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# THE THERMAL DETONATION OF LEAD AZIDE

## a Thesis by

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# Arthur S. Hawkes

### The Thermal Detonation of Lead Azide

The minimum detonation temperature of dextrin and service azide is sharply critical (within  $1^{\circ}C$ .) for a given batch, and may be raised by compression, wetting with butyl phthalate, or increasing the surface/volume ratio of the charge container. Large single crystals of lead azide have a lower minimum detonation temperature than have smaller crystals. These facts indicate that self-heating is a factor in the detonation of lead azide, the rate and amount of self-heat being influenced by the inter-particle thermal conductivity of the charge sample.

The induction periods preceding detonation at a given temperature are reproducible within experimental error, precluding the possibility that thermal detonation of lead azide is caused by the collision of material or energy chains, which would produce a more random distribution of induction period data.

The activation energy of the detonation of sensitized service azide is slightly larger than the activation energy of the pre-heating reaction, hence the sensitization effect of pre-heating cannot be due to the formation of a catalyst. The sensitization effect is permanent, but can be nullified by wetting of the sample with phthalate, indicating that pre-heating may merely cause a surface change which decreases the inter-particle thermal conductivity. THE THERMAL DETONATION OF LEAD AZIDE.

Knowledge of reactions in solids has lagged far behind that of gases and liquids, because of the difficulties involved, and only in comparatively recent years have extended attempts been made to remedy this deficiency. Consequently, explosions or detonations of solid compounds have been the subject of comparatively little work, and even in the past five years, which have shown the necessity for more exact information in this field, the amount made available on the kinetics and mechanism of detonation is quite limited.

The search for, and development of new explosives, under the stimulus of war, make fundamental studies of the initiation of detonation highly desirable, since an adequate background of experimental fact should facilitate interpretation of the behaviour of explosives and their practical development. Practical development is still in the empirical stage, while theoretical treatments have been based upon a minimum of findamental experimental work, and that of a type flexible enough to accommodate almost any newly proposed mechanism. Obviously, the deficiency that exists can only be remedied

in the laboratory, where, however, slow progress may be anticipated in view of the meagre information available and the ever present difficulty of investigating reactions in the solid state.

### HISTORICAL INTRODUCTION

It was natural that early attempts should be made to relate detonation in solids to detonation in gases, which had already been the subject of considerable investigation. Chapman (1), in 1899, developed mathematical equations which made possible the calculation of detonation velocities of compounds for which the thermodynamics and physical data were available. These calculations made no attempt to give, nor did they require, any information about the mechanism of propagation of a detonation, nor about the kinetics of the reactions involved. The equations gave reasonable results, limited by the accuracy of the known equations of state for the high pressure and temperatures involved in the detonation reaction.

Similar equations were developed independently by Jouguet (2, 3) in 1905, based on Hugoniot's (4, 5) theory of shock waves, and more recently improved by other workers, including von Neumman. (6)

Such work has little importance for the purely chemical aspects of detonation, although it may be used in the empirical development of explosive mixtures of improved detonation velocity, which, if all other factors are equal, gives a measure of the brisance (i.e. "shattering power") of the explosive. Provided the reaction zone is small compared with the diameter of the explosive charge, the reaction velocity of the explosive does not influence its detonation velocity. (7) Where true detonation is involved, and not rapid combustion, the detonation rate depends upon the chemical composition, geometry, density, mechanical confinement and physical properties of the explosive. For burning mixtures, such as cordite, the slow rate is determined primarily by the reaction rate rather than the physical properties.

Detonation velocities can now be measured with an accuracy that is remarkable (better than 1%), considering that they range between 2,000 and 10,000 metres per second. The modern method involves the use of a high speed rotating drum or rotating mirror cameras, (8, 9, 10, 11) which record the velocity in terms of the slope of a line made on a strip of film exposed by the light of the advancing flash of the detonation itself along a stick of explosive. The detonation velocity of an explosive is the stable velocity which it can itself sustain, and which will be constant if sufficient length of explosive is available for the stable value to be built up. Lower and higher values can be found, but they are unstable and the detonation may die out, or will approach the stable velocity, depending upon whether the shock wave from the initiating explosive produces a wave faster or slower than the minimum critical velocity for the

explosive. This critical velocity will depend upon the sensitivity of the explosive, hence it is almost zero for initiating explosives, or detonators, whereas TNT mixtures require "priming" with fairly high initial velocities.

The mechanism whereby an explosion is initiated and propagated in a solid has been considered by several workers. Berthelot (12) proposed that detonation by a shock wave or impact was due to heating caused by adiabatic compression, raising the reaction rate to explosive velocity. This theory, while not yet repudiated or abandoned, has met with much criticism, and more complex mechanisms have generally been proposed.

Muraour (13) and Semenov (14) proposed an energy chain mechanism to account for the high speed of propagation. A molecule is assumed to decompose, passing its heat of decomposition on to activate the decomposition of a neighbouring molecule, or, in the case of a branching chain, to activate two or more molecules. Muraour assumed that the presence of heavy metals, as in most initiators, favours the formation of energy chains.

Garner (15) considers this possibility for lead azide, assuming the decomposition to take place as follows:

> (a)  $\frac{1}{2}$  Pb<sup>+</sup> + N3<sup>'</sup> =  $\frac{1}{2}$  Pb + N2 + N - 51 Kcal (b)  $\frac{1}{2}$  Pb<sup>+</sup> + N3<sup>'</sup> + N =  $\frac{1}{2}$  Pb + 2N2 + 157 Kcal

The two reactions would occur in one stage, releasing 106 Kcal., which is sufficient heat to activate two or three neighbouring molecules requiring 38 Kcal. per mole. The detonation rate in lead azide is 5300 metres per second, so that the detonation wave traverses each molecular layer in about  $10^{-13}$  seconds. Since the lowest frequency of vibration of the Ngion in lead azide has been shown (16) to be 2 x 10 <sup>13</sup> vibrations per second, the detonation wave travels at about the maximum speed at which thermal vibrations could be transmitted from one ion to another. The energy then must be handed on within about  $10^{-13}$  seconds, or else will be dissipated and lost.

Criticism of this theory has been made (17) on the grounds that with such a rapid transmission of energy, the rate of decomposition should be (a) very rapid, complete decomposition occurring within a fraction of a second, and (b) almost independent of temperature, provided it is high enough to initiate any decomposition. A strong point of argument against the chain mechanism is the fact that the reaction is not affected by the addition of well-known chain breakers (18). It is not denied, however, that short energy chains may be a factor effective immediately preceding detonation arising from comparatively slow decomposition. Eyring (19), in his

recent theoretical treatments, has shown that detonation

need only be considered from a purely thermal viewpoint, and that chain mechanisms are not necessary for the mathematical development of the accepted relations governing detonation phenomena.

To explain the apparent variability in induction period leading to detonation, Muraour (20) proposed that initiation of detonation requires the simultaneous decomposition, in the same region, of a large number of Garner and Gomm (21) suggested that four molemolecules. cules are required in lead azide to form the so-called "reaction centre". This estimate was based on their data which showed the activation energy of the detonation reaction of lead azide was 200 Kcal., a value not confirmed in this laboratory, or elsewhere in the literature, Sutton (22) showed by X-ray analysis that the unit cell of the lead azide crystal contains eight groups of three molecules, and suggested that the "reaction centre" might be one of these three-molecule groups. In a later paper. Garner (23) revised his ideas, and showed, on the basis of probability, that more than two molecules could not be involved. At 290°C., in vacuum, the number of lead azide molecules decomposing per second per square centimetre of interface is 1.1 x 10<sup>16</sup>, or about 30 layers of ions decomposing per second. The probability that two molecules will be decomposed in adjacent places on the interface within a time interval of 10<sup>-13</sup> seconds, is

about  $4 \ge 10^{-9}$ , and that for a "ternary" decomposition is  $1.5 \ge 10^{-20}$ . The chance of a "binary event" is thus  $4 \ge 10^4$  times per second, and that of a "ternary event" is one in  $10^7$  seconds. Since, at this temperature, in vacuum, detonation occurs in 20 seconds, a binary decomposition could be the cause of detonation, but a ternary decomposition is too rare to be an effective cause.

The suggestion has also been made by Garner that detonation may occur when two chains intersect, thus producing a binary event. Robertson, Sinclair and Rideal(24) used the probability of a binary event to explain the erratic results obtained with potassium picrate. They placed single picrate crystals on a hot wire, and measured the rate of reaction during the induction period by calculating the rate of diminution of the molten globule. From this rate the probability of a binary event or a collision of energy chains could be calculated. However, this theory, as do the related theories, depends upon the experimental variability in induction period, and in this light merits further comment in the conclusions of this thesis.

Carl (25) proposes what he calls the "breaking theory" of initiation, and while he admits that it is open to criticism, suggests that it may indicate the way to further experimentation. He opposes Berthelot's view that detonation is a heat-induced reaction, with a relation between

sensitivity and rate, and claims the rate is largely due to physical properties, such as density and elasticity. and that the violence of the detonation is alone characteristic of the chemical properties of the explosive. A violent pressure wave will cause rupture of the valance bonds, and reaction ensues at these active faces. Small amounts of impurities as coatings on the crystals, render them more sensitive, which he suggests is due to their increased strength as a result of minimizing surface imperfections, and, in some cases, increased plasticity. The breaking wave would be sustained by release of gases and heat, and its passage through the explosive will be influenced by the elasticity of the medium. The optimum condition would occur in a perfectly elastic material which requires only a slight distortion to break its bonds. He argues further that endothermic compounds have, in addition to surface unsaturation, inherent internal weaknesses of the "strain" type. Thus he explains the reputed extreme sensitivity of large lead azide crystals, although Miles (26) prepared lead azide crystals two and three centimetres long, and crushed them with a spatula without ensuing detonation.

