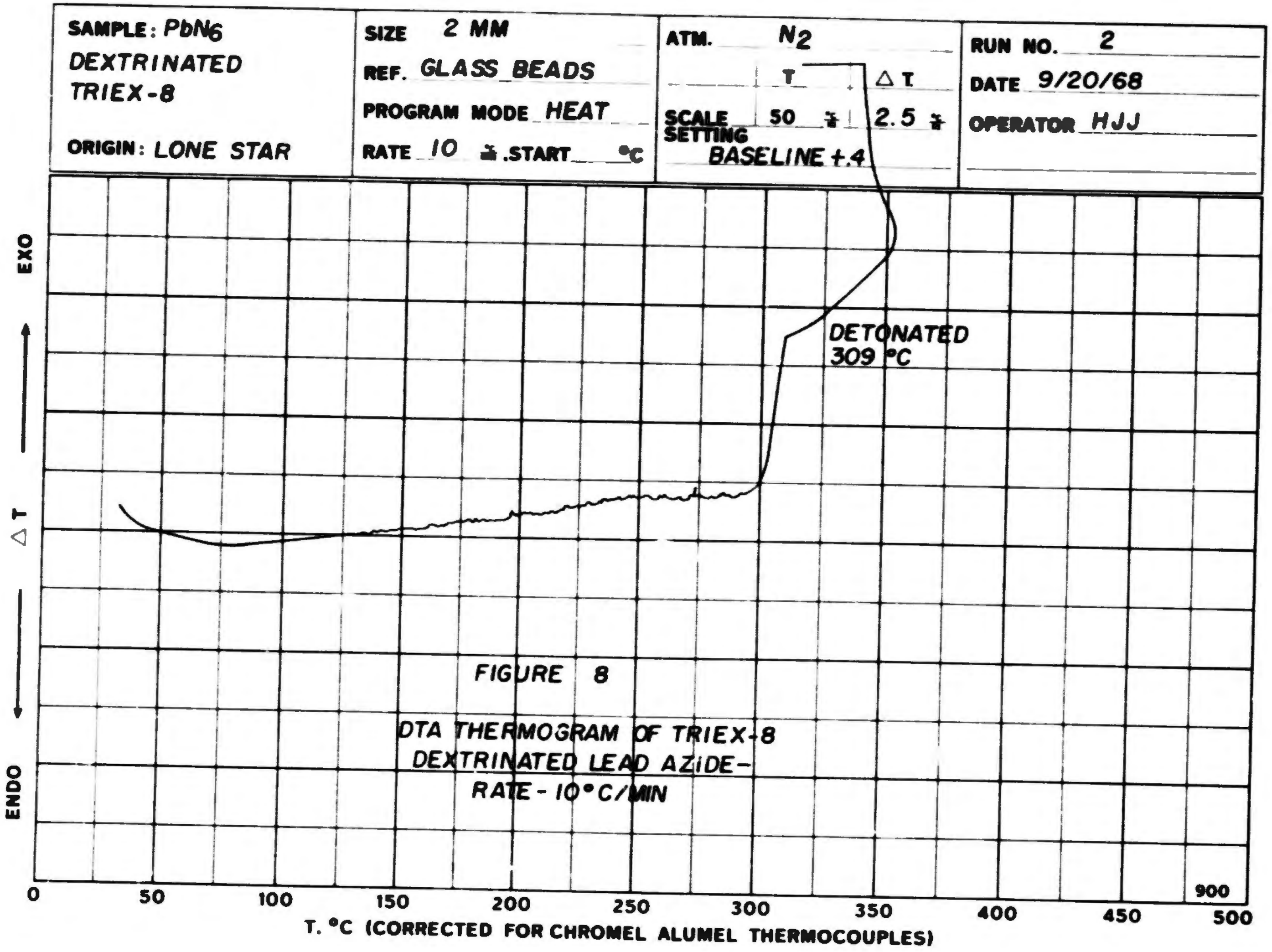


Fig 8 DTA thermogram of Triex-8 dextrinated lead azide. Rate, 10°C/min

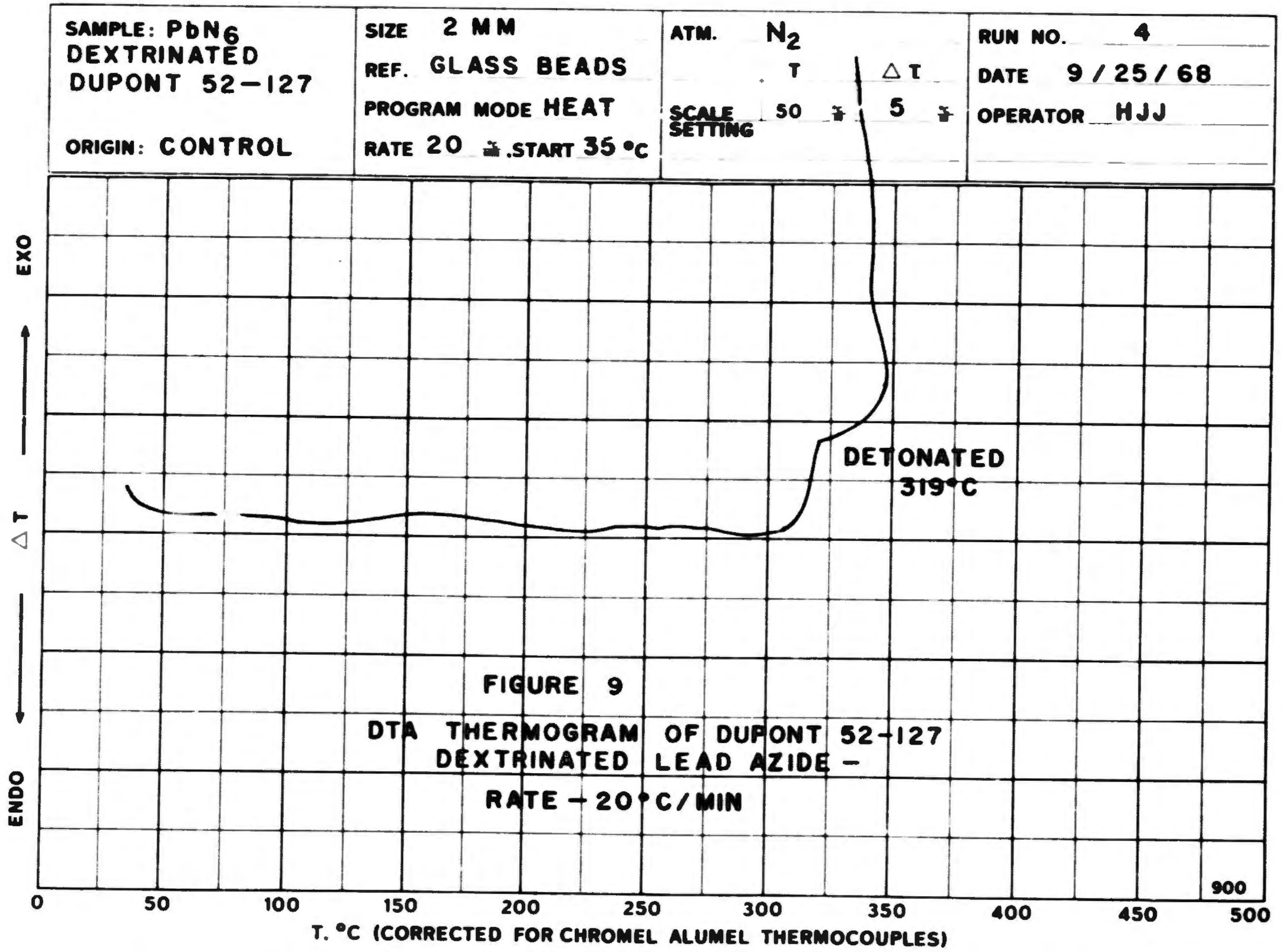


