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A DIFFERENTIAL THERMAL ANALYSIS INVESTIGATION TO DETERMINE THE SENSITIVITY OF LEAD AZIDE IN VARIOUS GASEOUS ATMOSPHERES

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ABSTRACT

The sensitivity of lead azide RD 1333 was investigated in various gases by differential thermal analysis (DTA) to determine which atmospheric conditions could affect its ignition temperature and "critical" weight. It was found that water vapor and, to a lesser extent, pure oxygen distinctly changed the decomposition temperature (exotherms) and critical weights of lead azide.

Small samples of lead azide thermally programmed in atmospheres containing essentially dry argon, nitrogen, carbon dioxide or air produced exotherms between 319 and 333°C. Atmospheres which contained even small amounts of water vapor caused a shift of the lead azide exotherm t_0 348—357°C and 377—298°C at a heating rate of 10°C min^{-1}. Critical weights changed from 0.7 mg in dry atmospheres to 11.0 mg in open air.

An autoignition temperature of 292°C for lead azide heated in an aluminum detonator cup and an apparent activation energy of 43 000 cal mole^{-1} were obtained. 10% additions of the fine copper, lead, or aluminum caused no change in the decomposition temperature in dry atmospheres. Aluminum addition lowered the critical weight from 0.7 to 0.5 mg in dry argon or nitrogen.

INTRODUCTION

Lead azide, $Pb(N_3)_2$, is a salt of hydrozoic acid, HN_3, and exists in two forms, orthorhombic (α, density 4.71 g cm^{-3}) and monoclinic (β, density 4.93 g cm^{-3}). It has a wide military use as a primary high explosive. Following a series of unexplained explosions involving non-electrical initiators, and subsequent to the conclusion that the factor common to all these explosions was lead azide, a study was initiated to investigate the high-temperature reactions of lead azide by differential thermal analysis (DTA).

A technique to differentiate between the thermal sensitivity of lead azide in different gaseous atmospheres and with different additives was adopted from a report published in 1968 [1]. This technique consisted of obtaining the critical mass of explosive below which it would not explode. The critical mass is a term used to denote the minimum mass of an explosive relative to a specific shape and environment necessary to sustain a chain reaction. At a fixed heating rate in a standard size cup, it should be reasonable to define the critical mass as the minimum weight which would explode, since an explosion can be considered to be a climax of a chain reaction. Thus, the

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critical mass as defined here is the minimum weight of sample which would explode in a fixed and specified condition at an elevated temperature. It is then a measure of the sensitivity of the tested explosive.

Thermal sensitivity is a means to determine relative sensitivity. It must not be construed as an indication of handling characteristics for lead azide.

TABLE 1

Lead azide RD 1333, Du Pont Lot 51-49
A. Chemical and physical requirements

Chemical test prescribed	Specification limits	Results
Color	White to Buff	White
Form	Aggregates shall be free from well-defined transluscent crystals. The particles shall be opaque, free-flowing powder and irregular in size and shape.	OK
Purity	97.5% minimum	98.43%
pH	5.0—7.5	5.8
Solubility in water	1.0% maximum	0.22%
HNO_3 insoluble	0.05% maximum. None shall be retained on a U.S. standard sieve 230	0
Iron	Trace (maximum)	Trace
Copper	Trace (maximum)	Trace
Chlorides	Trace (maximum)	Trace
Nitrates	Trace (maximum)	Trace
Acetates	Trace (maximum)	Trace
Lead CMC	0.60—1.20%	1.04
Bulk density	1.1 g ml^{-1} minimum	1.73 g cm^{-3}
Detonator function	The detonator shall form a hole in the specified lead disc, having a minimum diameter of 0.156 in.	OK
Workmanship	The lead azide shall be free from grease, wood slivers or chips, rubber or plastic particles, or other foreign particles.	OK

B. Ingredients used in the manufacture of lead azide RD 1333

Ingredients *	Analysis specified by MIL-L-46225C(MU)	DuPont purchase data
Lead acetate	None	Lead acetate, N.F. purchased from Mallinckrodt Chemical Works
Sodium azide	None	Sodium azide purchased from Canadian Industries, Inc.
"Empilan" AQ-100	None	"Empilan" AQ-100 purchased from Aceto Chemical Co., Inc.
Deionized water	None	Deionized water produced with plant facilities

* The crystal growth control agent specified in MIL-L-46225C(MU) was used in the manufacture of RD 1333 lead azide in the lot covered by this certification.

EXPERIMENTAL PROCEDURE

DTA was conducted on a Deltatherm III DTA accessory [2]. Two steel thermocups, to which alumel—chromel thermocouples were welded, were placed within an open cylindrical steel sample block with a separation of a few millimeters of open space. The sample and reference material (quartz) were placed in 0.14-in. diameter × 0.225 in. high steel cups situated inside the thermocups. Although this system would essentially relay the surface temperature, the tiny samples preclude any variation in temperature from the interior of the reference or sample. Thermograms were recorded on a Mosely 7100 B two-pen time base recorder. One pen recorded the temperature of the reference material and the other the temperature difference, ΔT, of the two cups at a space of 0.1 in. advanced on the time axis (abscissa).

TG was conducted on a Deltatherm III TG accessory. The sample was placed on a top-loaded balance inside a cylindrical area. Nitrogen was passed across the sample, but the system was open to air through the electronics section. A thermocouple to record the approximate temperature of the sample was located 1 mm from the bottom of the sample tube. The sample was placed in the same steel cups as were used for DTA. Thermogravimetric experiments were recorded on a two-pen time base recorder. One pen recorded the temperature from the above-mentioned thermocouple, the other responded to the weight loss of the sample.

Nitrogen, argon and oxygen came from commercial grade cylinders, the carbon dioxide was bone dry grade and the compressed air came directly from the air lines at Arradcom. The flow rate was controlled by a Matheson low flow flowmeter. The compressed air was dried by passing it through a 150 mm straight drying tube filled with a chemical drying agent.

An analysis of the lead azide used in all these experiments appears in Table 1. Metallic lead added to the lead azide was from Fisher Scientific and labeled finest powder, metallic copper was Fisher Scientific Electrolytic Dust, Purified and the aluminum was labeled atomized, 6 mμ from the Alcan Aluminum Company.

The height of the cup is critical if exotherms are to be obtained from tiny non-explosive samples of lead azide. The autoignition temperature was obtained by heating the lead azide RD 1333 (Table 1) in 0.167 in. high × 0.143 in. o.d. aluminum cups by a previously described procedure [2].

RESULTS

The results in Table 2 indicate that the critical mass for lead azide RD 1333, DuPont Lot 51-49, in dry, non-reactive gas is 0.7 mg at a temperature between 320 and 330°C for the experimental conditions used here. The critical mass diminished only when aluminum powder was added to the lead azide sample. The results also indicate that moist air and oxygen had affected the critical mass of lead azide to make the explosive less sensitive.

Further analysis of the same trends indicated by the data in Table 2 was conducted with sample sizes of less than the critical masses in the same

TABLE 2

Critical weights of lead azide, RD 1333, DuPont Lot 51-49
Heating rate 10°C min^{-1}.

