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REPORT No. 19/R/57

The Thermal Decomposition of some Organic Lead Compounds

USASCUK CONTROL NO.
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H. R. Broomhall

C. P. Conduit

L. D. Woollard

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SUBJECT: The Thermal Decomposition of Some Organic Lead Compounds (U)

TO: The Chief of Ordnance
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Attn: ORDGU-IN

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E.R.D.E. 19/R/57 XR.250/31

MINISTRY OF SUPPLY

2 EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT, U B

3 REPORT NO. 19/R/57

4 The Thermal Decomposition of some Organic Lead Compounds

by

5 H.R. Broomhall, C.P. Conduit and L.D. Woollard

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CONTENTS

Reference: XR.250/31

1. SUMMARY

The pyrolysis of a range of organic lead compounds used as ballistic modifiers has been studied using thermogravimetry and differential thermal analysis. The results show that the lead compounds of aliphatic carboxylic acids decompose to lead oxide in one stage which, in air, is largely oxidative in character. The compounds of the aromatic hydroxy acids, however, first yield intermediate basic compounds of varying stability and these ultimately decompose to lead oxide at high temperatures.

When heated in nitrogen dioxide vapour the lead compounds react with the gas but the products so formed from the aromatic series were found to ignite below 150°C. on further heating in nitrogen dioxide. Differential thermal analysis showed that in these latter cases the initial reaction involving the uptake of NO_2 is exothermal and that this effect can be detected if a propellant containing the lead salt is treated with excess nitrogen dioxide at an elevated temperature.

2. OBJECTS OF THE INVESTIGATION

To examine the thermal decomposition of some organic lead compounds of interest as ballistic modifiers in propellants.

3. INTRODUCTION

Organic compounds of lead are known to produce the platonisation effect when included in propellant compositions. The types of compounds used are in general the salts formed by lead with a wide range of organic carboxylic acids in both the aliphatic and aromatic series, although simple inorganic compounds such as the oxides have also been employed in some experimental formulations.

Much work has been carried out in attempts to elucidate the mechanism of the platonisation process which is usually also understood to include the super-rate ballistics associated with the "mesa" phenomenon. The processes occurring during the burning of a solid propellant may be illustrated as follows (1):

Solid Propellant	Condensed Phase Reaction Zone	Gas Phase Reaction Zone		
		Non-Luminous	Luminous	
Ambient Temperature	(Foam Reaction Zone) ← 10^{-2} cm. → NO_2 + Organic Molecules	← 7 x 10^{-3} cm. → NO, N_2, CO_2, H_2O + Aldehydes	← 10^{-3} cm. → NO + Aldehydes	
300°K	600°K	1600°K	3000°K	

/From .....

From this it is seen that the temperature of the gas-phase reaction zone is in the range 300° - 1300°C. and that a temperature gradient is present through the foam reaction zone in which decomposition of the material occurs with the formation of volatile products. The latter supply "fuel" to the combustion zones and their nature is determined by the ingredients of the propellant, which will therefore influence the nature of the combustion reactions and hence the ballistic behaviour. It is reasonable to suppose that the ballistic effect of added platonising agents depends in part on their mode of thermal decomposition in the foam reaction zone which lies in the temperature range from ambient up to 300°- 400°C., so that it seemed of interest to determine the nature of the reactions which lead compounds undergo on heating to these temperatures, with particular reference to the thermochemistry involved.

The two complementary techniques of thermogravimetry and differential thermal analysis were used in this investigation. In the former the sample is heated at a constant rate in a furnace and a continuous measure of its weight change is made using a recording balance. From the form of the curve of weight loss against temperature, some idea of the mode of thermal breakdown may be gained and in particular the formation of stable compounds is shown by the appearance of constant weight regions. In differential thermal analysis (D.T.A.) the sample is again heated at a constant rate and simultaneously its temperature is measured relative to that of an inert reference substance placed in the same furnace. The endothermal or exothermal effects accompanying the decomposition reactions then appear as positive or negative differential temperatures which are recorded using thermocouples embedded in the sample and reference material. For reasons which will become apparent later (Section 6.1), the D.T.A. experiments were carried out with the samples heated in both air and nitrogen whereas the thermogravimetry records were obtained in air only.

It was realised that heating in air represents a somewhat artificial condition since in the foam reaction zone of a burning propellant, much nitrogen dioxide must be present due to decomposition of the nitric esters. Accordingly, some of the lead compounds were examined by the above techniques in an atmosphere of NO_2.

4. EXPERIMENTAL METHODS

4.1 Thermogravimetry

The continuous weighing experiments were carried out using a Stanton Instruments Recording Balance. This instrument consists essentially of an ordinary aperiodic analytical balance of 0.1 mg. sensitivity. The sample is suspended from one side of the beam and is surrounded by the heating furnace. The movement of the balance beam due to a weight change of the sample is detected by a servo-operated capacity follower mechanism which also drives the pen of a strip chart recorder, thus giving a continuous weight versus time record. The full-scale chart deflection corresponds to a weight change of 10 mg., but an automatic weight loading device, which operates when the pen reaches the chart extremities, enables total weight changes of ±100 mg. to be accommodated. The record is read to 0.05 mg.

The method of heating the sample may be varied at will. The furnace and sample suspension system used in the present work are illustrated in Fig. 1. The furnace was of the type supplied by Messrs. Gallenkamp for differential thermal analysis. It consists of a 2-inch diameter alumina tube wound with a heating element (A) and surrounded by a box of asbestos wool heat insulation. The lower end of the furnace tube was fitted with an insert (B) shaped out of Sil-o-cel brick and drilled with two holes (C, D). The insert was held in place by a thick sheet of "Sindanyo" drilled as shown and fitted with a gas inlet tube (E), the latter being in communication with the furnace tube via (C).

/In order .....

In order to minimise gas currents within the furnace, the insert (B) was covered by a layer of broken Sil-o-cel (F). The temperature of the furnace was measured by a chromel-alumel thermocouple (G) placed with its junction close to the centre of the furnace and alongside the sample holder (H). The latter consisted of a small fused silica beaker of about 3 ml. capacity, which was supported by a stirrup (J) of stout platinum wire. This extended upwards to a point some 5 cm. above the top of the furnace. This sample assembly was suspended from the underside of the balance pan by a length of 0.006 inch nichrome wire which was held taut by a 20 g. brass weight (K).

The top of the furnace tube was restricted in area by two sheets of ceramic material (L) surmounted by an iris diaphragm (M). The latter could be moved for centering on the wire suspension and then stopped down to give as small an opening as possible (3 - 4 mm.) consistent with the slight pendulum oscillations executed by the suspension system. At room temperature, with a constant load on the balance, the random weight fluctuations shown on the balance record due to movement of the suspension amounted to no more than ± 0.1 mg. On switching on the furnace, these fluctuations increased with increasing temperature, reaching ± 0.5 mg. in the region of 600° - 700°C. The provision of extra shielding between the furnace and the balance did not reduce the effect which was ascribed to convection currents within the furnace itself.

The furnace heater was fed from a Variac transformer whose output voltage was adjusted during the experiment to maintain a constant rate of heating of 3° - 4°C. per minute up to the maximum temperature of 650°C. The furnace thermocouple was connected to a millivoltmeter calibrated in terms of temperature. The furnace temperature was entered on the balance record at 10 minute intervals. The sample weights were chosen so that the total weight loss did not exceed 100 mg. Assuming the final product in all cases to be lead oxide PbO, the range of weights generally lay between 150 and 600 mg.

The thermal decompositions were studied mainly in air, but no differences were noted if a slow stream of pure oxygen was passed through the furnace. For the experiments in nitrogen dioxide, the gas was obtained from a cylinder of the liquid by warming. It was passed through a perfluorohydrocarbon bubbler and led to the furnace inlet tube (E) through stainless steel tubing. Excess NO_2 escaped from the top of the furnace and this necessitated an arrangement for preventing contamination of the laboratory atmosphere. This is shown in Fig. 2. It consisted of a conical glass hood (A) standing on top of the furnace. The side-arm (B) was connected to an aspirator and an alkali abosrber. The iris diaphragm was moved to the top of the hood. Gentle suction from the aspirator prevented the escape of NO_2 vapour by causing a small inflow of air through the iris, the excess gas being drawn off into the absorber.

4.2 Differential Thermal Analysis

The practical principles of this technique have already been described (2), although in the previous work only metal block heaters were employed. In this present work on lead salts, the standard D.T.A. furnaces and accessories supplied by Messrs. Gallenkamps were found more convenient for use at higher temperatures. The furnace and sample holder are shown diagrammatically in Fig. 3., which also shows the arrangement of the thermocouples and gas inlet tubes.

The sample and reference substance were contained in the two-compartment fused alumina crucible (A) which lay in the well (B) of the hemi-cylindrical block of alumina (C). The latter fitted closely into the furnace tube. The left-hand end (D) of the alumina block was fully cylindrical and was pierced longitudinally by three 2 mm. holes, the outer pair of which formed the exits for the differential thermocouple leads and the centre one was used as an entrance for the particular gas required. A plate (E) similar to that used with the thermogravimetry furnace could be clamped over the end of the furnace and carried

/the .....

the main gas inlet tube (F). The right-hand end of the furnace contained a similar alumina block (G) and a two compartment crucible (H). One compartment of the latter was filled with the same reference substance (lead sulphate) as the true sample/reference crucible (A). In this was placed a thermocouple (J) used for measuring the absolute temperature of the furnace. The second compartment of the crucible (H) was left empty and held a second independent thermocouple (K) which was connected to the furnace temperature controller (see below).

The thermocouples were all of the chromel-alumel type, but it was found that if the junctions were left bare considerable attack by the lead compounds took place at high temperature. Accordingly, they were enclosed in short lengths of thin-walled stainless steel capillary tubing which could be easily removed for cleaning or renewal. The differential and absolute temperatures were measured using the same circuits and recorders as those described elsewhere (2). The zero shift circuit of the absolute temperature recorder was cut out and the mechanical zero used to set the recorder pen to the chart zero with the input on open circuit. It was found that zero drift of up to one scale division (≡14°C.) could occur during a run. Consequently a motor-driven switch was incorporated to open the absolute couple circuit for 40 seconds every 10 minutes in order to give a frequent zero check on the absolute temperature trace.

The furnace heating rate was controlled by a Kelvin-Hughes temperature program regulator. This received the output from the auxiliary thermocouple (K) which deflected a galvanometer forming part of a saturable reactor circuit included in a simple valve oscillator. The latter controlled an on-off switch in the furnace power circuit. The program was obtained by a suitably cut cam and in this work gave a linear temperature rise of 10°C./min.

The lead compounds examined in this work were mostly commercial samples as used in experimental propellant formulations and were not purified. Their compositions were checked chemically by estimation of (a) per cent. lead, (b) per cent. acid radical, (c) per cent. carbonate (since this was a likely impurity) and (d) spectrographic examination of sulphated ash to detect the presence of other heavy metal impurities. In most cases, additional confirmation of purity could be obtained from the total weight loss measured thermogravimetrically, since in all cases the final product of pyrolysis in air is lead monoxide.

Most of the thermogravimetric and D.T.A. experiments in an NO_2 atmosphere were not carried out in the usual way with steadily rising temperatures since explosive products were formed. The technique used in these experiments is described in Section 6.3.

5. RESULTS

The results obtained by both thermogravimetry and D.T.A. were found to be somewhat similar over a number of the lead compounds taken for study. In consequence, a complete set of weight-loss and differential temperature traces is not included here, but will be published separately. The records contained in this report are generally those of greatest interest to the discussion or are illustrations of typical behaviour within a series of related compounds. However, for completeness the results on all the compounds studied are summarised in tabular form in the appropriate sections below.

/6. .....

6. DISCUSSION OF RESULTS

6.1 The Lead Salts of Aliphatic Acids

The thermal decomposition of the lead salts of $\alpha\omega$-dicarboxylic acids was studied. The compounds ranged from the oxalate to the sebacate (excluding the malonate and azeleate); the formate, stearate and 2-ethylhexoate were included since the first is closely related to the oxalate, and the last two are used in Service propellants.