An excellent paper by Taylor and Weale (27), with later theoretic development, (28) describes remarkably accurate work with an impact machine fitted with a temperature-controlled anvil, and evolves the "tribo-chemical"

theory of detonation. Their work deals with the phenomenon of detonation of solid explosives by a study of the dynamics of the initiation of thin layers of explosives by impulsive forces. Statistical methods were used to analyse the results, and they were able to show the effect of temperature on impact sensitivity. They combine the temperature and the critical rate leading to detonation by impact, by the equation:

 $k = Ae - \frac{Q}{Rt} + BK$ 

where K is a simple function of the kinetic energy of the blow, and B a constant. They claim that percussive forces (K) alone are sufficient to produce detonation, and regard mass detonation as the passage through the explosive of a narrow reaction zone in which very rapid decomposition is taking place under the action of impulsive forces in the pressure wave, which is itself sustained by the energy of the explosive products. It is suggested that this decomposition is primarily due to the granules of explosive being ground together, with consequent tribo-chemical action. That is, the granules are sheared tangentially under the high normal pressures, and the rapid making and breaking of cohesional linkages, between the molecules in the shearing planes results directly in the production of high local concentration of activated molecules, providing reaction nuclei for further reaction, as postulated by Garner. Taylor and Weale

express the opinion that detonation in a single crystal must be differentiated entirely from detonation in a bulk explosive. However, it may be suspected that such a distinction is only necessary because the tribo-chemical theory does not include such phenomena.

Garner, in his 1931 paper (21), perfected one means of studying the thermal decomposition and detonation of initiating explosives, or detonators. His apparatus was a modification of that used by Farmer (29) for the study of mercury fulminate decomposition, and consisted of an evacuated glass system in which a small platinum bucket holding a single crystal could be lowered into a furnace. The decomposition was followed by measurement of the gas pressure with a McLeod or Pirani gauge. By the usual method of rate study, he showed that the activation energy for the decomposition of *d*-lead azide was 47.6 Kcal., and for  $\beta$ , 38.8 Kcal. Where the decompositions were studied at a temperature high enough to culminate in detonation, he calculated the "critical increment of detonation", or detonation activation energy, to be 200 Kcal. for lead azide. This he determined from the last part of his curves preceding detonation. This is in disagreement with values of 55 Kcal. for the slow decomposition, and 50 Kcal. for detonation of *L*-lead azide obtained by Andreev(30) and is not confirmed elsewhere in the literature.

Garner noted that the azide crystals blackened on their surface during the decomposition, apparently as a result of a deposit of free lead. These deposits occurred irregularly, being first concentrated along the crystal edges, and on splitting a crystal after its surface was completely darkened, he found that the interior remained white. Using as analogous reactions the dehydration of solid crystal hydrates, Garner argued that these deposits were the centres of reaction, and that further reaction could only occur at the interface, especially the interface between the lead deposit and lead azide. He postulated a branching mechanism from these nuclei, although he is not quite clear as to whether it is an energy or material chain that is involved. The probability of two chains meeting in this two-dimensional system, he claimed (22), is of the same order as that of two adjacent molecules decomposing simultaneously. so it is an event which might be responsible for detonation of lead azide.

In all investigations of the decomposition of lead azide, it is reported that the reaction seems to consist of distinct kinetic steps. At first, decomposition is slow, then abruptly increases, leading to a third and last stage (a first order reaction) which may or may not lead to detonation, depending upon the temperature. At high temperature, this last stage is almost non-detectable,

the second stage leading directly to detonation. It is a point of difference whether the second stage is caused by autocatalysis of some kind, or whether, as Garner maintains, the first stage is required to build up the reaction nuclei of deposited lead, and the second stage begins when the crystal surface has been completely covered, and the reaction begins to "drive" toward the interior of the crystal.

A similar phenomenon is evident with mercury fulminate. Farmer (29) by measuring CO2 liberation from fulminate in vacuo at 80°C., found a quiescent period of slow decomposition lasting 80 hours, followed by a rapid acceleration to constant evolution. If the sample were quenched after reaching the stage of rapid evolution, reheating showed that the pressure-time curve began again just where it had left off, showing no quiescent period. Washing the preheated samples with warm water or acetone partially restored the sample to its original condition. Garner and Hailes (31) believe that this effect of washing was due to the removal of the more active CNO ions from the reaction interface, and hence claimed that "the experiments cannot be adduced in favour of the autocatalysis theory." They assume that the reaction spreads along the "Smekal cracks" between the crystallites, with a branching chain mechanism.

Farmer assumed that an autocatalyst was formed in

the initial stages, but found that the preheated samples were not affected by addition of mercury, or mercuric or mercurous compounds, fresh fulminate (hence no inhibitor originally present there),  $CO_2$ , or air pressure, but was slightly retarded by alkalis and slightly accelerated by strong acids and organic bases. The induction period of quiescence was found to be shortened by exposure of samples to sunlight.

Other workers (32) have obtained similar results by detonating fulminate in glass tubes set into holes in a heated steel block, obtaining induction periods of 13 minutes at 140°C. to 4 hours at 116°C., corresponding to an activation energy of 37.8 Kcal. By inserting a thermocouple into the explosive sample, they measured the rise in temperature owing to self-heating. and found it to be as high as 33° C. above the bath temperature immediately preceding detonation. Preheating of the samples eliminated the initial period where no selfheating occurred. Dilution with Sb2S3 and KCl03 increased the induction period, owing to dissipation of self-heat, whence they suggested that dissipation of heat between the crystals is an important factor. Of special interest is their observation that the ratio of the induction periods for heating in H2 and He was 1:1.13. whereas the ratio of the thermal conductivities of these gases is 1:1.14, a relation which seems almost fortuitous. Andreev(30) similarly reports a "spontaneous heating" of lead azide with the progress of decomposition.

The influence of self-heating on the thermal initiation of detonation has been discussed in some detail by Robertson (33). Using admittedly scanty data, and some broad assumptions, he calculated a maximum selfheating effect of about 10°C. for a 7 mg.sample of lead azide, and suggested that "further light would be thrown on the initiation of detonation in lead azide by a determination of the thermal conductivity and of the reaction rate during the induction period", and that "if the selfheating effect is playing a part, dilution of lead azide with substances of different thermal conductivity should show a relation between increased thermal conductivity of the foreign substance and increased induction period and percentage of failures". The work of Phillips, Vaughan and Birks (32) with fulminate in the presence of H2 and He bears out this prediction. It is possible that Russian workers (34) too, have investigated this possibility, for they report studies on the thermal conductivity of explosives, in some cases before and after treatment with so-called phlegmatizers.

The decomposition of sodium and potassium azides is reported by Garner and Marke (35) who showed that if the reaction be carried out in a potassium-saturated atmosphere, the induction period for KN3 decomposition is considerably

shortened. The effect of Na vapour on NaNz is not so marked. They suggested that the inertness of these azides is probably related to the volatalization of the metallic products, this process absorbing energy and removing a metal-salt reaction interface.

Marke (36) also reported data for the decomposition of calcium azide, while Harvey (37) showed that BaN<sub>6</sub> decomposes similarly, blackening of crystals being observed, owing to the deposition of barium. He could deduce no relation between the rate of their formation and the rate of reaction as measured by nitrogen evolution, and proposed a branching mechanism "of a spatial character", similar to that proposed by Garner and Hailes for fulminate. He pointed out, however, that definite nuclei are formed, whereas a spatial branching would produce "clouds" of barium deposit throughout the crystal, such as fulminate exhibits.

Audrieth (38) points out that for some azides, once slow decomposition has been initiated, it can be made to continue at a lower temperature (39, 40) and suggests that the reaction may be catalyzed by liberated metal; for example

2 Ba  $(N_3)_2 \rightarrow Ba \equiv Ba_3 N_2 \rightarrow 5N_2$ 

Ubbelohde (41) in 1941, began work on detonation, particularly of azides. His procedure consisted of thrusting small detonator samples contained in blasting caps, into a hot molten bath, and measuring the induction period leading to detonation at a given temperature. He found that for service azide, the induction period, t, and the absolute temperature T, could be expressed by the familiar Arrhenius type of relation:-

In t =  $\frac{E}{RT}$  + B where E is the activation energy, and B a constant, depending upon the container, packing density, etc. His data gave very scattered points, and the periods he measured were all short (less than 10 seconds), but by use of least squares he obtained a straight line relation on plotting log t against the reciprocal absolute temperature. The value of E was shown to be 41.3 Kcal. for service and 23.4 Kcal. for dextrin azide. The time lag was found to increase on dilution of the service azide with powdered glass. A similar apparatus has recently been used at Bruceton (42), with an automatic electrical timing device for the measurement of extremely short induction periods. The value of E obtained for lead azide (apparently service azide) was 21.2 Kcal.

Ubbelohde found that samples of service azide which had been preheated, and quenched by chilling before the detonation occurred required a shorter period to produce detonation on a second heating. Such preheated samples were said to be sensitized. A similar sensitization could be produced by exposure of the service azide samples to sunlight, although dextrin azide could not be sensitized either thermally or photochemically. Such a sensitization is paralleled by experiments with the impact machine by other workers (e.g. Legge and Morrison (43)) where it has been shown that a charge that has suffered impact without detonation may often be caused to detonate subsequently by a blow lighter than the first.

Service and dextrin azides differ considerably in their thermal properties, dextrin azide being capable of detonation at a temperature (ca 275°C) as much as 40°C. lower than service azide, and never shows induction periods longer than 12-14 seconds, while service azide may exhibit induction periods of over a minute.At higher temperatures, the time lags of the respective types become more nearly equal.

The differences in thermal behaviour between service and dextrin azides is rendered more remarkable by the evidence of X-ray investigations of their respective structures as given in the Ubbelohde report (41). They are shown to be crystallographically identical, the service azide particles being generally whole crystals, but including some twins, whereas the dextrin azide particles are agglomerates, made up of probably 10<sup>6</sup> crystallites per grain.

Ubbelohde applies this information to account for their different apparent activation energies on the basis

of the much larger internal surface area presented by the dextrin azide crystallites. Assuming the reaction centres to be on the surface, dextrin azide should be capable of setting up a greater number of such centres, which, according to the Garner theory, should culminate in detonation of dextrin azide in a shorter time and at lower temperatures than would be the case with service azide with its smaller surface/weight ratio.

Ubbelohde expressed the opinion that detonation resulting from friction and impact must arise from a different mechanism than that involved in thermal detonation, for service azide is shown to be much more sensitive to friction and grit than is dextrin azide, and displays about the same sensitivity to impact, despite the fact that dextrin azide is much more sensitive to heat. This conforms with the data of other workers, and it is generally believed that an additional factor of particle hardness may be involved, (44) in addition to other factors not yet considered.

In seeking an answer to the question of how detonation is initiated and maintained in detonation type compounds, alternative methods of initiation are possible: by impact, by friction, by heat, etc. Since detonation must be regarded fundamentally as a chemical reaction, though one of exceptionally high rate, and as such must involve activation of the molecules concerned, it seemed logical in the present study to bring about the necessary activation by thermal means, and thus avoid the complications involved in interpreting the action of other methods of initiation.