Fig 9 DTA thermogram of Du Pont 52-127 dextrinated lead azide. Rate, 20°C/min

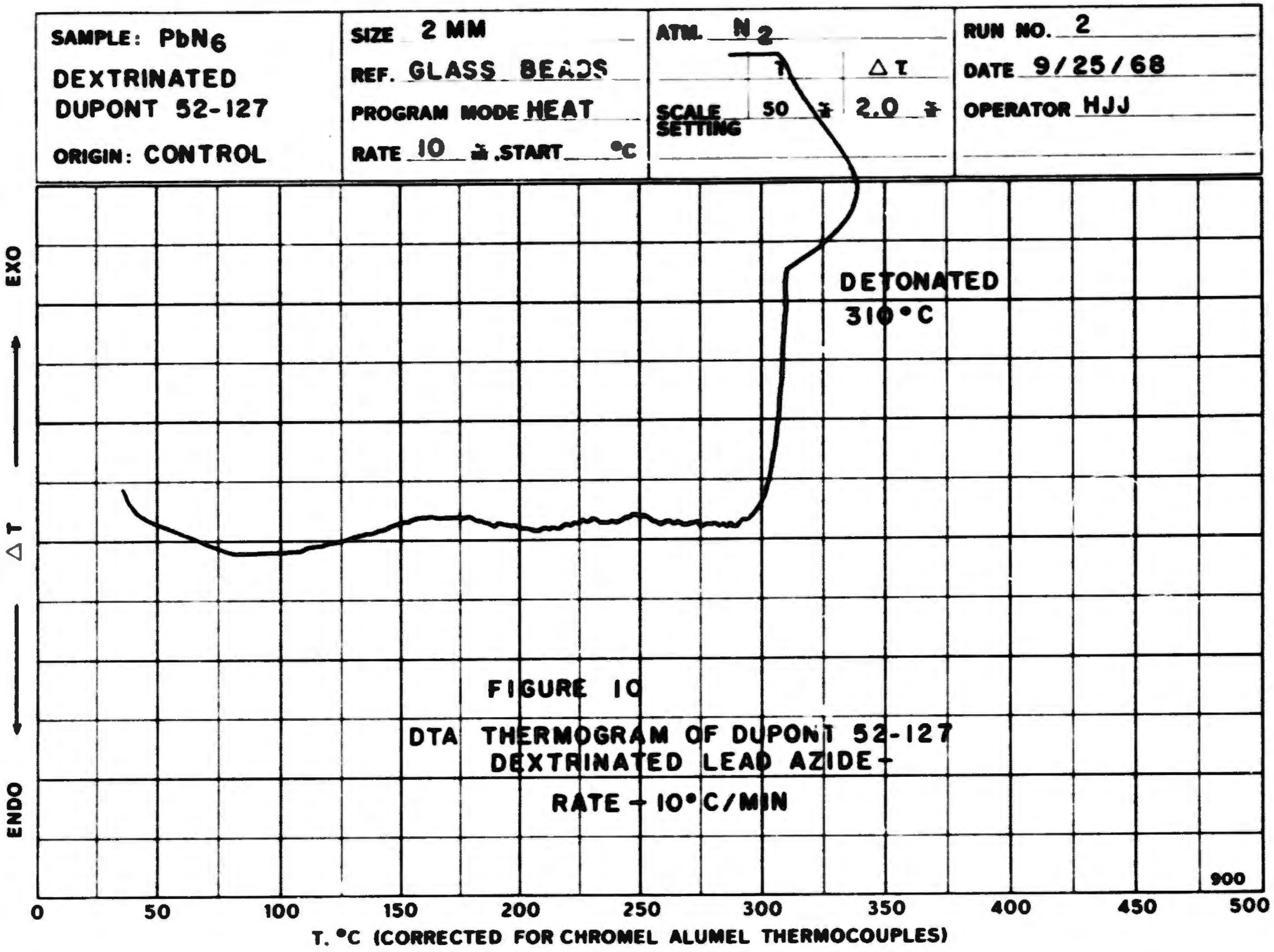
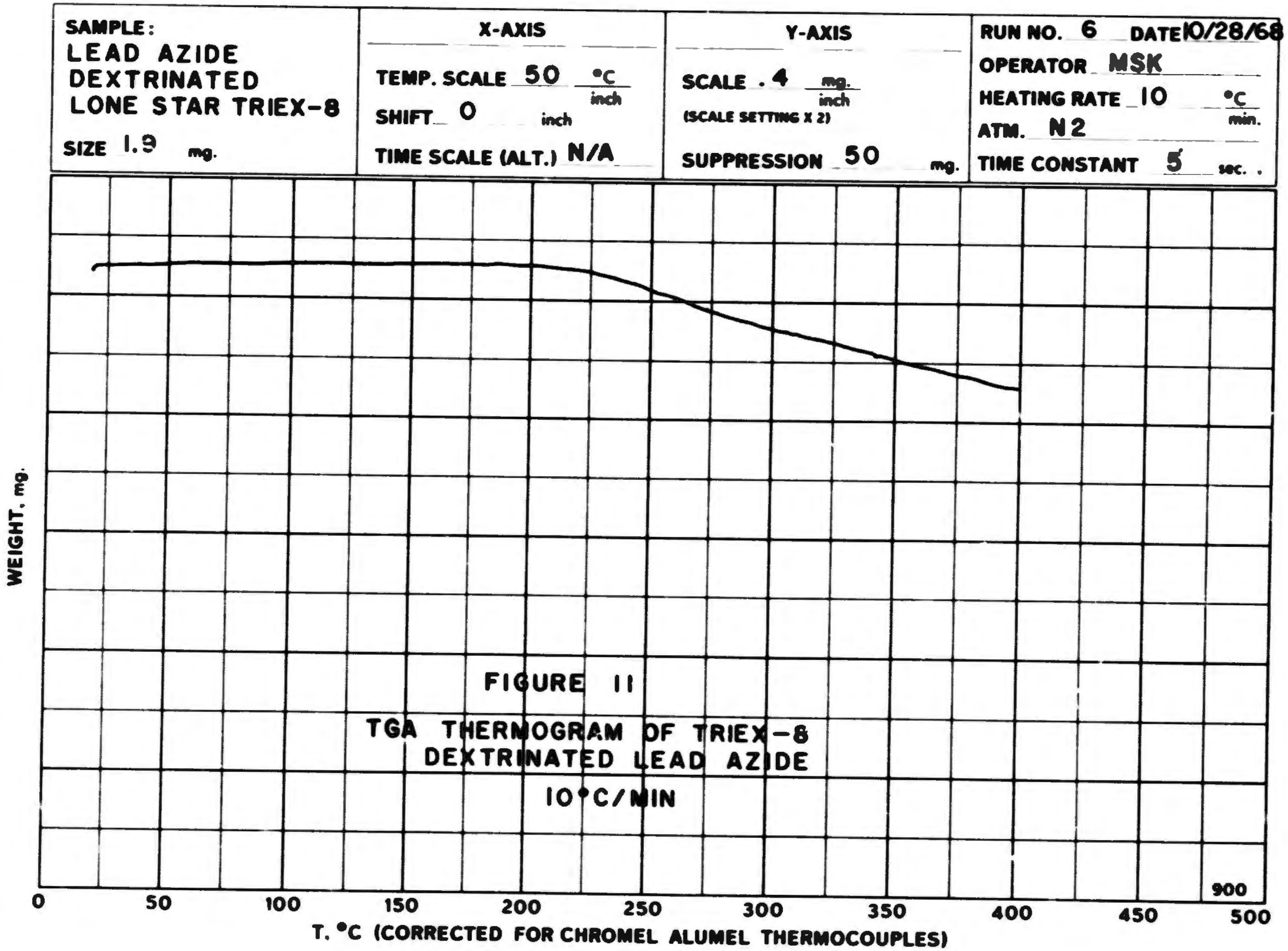