Thermogravimetric experiments in air showed that all these compounds decompose to lead oxide in one stage with no evidence of the formation of stable intermediates, although slight inflexions occur on the weight loss curves of the higher members of the series. The temperatures at which decomposition began and at which the sample reached constant weight are collected in Table 1. The weight loss curves for two of the compounds (oxalate and suberate) are shown in Figs. 4 and 5; these two examples are typical of the whole series.

TABLE 1

Lead Compound	Temperature Range of Decomposition, °C.	
	Initial	Final
Formate	200	300
Oxalate	330	390
Succinate	280	440
Glutarate	275	420
Adipate	250	460
Pimelate	270	400
Suberate	280	470
Sebacate	250	550
Stearate	255	520
2-ethylhexoate	150	450

There is little regularity in the decomposition temperatures through the $\alpha\omega$-dicarboxylic series. The reactions commence in the range 220° to 330°C. and reach completion between 400° and 550°C., although the end point tends to move to higher temperatures as the series is ascended.

Some idea of the mechanism of these thermal decomposition processes may be gained from an examination of the results of D.T.A. carried out under various conditions. Consider lead oxalate. This is known to decompose on heating in vacuo according to the following equation (3):

$$3PbC_2O_4 = 2PbO + Pb + 4CO_2 + 2CO \quad \text{.........} \; 1$$

The heats of formation ΔH_f of the reactants and products are given thus (4):

PbC_2O_4 (s) ΔH_f = -205 kcal/mole
PbO (s) -52 kcal/mole
CO_2 (g) -94 kcal/mole
CO (g) -26 kcal/mole

/Using .....

Using these values to set up a thermochemical equation shows that the above reaction is endothermal to the extent of 64 kcal/mole of lead oxalate decomposed. Fig. 6 shows the differential thermogram of the substance as determined in air, and it is seen that the decomposition is entirely exothermal and takes place within the same temperature range as that given by thermogravimetry. This opposite thermal behaviour in air indicates that reaction 1 does not hold for a sample heated in this way, and it is easily demonstrated that the only simple scheme having the required exothermicity must involve a reaction with oxygen, thus:

$$2PbC_2O_4 + O_2 = 2PbO + 4CO_2 \;\ldots\ldots\ldots\ldots\ldots\ldots\; \underline{2}$$

A thermochemical calculation shows that this reaction is exothermal with a ΔH value of 30 kcal/mole of oxalate. Confirmation of the oxidative character of the thermal decomposition of lead oxalate in air was obtained by carrying out D.T.A. in nitrogen. The thermogram is shown in Fig. 7, which confirms that under these conditions the reaction is indeed endothermal as required by an equation such as 1. Consistent with this, the final product contained globules of metallic lead, instead of consisting of pure lead oxide which was obtained on heating in air.

A similar treatment can be applied to the decomposition of lead formate which in vacuo may take place as follows:

$H\overset{O}{C}-OPb-O-\overset{O}{C}H$

$$2PbC_2H_2O_4 = Pb + PbO + 2H_2O + 3CO + CO_2 \;\ldots\; \underline{3}$$

This should be endothermal with a ΔH-value of 20 kcal/mole of formate. The differential thermal analysis record (Fig. 8) determined in air reveals that an endothermal effect does in fact commence at 220° - 230°C. but changes over to an exotherm at about 290° - 300°C. The latter temperature is that at which the thermogravimetry results indicate that the decomposition is largely complete, so that the observed exothermal reaction is probably the oxidation to PbO of the metallic lead produced. When carried out in nitrogen the decomposition is entirely endothermal (Fig. 9). A very small endotherm following the main one occurs at around 325° - 330°C. which is very close to the melting point of metallic lead (327°C.) and therefore confirms the formation of this substance during the pyrolysis in nitrogen. The decomposition of lead formate in air therefore occurs by two consecutive but slightly overlapping reactions:

$$2PbC_2H_2O_4 = Pb + PbO + 3CO + CO_2 + 2H_2O \;\ldots\ldots\; \underline{3}$$

$$\text{followed by } 2Pb + O_2 = 2PbO \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; \underline{4}$$

In agreement with this the thermogravimetry curve in air (Fig. 10) shows that towards the end of the main weight loss, a small weight increase takes place at about 300°C. followed by a slow fall to the theoretical loss expected for the overall reaction:

$$4PbC_2H_2O_4 + O_2 = 4PbO + 6CO + 2CO_2 + 4H_2O \;\ldots\ldots\ldots\ldots\; \underline{5}$$

The small weight increase represents the uptake of oxygen by reaction 4 before the end of 3 is reached.

The exothermal decomposition of lead oxalate in air cannot be explained by a similar two-stage process in which the second is an oxidation of metallic lead produced in the first, since in this case the decomposition temperature moves from 310° in air to 380°C. in nitrogen, whereas for the formate the initial endotherm occurs at the same temperature (220°C.) irrespective of the conditions.

/It is .....

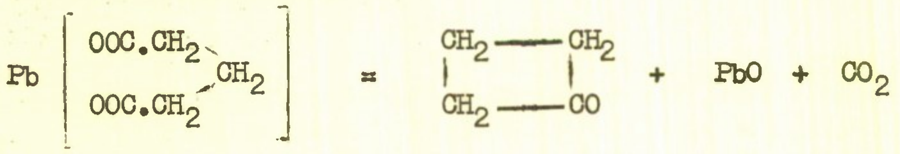
It is therefore possible to obtain some idea of the mode of thermal decomposition of an organic lead compound by comparing the differential thermograms carried out in air and in nitrogen. In this way it was found that for all the compounds listed in Table 1 above, the later stages of the decomposition reactions are oxidative in character, but, in some of the cases described in the notes below, this was preceeded by a decomposition of the salt per se. Thus, the end of decomposition in air consists of a burning off of the organic residues resulting from the earlier stages. The end-products from the heating in nitrogen always contained considerable amounts of carbonaceous material, whereas pure lead oxide resulted from heating in air. The following notes describe qualitatively the behaviour of some of the aliphatic lead compounds:

(i) Lead succinate.

This decomposes in air entirely by oxidation since the reaction is exothermal in air but endothermal in nitrogen.

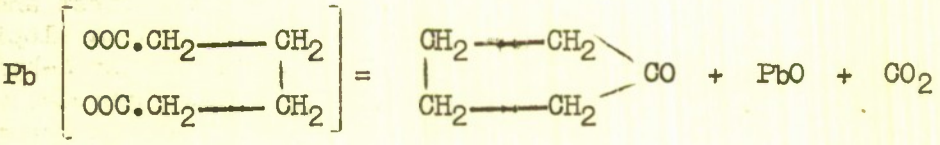
(ii) Lead glutarate.

The compound shows an endotherm followed by an exotherm in air but the latter effect is reversed in nitrogen. The first stage may be volatilisation of glutaric acid (or its anhydride) to give a basic salt, or it may be due to decarboxylation to give cyclobutanone:



(iii) Lead adipate.

This behaves similarly to the glutarate. In this case cyclic ketone formation is much more likely since the product is the five-membered cyclopentanone:



(iv) Lead sebacate.

The decomposition of this compound appeared to be entirely oxidative (see under lead succinate).

(v) Lead stearate and lead 2-ethylhexoate.

These decompose by general degradation to give a complex mixture of products which are oxidised at higher temperatures. The stearate showed two endothermal effects at 70° and 100°C., respectively. These correspond to the phase changes observed by Hattiangdi, Vold and Vold (5) in which the initially crystalline material is transformed into a mesomorphic state approaching that of an undercooled glassy liquid crystalline form.

Quantitative results of the thermogravimetry experiments together with the chemical analyses of the above series of compounds are collected in Appendix 1 (p. 16)

6.2 The Lead Compounds of Aromatic Acids

The compounds of this type were those derived from the various mono and dihydroxy-benzoic and naphthoic acids, although the phthalate and the 4-hydroxy-isophthalate were included, together with the lead compound of phthalimide.

/Thermogravimetry .....

Thermogravimetry experiments showed that in general these aromatic compounds decompose on heating in more than one stage, often with the formation of a relatively stable intermediate compound. Furthermore, a number of the compounds studied were known to contain water of crystallisation the loss of which on heating was clearly indicated on the weight-loss record. Typical behaviour is illustrated in Figs. 11 and 12 for lead salicylate and lead 4-hydroxybenzoate dihydrate. The temperatures marking the beginning and end of the various processes occurring during the complete pyrolysis of all the aromatic compounds studied are summarised in Table 2. The heating was carried out in air at a rate of 4°C. per min.

TABLE 2

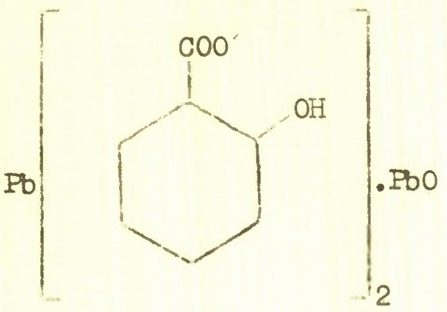
Lead Compound	Temperatures of Decomposition Reactions (°C.)		
	Dehydration	1st Stage	2nd Stage
Salicylate	-	200 - 255	325 - 450
4-hydroxybenzoate $2H_2O$ *	90 - 140	220 - 290	290 - 450
Resorc. 2:4-dihydroxybenzoate H_2O	130 - 160	190 - 255	290 - 390
Gentis. 2:5-dihydroxybenzoate $2H_2O$	100 - 160	190 - 300	400 - 480
Acetylsalicylate	-	170 - 280	365 - 470
3-phenylsalicylate *	-	200 - 280	280 - 600
Phthalate	-	310 - 390	420 - 510
4-hydroxy-isophthalate H_2O*	60 - 175	235 ——	—— 425
1-hydroxy-2-naphthoate H_2O*	120 ——	—— 220	300 - 590
2-hydroxy-3-naphthoate *	-	260 - 360	530
Phthalimide	-	140 - 270	295 - 520

For the compounds marked (*) the separation between the first and second stages of the decomposition was not sharp but appeared only as a sloping inflexion on the weight loss curve similar to that shown for the 4-hydroxybenzoate in Fig. 12. The 4-hydroxy-isophthalate decomposed in only one step which occupied the temperature range normally covered by the two-stage reaction characteristic of most of the other salts of the series. Quantitatively, the loss of water from the hydrated compounds agreed closely with the theoretical requirement with the exception of the 1-hydroxy-2-naphthoate. This was alleged to be a monohydrate, for which the theoretical weight loss is 3.4 per cent. The observed loss accompanying dehydration was 14.2 per cent., and further, the reaction reached completion only at 220°C. which is somewhat higher than that observed for the other hydrated salts examined. The quantitative results on this compound agree better with its being a dihydrate which decarboxylates simultaneously with dehydration, the theoretical weight loss for such a process being 13.5 per cent.

The interpretation of the two stages of the main pyrolytic reaction of these compounds is best obtained by reference to lead salicylate. The total weight loss to lead oxide was 50.0 per cent. compared with the theoretical figure of 53.6 per cent. However, chemical analysis showed that the sample used contained only 53.4 per cent. of salicylate radical instead of 57.0 per cent. for the pure compound, so that the percentage purity is only 93.8. The theoretical weight loss when adjusted to this figure for the purity then amounts to 50.3 per cent. which is in good agreement with the experimental result of 50.0 per cent. The weight loss of 22.8 per cent. to the intermediate

/compound .....

compound (point A in Fig. 11) compares with the value 25.2 per cent. for the formation of a basic mono-salicylate of the formula:



The discrepancy between the calculated and observed weight loss in this case may be explained by the fact that it is not possible to write a simple stoichiometric equation for the reaction. The volatile products may consist either of salicylic anhydride or of its pyrolysis fragments which are reported to be a mixture of carbon dioxide, phenol and phenyl salicylate. Other workers (6) have examined the pyrolysis of lead salicylate at 200°C. and find that the product consists of the "mono-salicylate", although no constitution is put forward for the latter.