Sample weight (mg)	Temperature at explosion (°C)	Atmosphere	Gas flow rate (ml min^{-1})
11.0	330	Open	0
8.0	329	Compressed air	30
2.0	333	Oxygen	30
2.0	331	Compressed air passed through ascarite	30
0.9	333	Compressed air passed through phosphorus pentoxide	30
0.7	324	Nitrogen	30
0.7	330	Carbon dioxide	30
0.7	323	Argon	30
0.5 (10% aluminum powder)	322	Argon	30
0.5 (10% aluminum powder)	324	Nitrogen	30

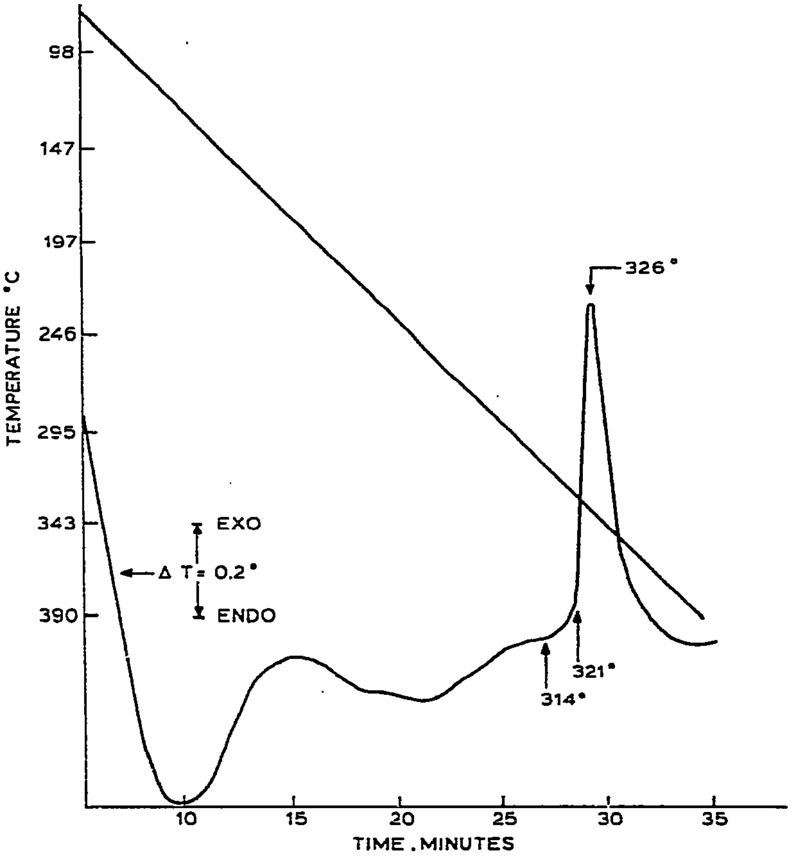

Fig. 1. DTA of lead azide RD 1333 in argon. Sample weight, 0.5 mg; gas flow rate, 22 ml min^{-1}; heating rate, 10°C min^{-1}.

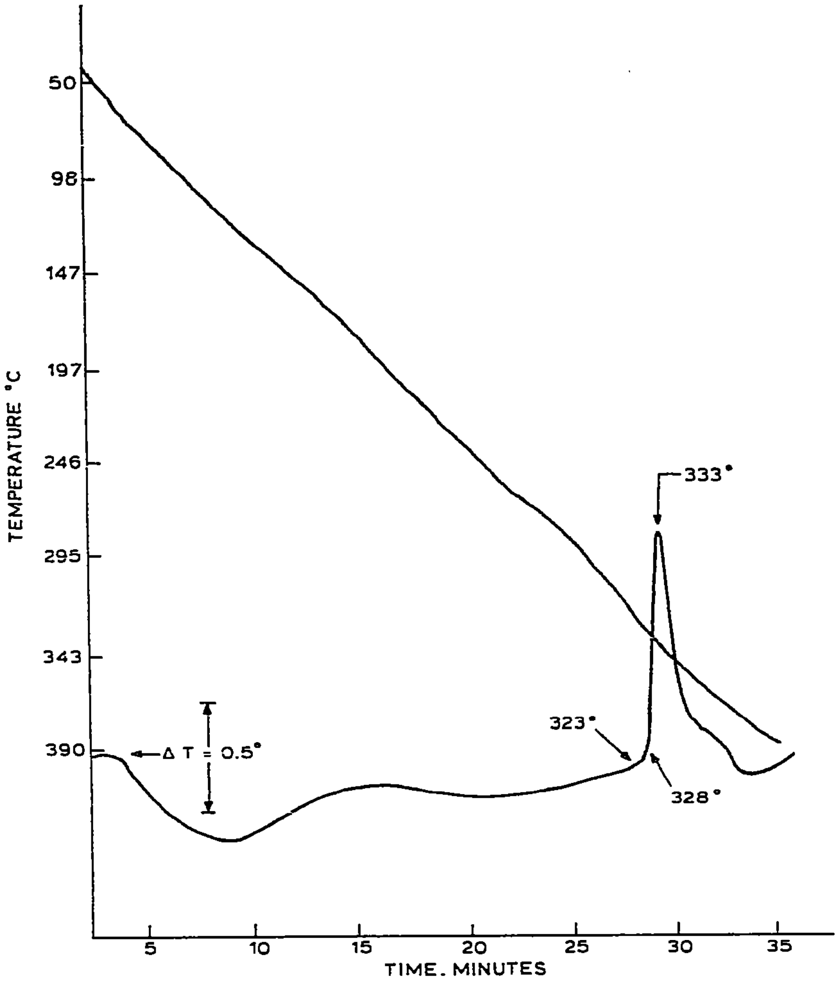

Fig. 2. DTA of lead azide RD 1333 in nitrogen. Sample weight, 0.6 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}.

atmospheres. The results from these thermograms are listed in Table 3 together with the previous results in which explosions occurred.

The data in Table 3 indicate that at least three distinctive exotherms exist for lead azide RD 1333, DuPont Lot 51-49, depending on the size of sample and the atmosphere which flows around it. The temperatures in Table 3 obtained from these exotherms are: the temperature at the initial departure from the base line, the temperature at the base of the steepest slope to the peak, the temperature at the peak of the exotherms, and the peak height, which is measured in $\Delta T°$ C.

The chemical reaction as interpretated from DTA is also included. A description of these exotherms, an interpretation of them, and their importance to understanding spontaneous detonation are discussed in the following paragraphs.

Table 4 includes DTA data from samples of lead azide at or below the critical weight mixed with fine powders of aluminum, copper, and lead. The data in Table 5 come from recent thermocurves of mostly small samples of

TABLE 3

DTA of lead azide RD 1333, DuPont Lot 51-49, in steel cups

Heating rate 10°C min^{-1}.