Fig 10 DTA thermogram of Du Pont 52-127 dextrinated lead azide. Rate, 10°C/min



SAMPLE:
LEAD AZIDE
DEXTRINATED
LONE STAR TRIEX-8
SIZE 1.9 mg.

X-AXIS
TEMP. SCALE 50 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) N/A

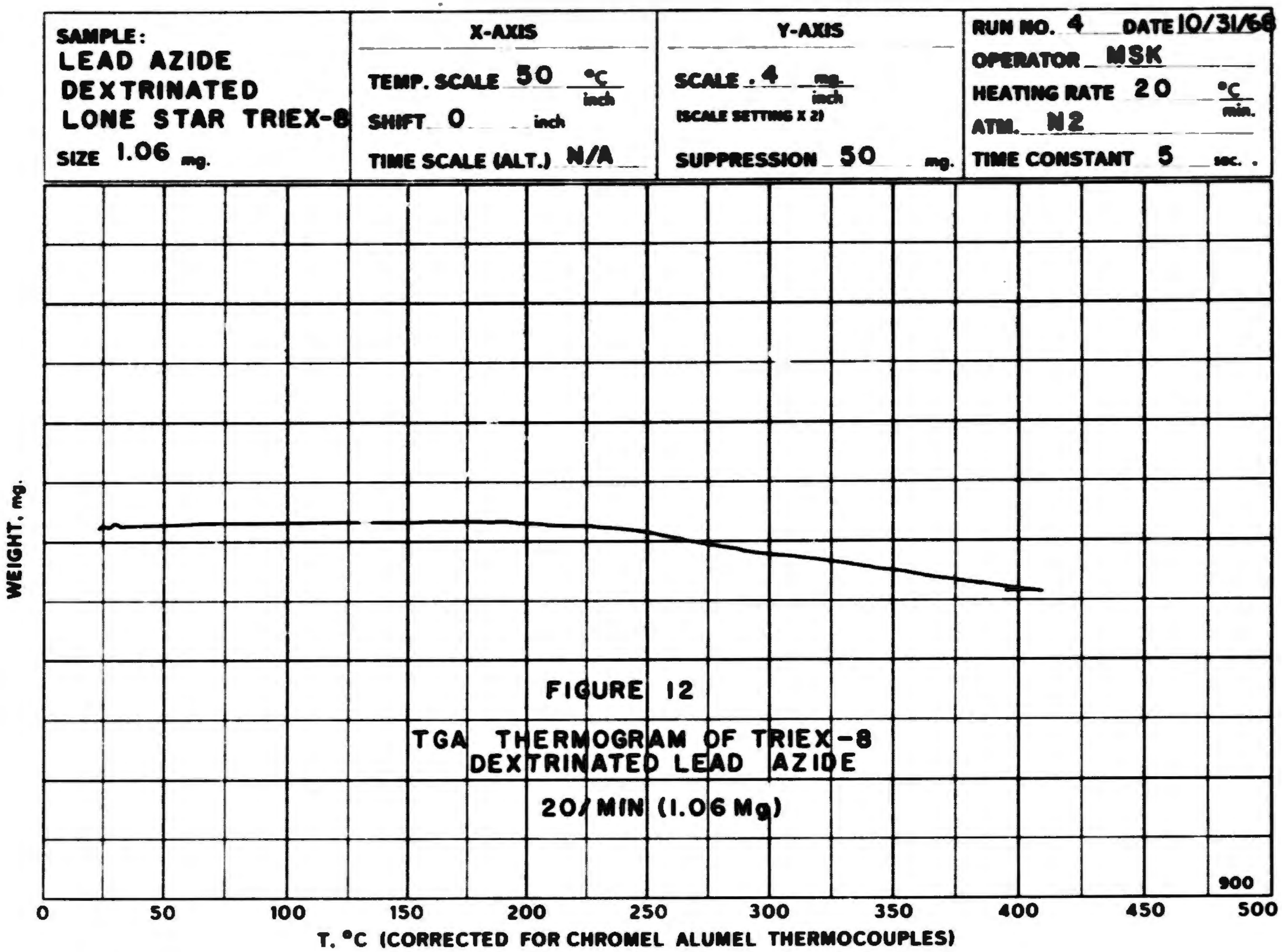
Y-AXIS
SCALE .4 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 50 mg.