An analysis of the weight loss curves for all of the aromatic compounds studied in this work showed that in those cases in which intermediate compound formation takes place, the first stage is the loss of approximately one equivalent of the acid to give a basic salt analogous to the monosalicylate. The quantitative results are tabulated in Appendix 2 (p. 17) together with notes on the chemical analysis of the compounds.

As in the case of the aliphatic compounds described in Section 6.1, a series of differential thermal analysis experiments in both air and nitrogen were carried out in order to obtain further information on the types of reaction which occur during the pyrolysis of the aromatic compounds. The thermograms for lead salicylate are shown in Figs. 13 and 14 for air and nitrogen respectively. In both cases there is an endothermal effect commencing at 210°C. corresponding to the formation of the basic mono-salicylate, and, using the same reasoning as that outlined for the aliphatic compounds, it is clear that the process consists of volatilisation rather than oxidation. In air, a second effect commences at about 330°C. in agreement with the second stage of the weight loss curve (Fig. 11). This effect is exothermal in air but becomes endothermal in nitrogen and moves to a higher temperature (400°C.). Hence, the decomposition of the mono-salicylate takes place in air by an oxidative reaction. Other workers (7) have studied the decomposition of the mono-salicylate in vacuo at 400°C. and have found that one molecule of carbon dioxide is evolved per molecule of compound decomposed, and that the residue consists mainly of pyrophoric lead. Consistent with this, if air was admitted to a nitrogen D.T.A. run at the higher temperatures (ca. 600°C.) a very intense exothermal reaction took place.

The dehydration of those compounds containing water of crystallisation was marked by an endotherm at the appropriate temperature, so that in general all the features of the thermogravimetry experiments were confirmed by D.T.A.

With two exceptions, all the compounds listed in Table 2 gave D.T.A. curves similar in form to that of that salicylate, showing that the mode of thermal decomposition is much the same in each case. Thus, in air, a generalised reaction scheme may be written:

/1st stage .....

1st stage $Pb[A]_2 \rightarrow Pb[A]_2.PbO$ (+ HA) 6

2nd stage $Pb[A]_2.PbO + O_2 \rightarrow PbO$ + oxidation products 7

In some cases 7 may commence before 6 is quite complete so that the range of stability of the intermediate basic salt is then very small.

The two exceptions mentioned above consist of the phthalate and the 2-hydroxy-3-naphthoate. For each of these the first stage of the decomposition in air is exothermal, showing that the reaction consists of an oxidation of the organic part of the molecule. It is probably significant that these two compounds have the highest decomposition temperatures of any in the series (320° and 260°C., respectively). Thus, these two salts appear to be exceptionally stable with respect to reactions analogous to 6 above, which is replaced by an oxidation reaction similar to 7, although the result is the formation of the corresponding basic salt. In nitrogen, the first reaction of each of these two compounds becomes endothermal and moves to higher temperature, namely to 360°C. for the phthalate and to 300°C. for the 2-hydroxy-3-naphthoate. This is in contrast with the compounds such as the salicylate in which the first reaction (volatilisation) is both endothermal and remains at the same temperature irrespective of the heating conditions. Other features of interest in this series of compounds are discussed as follows:

(i) It was stated earlier in this Section that the 1-hydroxy-2-naphthoate gave an unexpectedly high weight loss during dehydration, this being consistent with the loss of two molecules of water of crystallisation accompanied by decarboxylation. The differential thermogram confirmed the composite nature of this process by the appearance of two strong shoulders on either side of the main endothermal effect occurring in the range 120° - 220°C. Decarboxylation of this substance at such a comparatively low temperature is in marked contrast with the high thermal stability of the isomeric 2-hydroxy-3-naphthoate discussed above.

(ii) Other pairs of isomeric compounds also differ in thermal stability. Among these are the salicylate and 4-hydroxybenzoate, and the 2:4 and 2:5-dihydroxybenzoates. Inspection of Table 2 shows that in these cases it is the stabilities of the intermediate basic salts which vary, and it is of interest that the lower stabilities are associated with the presence of a hydroxyl group in the ring position para to the carboxylate group. The differential thermograms, as already stated, show that the second stage of decomposition, i.e., the breakdown of the basic salts, is oxidative in character. Any attack by oxygen on the benzene ring system in these compounds will be retarded by the deactivating influence of the COO^- group. Thus, the oxidation of the compound should be facilitated by those factors which accelerate decarboxylation and it is known (8) that the decarboxylation of aromatic acids tends to be assisted by the presence of hydroxyl groups para to the carboxylate group. On this basis therefore, the lower stability of the basic 4-hydroxybenzoate and the 2:4-dihydroxybenzoate compared with their respective 2 and 2:5 isomers is to be expected.

6.3 Thermal Decompositions in Gaseous Nitrogen Dioxide

The pyrolysis of some of the above lead compounds was studied in an atmosphere of nitrogen dioxide in order to simulate to some extent the conditions existing in and below the foam reaction zone of a burning propellant. Initially only the thermogravimetry technique was used and a few representative samples from the aliphatic and aromatic series were chosen for study.

/The .....

The curve of weight change versus time with a temperature rise of 3°C./min. is shown for lead salicylate in Fig. 14. A considerable and rapid gain in weight occurred on admitting nitrogen dioxide to the furnace, even in the cold, and the effect continued on heating up to a temperature of 75° - 80°C. Thereafter the sample lost weight slightly, and at 90°C. it ignited violently. Lead phthalate also showed an initial weight increase, but this was followed by a succession of gains and losses up to 330°C. at which temperature the sample ignited. In the aliphatic series, a similar behaviour was exhibited by lead glutarate, the final ignition occurring at 250°C. The weight changes observed on heating under these conditions could not be interpreted quantitatively to determine the nature of the reaction products, although it was considered that nitration reactions took place with the aromatic compounds to give the lead salts of nitrohydroxy acids somewhat akin to well-known initiatory materials such as lead styphnate, and that the latter were responsible for the sharp detonations which often accompanied the ignition of the sample. Other workers (9) have shown that the products formed by reacting nitrogen dioxide with lead salicylate in solution at 0°C. consist of lead nitrate and nitrosalicylic acid, though some of the latter is decarboxylated with evolution of carbon dioxide. These points are considered again later.

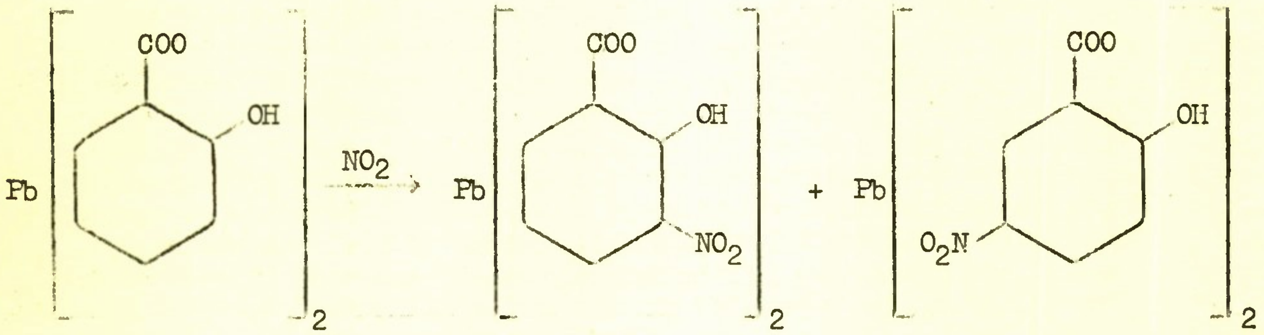
To avoid damage to the balance due to the detonation of the samples, continuous weighing in nitrogen dioxide was abandoned and instead heating in the gas was carried out to determine the ignition temperatures of all the lead compounds used in this work since it was thought that such values might be of use in the discussion of the ballistic modifying effect of the various compounds. Table 3 gives the ignition temperatures as determined in this way, together with notes on the nature of the phenomenon.

TABLE 3

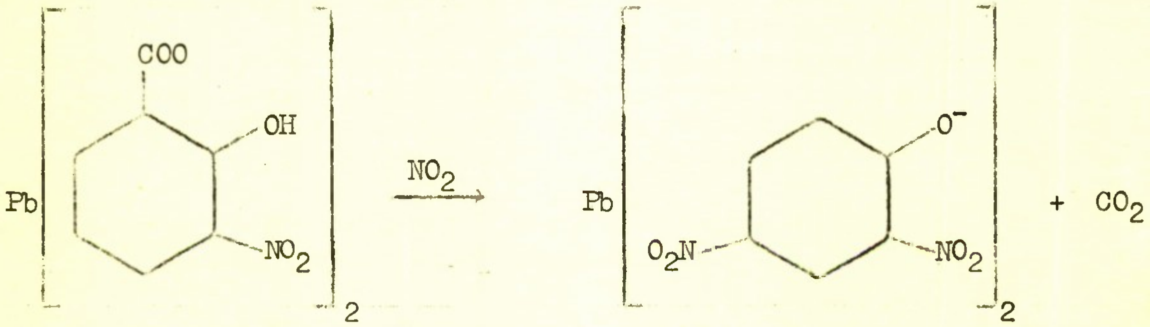
Lead Compound	Ignition Temperature in NO_2, °C.	Remarks
Salicylate	90	Detonation
4-hydroxybenzoate	150	"
2:4-dihydroxybenzoate	140	Mild ignition
2:5-dihydroxybenzoate	ca 130	" "
Acetylsalicylate	76	Detonation
3-phenylsalicylate	116	Mild ignition
Phthalate	330	Detonation
4-hydroxy-isophthalate	225	"
1-hydroxy-2-naphthoate	120	Mild ignition
2-hydroxy-3-naphthoate	140	Detonation
Phthalimide	-	No ignition
Formate	-	" "
Oxalate	-	" "
Succinate	240	Mild ignition
Glutarate	250	" "
Adipate	220	" "
Pimelate	250	" "
Suberate	155	" "
2-ethylhexoate	-	No ignition
Stearate	-	" "

/In .....

In the aromatic series most of the compounds ignite below 150°C., although for the phthalate and the 4-hydroxy-isophthalate the temperature is appreciably higher than this (330° and 225°C., respectively). It is significant that the lower range of ignition temperatures (<150°C.) occurs for those compounds containing only one carboxylic acid grouping together with one or more hydroxyl groups. The first stage in the reaction with nitrogen dioxide is most likely to be nitration. In the case of a simple aromatic acid such as benzoic this reaction takes place with only moderate case on account of the deactivating influence of the carboxyl group. The hydroxyl group has the opposite tendency to a more marked degree, so that in the compounds here considered the nitration reaction should proceed easily, much as with a phenol. Lead salicylate would be expected to give a mixture of the 3 and 5-nitrosalicylates:



It is unlikely that in the continued presence of nitrogen dioxide the initial nitro-derivatives would be stable. They would be further nitrated and/or decarboxylated, since it has been found (10) that the free acids are decarboxylated on heating with aqueous sodium nitrite.



The dinitrophenolate produced may then undergo further nitration to give a sensitive polynitro compound or it may itself be sufficiently sensitive to ignite on further heating. The higher thermal stability of lead phthalate is probably associated with the presence of two deactivating carboxylate groups which make the initial nitration more difficult. Secondly, decarboxylation of any nitrophthalate which is formed leads to a simple nitrohydrocarbon and not to a nitrophenolate. The former would be expected to be less sensitive to heat than the latter and therefore to ignite at a higher temperature. In the case of the 4-hydroxy-isophthalate, a nitrophenolate would be the ultimate product of nitration and decarboxylation but only after the removal of both carboxylate groups, and it is reasonable to expect that the ignition temperature would lie between that of the hydroxymonocarboxylates and that of the normal phthalate, as observed.