Sample weight (mg)	Atmosphere	Flow rate (ml min^{-1})	Exotherm 1				Exotherms 2—3					
			Initial temp. (°C)	Slope temp. (°C)	Peak temp. (°C)	ΔT (°C)	Chemical reaction	Initial temp. (°C)	Slope temp. (°C)	Peak temp. (°C)	ΔT (°C)	Chemical reaction
1.7	Open to air	0					None	371	384	392	1.00	Decomposed
1.2		0					None	364	376	392	1.00	Decomposed
8.0	Compressed air	30	326	329	329	7.00+	Explosed					None
6.0		30	329	331	331	3.30	Decomposed					None
4.0		30	328	329	329	3.20	Decomposed					None
4.0		30	322	326	326	1.50	Exploded					None
2.0		30	328	328	330	0.02	Decomposed	362	390	392	1.40	Decomposed
2.1	Compressed air passed through ascarite	30	326	329	331	2.40	Exploded					None
2.0		30	329	330	330	0.50	Decomposed	390	398	405	1.50	Decomposed
1.8		30	326	328	334	0.26	Decomposed	370	395	400	1.50	Decomposed
2.0		30	326	328	330	+	Exploded					None
1.5		30	320	329	331	0.65	Decomposed					None
1.1		30					None	379	387	395	0.70	Decomposed
0.8		30					None	383	391	398	1.90	Decomposed
0.5		30					None	355	362	367	0.08	Decomposed
2.1	Compressed air passed through ascarite	30	322	325	366		Exploded					None
1.0		30					Exploded					None
0.9	P_2O_5 * A	30	326	331	333		Exploded					None
0.9	A	30	324	329	333	0.30	Decomposed					None
0.7	B	30	324	329	331	1.00	Decomposed					None

0.7	B	30	328	333	336	0.50	Decomposed	376	381	391	0.60	Decomposed
0.7	B	30	324	333	336	0.70	Decomposed	373	378	384	0.95	Decomposed
0.9	B	30	329	334	338	0.60	Decomposed	373	377	385	0.80	Decomposed
0.8		30	333	336	339	0.25	Decomposed	371	379	386	0.30	Decomposed
0.7	Dry carbon dioxide	30	324	329	330	0.30	Exploded					None
0.5		30	326	329	333	0.60	Decomposed					None
5.1	Oxygen	30	314	331	332	4.00+	Exploded					None
2.0		30	314	333	334	1.00	Exploded					None
1.0		30	313	329	331	0.80	Decomposed					None
0.5		30		333	338	0.04	Decomposed	360	374	381	0.30	Decomposed
0.7	Argon	30		324	324		Exploded					None
0.6		30	323	328	333	0.75	Decomposed					None
0.6		30	324	325	331	1.00	Decomposed					None
0.5	Nitrogen	30	324	329	334	2.00	Decomposed					None
0.4		30	328	328	334	0.20	Decomposed					None
0.7		0					None	357	360	369	0.23	Decomposed
0.7	Argon	26	295	309	309		Exploded					None
0.7		30	316	319	323	1.50+	Exploded					None
0.6		30	314	319	321	1.30	Decomposed					None
0.5		30	314	321	329	1.10	Decomposed					None
0.5		30	316	321	328	0.40	Decomposed		345	357	0.06	Decomposed
0.5		30	314	315	329	0.10	Decomposed	338	348	353	0.20	Decomposed
0.5		6	324	329	333	0.50	Decomposed	350	352	355	0.20	Decomposed
0.5		9	314	319	324	0.40	Decomposed	338	343	348	0.2	Decomposed
0.5		12	314	319	326	0.50	Decomposed		340	348	0.1	Decomposed
0.5		15	314	319	324	0.70	Decomposed					None
0.5		22	314	321	326	0.70	Decomposed					None
0.5		22	314	321	324	0.78	Decomposed					None
0.5		29	317	324	329	0.60	Decomposed		343	350	0.01	Decomposed
0.5		12	312	319	326	0.30	Decomposed		337	348	0.08	Decomposed

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* (P_2O_5) A = phosphorus pentoxide, fresh from bottle; B = phosphorus pentoxide, one day old.

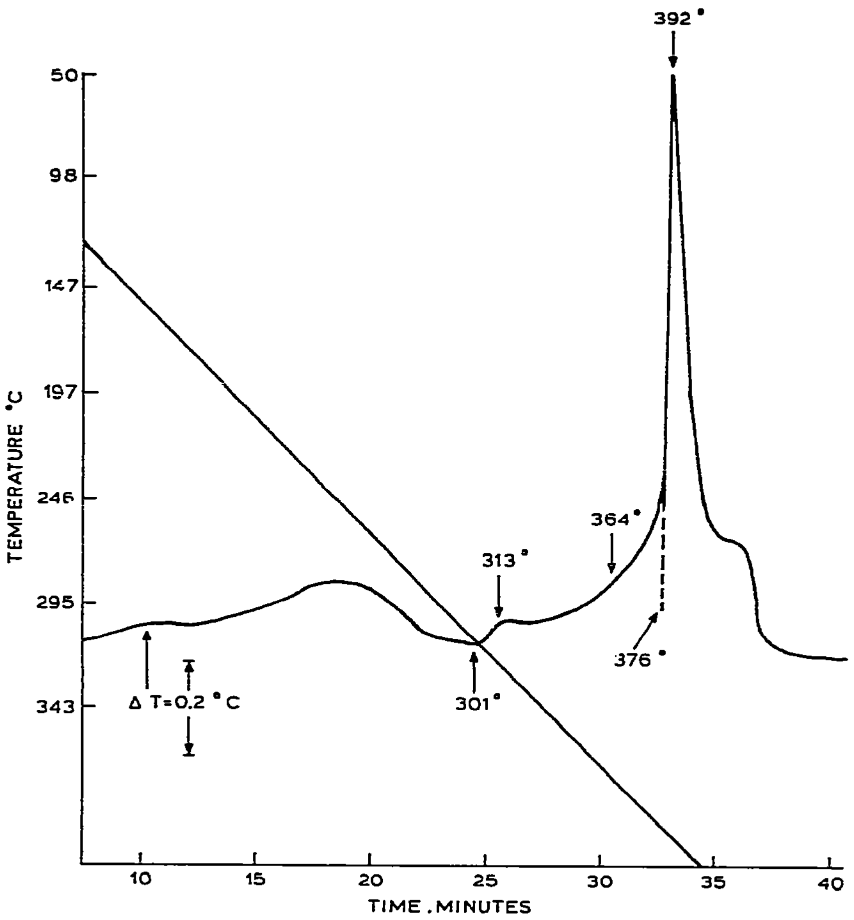

Fig. 3. DTA of lead azide RD 1333 in a system open to the air. Sample weight, 1.2 mg; heating rate, 10°C min^{-1}.

lead azide of less than the critical weight. This data is used to calculate the autoignition temperature and the activation energy by a modified Kissinger technique [2]. Table 1 contains specification limits for RD 1333 as well as a chemical analysis and the ingredients used to manufacture lead azide RD 1333.