The method of Ubbelohde appeared to be adaptable to the purpose in view. Furthermore, lead azide presented itself as an excellent material to investigate, primarily because of its two commercial forms, the so-called "service" and "dextrin" azides, differing in detonation properties despite their identical chemical and crystallographic properties.

E. Detail of crystal boat and holder.

D. Detail of single-crystal heating furnace.

C. Detail of objective lens and cooler.

B. Detail of charge container and holder.

A. Bulk detonation heating bath.

# APPARATUS

# FIGURE I



20a

#### APPARATUS

### A. BULK DETONATION:

For detonation experiments on bulk samples the large heating bath shown in Fig. 1A was used. It consisted of a mild steel cylinder 3 inches in diameter and 6 inches long, with a 0.75 inch diameter hole drilled to a depth of 4.5 inches. The block was first wrapped with a thin sheet of absestos paper, over which was wound Nichrome wire to provide a 500 watt heating element. The block with its wiring was then well lagged with layers of asbestos paper to a thickness of about one inch. The lagged block was placed in a shallow container partly filled with ground asbestos, which served as a thermal insulator for the bottom. The top remained uncovered.

Tin was used as the thermostat liquid, since its melting point (232°C) was well below any temperatures used, and its low vapour pressure and resistance to oxidation made it convenient. Oxide slag was easily removed from its surface, where it collected as a solid pulp.

Temperature was maintained manually by a series of rheostats. For rapid temperature adjustments, current was shorted directly through the heating circuit around the block, and shunted through the outside resistances for finer adjustments as the desired temperature was approached. An ammeter was wired in series with the heating element so that corrections for line voltage fluctuations could be made in the course of an experiment.

Temperature was measured with a chromelealunel thermocouple, the electromotive force of which was determined with a portable Cambridge potentiometer, accurate to better than 0.01 millivolts (corresponding to 0.25°C). The hot junction of the thermogouple was placed in a sheath of 5 mm. pyrex tubing, about 5 inches long, which was packed with finely ground pyrex after the junction had been inserted, thus ensuring fairly rapid thermal equilibrium between the thermostat liquid and the couple junction itself. The couple was calibrated by determining its thermoelectric power at o°C., 232°C. (m.p. of tin) and 327°C. (m.p. of lead).

Twenty milligram samples of azide were generally used. These were weighed on to a piece of glazed paper, and then brushed lightly into the detonation tubes, which were No. 8 aluminium blasting caps. The bottoms of these tubes were rounded on a steel jig, to ensure uniform distribution of the charge from sample to sample. A small hole was drilled through each cap about a centimetre from the top to permit the cap to be wired to a holder as shown in Fig. 1B.

Where glass tubes were required, they were made by drawing out 6 mm. pyrex tubing to a capillary of the required bore. These capillaries were then fused to close one end, and the weighed charge introduced. The glass

tube was then fitted into a detonation cap whose bottom half had been cut off. The remainder of the cap was stuffed with cotton batting, and the capillary wedged into its lower (now open) end. The cap, with its appended capillary, was then fixed to the cap holder in the usual manner.

A steel screen with a safety glass window was placed between the heating block and the operator, to give protection against spattering by molten tin thrown out of the well by the detonating charge. The cap holder was attached to an inverted-U-shaped steel rod, which fitted into a guide on the operator's side of the screen, enabling the charge to be lowered vertically into the thermostat, while the operator remained in front of the screen. The metal control arm was counterbalanced to make the operation smoother.

The general technique was as follows: The sample was fitted to the capholder, and the control arm adjusted in its guides. When the temperature of the tin had reached a steady value at the desired level, the hot junction of the thermocouple was removed from the thermostat, and, by means of the control arm, the charge container was thrust into the thermostat fluid. The level of the fluid was kept adjusted so that when the capholder was firmly seated over the mouth of the well, the charge container was immersed in the fluid to a depth of about one inch. A stop watch was started at the instant the charge was thrust into the thermostat, and stopped at the sound of detonation.

Where samples were to be preheated for a time less than their induction period, the control arm was raised quickly after the required time, swung to one side, and immediately lowered again to bring the charge container down into an ice-water bath beside the thermostat. After some practice, the manipulation required for such quenching could be performed in about one second, or less. The preheated samples were allowed to chill for two minutes before being removed from the cooling bath.

After each detonation, it was necessary to remove the tin which had spattered up the sides and on top of the thermostat block and to readjust the level of the molten tin to a constant depth. The hot junction of the thermocouple was then placed in the bath, and the above procedure repeated.

B. SINGLE CRYSTAL DETONATION:

To study the behaviour of single large crystals of lead azide, the apparatus shown in Fig. 1,C,D, & E was designed. Here the heating bath, or furnace (K) as shown in Fig. 1D, was made from a short length of heavy capillary tubing (pyrex) with a 2 mm. bore. A fine hole was blown through one side, as shown, to admit a platinum-platinumrhodium thermocouple junction. The furnace was wound with about a foot of Nichrome wire (resistance of about 1 chm), and then lagged with layers of asbestos sheeting to give an insulating layer about 2 cm. thick. The whole furnace unit was then mounted in the hole of a microscope stage (L) and the thermocouple (M) inserted through the asbestos insulation and furnace wall, so that its tip was just in line with the inside walls of the capillary. The glass sheath covering the couple leads was fixed to the stage with waterglass so that it could not shift.

To protect the objective lens of the microscope from the furnace heat, it was necessary to arrange for its cooling, as in Fig. 1C. A microscope slide (N) was wired over the end of the objective, and two short pieces of wire placed between the slide and the lens mount, so that they were parallel, and kept at a constant distance apart (about 1 mm.). A stream of water from a fine jet (O) was played constantly on to the slide, so that there was a moving film of water to carry any heat from the furnace away from the lens, the film being of constant thickness between the objective and its protecting slide. By this means, the microscope objective could be brought up close to the end of the furnace (within 1 or 2 mm.) without suffering any ill effects from overheating.

Fig. E shows the glass boats used to hold the crystals. These were made of 2 mm. pyrex rod, which was cut to length and flattened on a carborundum surface to the semi-cylindrical shape shown. To hold the crystal firmly in position, a thin pyrem thread (P) was fused to one end of the boat, the opposite end being left free. By raising the free end of the thread the crystal could be placed in position on the boat, and held by the glass "clip" being allowed to press down upon it.

The boat carrying a crystal was inserted through the back of the furnace and pushed in until the front end was flush with the front of the furnace. The dimensions of the crystal in the cold furnace was measured with a micrometer scale fitted into the microscope eye-piece. The boat and crystal were then removed, and a current passed through the heating element until the furnace was brought to the required temperature as indicated by the thermocouple. Temperature was manually controlled with rheostats in the heating circuit. The boat was then replaced quickly, a stop watch started at the same time, and the microscope adjusted to focus on the crystal so that its detonation or other action could be watched.

### MATERIALS

Service lead azide was obtained from the Canadian Industries Ltd. The samples were pure white, and showed little twinning, the crystals being generally well formed lead azide. Dextrin azide, obtained from the same source, was a light yellow colour, and of a fluffy nature, the grains appearing under the microscope as agglomerates.

The large crystals of lead azide used in the microscopic studies were made using the method described by Miles (26). About 1.3 g. of service azide was dissolved in 60 c.c. of solution containing 8.5g sodium acetate, at 75°C., the solution filtered hot, and poured into a small heated dewar vessel. On standing overnight, many large crystals were formed. They were filtered off, and dried at room temperature. Many of the crystals were 3-4 mm. long, but were relatively insensitive, not detonating when crushed or broken. Pieces of convenient length for the small furnace boats were cut to size with a razor blade.

### EXPERIMENTAL AND RESULTS.

## PRECISION OF MEASUREMENT:

As observed by other workers, an induction period precedes detonation of lead azide at a given temperature. It is to be noted that this period referred to here differs from the one observed in decomposition experiments such as those made by Garner, and others. In the present studies, it represents the time lag between immersion and detonation of the sample at a given temperature, whereas in the thermal decomposition experiments it represents the duration of the quiescent period, i.e. the period preceding the accelerated decomposition reaction.

The precision with which the induction period could be measured with the large heating bath is shown by the following typical results in Table I, obtained when 20 mg. samples of lead azide were detonated.

For the dextrin azide values, the maximum deviation from the average was 5% at 280°C., and about 8% at 295°C. With service azide the percentage error was even smaller, rarely exceeding 5%.

The error is probably due mainly to cooling (ca  $0.5^{\circ}$ C) of the bath during the induction period, as a result of heat conduction along the control arm. Errors in timing and variations in crystal size between samples would also affect the precision of the measurements.

#### TABLE I

Induction Periods for Lead Azide (20 mg. samples)

Temp.(°C.)			<u>t (s</u>	ec.)	Av.t (sec)		
Dextrin	Azide				-		
	280	10.0 9.5	9.8 9.8	10.4 10.0	10 <b>.0</b> 9 <b>.4</b>	9.7 9.9	9.9
	295	7.6 8.0	7.6 7.8	7.6 7.7	7.4 8.0	7.0 7.0	7.6
Service	Azide						
	320	<b>48.</b> 8	48.6	49.2 48.4	48.8 48.8		48.8
	365	3.8	4.2	3.8	4.0 4	•0	4.0

The manner of distribution of the charge in the bottom of the detonation tube, as well as the actual weight of the sample would also be variable factors. Table II shows how change in weight is reflected in change of induction period.

Comparing the average induction periods at 295°C. for 10 mg and 20 mg. samples of dextrin azide, it can be seen that t changes by 2.2 sec. With service azide there was a sharp decrease (5.7 sec.) in t at 320°C. when the sample weight was increased from 15 to 20 mg., and a considerably smaller decrease (0.5 sec) on increasing the weight from 20 to 25 mg. Hence, with samples below 20 mg., slight inaccuracies in weighing might well produce a considerable variation of the induction period. It was decided to use
samples of 20 mg., however, since the detonation of larger samples is of sufficient violence to cause considerable inconvenience from scattering thermostat liquid.

### TABLE II

Effect of Weight on Induction Period.