RUN NO. 6 DATE 10/28/68
OPERATOR MSK
HEATING RATE 10 °C/min.
ATM. N2
TIME CONSTANT 5 sec.

FIGURE 11

TGA THERMOGRAM OF TRIEX-8
DEXTRINATED LEAD AZIDE
10°C/MIN

Fig 11 TGA thermogram of Triex-8 dextrinated lead azide. Rate, 10°C/min



SAMPLE: LEAD AZIDE DEXTRINATED LONE STAR TRIEX-8
SIZE 1.06 mg.

X-AXIS
TEMP. SCALE 50 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) N/A

Y-AXIS
SCALE .4 mg./inch (SCALE SETTING X 2)
SUPPRESSION 50 mg.

RUN NO. 4 DATE 10/31/68
OPERATOR MSK
HEATING RATE 20 °C/min.
ATM. N2
TIME CONSTANT 5 sec.

Fig 12 TGA thermogram of Triex-8 dextrinated lead azide. Rate 20°C/min (1.06 mg)

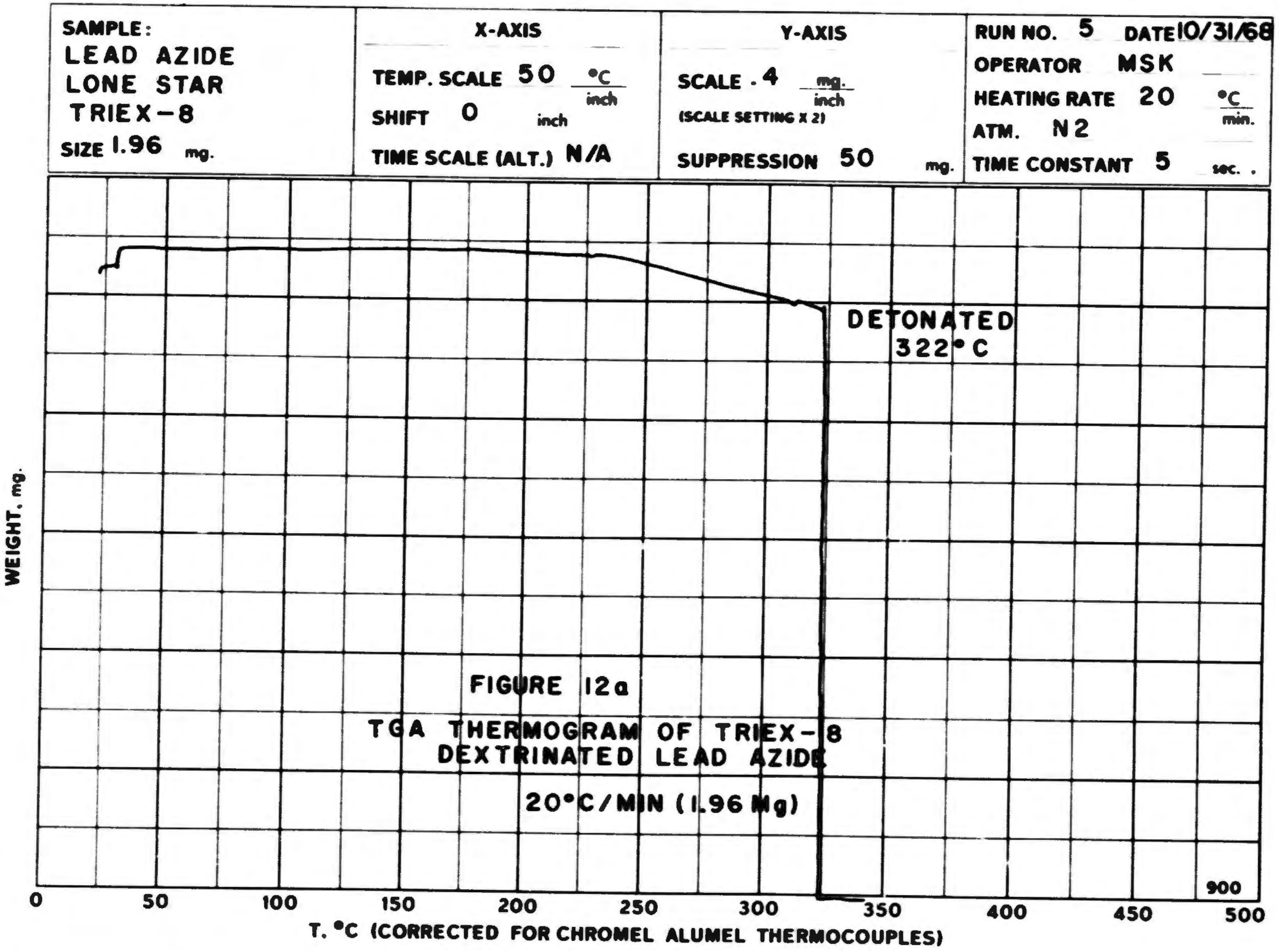


Fig 12a TGA thermogram of Triex-8 dextrinated lead azide. Rate 20°C/min (1.96 mg)