DISCUSSION

The first exotherm (lowest in temperature) has been assigned to decomposing or exploding lead azide [1] (Figs. 1 and 2). This exotherm appears between 319 and 333°C depending on the size of the sample and the thermal conductivity of the surrounding atmosphere. Thermocurves of lead azide RD 1333, DuPont Lot 51-49, samples of less than the critical weight in moist atmospheres show a decrease in the height or a disappearance of the first exotherm and the appearance of a large exotherm at a higher temperature (Fig. 3 and Table 3). TG of samples of lead azide RD 1333, DuPont Lot 51-49,

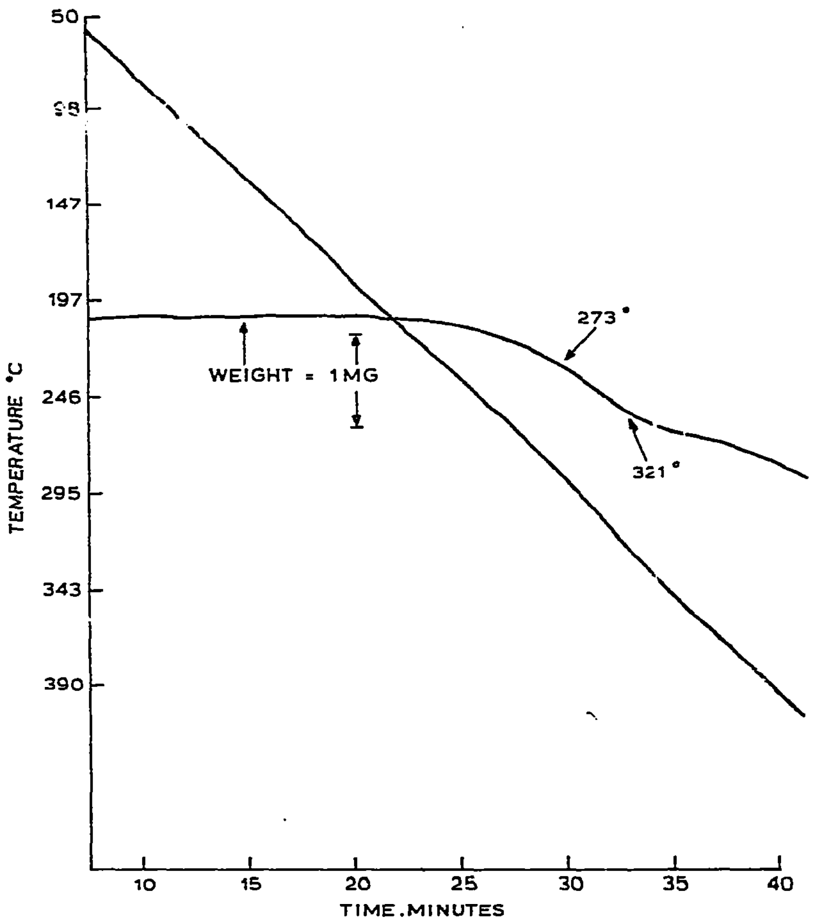

Fig. 4. TG of lead azide RD 1333 in argon. Sample weight, 8.0 mg; gas flow rate, 5 ml min^{-1}; heating rate, 10°C min^{-1}; total weight loss, 1.7 mg.

tested in a system open to the atmosphere but with a 5 ml min^{-1} flow of nitrogen across the sample holder indicated that the largest weight loss occurred between 273 and 320°C. The weight loss was perceptible, however, beginning at 220°C (Fig. 4). Since no distinguishable exotherms appeared on any thermocurves below 319°C, the indications are that a slow oxidation reaction takes place which converts the lead azide to basic lead azide when any moisture is present. Conversion of the lead azide to $PbN_6 \cdot PbO$ would result in an 11.7% theoretical weight loss [3]. This is in agreement with the weight loss up to 310°C.

An identification of exotherms 2 and 3 (over 333°C) was attempted by means of a literature search. These exotherms were indentified as being produced by decomposing basic lead azide which exists in two modifications $PbN_6 \cdot PbO$ and $2\ PbN_6 \cdot 5\ PbO$ [3]. It is reported that only 0.11—0.20 wt.% of water vapor (1×10^{-3} mg of water) is sufficient to produce basic lead azide. The mechanism by which lead azide is hydrolyzed by water vapor to basic lead azide appears in ref. 4.

Appreciation of the efficacy of water on lead azide was an incidental result of decomposing lead azide in an atmosphere of compressed air. The

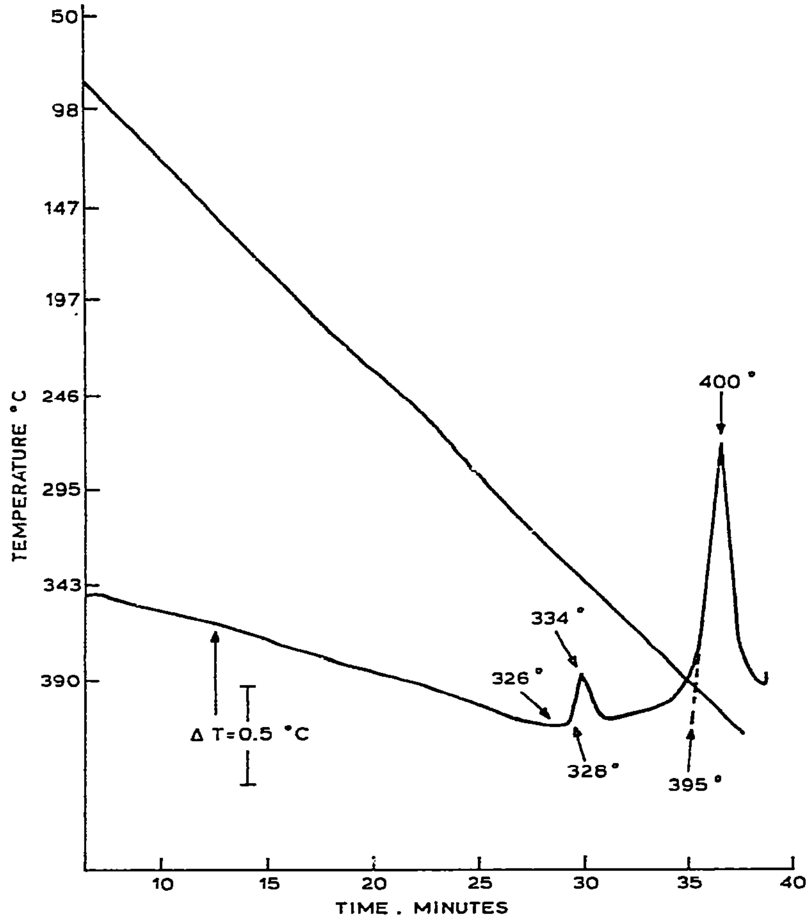

Fig. 5. DTA of lead azide RD 1333 in air passed through ascarite. Sample weight, 1.8 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}.

compressed air was piped over 2000 ft. from a compressor to where it was used in the thermal analyzer. Although a trap existed for separating water from the air, the air was not dried. Since only 0.11—0.20% water vapor is needed to produce basic lead azide, the compressed air probably always contained at least this minimum amount.