/The .....

The reaction schemes outlined above should take place also in the foam reaction zone of a burning propellant due to the nitrogen dioxide produced by the breakdown of the nitric esters. It was thought to be of interest to determine something of the thermochemistry of the reactions of nitrogen dioxide with lead compounds. As shown above, the lead salts of the hydroxymonocarboxylic acids take up NO_2 on heating. After reaching a maximum, a loss in weight commences but is quickly terminated by ignition of the sample. The latter process is clearly exothermal, but it was considered important to discover the nature of the thermal effects associated with the uptake of nitrogen dioxide. This was done for the salicylate as follows.

A sample was placed in the D.T.A. apparatus with the usual thermocouple system. The furnace temperature was raised to 70°C. and held constant. When at this point NO_2 vapour was admitted to the furnace, the differential temperature record showed a large exothermal effect which reached a maximum in about one minute and then returned exponentially to zero. The 2:4-dihydroxybenzoate which ignites at the higher temperature of 150°C. was also examined by this technique except that the reaction was carried out at 120°C. A similar exotherm was obtained but was of somewhat lower intensity than that given by the salicylate. This suggests that the initial reaction of nitrogen dioxide with those compounds which ignite in the gas below 150°C. is exothermal in all cases. As we have seen, the initial nitration of lead phthalate does not take place so readily as that of the hydroxy acids, and, when this substance was examined by the technique described above, no thermal effect could be detected at 120°C. If anything, a very slight endotherm appeared on the differential temperature trace. In the aliphatic series, lead stearate gave no thermal effect on being treated with nitrogen dioxide at 100°C.

6.4 The Reactions of Lead Salts in Propellants

Having established that most aromatic lead compounds react exothermally with gaseous nitrogen dioxide it appeared possible that the thermochemistry of the reaction might play a part in the platonisation process. However, since most platonised formulations contain only a few per cent. of the ballistic modifier, it was thought desirable to determine whether a platonised propellant on reaction with gaseous nitrogen dioxide shows any thermal effects over and above those due to reactions involving the stabiliser.

Differential thermal analysis of colloidal propellants has shown (2) that at low rates of heating (0.5°C/min.), self-heating commences at about 130°C. and increases until ignition takes place at around 160°C. The self-heating effect corresponds with the uncontrolled production of nitrogen dioxide by decomposition of the nitric esters and it occurs at a temperature assigned to the foam reaction zone. In order to avoid complications due to this self-heating of the sample, a temperature of 125°C. was chosen for the study of the reactions of the propellant with excess gaseous nitrogen dioxide. The sample was raised to the experimental temperature in the furnace in air after which nitrogen dioxide vapour was admitted. Three propellants were examined. They had similar basic compositions but two of them were modified by the addition of 2 per cent. of lead salicylate and 2 per cent. each of the salicylate and 2-ethylhexoate, respectively. The compositions are given in Table 4.

/TABLE 4 .....

TABLE 4

Ingredient	Per cent.		
	F.488/699	F.488/611	F.488/649
Nitrocellulose	53.0	53.0	53.0
Nitroglycerine	37.7	37.7	37.7
Dibutyl phthalate	7.3	7.3	7.3
Carbamite	2.0	2.0	2.0
Lead salicylate	-	3.0*	2.0*
Lead 2-ethylhexoate	-	-	2.0*

* Additions

An experiment was carried out with each of these compositions using lead sulphate as the inert reference material. The maximum differential temperatures produced by the reaction with nitrogen dioxide were 3°, 9° and 5° for the F.488/699, F.488/611 and F.488/649 compositions, respectively. Thus, the larger effect for the two latter propellants must be due to the presence of the lead salts. This was confirmed by replacing the lead sulphate by the non-leaded F.488/699 composition as the reference material and repeating the above experiments with the two leaded samples. The maximum differential temperatures obtained now became 6° and 3°C. for F.488/611 and F.488/649, respectively. The values predicted from the results obtained by running each of the three samples against lead sulphate are 6° and 2°C. As a final check to ensure that the effects were not due to thermal asymmetry in the furnace, some F.488/611 composition was placed in both the sample and reference holders. Admission of nitrogen dioxide at 120°C. caused a thermal effect of less than 0.5°C., showing that almost equal amounts of heat were produced in each portion of the same sample.

Thus, there is little doubt that the presence of lead salicylate in a propellant even at the 2 per cent. level (F.488/649), results in a more highly exothermal reaction with nitrogen dioxide than in formulations not containing a lead salt, and the higher thermal effect in F.488/611 is probably to be ascribed to the higher proportion of salicylate in this latter composition. It is likely that this effect is induced by the aromatic hydroxycarboxylic acid lead compounds which themselves react exothermally with nitrogen dioxide, and further work is in progress to determine whether the effect is indeed general for this class of ballistic modifiers.

7. ACKNOWLEDGMENTS

Appreciation is due to Dr. D.L. Hodge and Mr. R. Pape for a number of useful discussions and for supplying many of the lead compounds used in this work.

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/APPENDIX I .....

APPENDIX 1

Thermogravimetry and Chemical Analysis of the Lead Compounds of Aliphatic Acids

Lead Compound	Per cent. Pb		Per cent. Acid Radical		Per cent. Weight Loss by Thermogravimetry	
	Found	Required	Found	Required	Found	Required
Formate	69.8	69.7	27.0	30.3	25.0	24.9
Oxalate	70.2	70.2	29.4	29.8	24.2	24.4
Succinate	64.0	64.1	35.5	35.9	31.2	31.0
Glutarate	60.9	61.5	38.0	38.5	33.8	33.8
Adipate	56.4	59.0	35.0	41.0	38.9	36.5
Pimelate	56.2	56.7	43.8	43.3	37.6	38.9
Suberate	54.4	54.6	45.6	45.4	40.9	41.2
Sebacate	49.8	50.9	47.2*	49.1	44.5	45.7
2-ethylhexoate	41.1	42.0	56.9*	58.0	57.1	56.2
Stearate	30.0	26.8	69.3*	73.2	66.8	67.2

The per cent. Pb figures were obtained gravimetrically by the $PbSO_4$ method. The formate and the oxalate radicals were estimated volumetrically with alkaline and acid $KMnO_4$ respectively. The remaining acid radicals were determined by an ion exchange technique followed by an alkali titration, but this did not work well for the higher members of the series, marked (*).

/APPENDIX 2 .....

APPENDIX 2

Thermogravimetry and Chemical Analysis of the Lead Compounds of Aromatic Acids

Lead Compound	Per cent. Pb		Per cent. Acid Radical		Per cent. Weight Loss by Thermogravimetry					
					(i) Dehydration		(ii) 1st Stage		(iii) Total Loss	
	Found	Required	Found	Required	Found	Required	Found	Required	Found	Required
Salicylate	46.0	43.0	53.6	57.0	-	-	22.8	26.8	50.0	53.6
4-hydroxybenzoate $2H_2O$*	40.1	40.0	52.8	53.0	6.8	7.0	-	-	55.2	56.9
2:4-dihydroxybenzoate H_2O	39.1	39.0	57.6	57.8	2.9	3.4	34.8	29.8	60.1	58.0
2:5-dihydroxybenzoate $2H_2O$	37.8	37.7	52.3	55.7	5.9	6.6	34.6	33.0	58.0	59.4
Acetylsalicylate	40.2	36.6	67.9	63.4	-	-	30.4	31.8	55.7	60.5
3-phenylsalicylate*	31.2	32.7	-	67.3	-	-	-	-	64.0	65.7
Phthalate	55.6	55.8	43.2	44.2	-	-	24.9	19.8	37.8	39.9
4-hydroxy-isophthalate H_2O*	49.9	51.1	43.9	44.4	4.8	4.5	-	-	43.8	44.9
1-hydroxy-2-naphthoate H_2O*	34.0	34.5	62.7	62.4	14.2	3.0	-	-	62.4	62.7
2-hydroxy-3-naphthoate*	35.0	35.6	-	64.4	-	-	-	-	61.5	61.5
Phthalimide	37.7	41.5	-	58.5	-	-	21.6	27.7	56.7	55.4

The acid radicals were determined as follows: Salicylate, 4-hydroxybenzoate, 2:4-dihydroxybenzoate, acetylsalicylate and 4-hydroxy-isophthalate by a volumetric bromination method; 2:5-dihydroxybenzoate by ion exchange; 1-hydroxy-2-naphthoate by isolation and weighing of the free acid. The compounds for which no acid radical results are given were examined by all of the methods mentioned above, but did not give reproducible results. For the compounds marked (*) the first and second stages in the pyrolysis were separated by an inflexion which made it difficult to define with accuracy the end of the first stage. Accordingly, no weight-loss results for this stage are given in these cases. The theoretical weight loss in the first stage is based on the reaction:- $2Pb(A)_n \rightarrow Pb(A)_n.PbO$, whilst the total weight loss assumes the overall reaction to be $Pb(A)_n \rightarrow PbO$.

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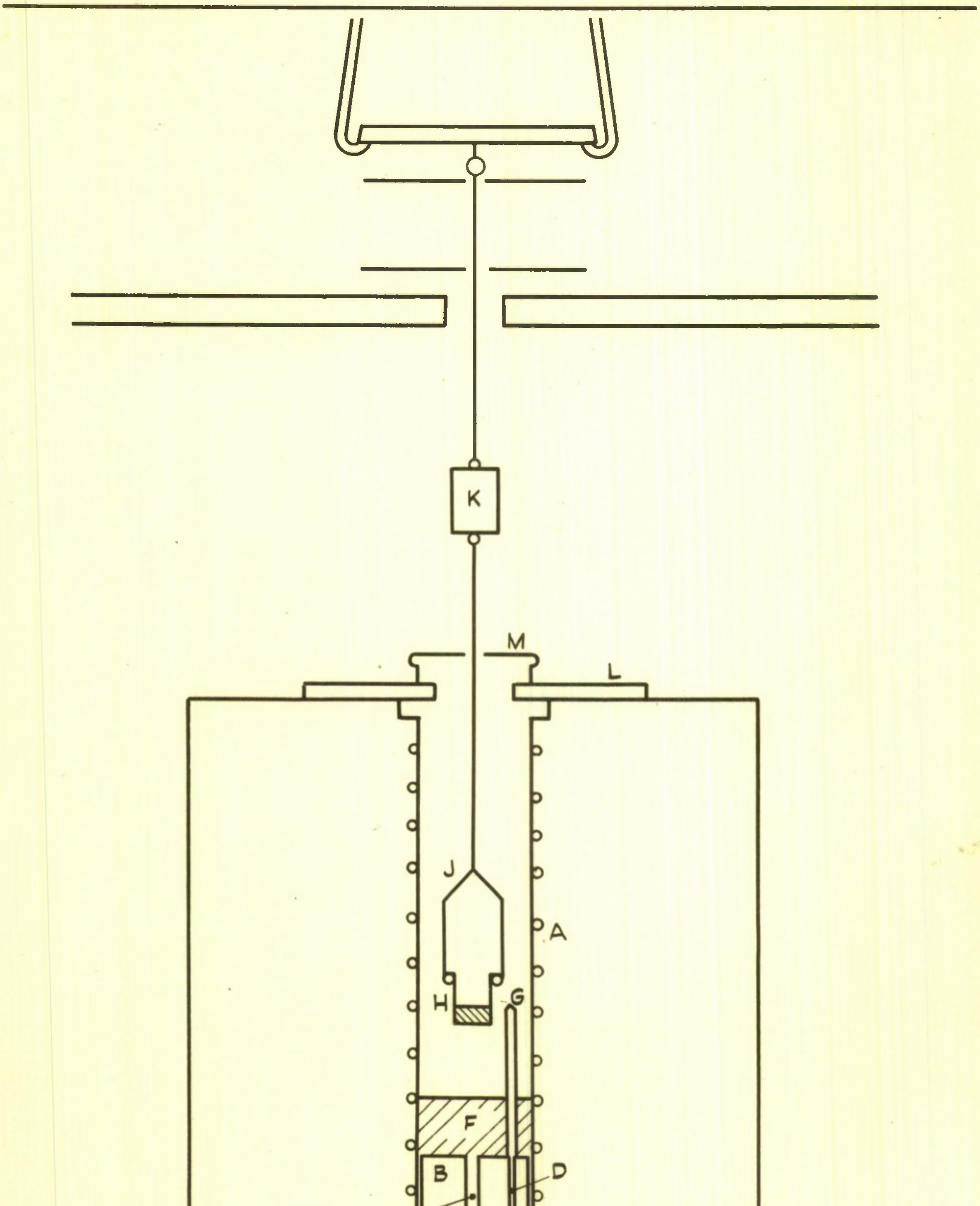


FIG. 1.