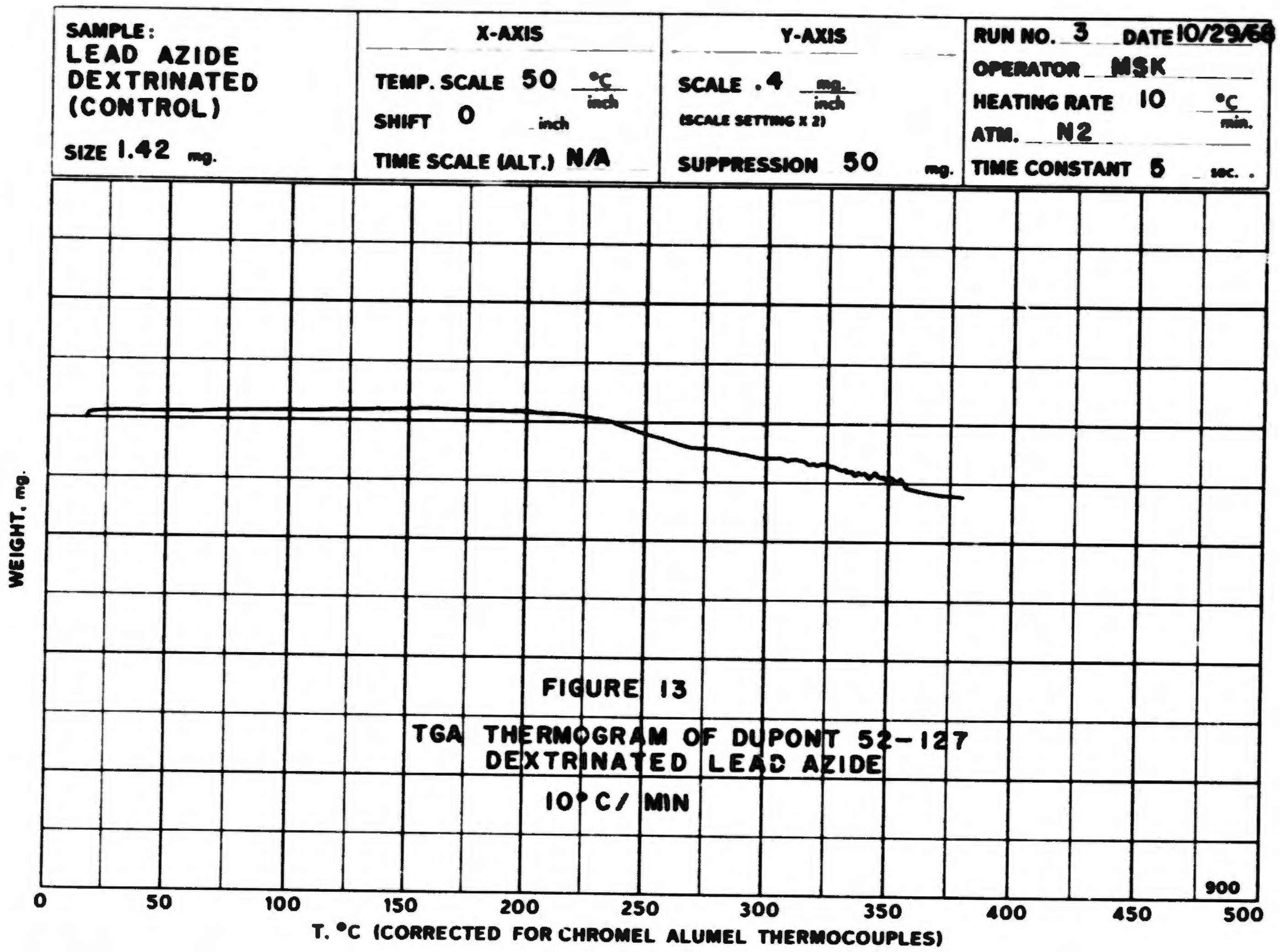


Fig 13 TGA thermogram of Du Pont 52-127 dextrinated lead azide. Rate 10°C/min

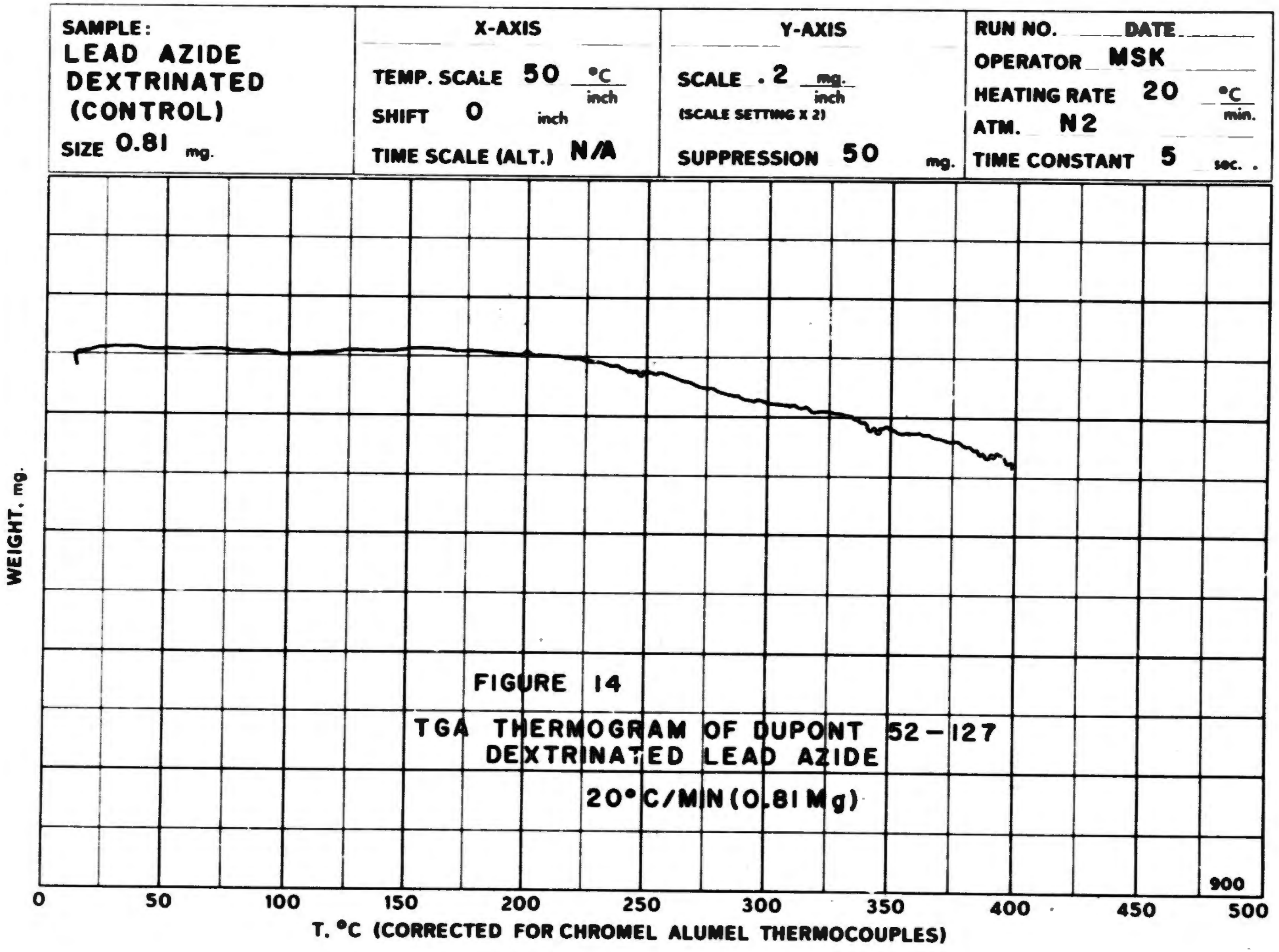
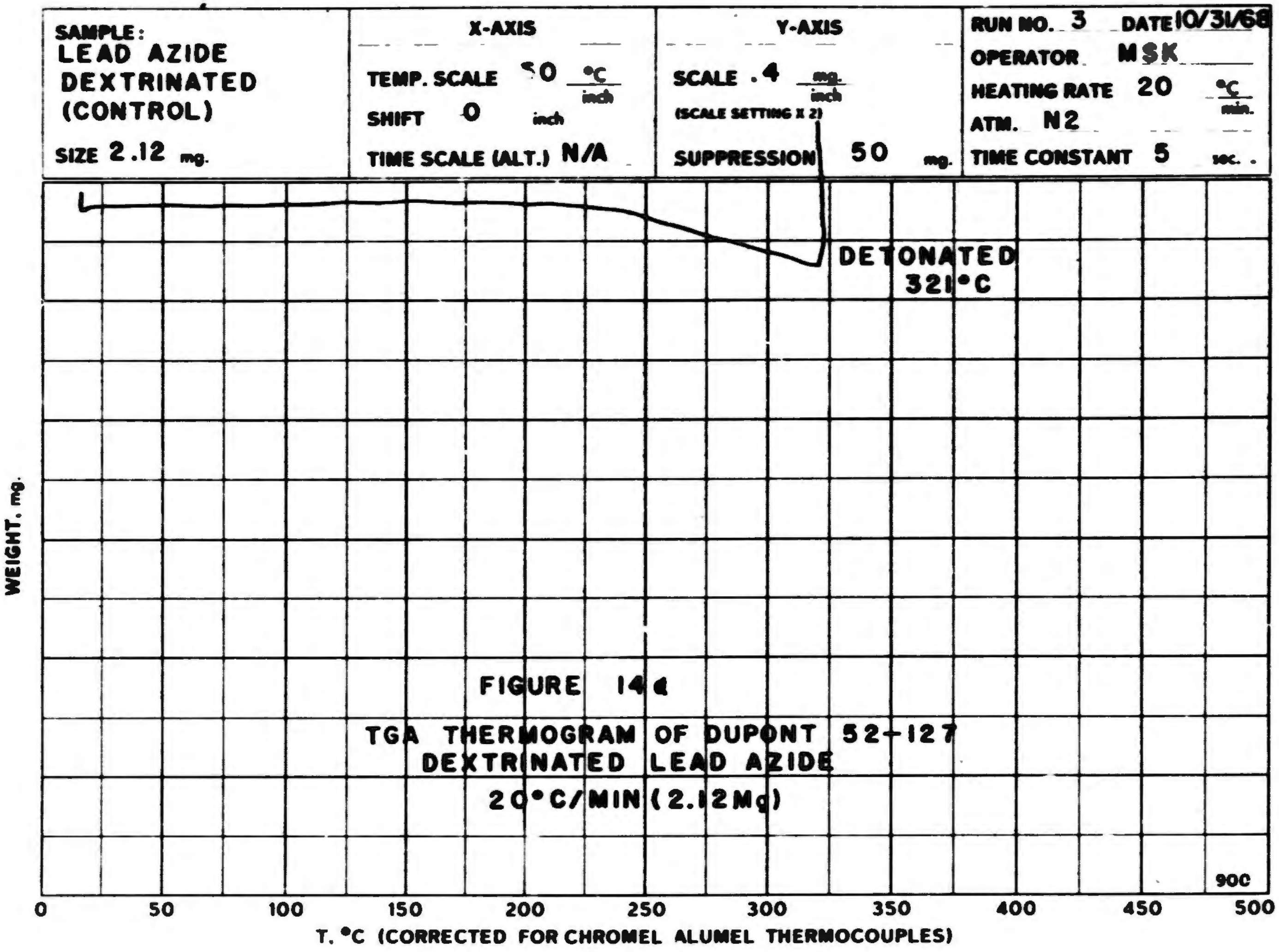


Fig 14 TGA thermogram of Du Pont 52-127 dextrinated lead azide. Rate 20°C/min (0.81 mg)


SAMPLE: LEAD AZIDE DEXTRINATED (CONTROL)