All experiments with lead azide conducted in undried compressed air showed the basic lead azide peak at approximately 390°C whenever a sample size of less than 0.0020 g was analyzed. The weight specification is necessary since larger samples of lead azide produced sufficient heat at 323—333°C to explode.

The next task was to determine which component of the compressed air was responsible for the larger critical weights and higher temperature exotherms of lead azide RD 1333, DuPont 51-49. Carbon dioxide was removed from the compressed air by passing the air through a tube of ascarite (a mixture of sodium hydroxide and asbestos). This mixture also has the ability to dry the air to a residual water content of 0.16 mg of water per liter of air [5]. Lead azide, tested in air passed through ascarite, showed a reduced critical weight, but still produced large, higher-temperature exotherms

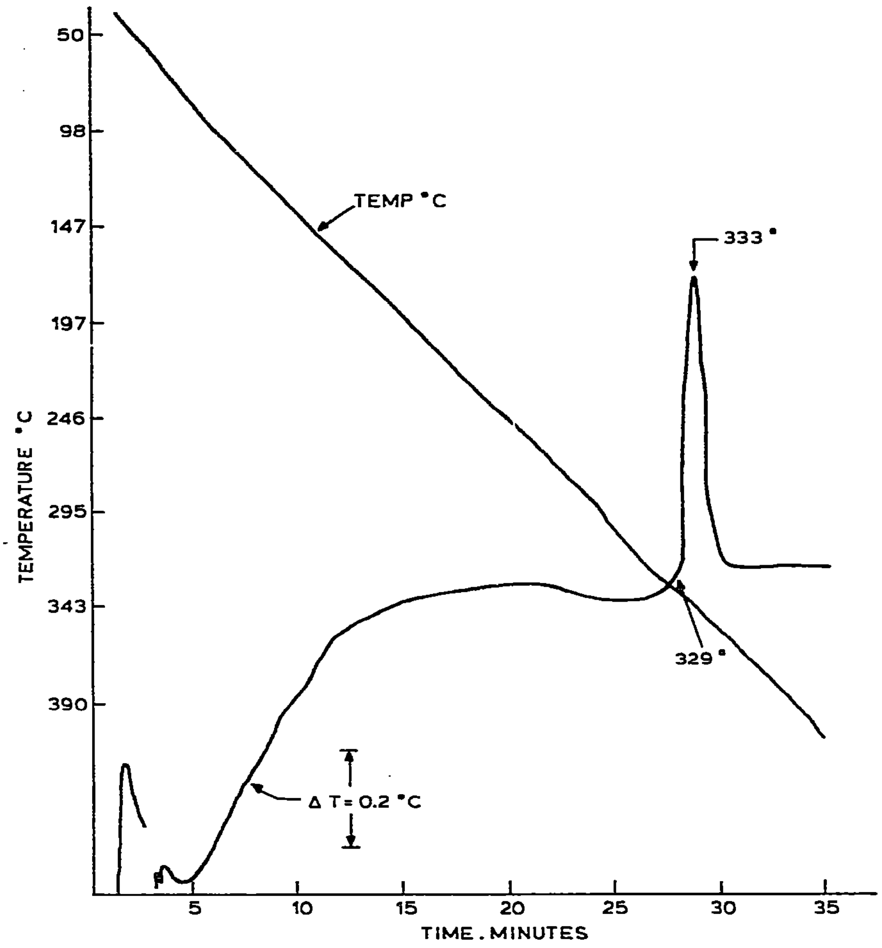

Fig. 6. DTA of lead azide RD 1333 in dry carbon dioxide. Sample weight, 0.5 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}.

(Fig. 5 and Table 3). A dry atmosphere of carbon dioxide resulted in lead azide thermocurves identical to the thermocurves of lead azide obtained in argon (Fig. 6 and Table 2). The conclusion from these analyses was that carbon dioxide does not react with the lead azide. It is the dessication property of ascarite which resulted in the diminshed critical weight of the lead azide.

Compressed air was next passed through phosphorus pentoxide (P_2O_5), a more efficient drying agent (residual water content 2 × 10^{-5} mg of water per liter of air [5]) but one of limited capacity. The use of fresh P_2O_5 resulted in the disappearance of the higher-temperature exotherms (above 333°C) (Fig. 7 and Table 3). The critical weight in compressed air decreased to within 0.2 mg of the minimum explosion weight which occurs in a dry argon atmosphere. The effect of water vapor on the thermal performance of lead azide was thus found to be quite drastic. On the second day that the P_2O_5 was utilized unreplenished to dry the compressed air, the higher-temperature exotherms reappeared and the critical weight was noticed to have also risen (Fig. 7 and Table 3). The first day's test on lead azide with P_2O_5-dried air produced a black residue which could contain lead. The residue from the

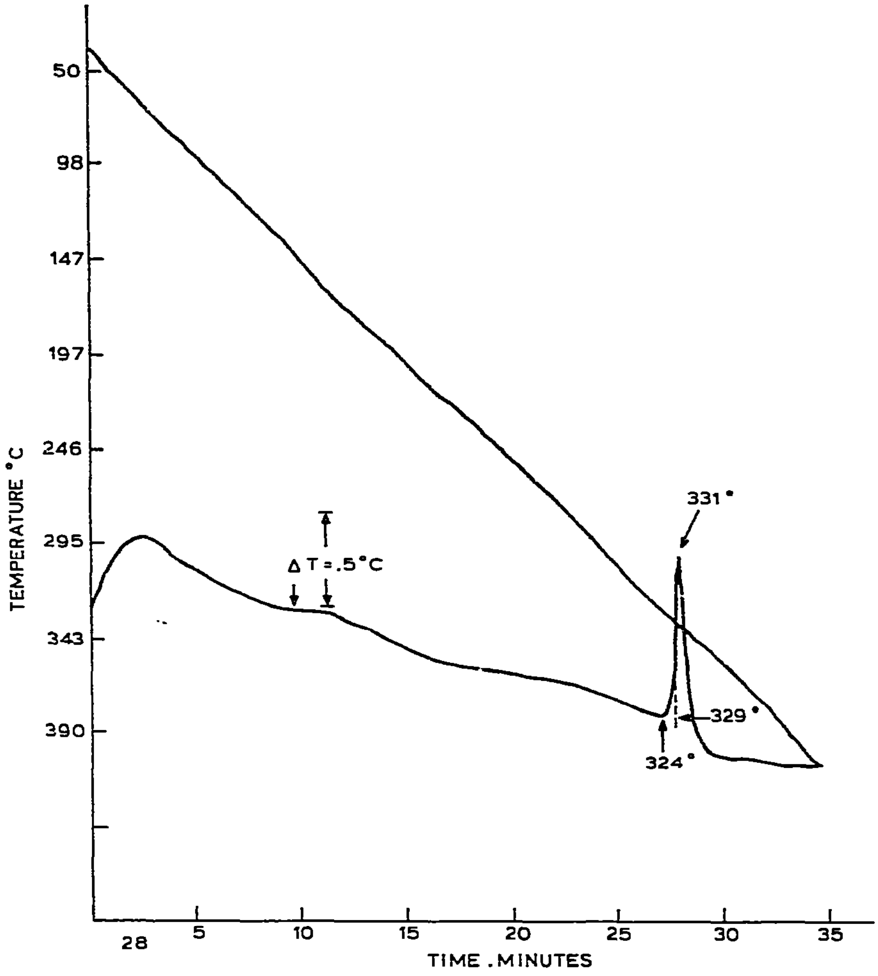

Fig. 7. DTA of lead azide RD 1333 in air passed through fresh phosphorus pentoxide. Sample weight, 0.7 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}

lead azide decomposition (produced by the second day's use of the same P_2O_5) was orange. (The color of Pb_2O_3, which is the stable lead oxide between 375 and 460° C, is orange.)