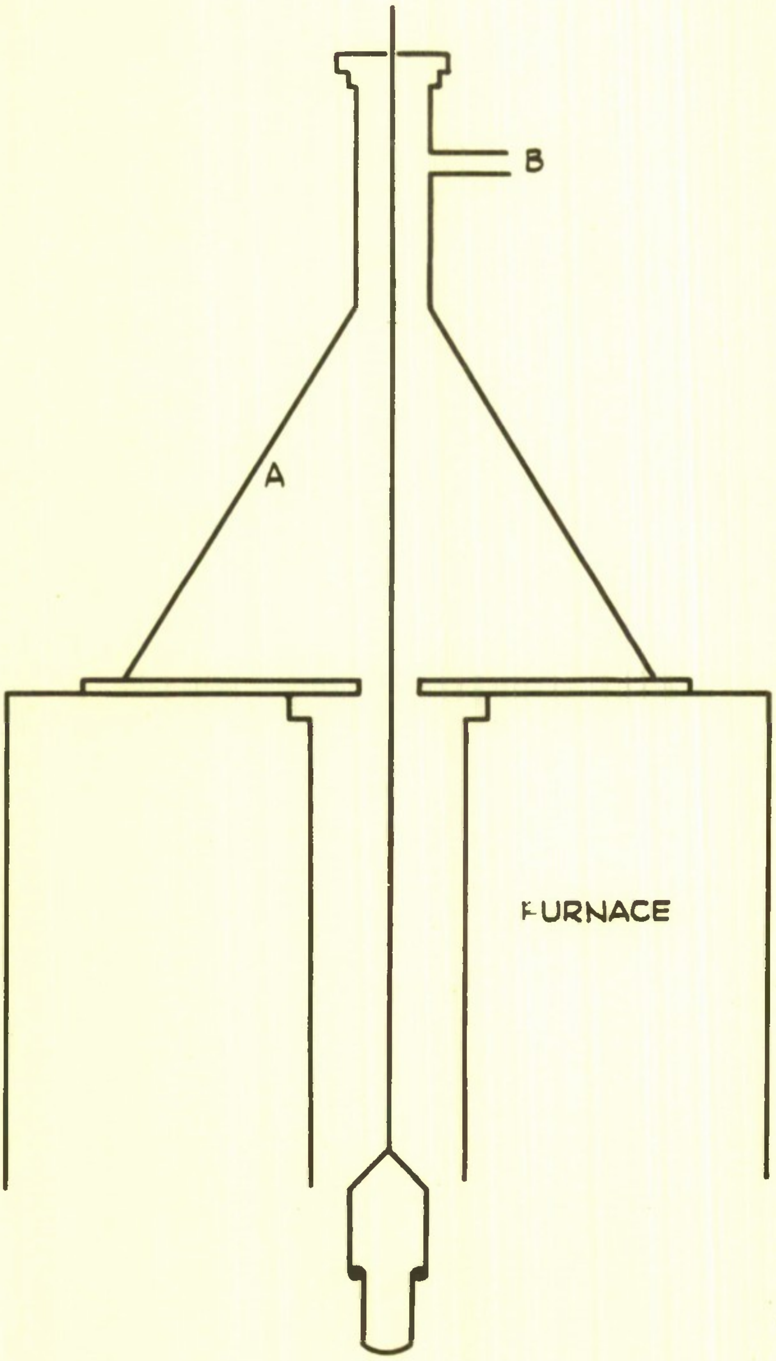
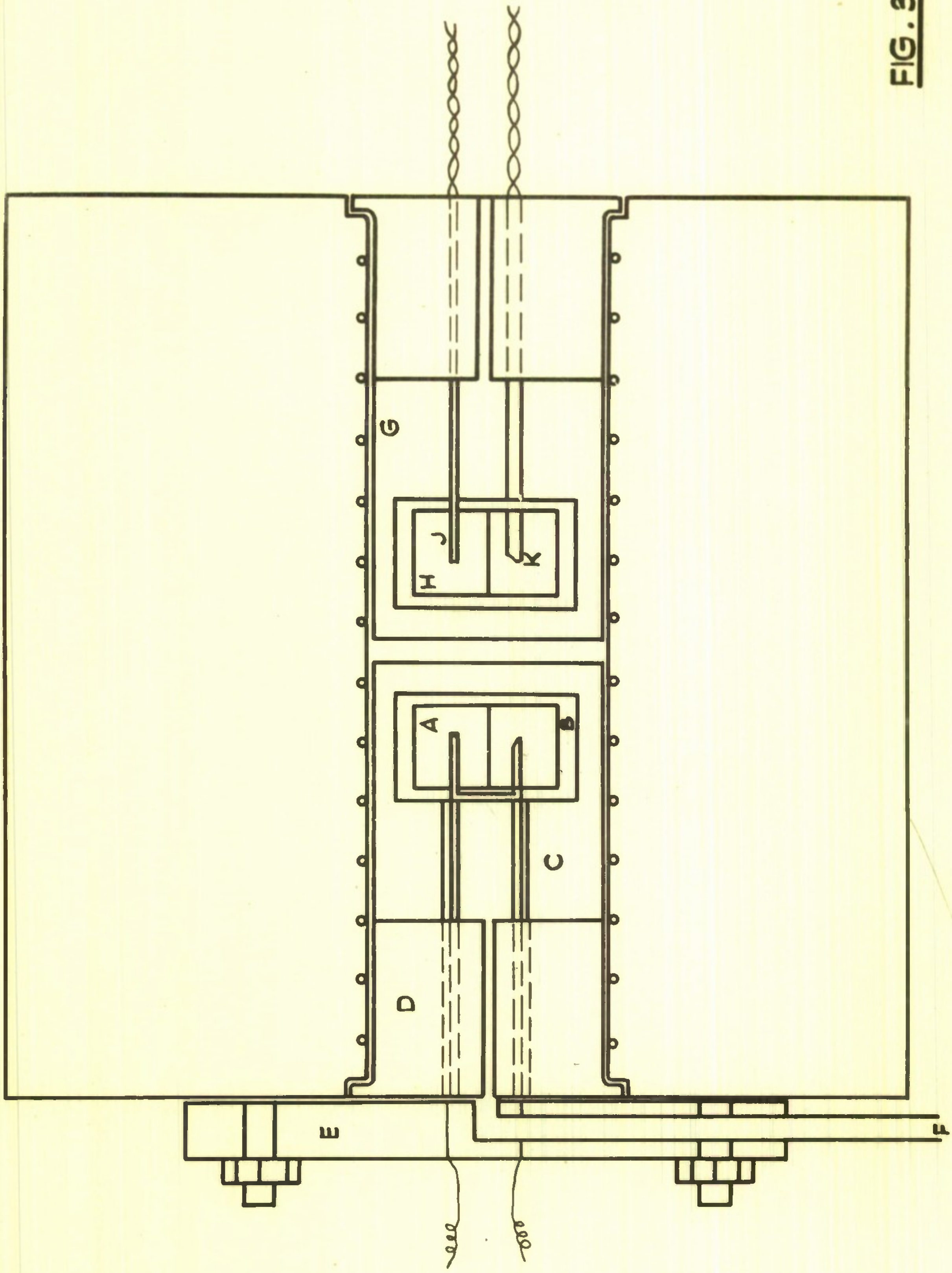


FIG. 2.

FIG. 3.



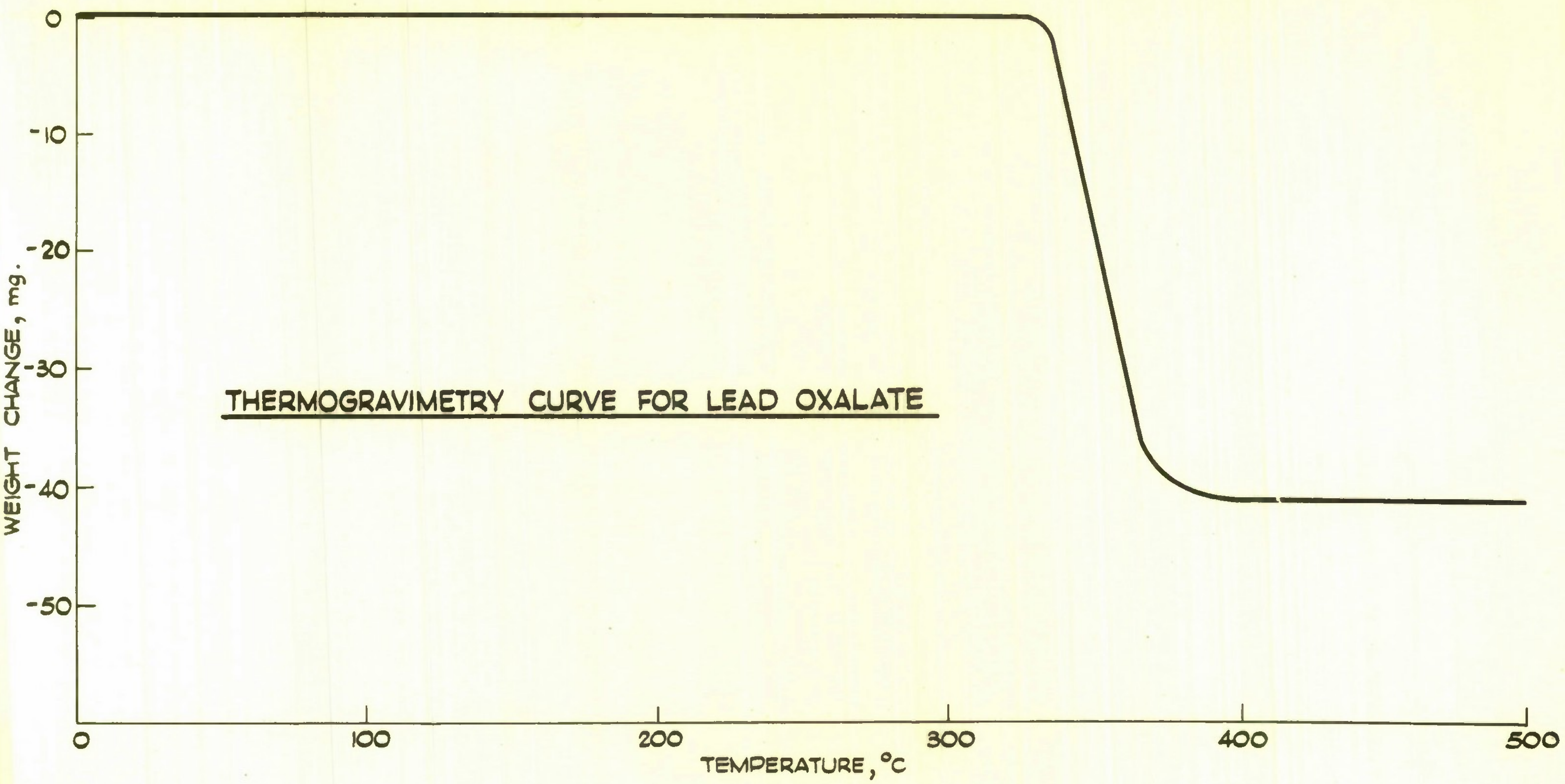

THERMOGRAVIMETRY CURVE FOR LEAD OXALATE

FIG. 4.