Weight (mg.)	Temp.( <sup>o</sup> C.)	t (sec.)	Av.t (sec.)
Dextrin Azide			
10	295	5.4 5.1 5.9 5.4 5.6 5.0 5.4	5.4
20	295	7.6 7.6 7.6 7.4 7 8.0 7.8 7.7 8.0 7	7.0 7.0 7.6
Service Azide			
15	320	57.2 56.2 56.0	56.5
20	320	50.3 50.8 51.3	50.8
25	320	49.8 50.8 50.4	50.3

### Minimum Detonation Temperature

### (a) In No. 8 Blasting Caps:

It was found that a well defined minimum temperature exists, below which detonation of lead azide will not occur, even after prolonged heating, but above which detonation occurs with every trial. This temperature varies a few degrees with different batches tested, as seen from the typical data in Table III, but for a given batch, the minimum detonation temperature was sharply critical within 1°C., or within 0.5°C., if considerable care were taken.

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# TABLE III

Minimum Detonation Temperature of Lead Azide.

Ten	вр.( <sup>о</sup> С.)	Heating	Remarks
Dextrin Azide	(a)	Time (sec.)	
	295	8.6	detonation
	285	10.0	detonation
•	281	10.0	detonation
	275	11.7	detonation
	270	13.6	detonation
	269	60	no detonation
	269	60	no detonation
	268	60	no detonation
Dextrin Azide	(b)		
	<b>27</b> 8	10.2	detonation
	275	11.0	detonation
	273	60	no detonation
	273	12.1	detonation
·	273	12.0	detonation
• •	273	60	no detonation
	272	60	no detonation
	271	60	no detonation

		TABLE III (cont'd)	
Service Azide	(2)		
	315	78.4	detonation
	314	150	no detonation
	314	87.8	detonation
	31.4	96.5	detonation
	313	150	no detonation
	313	150	no detonation
Service Azide	<b>(</b> b)		
	317	78.3	detonation
	316	76.8	detonation
	316	73.8	detonation
	315	120	no detonation
	315	120	no detonation
	315	84.7	detonation
	315.5	82.8	detonation
	315	88.1	detonation
	315	120	no detonation

The dextrin azide batches shown in Table III had a minimum detonation temperature of  $270^{\circ}C$ . and  $273^{\circ}C_{\circ}$ , and the service azide detonated at  $315^{\circ}C - 315.5^{\circ}C$ . respectively. Some dextrin azide batches required a bath temperature of  $276^{\circ}C_{\circ}$ , before detonation occurred.

### (b) In glass capillaries:

To determine whether the surface/volume ratio contributed to variation of the minimum detonation temperature, dextrin azide samples were detonated in glass capillaries of different bores. The results are shown in Table IV. The height of the column of azide in the tubes gives a measure of the surface/volume ratio for each 20 mg. sample, the ratio increasing with the column height.

### TABLE IV

Eft	fect	of Su	rface	/Volume	Rat	io on	
Minimum	Deto	natio	n Tem	peratur	e of	Lead	Azide

Height (mm.)	Temp.(°C.)	Heating	Remarks
Dextrin Azide:		Time (560.)	
1.5	285	10.6	detonation
2.0	283	10.8	detonation
2.2	280	45	no detonation
2.5	282	10.8	detonation
2.5	281	30	no detonation
2.6	282	10.4	detonation
2.6	282	10.4	detonation
2.7	281	10.9	detonation
2.8	280	30	no detonation
3.0	281	30	no detonation
3.5	283	30	no detonation
18.0	305	30	no detonation
27.0	310	2.0	detonation
27.5	305	30	no detonation
27.5	317	1.5	detonation
28.0	310	60	no detonation

The minimum detonation temperature was about 281°C. for a column height of 2.5 mm., and between 310° and 317°C. for a height of 27-28 mm.; the minimum detonation temperature in No. 8 blasting caps for this batch was 272°C. Similarly, service azide showed a minimum detonation temperature of 323°C. for a column height of 10.0 mm., as compared with 314°C. in a No. 8 blasting cap.

It is evident that the minimum detonation temperature is markedly influenced by the surface/volume ratio, a higher temperature being required as the ratio is increased, despite the fact that the rapidity with which the azide is heated would be improved in the capillaries.

It can be assumed that on heating lead azide, an exothermic decomposition occurs, liberating, according to Garner (15), 106 Kcal. per mole. If this heat is not immediately dissipated, the temperature of the lead azide sample will increase, with a consequent increase in the reaction rate. Since the rate of loss of heat varies directly with the temperature gradient, while the rate of the reaction increases logarithmically with the temperature, reaction could readily develop an explosive rate under favourable conditions. The minimum detonation temperature, on this view, is that temperature which will enable the reaction to accelerate itself by self-heating. When the reaction is initiated by heating lead azide below this critical temperature, it is never able to produce heat rapidly enough to

overcome the rate of loss of heat from the decomposing sample to the bath, and the decomposition would proceed non-violently.

If the heat produced by the pre-detonation decomposition of lead azide can be dissipated more readily, as it would be as the capillary bore is decreased, a higher bath temperature should be required to produce an internal temperature sufficiently high to cause the reaction to attain explosive velocity. The conductivity of shearample, then, particularly the inter-crystal conductivity, would seem to be a major factor governing the thermal sensitivity of lead azide. It seems reasonable to assume that the essential difference between service and dextrin azides is their relative inter-crystal conductivity, that of service azide being the larger, probably as a result of better packing of its more uniform particles, and possibly because of an insulating effect of the dextrin between the crystallites of the dextrinated material. Ascribing the difference in behaviour to physical rather than chemical differences would be in accord with the fact that the two forms are crystallographically identical.

(c) Compression Treatment:

On the basis of the above argument, improved thermal contact between the particles should increase the minimum detonation temperature. An effort was made to bring about such an improvement by compression, in an attempt to

approximate the glassy product, or "ice", that Legge and Morrison (43) observed with unexploded detonator charges after impact. By applying pressure to the lead azide in (20 mg.) contained aluminium tubes, a packed mass was obtained, the service azide packing more firmly than the dextrin. As seen in Tables V and VI, both types showed an appreciable elevation of the minimum detonation temperature as a result of the treatment.

#### TABLE V

Effect of "Packing" on the Minimum Detonation Temperature of Dextrin Azide Min. Det. Temp. (untreated) = 275°C.							
	Temp.( <sup>o</sup> C.)	Heating Time (sec.)	Remarks				
	305	1.0	detonation				
	295	4.7	detonation				
	290	60	no detonation				
	285	60	no detonation				
	280	60	no detonation				

Obviously, the minimum detonation temperature for both service and dextrin azides was increased by the compression treatment, the former by about  $5^{\circ}$ C., the latter by at least  $15^{\circ}$ C.

### TABLE VI

Temp.( <sup>o</sup> C.)	Heating Time (sec.)	Remarks
325	19.3	detonation
322	29.8	detonation
321	47.4	detonation
320	74.2	detonation
320	150	no detonati
319	150	no detonati
315	150	no detonati
<b>31</b> :5	150	no detonati

Effect of "Packing" on the

### (d) Phthalate Treatment:

Further attempts to raise the minimum detonation temperature were made by adding a few drops of dibutyl phthalate to the azide samples (20 mg.). A capillary dropping tube was used to measure the phthalate, about 42.5 mg. being added in every case. Tubes were shaken until the crystals were thoroughly wetted. Results are shown in Tables VII and VIII.

These data show that the minimum detonation temperatures of service and dextrin azides, treated with phthalate, are increased approximately 7° and 40°C. respectively, over the corresponding temperatures for the untreated materials. It is to be noted that the

### TABLE VII

Min	imum Detonati	on Temperature of	Service Azide.
	Temp.( <sup>Ġ</sup> C)	Heating Time (sec.)	Remarks
	325	72.0	Detonation
	322	75.6	11
	321	86.0	1
	320	150	No detonation
	320	150	No detonation
	315	150	No detonation
	310	150	No detonation

# The Effect of Wetting by Phthalate on the

# TABLE VII

The Effect of Wetting by Phthalate on the Minimum Detonation Temperature of Dextrin Azide.

Temp. ( <sup>O</sup> C.)	Heating Time (sec.)	Remarks
320	65.5	Detonation
320	68.8	Detonation
317	86.8	Detonation
313	150	No detonation
310	150	No detonation
	٠	

induction periods are very long for dextrin azide when treated with phthalate.

The results of the compression and phthalate treatments indicate that dextrin azide may be made to resemble service azide insofar as the minimum detonation temperature is concerned. The difference in behaviour may be accounted for by assuming that the thermal conductivity of the bulk service azide is better than that of dextrin azide, and is relatively less improved by such treatments.

### Length of Induction Period

As mentioned earlier, the relation between the induction period and temperature was confirmed by Ubbelohde for lead azide and is expressed by the following relation:  $\frac{E}{RT} + B$ 

From Ubbelohde's data (41), it appears that t may vary from 7 to 13 seconds for service azide at 330°C., and that the minimum detonation temperature is by no means critical, but has a sepread of as much as 20°C. between 0 and 100% detonation of samples tested. Results obtained in the present study show considerably more accuracy, and cover a greater temperature range for induction period data;. These results are shown in Table IX for 20 mg. samples in rounded No. 8 blasting caps.

### TABLE IX

Induction Period for Service and Dextrin Azides.

	Temp. ( <sup>O</sup> C. )		Ind perio	duction d (se	on ec.)		erage (sec.)	,
(a)	Service Azide.							
	320 <sup>0</sup>	48.8	48.6	49.0	48.8		48.8	
· .	325 <sup>0</sup>	30.2	30.4	31.8	30.6	31.2	30.8	
	335 <sup>9</sup>	14.4	14.4	14.5	14.6		14.5	
. •	345 <sup>0</sup>	8.6	8.6	8.7			8.7	
	355 <sup>0</sup>	5.3	5.6	5.7	5.6		5.6	
	365 <sup>0</sup>	3.8	4.2	3.8	4.0		4.0	
	375 <sup>0</sup>	2.6	2.4	2.6			2.6	
						κ.		
(Ъ)	Dextrin Azide		• •		. '			
	277	11.7	11.8	11.4	11.4	11.8	11.6	
	280	10.5	10.7	10.3	9.9	10.1	10.3	
•	285	9.0	8.8	9.0	8.8		8.9	
	305	6.8	6.8	6.4	6.4	6.8	6.6	
	325	<b>5.</b> 0	4.8	5.2	5.5 5.2	5.3 5.6	5.3	
	345	3.4	4.4	3.6	3.9 4.0	3.4 4.1	3.8	
	365	3.1	2.8	3 3.2	2.7	2.6	2.9	

## FIGURE II

Induction period variation with temperature for service and dextrin azide, with and without wetting with phthalate.