SIZE 2.12 mg.

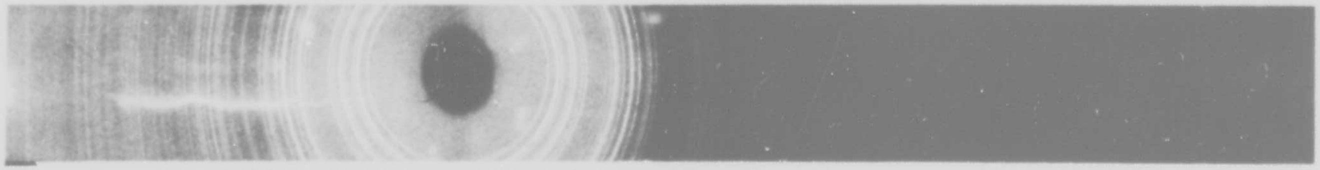
X-AXIS
TEMP. SCALE 50 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) N/A

Y-AXIS
SCALE .4 mg./inch (SCALE SETTING X 2)
SUPPRESSION 50 mg.

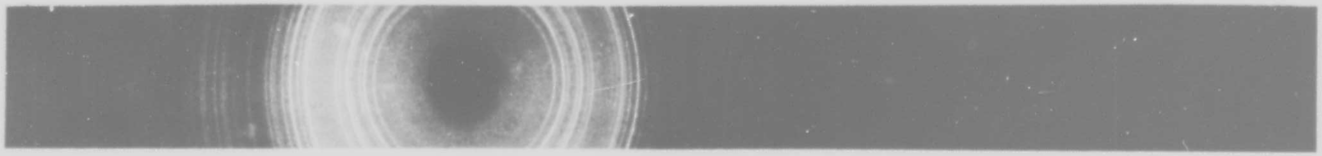
RUN NO. 3 DATE 10/31/68
OPERATOR MSK
HEATING RATE 20 °C/min.
ATM. N2
TIME CONSTANT 5 sec.