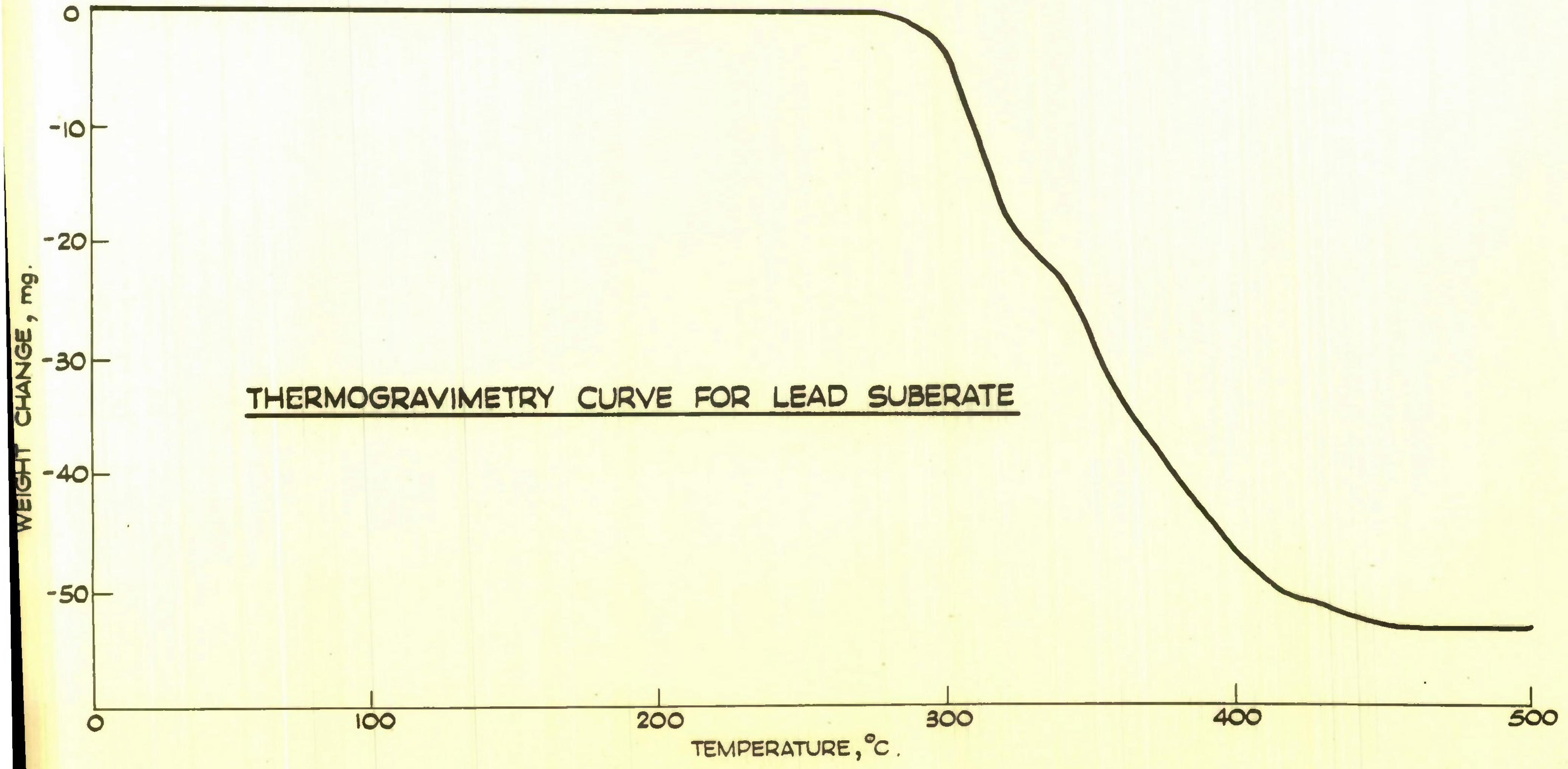
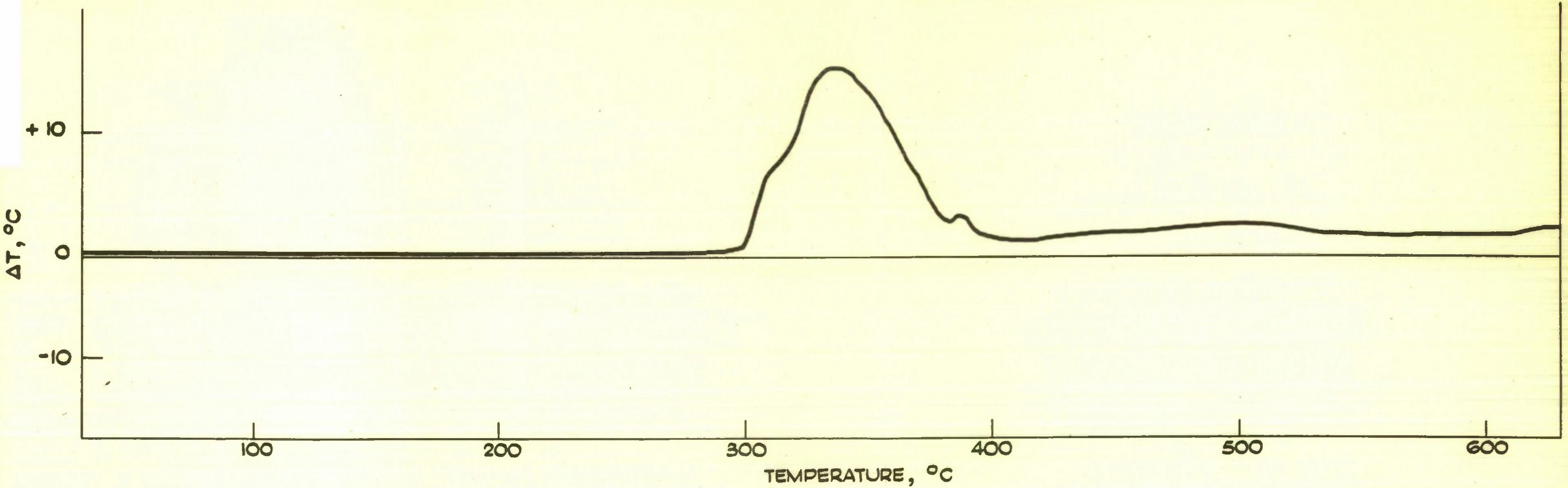
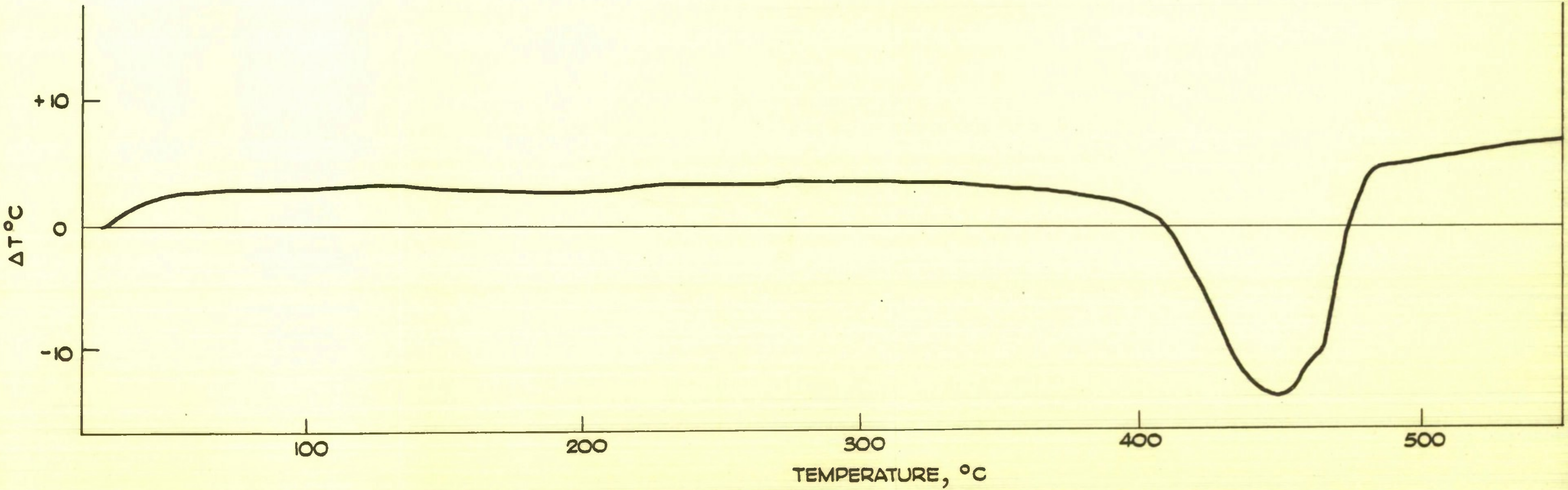

THERMOGRAVIMETRY CURVE FOR LEAD SUBERATE

FIG. 5.



D.T.A. OF LEAD OXALATE IN AIR.

FIG. 6.



D.T.A. OF LEAD OXALATE IN NITROGEN

FIG. 7.

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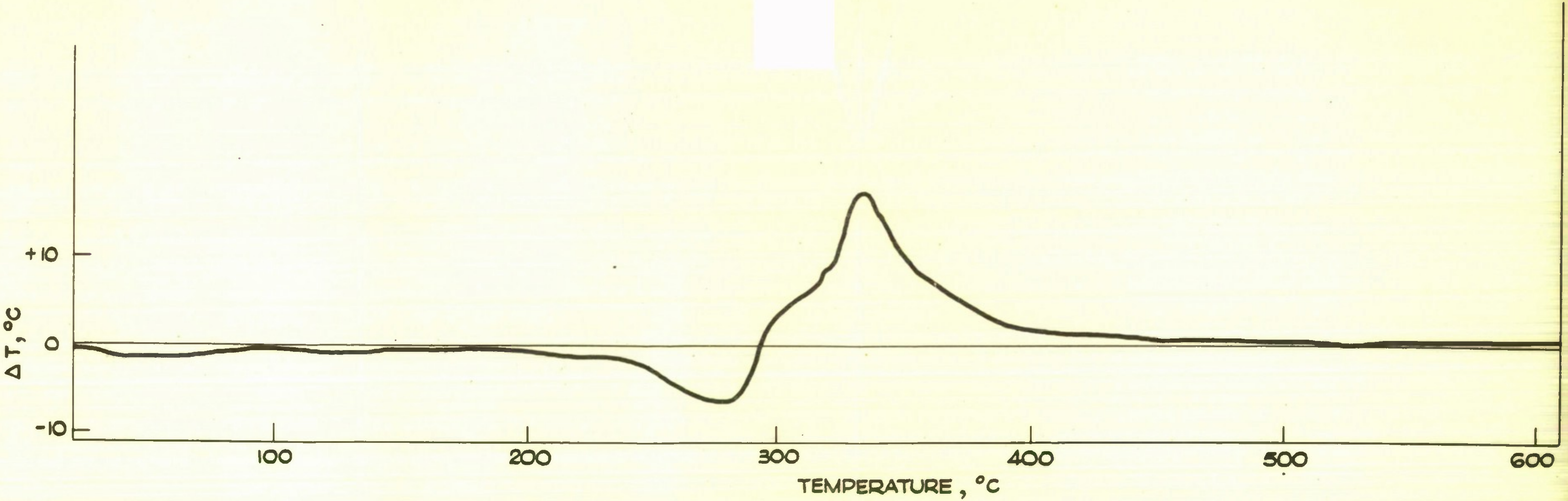
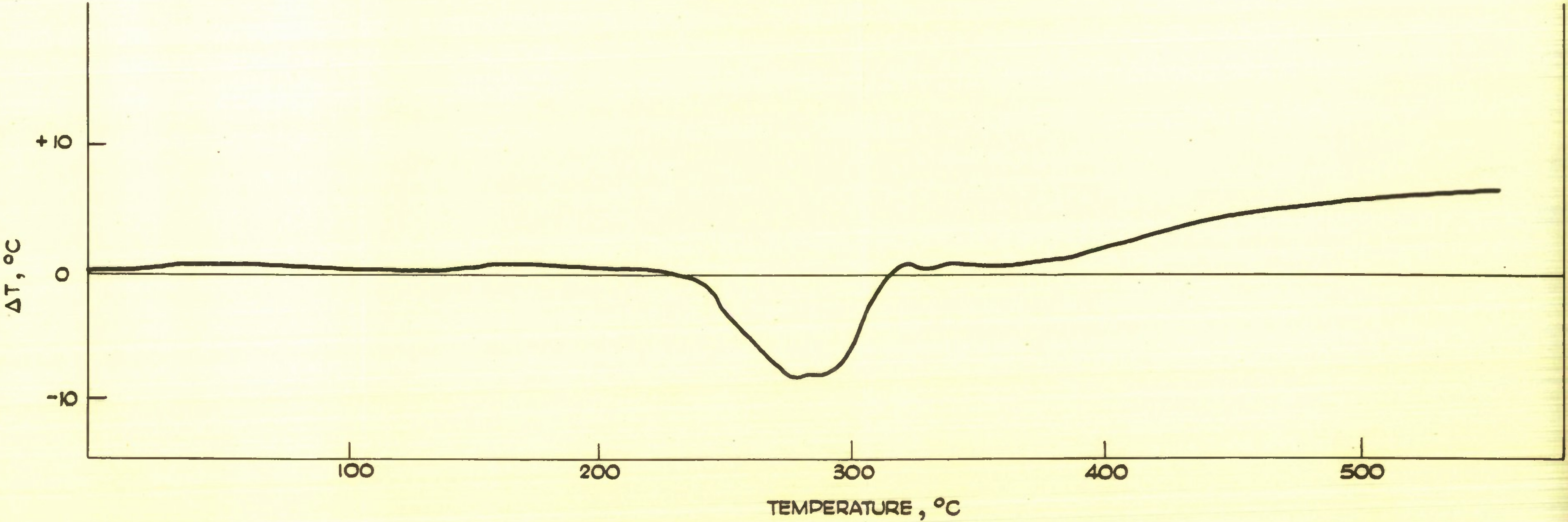