40a

# FIGURE ITI

Log t against reciprocal absolute temperature for service and dextrin azide, with and without wetting with phthalate.



A plot of t against T (Fig. II) shows that the temperature coefficient of the induction period is much larger for service azide than for dextrin azide. The curves intersect, with slight extrapolation, at a temperature of 375°C. This is to be compared with a temperature at intersection of 416°C. reported by Ubbelohde from his data.

Plotting log t against  $\overline{\overline{T}}$ , a straight line is obtained ed for dextrin, and a slightly curved line for service azide, (Fig. III) from which values for E may be calculated, the value for service azide being, of course, much higher than for dextrin. The calculated value for the activation energy of detonation of dextrin azide is 10.6 Kcal., but since a straight line is not obtained for service azide, the value of E varies from about 31 Kcal. at the bottom of the curve, to about 65 Kcal. at the top. Such a change in activation energy could not be due to a temperature effect over the small temperature range considered.

If the two azides are essentially the same, the observed difference in the slopes of the two lines can scarcely be due to true differences in activation. To determine whether the difference might be attributed to a difference in intercrystal thermal conductivity, samples were treated with dibutyl phthalate as previously described, and detonated over a range of temperatures, with the results given in Table X.

		Azides	wette	d with	Phtha	late.	
	Temp. (°	C.)	Induc	tion P	eriod	(sec.)	Average
(a)	Service	Azide (	+ Phth	alate)			<u>t (860.)</u>
	335	62.0	58.8	62.2	56.3		<b>59.</b> 8
	345	29.1	31.4	29.5	27.5		29.4
	355	5.8	5.7	5.8	6.4		5.8
	360	2.8	2.9	3.1	2.6		2.85
(Ъ)	Dextrin	Azide (	+ Phth	<u>alate</u> )			
	330	53.8	71.5	63.1	52.4		60.2
	335	32.7	34.0	29.2	28.8	<b>30.</b> 2	31.0
	345	9.2	9.3	8.8	8.6	9.1	9.0
	<b>3</b> 55	3.9	3.8	4.3	4.0 3.6	<b>4.</b> 0 <b>4.</b> 3	4.0
	365	2.0	1.8	<b>2.</b> 0	1.6		1.9

### TABLE X

Induction Periods for Service and Dextrin

Plotting t against T for this series (Fig. II) shows that the curves for the two types of azides are now more nearly similar, while a plot of log t and  $\overline{\overline{T}}$  (Fig. III) indicates nearly linear relations of essentially the same slope for the two forms of azides. The value of E for service azide varies from 87 Kcal. at the top of the curve (low temperature) to 66 Kcal. at the bottom (high temperature); while for dextrin azide, E varies from 97 Kcal. at the top to 60 Kcal. at the bottom. These values, obtained under identical conditions, confirm the essential chemical

identity of service and dextrin azides.

### Sensitization by Pre-Heating

As mentioned previously, Ubbelohde found (41) that the induction period leading to the detonation of service azide may be shortened by pre-heating. Samples were preheated at a given temperature for a fraction of the full induction period at that temperature, and the pre-detonation reaction then quickly quenched by thrusting the container into ice-water for two minutes. The second heating period, resulting in detonation, was shorter than the single induction period required at the same temperature by an amount which depended upon the time and temperature of preheating. The azide may be said to be sensitized.

Service azide is readily capable of sensitization, as shown by the data in Table XI, where  $t_1$  is the duration of the pre-heating period,  $t_2$  the duration of the second heating to produce detonation, T the temperature for both heating periods, and t the time required for detonation by a single heating period at the same temperature.

For all these data,  $t_2$  was less than t, the time for detonation by a single heating, by an amount which depends upon  $t_1$ , and the sum of  $t_1$  and  $t_2$  was always larger than t. Of interest is the fact that samples may be preheated to within one or two seconds of detonation, and yet require a considerable heating period,  $t_2$ , to produce detonation after the sample has been quenched. This fact

			Sens	itiza	tion	of Service	Azio	le	
Т	1	330 <sup>0</sup> 0	с.	t <b>=</b>	20.3	sec.			
		tl	(sec.)		$t_2$	(sec.)	t <sub>1</sub> +	$t_2$	(sec.)
		<u></u>	5			18.3		23.	.3
			5			18.3		23.	.3
			8			16.6		24.	. 6
			8			15.9		23.	9
			10			14.3		24.	3
			10			15.9		23.	9
			10			13.7		23.	7
			15			12.2		27.	2
			15			12.4		27.	4
			18			12.4		30.	4
			18			11.0		29.	0
			19			10.0		29.	0
			19			10.6		29.	6
			20		exp	loded on wi	thdra	awa]	••
'n	i =	<b>3</b> 20	°C. t	= 4	7.0	sec.			
			15			34.8		49.	8
			25			24.8		49.	,8
			30			24.8		54.	8
			35			22.8		57.	8
			<b>4</b> 3			22.2		65.	2
			45		expl	oded on wit	hdraw	val.	

$\mathbf{T}$	A:	BL	Έ	Х	Ι

would suggest that most of the reaction culminating in detonation occurs in a very short time preceding the detonation, and, that at the temperature used here, considerable time is required to reproduce conditions causing detonation.

It seems unlikely that the rate of the pre-detonation reaction is influenced mainly by self-catalysis, since any catalytic products formed during  $t_1$  should be present in sufficient quantity to make  $t_2$  much shorter than it is, unless practically all of the catalyst is produced in the fraction of a second immediately preceding detonation, or is destroyed by quenching. However, the fact that sensitization is possible suggests that a catalytic effect may exist to some extent.

To study the possible extent of sensitization, preheating temperatures below the minimum detonation temperature were used, permitting long pre-heating periods that would not result in detonation. After the usual quenching, the samples were re-heated at a temperature high enough to produce detonation, this second period giving a measure of the extent of the sensitization. Results are shown in Table XII, where  $T_1$  is the pre-heating temperature,  $t_1$  the period of pre-heating,  $T_2$  the second heating temperature, and  $t_2$  is the time required to produce detonation in the sensitized samples at the temperature  $T_2$ .

From these data it is apparent that the sensitization effect is limited, as  $t_2$  can only be reduced in this

### TABLE XII

	below the	Minimum	Detor	nation Temp	erature.	
T1 t1	= 310 <sup>0</sup> C. = (sec.)	T <sub>2</sub> t <sub>2</sub>	320 <sup>0</sup> ( (sec.	C. ,)	Av. t	(sec.)
	20	38.2 38	.8 36	0 38.6		38.4
	30	30.0 32	.8 31.	.8 31.0		31.4
	40	27.5 25	.2 25.	4 28.0		26.5
	50	24.3 22	.9 23	0 24.0		23.6
	60	21.0 23	.3 23.	. 4		23.6
	70	23.2 21	.9 21.	.6		22.2
	80	22.1 20	.8 21.	.2		21.4
	90	20.3 18	.8 20	.5		19.9
	100	20.2 19	.2 19.	5 19.9		19.7
	120	18.0 19	.2 19.	0 18.7		18.8
	150	21.9 18	.6 20	,1		20.3
	175	26.3 23	.4 24	,0		24.4
	200	90 90	90	(no detona	tion)	

Sensitization of Service Azide by Pre-heating below the Minimum Detonation Temperature.

way to about 19 seconds from a normal induction period of about 50 seconds. If pre-heating is extended to attempt to exceed this limit,  $t_2$  increases, and in fact, with a pre-heating period of 200 seconds at  $310^{\circ}$ C., the samples can no longer be made to detonate at  $320^{\circ}$ C.; the minimum detonation temperature has evidently been raised above this latter temperature. Table XIII shows the data obtained upon closer examination of the effect of pre-heating samples for a  $t_1$  of 40 seconds and over, i.e., a continuation of the process recorded in the latter part of Table XI.

### TABLE XIII

### Sensitization of Service Azide

$T_{1} = 320^{\circ}C.$ $t_{1}$ (sec.)	$T_2 = 320^{\circ}C_{\bullet}$ $t_2 (sec_{\bullet})$	Av.t (	(sec.)
40	21.4 22.2 21.4		21.7
42	21.2 21.6 21.4		21.4
43	18.9 21.4 20.6 21.3		20.5
44	21.2 21.0 21.1		20.5
45	21.0 18.6 21.3 18.2		
46	20.8 21.4 20.2 19.4		
47	17.5 20.4 21.0 20.7		
48	19.4 21.1 19.9 19.4 21.8		
49	exploded on withdrawal		
49	11 11 11		
49	11 II II		

Table XIII shows no such clear limit of sensitization as was found in the data in Table XII. The limit may exist, but experimental error prohibits its detection, since, as may be seen from the scattering of values for t2 corresponding to t1 values exceeding 44 seconds, average t2 values could not be considered as evidence of a clear line of demarcation for such a limit. It was found that the minimum detonation temperature of samples pre-heated at  $320^{\circ}$ C., for 47 seconds showed an increase of only  $1^{\circ}$ C., which does not compare with the increase of at least  $5^{\circ}$ C. apparent at the end of Table XII. Evidently, then, these samples preheated to the limit of  $320^{\circ}$ C. are not in the same condition as samples pre-heated for 200 seconds at  $310^{\circ}$ C., but are probably the same as samples pre-heated for 80 seconds at  $320^{\circ}$ C., and it may be safely assumed that at  $320^{\circ}$ C. the sensitization limit cannot be attained.

Samples of service azide were pre-heated, and examined by X-ray diffraction to see if any marked change had occurred. The diffraction photographs are shown in Fig. IV, where (a) is the untreated service azide, (b) is the service azide partially sensitized by pre-heating for 40 seconds at 310°C., and (c) is the service azide fully sensitized by pre-heating for 120 seconds at 310°C.

The diffraction patterns are all identical, showing that no chemical reaction could have occurred on pre-heating to change the composition of the sample by more than 5%.

Examination of sensitized samples under a petrographic microscope indicated that there was no change in crystal form. The optical properties appeared to be unchanged, but darkening of the crystals caused by pre-heating made it difficult to establish this point beyond all doubt.

Many unsuccessful attempts were made to sensitize

## FIGURE IV

X-ray photographs of sensitized service azide A. Untreated service azide.

B. Service azide preheated for 40 seconds ab 310°C.
C. Service azide preheated for 120 seconds at 310°C.



various batches of dextrin azide by pre-heating above the minimum detonation temperature, as was done with service azide. However, it was found by pre-heating slightly below the minimum detonation temperature for short periods, and subsequently detonating the samples above that temperature, that slight sensitization could be obtained. These results are shown in Table XIV, for a dextrin azide batch where the induction periods for a single heating at 280°C. gave an average of 9.0 seconds.