In order to complete the investigation concerning the effect of compressed air on lead azide, thermal analysis was conducted in an atmosphere of oxygen from a commercial cylinder. The specifications for commercial grade oxygen call for a dew point of better than —70° F which is equivalent to 1 × 10^{-5} mg of residual water per liter. Any alteration in the performance of lead azide would then be due to oxygen and not water vapor. The critical weight of the lead azide increased slightly (Table 2) and higher-temperature exotherms appeared when a small sample size was used (Fig. 8). The extent of the change was considered minor in comparison with the drastic changes brought about by water vapor. The mechanism of formation of basic lead azide is the hydrolysis by water vapor of lead azide at temperatures above 180° C [3]. Perhaps another, but less important, mechanism may be the direct reaction of oxygen with free lead to also form basic lead azide.

If the sensitivity of lead azide can be controlled with water vapor, then the possibility exists that the absence of water vapor could lead to spontaneous detonation. The mechanism to control the sensitivity of lead azide would be the production of basic lead azide nuclei during the induction period of the lead azide decomposition reaction. The probability then exists that the autocatalytic decomposition [4] can be poisoned during its induction period by oxidation of the reaction catalyst, free lead.

The mechanism for the autocatalytic decomposition [6] is

$$2\ N_3^- \rightarrow 3\ N_2 + 2\ e$$

$$Pb^{2+} + 2\ e \rightarrow Pb$$

In a review and analysis of previous decomposition studies on lead azide, there is accumulated data for lead azide decomposed in a vacuum (no water vapor) and lead azide decomposed in air (water vapor present) [3]. It is reported that the decomposition of lead azide is autocatalytic and results in a S-shaped curve of gas volume vs. time. The decomposition of basic lead azide, on the other hand, produces a linear plot of gas volume vs. time. A possibility exists that the presence of moisture is necessary to poison a spontaneous chain reaction of dry lead azide by producing basic lead azide.

The data from ref. 4 that less than 8.9 mm of water vapor must be present to obtain an autocatalytic reaction is corroborated by the data in Table 3.

TABLE 4

DTA of lead azide RD 1333, DuPont Lot 15-49, with 10% metallic additive

Heating rate 10°C min^{-1}.

Sample weight (mg)	10% additive	Atmosphere	Flow rate (ml	Exotherm I				
				Initial temp. (°C)	Slope temp. (°C)	Peak temp. (°C)	ΔT (°C)	Action
0.6	None	Nitrogen	30	316	324	332	1.30	Decomposed
0.5	Aluminum	Nitrogen	30	316	324	327	1.10	Decomposed
0.5	Aluminum	Nitrogen	30	314	324	324	0.80+	Exploded
0.6	Aluminum	Nitrogen	30	317	326	330	0.80+	Exploded
0.4	Aluminum	Nitrogen	30	313	324	330	1.60	Decomposed
0.6	Copper	Nitrogen	30	317	325	329	1.10	Decomposed
0.5	Copper	Argon	30	306	321	323	1.40	Decomposed
0.5	Copper	Argon	30	305	321	325	1.20	Decomposed
0.5	None	Argon	30	312	319	324	1.70	Decomposed
0.4	Aluminum	Argon	30	312	322	329	0.70	Decomposed
0.5	Aluminum	Argon	30	314	319	327	0.80	Decomposed
0.5	Aluminum	Argon	30	312	319	322	0.90+	Exploded
0.5	Lead	Argon	30	312	319	322	1.80	Decomposed
0.5	Lead	Argon	30	314	322	326	0.90	Decomposed
0.5	Lead	Argon	30	312	319	326	0.80	Decomposed
0.5	Lead	Argon	30	314	320	326	0.80	Decomposed

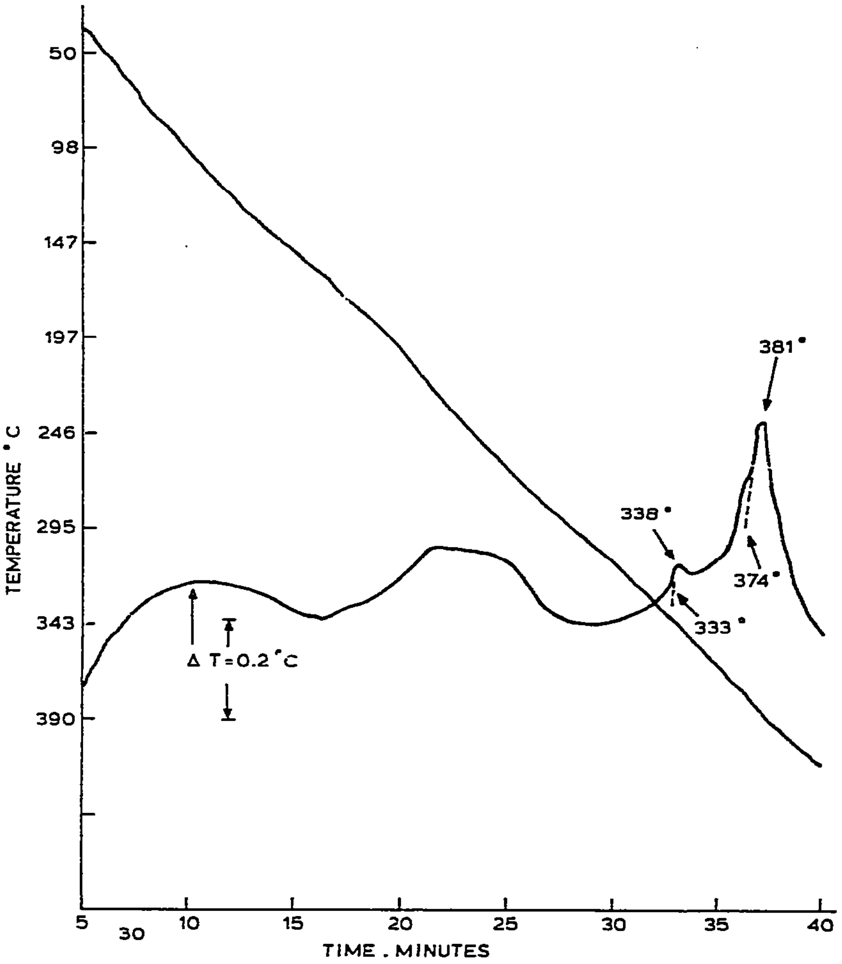

Fig. 8. DTA of lead azide RD 1333 in oxygen. Sample weight. 0.5 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}.