D.T.A. OF LEAD FORMATE IN AIR.

FIG.8.



D.T.A. OF LEAD FORMATE IN NITROGEN. FIG. 9.

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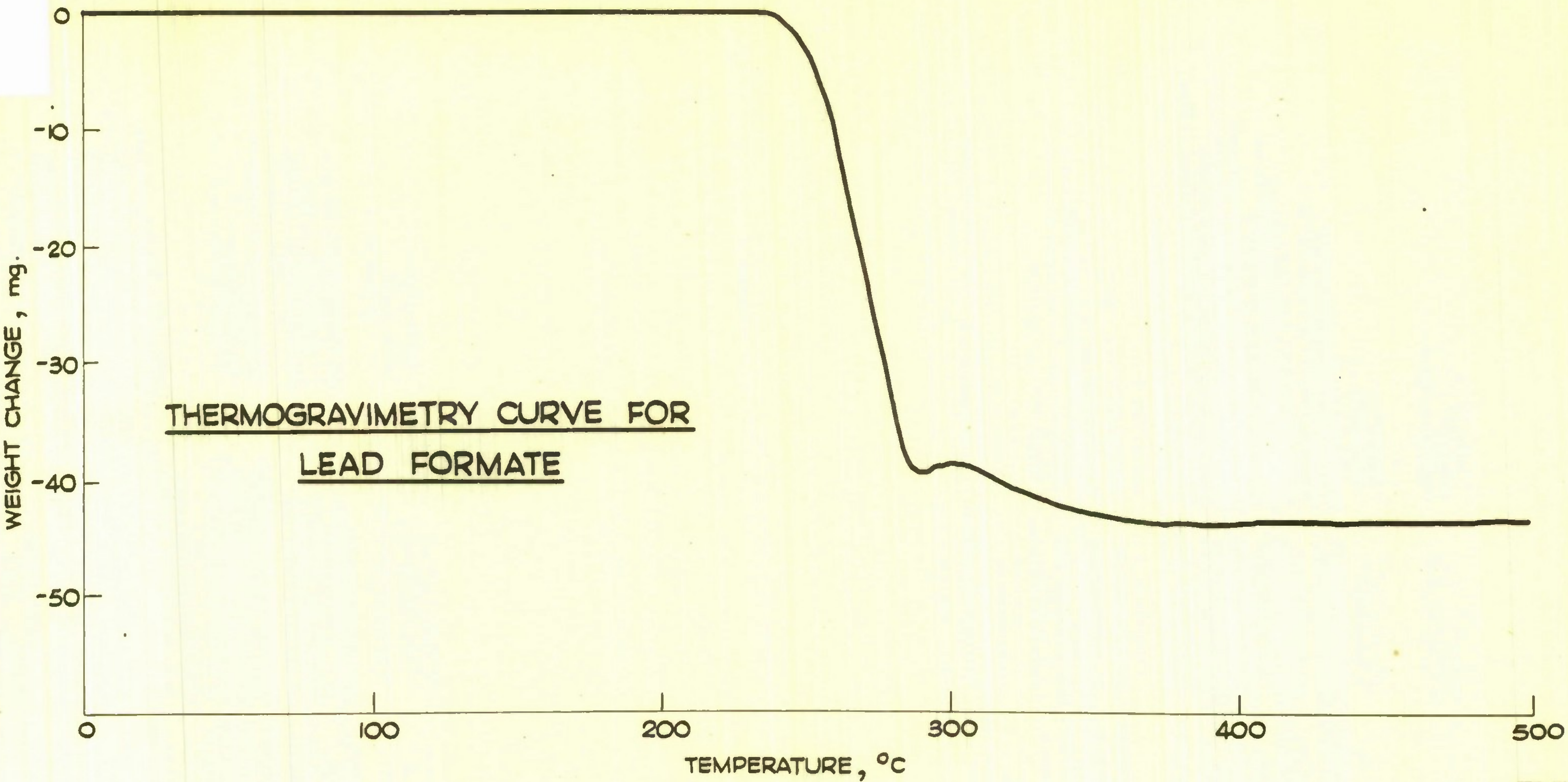
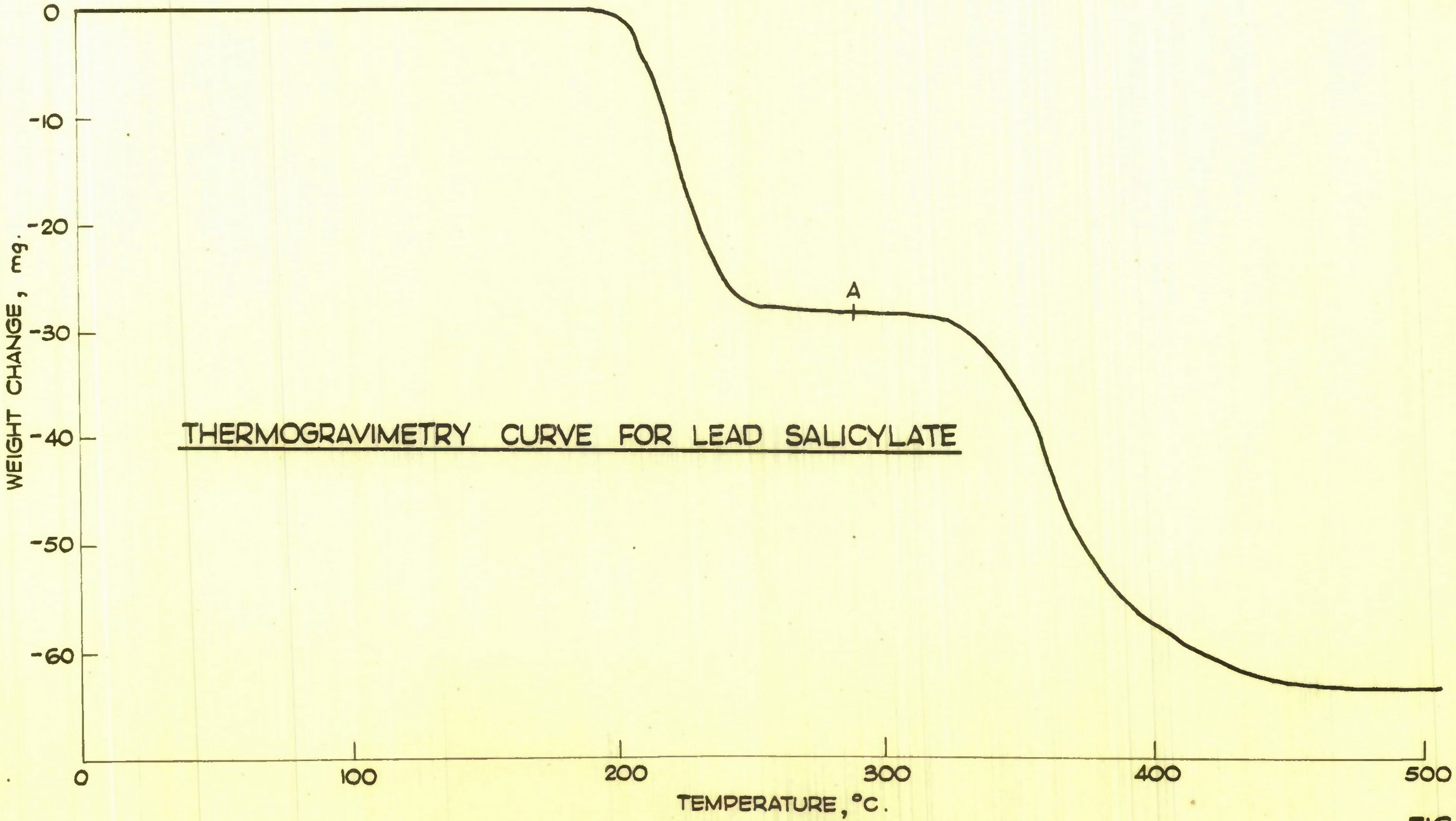