### TABLE XIV

S	ensit	izati	on	of	Dextrin	Azide

T <sub>1</sub> = 275 <sup>0</sup> C.	$t_1 (sec.)$	$T_2 = 280^{\circ}C.$	$t_2$ (sec.)
<u> </u>	7		10.6
	10		60 (no detonation)
	5		10.4
	3		8.0
	3		8.4
	2		8.1
	2 +		8.1
	1 +		8.2
	1 <b>+</b>		8.4

The values  $l \neq and 2 \neq indicate$  that samples were pre-heated for slightly more than l or 2 seconds, respectively. It is noteworthy that where  $t_l$  is more than 5 seconds, the samples were desensitized, and in fact would not detonate at 280°C. when pre-heated for 10 seconds. The minimum detonation temperature of dextrin azide is obviously raised from the normal value of 276°C. by pre-heating for even such short periods, perhaps because of the effects of the decomposition products of the occluded dextrin itself.

It was found possible to sensitize dextrin azide if it were first wetted with phthalate in the manner previously described. For a batch which showed, when wetted, an induction period for single heating at 335°C. of about 41 seconds, it was found by pre-heating 4 wetted samples at 335°C. for 25 seconds, that detonation occurred on a second heating at 335°C. after 21.0, 17.9, 18.0, and 23.8 seconds respectively. Here again, dextrin azide is shown to behave similarly to service azide.

### Duration of Pre-Heating Effect

To investigate the duration of the sensitization produced in service azide four series of experiments were made. In each series, samples of service azide were preheated for 20 seconds at 320°C., and stored at room temperature under the following conditions:

- Series A: Stored over concentrated sulphuric acid, in the dark.
- Series B: Stored over concentrated sulphuric acid, in an atmosphere of nitrogen, in the dark.

Series:C: Stored over water, in the dark.

Series D: Stored over water, exposed to diffuse light.

Duration of Sensitization									
Series A:	tl(sec.)	Storage time (hours)	t <sub>2</sub> (sec.)						
	20	68	<b>3</b> 2.3						
		93	34.4						
		93	33.7						
		117	33.9, 29.8						
		143	28.1, 26.6						
		164	32.4, 28.8						
		174	38.0, 30.3, 31.0						
		187	29.5, 29.4						
		220	28.8, 28.2						
		268	33.4						
		408	32.8						
		571	32.6						
		763	40.2, 33.0						
		935	44.6, 27.0						
		1122	35.7, 36.2						
	5	<b>7</b> 62	45.6						
		935	43.6						
	<b>4</b> 5	311	19.6						
		763	28.0						
		935	23.2						

TABLE XV

	TABLE XV cont'd.							
Series B:	tl(sec.)	Storage t <b>ime</b> (hours)	t <sub>2</sub> (sec.)					
	20	46	27.0, 29.0					
		72	26.0, 27.2					
		93	28.9, 30.2					
		117	27.6, 27.0					
		150	26.0					
		170	28.8					
		197	28.8					
		337	29.2					
		500	27.8					
		692	27.0					
		864	26.6, 31.0					
		1051	26.8, 28.2					
	45	239	20.5					
		864	22.4					

	TAB LE XV cont'd.								
•	Series C:	tl(sec.)	Storage time (hours)	t <sub>2</sub> (sec.)					
		20	23	28.6					
			57	28.6					
			74	29.8					
			95	31.9					
			120	32.6					
		•	143	37.4					
			167	36.5					
			190	30.2					
			238	34.2					
			286	34.0					
			431	45.0, 35.3					
			604	150,150 (no detonation)					
			790	150 (no detonation)					
			790	t <sub>2</sub> at 324°C.= 20.5,20.0					
	<u>Series D</u> :	20	28	29.0					
			46	33.4					
		<b>,</b> ,	70	32.8, 29.3					
			104	30.3					
			122	33.1					
			140	28.6					
			165	31.1					
			189	32.3					
			212	34.0					
		· ·	236	30.8					
			283	38.6					
			331	120,120 (no detonation)					
			404	150 (no detonation)					

Samples were removed from time to time, and heated to detonation at  $320^{\circ}$ C. The results are shown in Table XV.

With Series C and D, were included some samples preheated and detonated at 324°C. These were found to behave similarly except that they did not exhibit a failure to detonate after standing over water for a long period, but retained their sensitization throughout. This led to the conclusion that the failures shown in Table XV may have been due merely to an increase in the minimum detonation temperature of the samples, and not to any loss in sensitization. The minimum detonation temperature of such samples was determined, and it was found to have increased to  $322^{\circ}$ C., an increase of  $6-7^{\circ}$ C. However, at temperatures where detonation did occur, the sensitization effect was still evident.

It was noticed that after storing over water, the sensitized azide samples tended to bind together in the tubes, becoming lumpy and no longer free-flowing. Subsequent drying over sulphuric acid did not improve their condition, nor did it restore them to a lower minimum detonation temperature. This binding, resulting from condensation from the water-saturated atmosphere surrounding the samples, was probably the cause of the change in the minimum detonation temperature.

### Effect of Heat Treatment on Sensitized Service Azide

The effect of slow cooling of preheated service azide was studied by treating samples as follows: The samples were preheated, then raised so that the bottom of the charge container was just about at the level of the thermostat liquid for 30 seconds, then raised again until the bottom of the container was about 1 inch below the top of the heating block for another 30 seconds, then cooled in the air for 5 minutes, the first minute of which the container was held about 2 inches directly above the block. No ice water was used to quench any of the samples. Finally the samples were detonated at  $320^{\circ}$ C. The data obtained are given in Table XVI.

Effect	of	Slow	Cooling on	Pre-heated	Service	Azide
T1 =	310	o°c.	tl(sec.)	T <sub>2</sub> = 320°	°C. t <sub>2</sub> (	sec.)
			50			24.4
			50			23.2
			50			24.5
			90	,		20.8
			90			21.6
			90			20.8

TABLE XVI

Comparing these data with those shown in Table XII, it is clear that the rate of cooling has no appreciable effect on the extent of the sensitization produced by pre-heating. The sensitized azide is a comparatively stable product.

It may be assumed that the pre-heating effect is permanent at least for a period of over three months. The variation in t2 in stored samples was somewhat larger than would be expected, and was noticeable in each of the series except B, where the nitrogen atmosphere seemed to have been more effective in preserving the samples. The mean deviation from the average t2 for samples that have stood for less than 2 hours was about half that of the mean deviation from the average t2 in any of the above series. The larger variation may have been due to the fact that the tests were made over a considerable period of time, where slight variations in the thermocouple or general technique may have increased the experimental error. This explanation seems unlikely, however, for even t<sub>2</sub> values obtained in duplicate on some days showed a considerable difference, as may be seen in Table XV.

### Effect of Phthalate on Sensitized Service Azide

If the sensitization of service azide by pre-heating produces a distinct chemical change in the crystals, then the addition of phthalate to sensitized samples should not obliterate the pre-heating effect. To investigate the effect of phthalate on sensitized service azide, samples were pre-heated to the limit of sensitization above and below the minimum detonation temperature (cf. Tables XII and XIII). They were then wetted with phthalate in the usual manner, and detonated at  $335^{\circ}$ C. The results are shown in Table XVII. For untreated samples similarly wetted with phthalate, the induction period for a single heating at this temperature was 37.3 seconds (average).

T.	A	B	L	E	2	٢	V	Τ	I

	Effect	of Phthal	ate on Sensi	tized	l Serv	rice A	Azide	
		t <sub>l</sub> (sec.)	T <sub>2</sub> = 335 <sup>o</sup> C.	t <sub>2</sub>	(sec.)	) _	A1 ( 5	.t <sub>2</sub> sec.)
Tl =	310 <sup>0</sup> C.	100		44.2	34.2	41.4		39 <b>.</b> 9
		120		49.4	45.4	36.6	37.4	42.2
		150		40.0	42.2	37.4		39.9
<sup>T</sup> 1 =	320 <sup>0</sup> C.	42		45.2	42.2	38.6	37.2	40.8

The samples heated for 120 seconds at  $310^{\circ}$ C. should be sensitized to the limit and hence those heated for 150 seconds should be beyond the maximum limit, i.e., their  $t_2$ values should be longer than for those pre-heated for 120 seconds. However, after phthalate had been added it was clear that the sensitization had been lost, for the  $t_2$ values then gave an average approximately the same as that obtained for the induction period for a single heating of phthalate-treated service azide at  $335^{\circ}$ C. The sensitization is similarly lost from samples pre-heated at  $320^{\circ}$ C. (above the minimum detonation temperature) for 42 seconds and treated with phthalate. The induction periods of sensitized service azide and dextrin azide can be increased considerably by wetting with phthalate. A possibility presents itself, then, that sensitized service azide has a short induction period for a reason similar to that given for the behaviour of dextrin azide, namely, it has a poorer thermal conductivity than has untreated service azide.

### Detonation of Mixtures of Service and Dextrin Azides

Since service and dextrin azides differ so markedly in their thermal detonation properties, it should be of interest to investigate these properties for mixtures of varying propertions of the two types. Mixtures were weighed out accurately in the proportions indicated in Table XVIII and 20 mg. samples of each mixture were detonated at 320°C. The results are shown in Table XVIII with the percentage of service azide given for each mixture, the remainder of the mixture consisting of dextrin azide. The minimum detonation temperature of each mixture was also determined, with the results shown.

The data from Table XVIII are plotted on Fig.V. It is seen that the properties of the mixtures are extremely sensitive to small changes in the ratio of components. When the samples were detonated at 320°C., as was done here, the curve is discontinuous at 75% service azide, when t is plotted against composition of the mixture, since the minimum detonation temperature of this mixture is 321°C. Obviously

# FIGURE V

Induction periods of service-dextrin azide mixtures at 320°C., and their minimum detonation temperatures.


this discontinuity would widen at a lower temperature, and would not occur at a higher temperature. It should also be noticed that the discontinuity occurs at percentages of service azide slightly above those whose mixtures show properties similar to dextrin azide, as far as the length of the induction period is concerned, despite the fact that they may contain as much as 70% service azide.