FIGURE 14a
TGA THERMOGRAM OF DUPONT 52-127 DEXTRINATED LEAD AZIDE
20°C/MIN (2.12Mg)

Fig 14a TGA thermogram of Du Pont 52-127 dextrinated lead azide. Rate 20°C/min (2.12 mg)



LEAD AZIDE LOT DUPONT 52-127



LEAD AZIDE LOT TRIEX-8

Fig 15 X-ray diffraction patterns of dextrinated lead azide

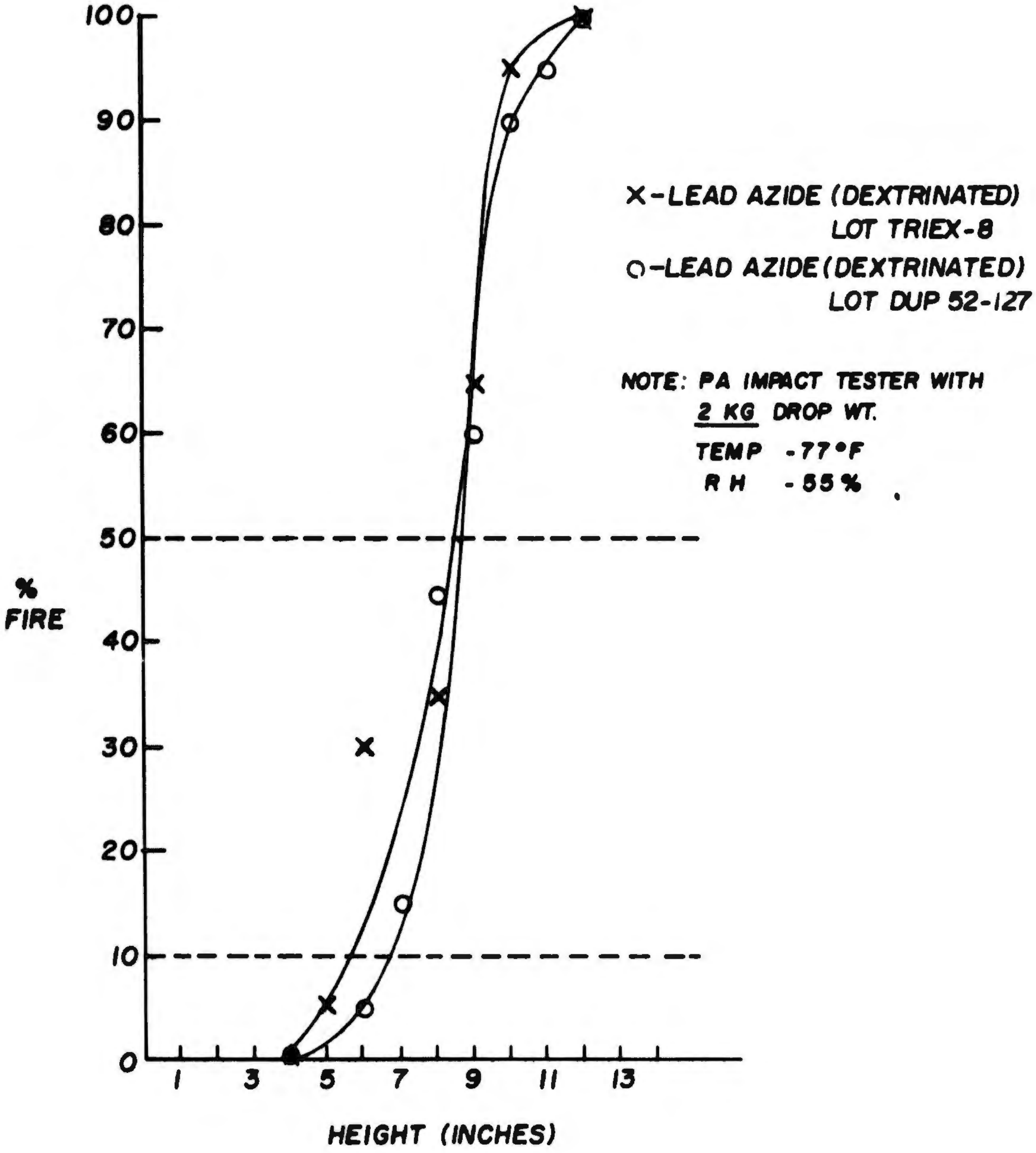


Fig 16 Impact sensitivity curves comparing lots of dextrinated lead azide

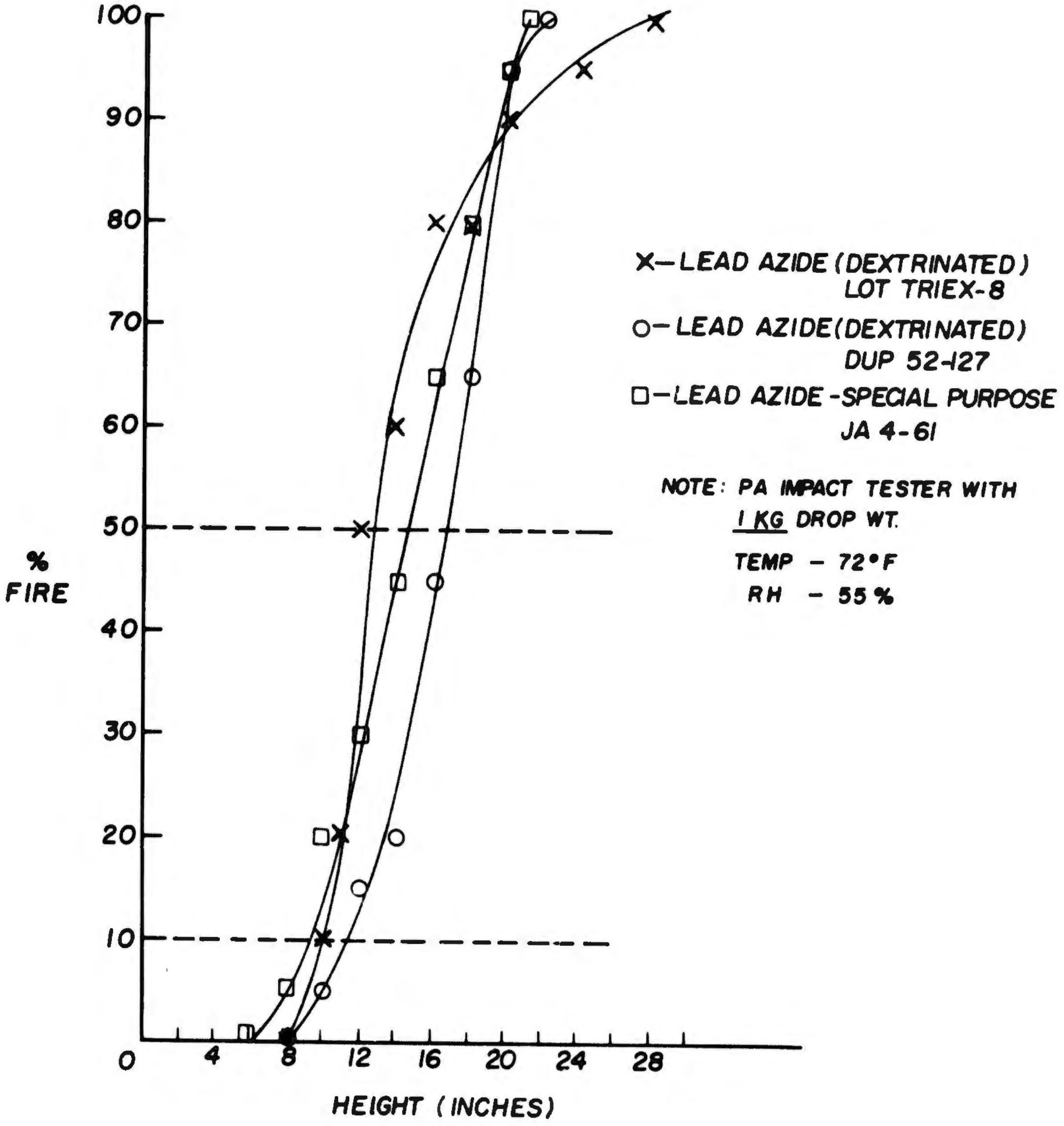


Fig 17 Impact sensitivity curves of different lots of dextrinated lead azide with special purpose lead azide

APPENDIX

Photomicrographs from Lone Star Army Ammunition Plant of different samples of dextrinated lead azide

Fig A Photomicrograph of a large conglomerate in lot Triex-8 dextrinated lead azide (260X)

Fig B Photomicrograph of another large conglomerate in lot Triex-8 dextrinated lead azide (260X)