When the water vapor level was less than 8.9 mm, only the lead azide 320° C exotherm was prominent. As the moisture concentration increased slightly, such as when a slower flow of argon was used or when the drying agent became less efficient, both the lead azide and basic lead azide exotherms were observed (Figs. 9 and 10).

In an atmosphere of compressed air dried with fresh phosphorus pentoxide (drying efficiency 2×10^{-5} mg of residual water per liter of air), only the lead azide 320° C exotherm appeared (Fig. 7). When the compressed air was dried with ascarite (drying efficiency 0.16 mg of residual water per liter of air) and passed over the lead azide sample, the basic lead azide exotherm at 380° C appeared. The 320° C lead azide exotherm was indicative of an autocatalytic decomposition. The 350 and 380° C basic lead azide exotherms were indicative of a decomposition which was linear for gas volume vs. temperature.

Dry carbon dioxide, nitrogen and argon did not react with lead azide. The critical weight and the decomposition temperature of the lead azide RD

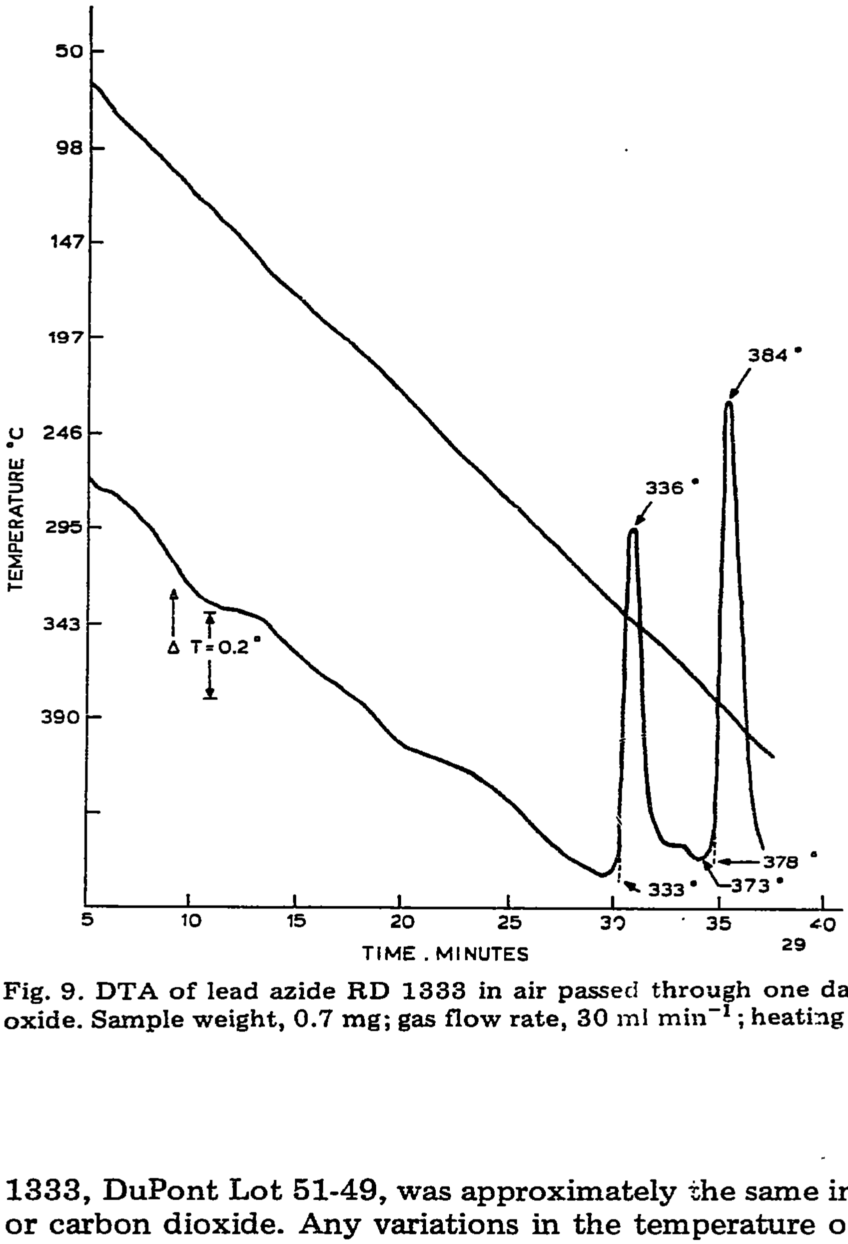

Fig. 9. DTA of lead azide RD 1333 in air passed through one day old phosphorus pentoxide. Sample weight, 0.7 mg; gas flow rate, 30 ml min^{-1}; heating rate, 10°C min^{-1}.

1333, DuPont Lot 51-49, was approximately the same in dry argon, nitrogen or carbon dioxide. Any variations in the temperature of the lead azide exotherm or the explosion temperature are probably due to differences in the thermal conductivities of argon, nitrogen and carbon dioxide at 319—333°C. The information accumulated in this report indicates that the surfaces of lead azide crystals are very reactive to hydrolysis by water vapor at elevated temperature; the formation of the less sensitive basic lead azide nuclei is dependent on the vapor pressure of water. Only when all moisture and perhaps oxygen are consumed in a sealed component can the catalytic lead nuclei be found [7].

The data in Table 4 represent an attempt to find the effect of metallic impurities on lead azide. 10% fine aluminum, copper or lead were mixed with lead azide RD 1333, DuPont Lot 51-49. The intention of these experiments was to test less than the critical weight of lead azide in argon or nitrogen and