#### TABLE XVIII

	Detonation	of Serv	vice-Dextrin	Azide Mixtures	at 320°C.
%	Service Azide	t(sec.	• )	Av.t(sec.)	Min.Det. Temp.( <sup>o</sup> C.)
0	5.4	5.5 5.3	3 5.6 5.5	5.5	276
20	5.6	5.5 5.7	7 5.5	5.5	283
40	6.1	6.0 6.2	2 6.1	6.1	298
50	6.6	6.4 6.6	6.5	6.6	308
60	7.1	6.8 7.0	0 7.0	7.0	312
70	8.0	8.0 7.5	5 7 <b>.</b> 1 7 <b>.</b> 1 7 <b>.</b> 2	7.9 7.5	312
71	11.7	10.4 11	L.4 12.2 10.1	11.1	319
74	£ 27.4	20,9 25	5.2	(26.3)	320
75	5 120 1	120 120	(no detonati	on) –	321
76	39.8	40.6 39	9.8	39.9	319,5
77	39.2	39,3 39	9.0	39.2	319.5
80	) 37.0	37.9 37	7.6	37.5	319.5
90	42.8	40.6 43	3.2 42.8	42.3	317
10	00			51.8	316

\_\_\_\_\_

## FIGURE VI

Variation of induction periods with temperature for service-dextrin stide mixtures.

A -	100%	service	azide
в -	90%	<b>H</b>	ľ
С -	80%	Î Î Î	n
D -	75%	n n n	n
<b>E</b> -	70%	<b>U</b>	n.
ŕ-	60%	<b>H</b>	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1
<b>G</b> -	30%		<b>n</b> .



•

## FIGURE VII

Log t against reciprocal absolute temperature for service-dextrin azide mixtures.

А	-	100%	service	azide
В	-	90%	11	"
С	-	80%	ň	11
D	-	753	17	**
Ε	-	70%	11	11
F		60%	11	11
G	<del>-</del> .	30%	11	11
Ħ	-	0%	11	11



The temperature coefficients for the detonation of these various mixtures were obtained by heating samples to detonation over a range of temperatures. The results are shown in Table XIX, and plotted in Fig.VI.

The data in Table XIX were used to plot log t against <u>1</u> T in Fig. VII. As might have been anticipated from Fig. V, an abrupt change in the detonation properties of the mixtures is evident in the lower temperature range.

To investigate further the reason for such an abrupt change, tests were made to determine the relative densities of these mixtures. A fine bore pyrex capillary was made, and 50 mg. samples of each mixture were weighed and poured in. The tube was tapped and rubbed with a file edge (the usual melting-point-tube technique) to ensure that the sample would settle firmly to the bottom. Measurements of the length of the sample were made from time to time during such "packing", and when three successive measurements checked exactly, it was assumed that the settling was complete. This final length weighed into it, repeating the above procedure. The results are shown in Table XX where the length given is the height of the samples in the capillary tube.

Detonati	lon of	Service-Dextrin Azide Mixtures	
	т( <sup>о</sup> с.	) $t(sec.)$ Av.t(	(sec.)
30% Service Azide	300	8.3 8.4 8.4	8,4
	315	6.7 6.5 6.5 6.4	6.5
	340	4.8 4.9 4.8 4.7	4.8
	360	3.4 3.2 3.4 3.4	3.4
6C% Service Azide	315	7.0 7.0 7.2 6.8	7.0
	320	6.7 6.4 6.4 6.2 6.4	6.4
	340	5.4 5.4 5.0 5.4	5.4
	<b>36</b> 0	4.2 4.0 4.1 4.0	4.1
70% Service Azide	320	8.2 8.6 8.7 8.4	8.5
	340	5.8 6.2 6.2 5.8 5.6	5.9
	360	4.3 4.0 4.0 4.0	4.0
75% Service Azide	325	9.7 10.0 8.8 7.8 7.7 9.4 8.2	8.8
	330	6.6 7.2 7.2 7.3	7.2
	340	6.5 6.8 6.8 6.7 6.7	6.7
	360	4.0 3.9 4.2 4.3 4.2	4.1
	370	2.9 3.2 3.0 2.6 3.1	3.0
80% Service	320	39.4 38.0 36.5 33.2 34.0 35.5	36.1
AZIGE	330	10.6 9.4 9.5 11.0	10.1
	340	7.1 6.8 7.1 7.0	7.0
	360	3.9 4.2 4.0 4.1	4.0
90% Service Azide	320 330 340 360	$42.9 \ 42.5 \ 38.8 \ 37.7 \ 40.3 \ 37.3 \ 16.2 \ 16.2 \ 17.2 \ 17.0 \ 16.4 \ 16.9 \ 8.4 \ 8.4 \ 8.6 \ 8.0 \ 8.5 \ 4.2 \ 4.2 \ 4.2 \ 4.2 \ 4.1$	39.6 16.5 8.4 4.2

## TABLE XIX

Detonation of Service-Dextrin Azide Mixtures

	Relative	Densi	ty of S	Service	-Dext	rin Azi	lde Mixtures
%	Service Azide	Ler	ngth of	f Sampi	Le(mm.)	) _	Av.length(mm.)
	0	117.4	118.8	117.4	118.2		117.9
	70	100.3	100.9	102.3	101.2	102.3	101.4
	75	99.6	99.3	99.1	99.2		99.3
	80	100.9	99.5	100.5	98.5		99.8
	100	106.4	103.7	103.7	100.9	103.7	103.7

#### TABLE XX

The relative packing densities, which give a measure of the "packing ability", will bear an inverse ratio to the lengths given in Table XX. Thus it is clear that the 75% service azide mixture "packs" better than any other, which would be expected to lead to better inter-particle thermal conductivity. This property would manifest itself in a high minimum detonation temperature, one which, in fact, should be higher than that for pure service azide, which is indeed true, as has been shown.

#### Detonation of Mixtures of Pre-Heated Service and Untreated Service Azide

Pre-heated service azide resembles dextrin azide in that it has a fairly short induction period. Detonation mixtures made up of sensitized service and untreated service azide should give data to show whether the effect of dextrin azide in the service-dextrin azide mixtures is the result of its shorter induction period alone, or to some other factors.

# TABLE XXI

	Detonat	ion o	of Mi: Serv:	xture ice A	s of a zide l	Sensi Mixtu	tized-Unt res	reated
% Untr Service	reated Azide	-	t <sub>2</sub> (se	c.)			Av.t <sub>2</sub> (sec.)	Min.Det. Temp.( <sup>o</sup> C.)
0	31.9 30.9	28.8 28.0	28.4 31.8	29.5	31.0		<b>30.</b> 0	316
10							-	316.5
16.6	30.6	30.8	32.5	30.6	31.4	32.8	31.5	-
17							-	317
18							-	317
20	34.0	30.8	34.4	34.4	32.4	31.6	33.1	317
22							-	317
25	35.2 33.0	32.8 33.4	34.3	34.6	31.8		33.6	-
28							-	<b>316</b> .5-317
33.3	37.8 36.6	36.8 35.4	37.4	35.0	35.2		3 <b>6.</b> 3	-
35							-	316.5
40	39.2 35.5	38.4 40.4	38.0 37.0	41.6 39.1	36.8		38.6	-
50	40.8	44.2	42.6	41.6	40.4	<b>41.</b> 0	41.8	316
60							-	316
70	47.2 48.4	46.0 46.4	46.9	46.4	48 <b>.</b> 4		<b>46.</b> 8	316
80							-	316
85							-	316
90							-	<b>315</b> ,5
100	51.1 52.4	52.6 52.0	52.8 51.0	50.9	50.6		51.7	<b>315-315</b> .5

## FIGURE VIII

Induction periods for preheated-untreated service azide mixtures at 320°C., and their minimum detonation temperatures.



Service Azide was pre-heated, in the usual 20 mg. quantities, for 25 seconds at 320<sup>0</sup>C. Quantities of this sensitized material were then used to make up mixtures of pre-heated and untreated service azide, which were detonated in 20 mg. quantities at 320<sup>0</sup>C. The minimum detonation temperatures of these mixtures were also determined. The results are shown in Table XXI.

The data from Table XXI are plotted on Fig.VIII, and show a smooth curve for the induction period against per cent. untreated service azide. As expected from these mixtures, no sharp break appears during the transition over the range of mixtures, with the exception of one point off the curve at 30% service azide. The unusual curve obtained for the service-dextrin mixtures, then, must be due to factors other than the short induction period of dextrin azide.

If the factor which produces this unusual effect for service-dextrin azide mixtures is the thermal conductivity between the particles, then the addition of phthalate as a wetting agent should remove this marked effect. Mixtures containing 30%, 75% and 80% service azide were made up, and 20 mg. samples were treated with phthalate. These mixtures were detonated at 340°C., with the result shown in Table XXII.

#### TABLE XXII

Effect of Phthalate Wetting on Service-Dextrin Azide Mixtures

% Servic Azide	e	t 	c(sec.	.)				Av.t(sec.)
30	28.1	26.5	27.0	27.5				27.3
75	33.4	33.5	35.5	33.7	34.8			34.2
80	30.0 33.0	29 <b>.7</b> 32 <b>.</b> 4	35.8 36.1	36.2 34.4	32.6 29.0	32.8 29.1	29.0	32.3

Evidently, the spread between induction periods for mixtures below and above 70% service azide recorded in Table XVIII, is reduced by wetting of phthalate. If the phthalate merely serves to improve the inter-particle thermal conductivity, then conductivity would seem to be a major factor affecting the detonation properties of the mixtures.

#### Activation Energy of Sensitized Service Azide

If the pre-heating of service azide produces a catalyst which renders it sensitized, then the activation energy of the reaction of the sensitized material leading to detonation should be appreciably lower than the activation energy of the reaction which produces the sensitized material. This condition must be met whether the catalytic effect is caused by decomposition intermediate, stable or unstable or is the result of "reaction centres" being formed in the initial stages of the reaction. To determine the activation energy of sensitized service azide, samples were pre-heated for 20 seconds at  $320^{\circ}$ C., quenched, and then detonated by heating over a range of temperatures. The data obtained are shown in Table XXIII. For all these samples,  $T_1 = 320^{\circ}$ C.

#### TABLE XIII

#### Detonation of Sensitized Service Azide

$T_2(^{o}C_{\bullet})$	$t_2$ (sec.)	Av.t2 (sec.)
320	30.8 28.7 30.4 27.8 31.2 29.0	29.7
330	16.6 16.6 17.2 16.6 15.8	16.6
340	8.6 8.4 8.1 8.6 8.8 8.2	8.5
350	5.6 5.6 5.1 6.2 5.8 5.8	5.7
365	3.1 3.6 3.5 3.5 3.4	3.4
375	2.3 2.0 2.1 1.9 2.4 2.0	2.1

A plot of log  $t_2$  against  $\overline{T}$  for these data gave the curve shown in Fig. IX. The activation energy calculated from the equation

 $\ln t_2 = \frac{E}{RT} + B$ gave a value for E of 41.0 Kcal.