Fig C Photomicrograph of Du Pont 52-132 dextrinated lead azide (260X)

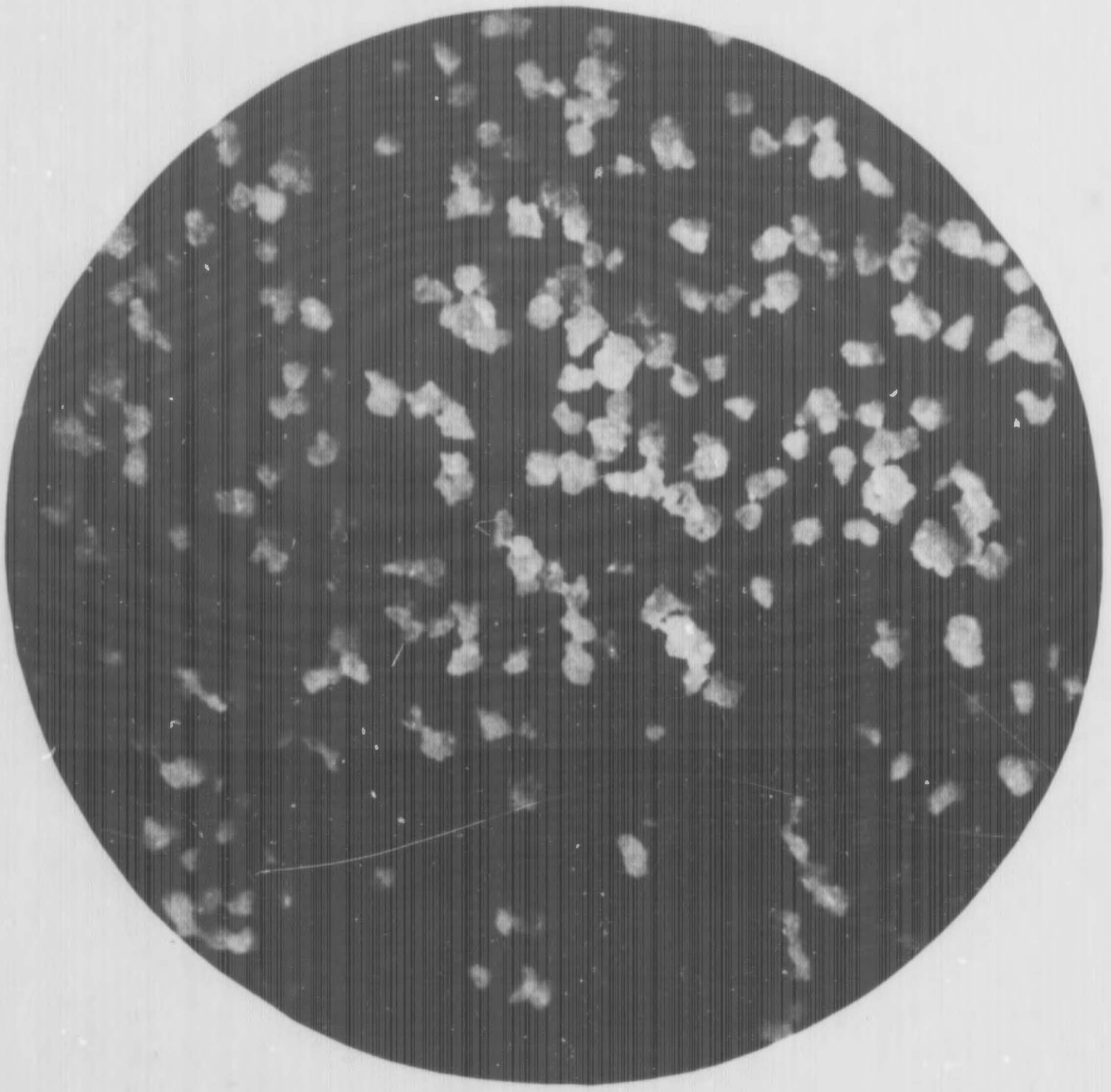


Fig D   Photomicrograph of batch 113 OMC-68-7 dextrinated lead azide (260X)

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13. ABSTRACT

Laboratory tests including the 100°C vacuum stability test, DTA, TGA, x-ray diffraction analysis, impact sensitivity and electrostatic spark sensitivity were conducted on two different samples of dextrinated lead azide. One of the two samples was 25 years old while the other was recently manufactured. The results obtained with both materials and the values given in the literature were in close agreement.

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X-ray diffraction						
Impact sensitivity						
Electrostatic spark sensitivity						
Triex-8						
Du Pont 52-127 dextrinated lead azide						