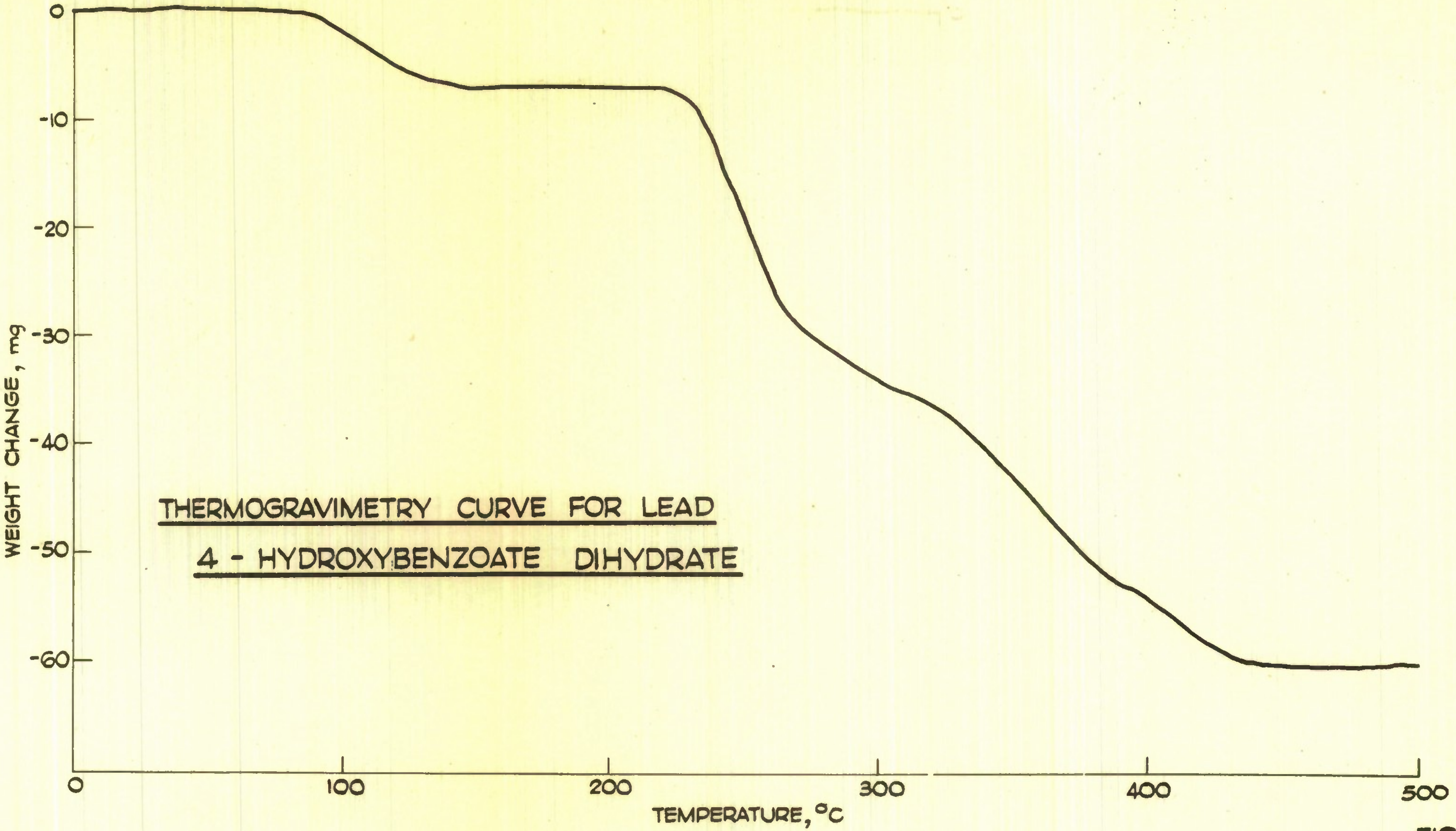
THERMOGRAVIMETRY CURVE FOR LEAD FORMATE

FIG. 10.



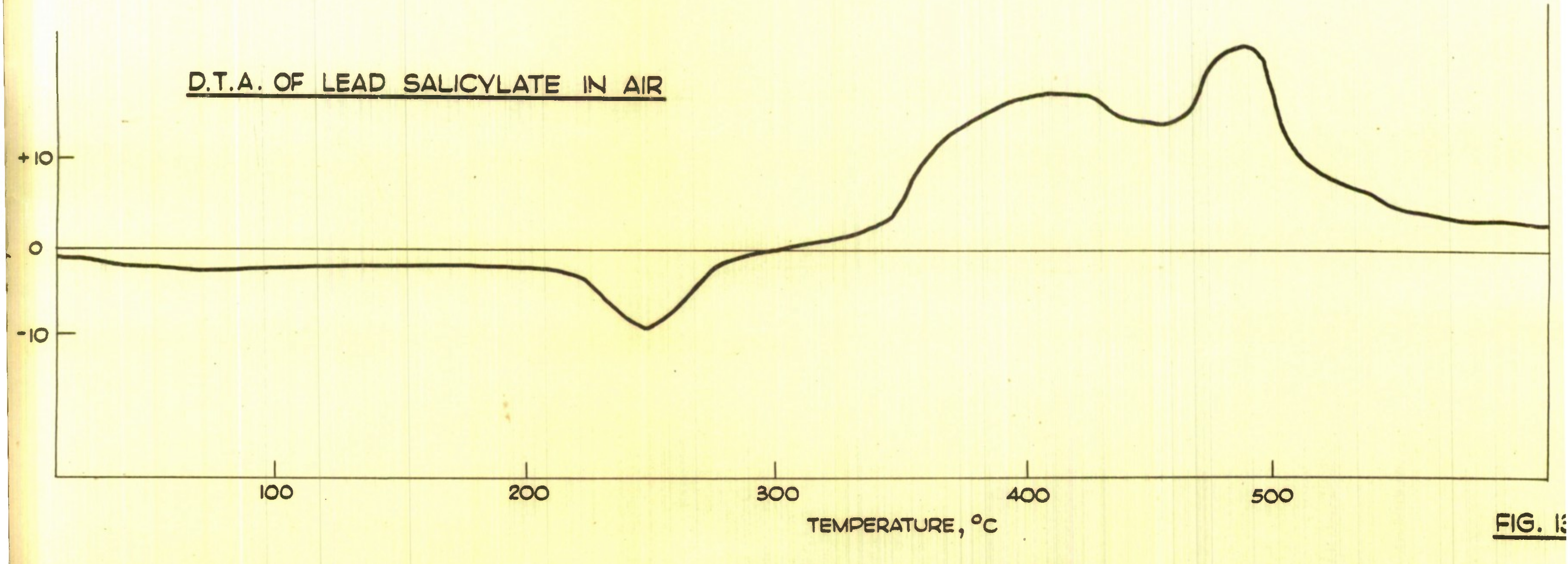
THERMOGRAVIMETRY CURVE FOR LEAD SALICYLATE

FIG. 11.



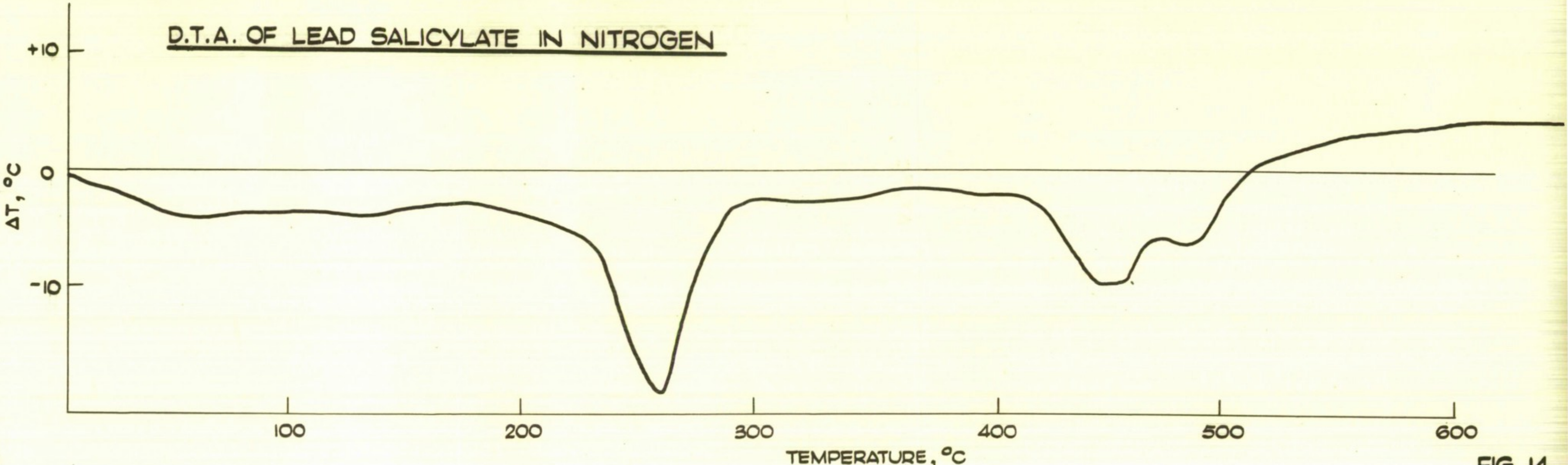
THERMOGRAVIMETRY CURVE FOR LEAD 4 - HYDROXYBENZOATE DIHYDRATE

FIG. 12.



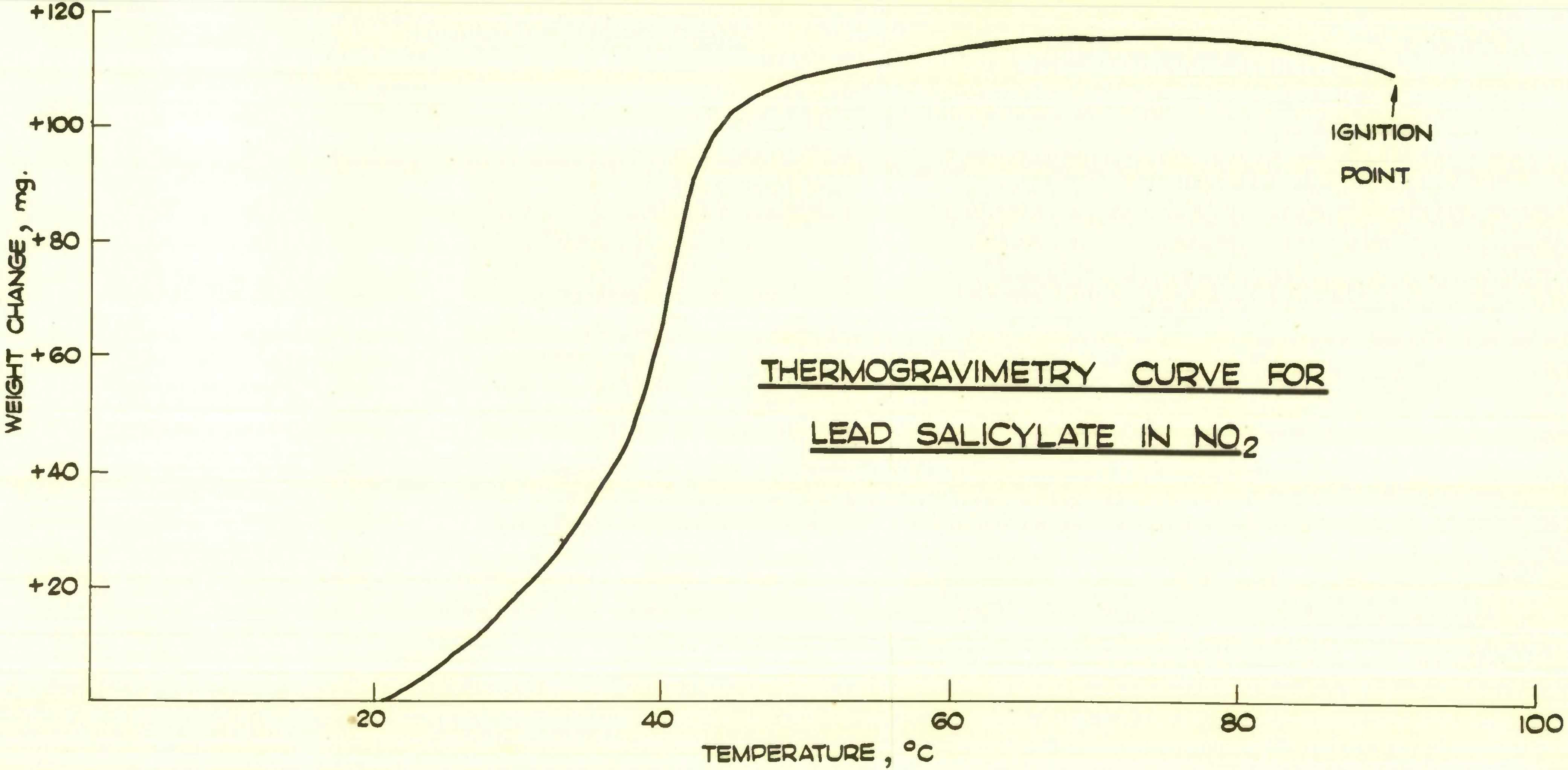
D.T.A. OF LEAD SALICYLATE IN AIR

FIG. 1



D.T.A. OF LEAD SALICYLATE IN NITROGEN

FIG. 14.



THERMOGRAVIMETRY CURVE FOR LEAD SALICYLATE IN NO_2

FIG. 15.

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