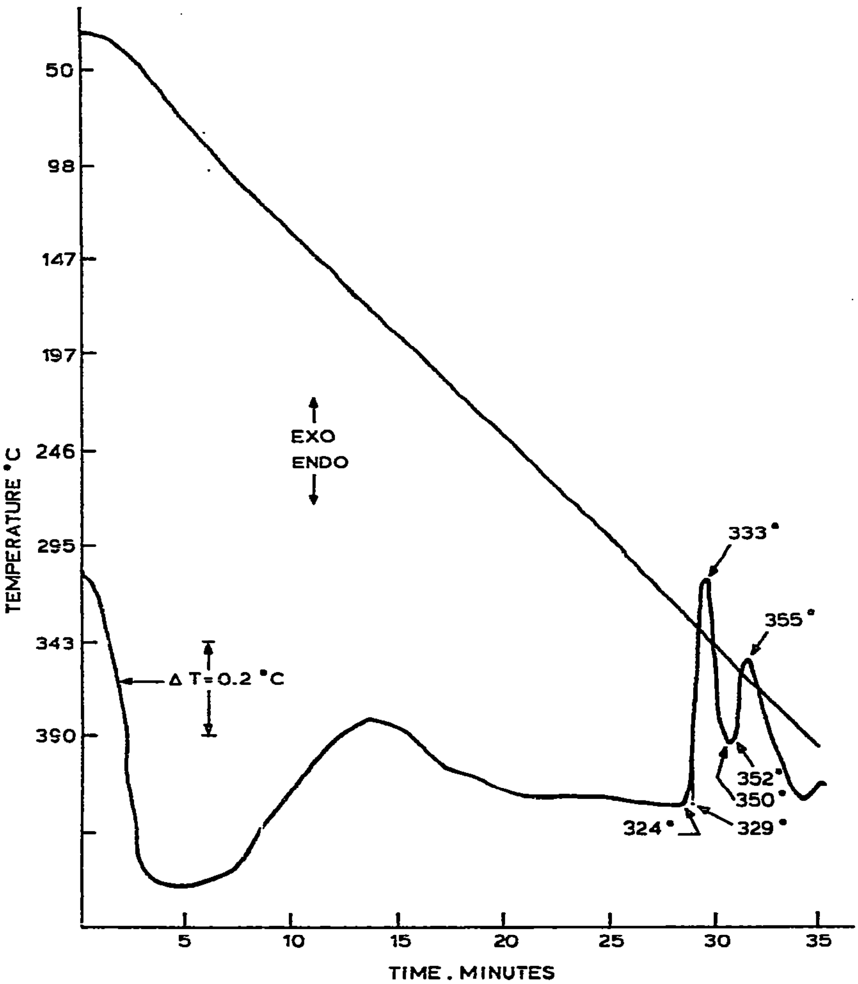

Fig. 10. DTA of lead azide RD 1333 in argon. Sample weight, 0.5 mg; gas flow rate, 6 ml min^{-1}; heating rate, 10°C min^{-1}.

observe differences in explosion temperature. No temperature changes occurred as can be seen in Table 4, but the 10% aluminum reduced the critical weight of lead azide. An exothermic chemical reaction between aluminum and nitrogen freed from decomposed lead azide must be considered probable. Copper in the presence of moisture has been reported to form the dangerous sensitive compound copper azide [8]. In these experiments, the lead azide in contact with copper was decomposed in dry atmospheres of argon and nitrogen and no evidence of sensitization appeared.

The autoignition temperature of lead azide RD 1333 was found by a procedure described earlier [2] and from the data listed in Table 5 to be 290° C. Below this temperature, lead azide appears to decompose into nitrogen and lead without explosion. An activation energy of 43 000 cal mole^{-1} from Fig. 11 is close to the theoretical value of 41 300 cal mole^{-1} reported for pure lead azide [8]. Examination of the chemical analysis in Table 1 would suggest that RD 1333 of purity 98.43% should be most similar to pure lead azide for activation energy.

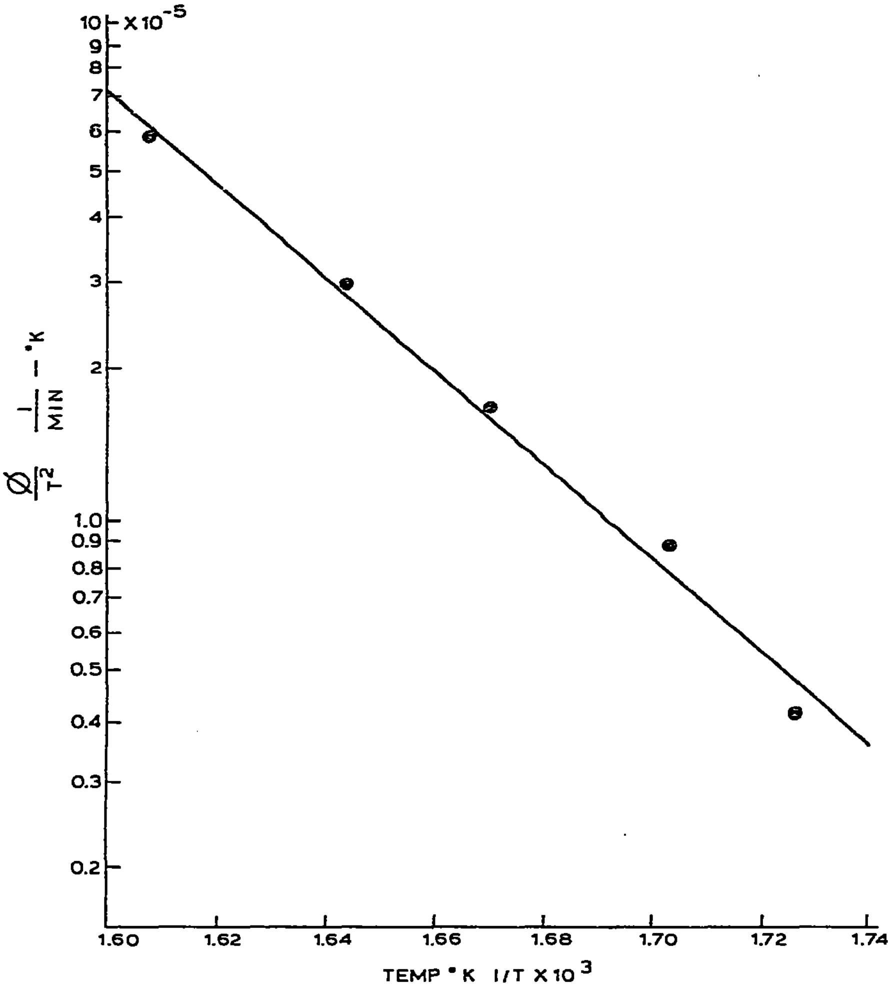

Fig. 11. Heating rate vs. absolute temperature of DTA exotherm peak of lead azide RD 1333. Activation energy, 43 236 cal mole^{-1}.

TABLE 5

DTA data for calculation of activation energy

Atmosphere: 20 ml min^{-1} nitrogen.

	Heating rate (°C min^{-1})	Sample weight (mg)	Melting point indium in reference cup (°C)	Slope temp. (°C)	Peak temp. (°C)	Action
	1.30	3.00		303.0	306.5	Decomposed
	1.40	3.28		301	305.5	Decomposed
Average (2)	1.35			302.0	306.0	
	3.05	1.62		311	316	Decomposed
	3.00	3.22	157	309	313	Decomposed
	3.00	254		310	312	Decomposed
Average (3)	3.02			310.0	313.7	
	5.8	1.21	158	321.0	327.0	Decomposed
	5.7	1.56	157	321.5	325.0	Decomposed
	6.3	1.40	157	320.5	324.0	Decomposed
Average (3)	5.9		157.3	321.3	325.3	
	11.0	1.00	159	330.0	336.0	Decomposed
	10.0	0.86	160	330.0	336.0	Decomposed
	10.5	1.70	160	329.5	336.0	Decomposed
	11.0	0.85	160	328.0	333.5	Decomposed
Average (4)	10.6		160	329.4	335.4	
	22.0	0.54	160	340.0	348.0	Decomposed
	22.2	0.50	158	338.0	345.0	Decomposed
	21.8	0.53	161	341.0	349.0	Decomposed
	22.5	0.45	162	343.0	352.0	Decomposed
Average (4)	22.1		161	340.5	348.5	
	1.35	5.00	157	301		Exploded
	2.75	2.66	158.5	312		Exploded
	3.00	8.16		309		Exploded
	3.00	12.00	159	306		Exploded

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