#### Activation Energy of the Pre-Heating Reaction

As suggested above, if a chemical reaction occurred during the process of sensitization by pre-heating, it should be possible to evaluate its activation energy. To determine this activation energy, service azide samples were pre-heated

## FIGURE IX

Log of induction period against reciprocal absolute temperature for sensitized service azide, and log of preheating time required for constant sensitization against reciprocal absolute temperature.

 O Detonation of sensitized service azide
Preheating of service azide to constant sensitization.



**6a** 

at various temperatures for a time sufficient to sensitize them to a constant amount. Actually,  $T_1$  and  $t_1$  were varied, so that on a second heating at  $T_2 = 320^{\circ}C_{\circ}$ ,  $t_2$  would be fairly constant at about 24 seconds. The results are shown in Table XXIV.

#### TABLE XXIV

Pre-Heating of Service Azide to Constant Sensitization.

T1 (°C.)	$t_1(sec_{\bullet})$	$T_2 = 320^{\circ}C.$		tź	2( sec.	)
300	100		24.	4	24.2	<b>23.</b> 3
310	51 <sup>a</sup>					
320	35		24.	4	24.2	
330	20		23.	5	25.1	24.2
<b>34</b> 0	11p					

a,b

The values at  $310^{\circ}$ C. and  $340^{\circ}$ C., unlike the others, were not obtained directly. The value of 51 seconds at  $310^{\circ}$ C. was obtained by interpolation from the data given in Table XII. The value of 11 seconds at  $340^{\circ}$ C. could only be estimated, since the induction periods for a single heating at  $340^{\circ}$ C. gave an average of 11.5 seconds, and pre-heating up to 10 seconds at  $340^{\circ}$ C. reduced  $t_2$  at  $320^{\circ}$ C. to only 29.2 seconds. Thus it was estimated that a pre-heating time of about 11 seconds at  $340^{\circ}$ C., if it were technically possible, should give a t2 of about 24 seconds at  $320^{\circ}$ C. The value shown should not be in error by more than 0.5 seconds at the most.

The data in Table XXIV were used to plot log t<sub>1</sub> against reciprocal absolute temperature, the resulting curve being shown in Fig. IX. From the straight line relation an activation energy of 37.1 Kcal. was calculated, which approximates closely the value of 41 Kcal. obtained for the detonation of sensitized azide. This agreement might be made even closer if a different degree of sensitization had been chosen as a standard, that is, if pre-heating times had been changed to give  $t_2$  at 320°C. some other fixed value. The 24 second value was chosen as it represents about half the single induction period required at  $320^{\circ}$ C.

The agreement is sufficiently close to suggest that there is little, if any, difference between the reaction causing sensitization and the reaction producing detonation. It gives strong indications that a catalyst is not formed in the early stages of the reaction, since a catalytic effect should be made manifest by a smaller activation energy for the latter part of the detonation reaction; that is, the activation energy for the detonation of sensitized service azide should be very appreciably smaller than the activation energy for the pre-heating effect which produces a sensitized product. The slight difference obtained here is actually in the opposite direction - that is, the activation energy for sensitization is slightly smaller than that for the detonation after pre-heating.

#### DETONATION OF SINGLE CRYSTALS

The apparatus (see Fig. IC, D, E) used for this work has already been described, as well as the method of preparation of large single crystals of lead azide. It was hoped to be able to project the crystal image through the microscope on to a screen, or a moving strip of film, the larger image size permitting more accurate measurements of changes in crystal size, as well as providing a permanent record of the stages leading to thermal detonation of a single crystal. However, for preliminary work it seemed inadvisable to use a high-precision microscope with such a high-temperature stage. The risk of injury to the objective through heat seems to have been eliminated however, and subsequent work should permit the use of a more precise instrument.

#### Minimum Detonation Temperature of Single Crystals

The principal factor determining the minimum detonation temperature of single lead azide crystals was found to be their size, the larger particles detonating at lower temperatures. Some examples illustrating this effect of size are given in Table XXV. The crystal dimensions are given in terms of divisions of the micrometer scale (1 mm. = 65 divisions), the first figure being the length, the second the height of the crystal above the boat (i.e., the thickness)

and the third, the width bearing on the boat surface. The cross-sectional areas are given since these must determine mainly the rate of conduction of heat between the crystal and the boat. The crystal length being by far the largest dimension, would not be expected to bear any relation to the rate of heat loss from the crystal.

#### TABLE XXV

#### Effect of Crystal Size on Minimum Detonation Temperature

Crystal Size	Temp. ( <u>°C.</u> )	Cross-sectional area $(div_{\bullet})^2_{\bullet}$	Remarks
43 x 8 x 14	320	112	no detonation
53 x 13 x 10	320	130	no detonation
53 x 18 x 15	320	270	broke up at 25 sec.
44 x 8 x 14	325	112	no detonation
49 x 16 x 16	325	256	broke up at 22 sec.
66 x 9 x 14	332	126	no detonation
61 x 18 x 15	332	270	broke up at 15 sec.
39 x 9 x 14	<b>34</b> 0	126	no detonation
50 x 8 x 18	340	144	broke up at 17 sec.
52 x 10 x 16	340	160	broke up at 17 sec.
49 x 13 x 17	340	221	broke up at 18 sec.
58 x 8 x 17	347	136	broke up at 13 sec.

At temperatures below about 350°C., the crystals did not detonate with a loud sound, but broke up abruptly with a faint crackle. "Detonation" of this kind was not complete, but is classed here as detonation, for on extending the temperature to higher ranges, a smooth curve is obtained on plotting induction period against temperature, when the time lag preceding this "breaking-up" at lower temperatures is taken as the induction period preceding detonation.

From the dimensions of the crystals not detonating at 320°C., it is obvious that they are all smaller in width and thickness than those that did detonate. One sample shown in Table XXV would not detonate even at a temperature as high as 340°C., while larger crystals detonated at temperatures as low as 320°C. Such behaviour may be interpreted as showing that in the larger **crystals**, the dissipation of heat from the pre-detonation decomposition is slower than for the smaller crystals, and hence a lower bath temperature is sufficient to produce detonation.

Activation Energy of Detonation -- Single Crystals

Data were obtained for single lead azide crystals to determine E from the equation

$$\ln t = \frac{E}{RT} + B$$

by detonating single crystals of approximately the same size over a range of temperatures, and timing their induction period to the nearest second. The data are given in Table XXVI.

t/T Re	stations for Single Lead	Aziae Cr	stals
Temp.( <sup>O</sup> C.)	Crystal Size(div.)	t(sec.)	Av.t(sec.)
390	70 x 14 x 20	7-8	7
390	70 x 18 x 23	7	
<b>34</b> 8	70 x 20 x 16	11-13	12
<b>34</b> 8	61 x 22 x 20	12-14	
334	57 x 18 x 20	14-16	15
334	62 x 15 x 18	15-17	
320	59 x 11 x 18	19-20	18
320	56 x 17 x 20	16-19	

#### TABLE XXVI

A value of 10 Kcal. is obtained for E by substituting the above values in the equation

 $lnt = \frac{E}{RT} + B$ 

a remarkably small activation energy compared with those obtained for detonation of the bulk service azide samples, although it compares with the value of E for dextrin azide (10.6 Kcal.).

#### Sensitization of Single Crystals

Attempts were made to sensitize single crystals of lead azide by pre-heating, the reaction being quenched by quickly withdrawing the boat from the furnace, and placing it in a gentle stream of air to facilitate rapid cooling.

It was not possible to detect sensitization when the crystals were pre-heated above their minimum detonation temperature. The induction period at temperatures high enough to give accurately reproducible results is too short to permit conclusively the detection of a shortened period, but the indications are that very slight sensitization may occur. Results are shown in Table XXVII. The induction period for a single heating at 320°C. was 18-20 seconds, with no values lower than 18 seconds.

	Sensitization of Single Crystals						
T1(°C.)	tl(sec.)	<b>T<sub>2</sub>(°</b> C•)	t <sub>2</sub> (sec.)				
295	25	320	20				
**	17	. 11	16				
11 4	Ħ	- 11	16				
n	Ħ	11	18				
n	11	11	16-18				
n	T	11	17				

TABLE XXVII

The data in Table XXVII are typical of the results obtained, and it must be said that they do not show beyond reasonable doubt that appreciable sensitization is possible on pre-heating single crystals. There is a slight indication that such a phenomenon does occur since values of  $t_2$ obtained are slightly lower in some cases than the values of t for a single heating at the same temperature. If  $t_1$ is increased any further,  $t_2$  becomes longer than t.

Examination of crystals subjected to pre-heating showed darkening at the crystal ends and subsequently along the edges, or wherever roughness was visible due to crystal imperfections. Crystals heated to within 1-2 seconds of detonation and then quenched were not by any means completely covered by these dark brown deposits, and on breaking such crystals, it was seen that the deposits occurred only on the outer surfaces, and had not yet begun to penetrate the interior.

### Self-Heating of Single Crystals

If the pre-detonation reaction of lead azide releases heat sufficient to raise its temperature appreciably, then this may exhibit itself in thermal expansion of the crystals. To investigate this possibility, every crystal detonated was closely watched to see if any crystal expansion occurred before the actual detonation. In every case it was found possible to predict detonation 1-2 seconds before it actually took place, by noting the time at which an apparently abrupt swelling of the crystal occurred. In a few cases (probably 10% of the trials made) the crystal increased its length suddenly after several seconds of quiescence, followed within 1-2 seconds by detonation.

It was impossible to measure the new crystal length resulting from this expansion in the short time allowed, but by lining up the ends of the crystal with a line of the eyepiece, it was noted that the expansion amounted to about 0.3 divisions for a crystal about 60 divisions long. Assuming the same expansion to occur at the other end of the crystal, the crystal increased its length by about 0.6 divisions.

The approximate coefficient of thermal expansion of these lead azide crystals was obtained by making many measurements of crystal length at room temperature, and again at  $310^{\circ}$ C. The crystals were found to expand about 0.4 divisions over this temperature range for a crystal length of about 60 divisions.

If the coefficient of linear expansion is reasonably constant between room temperature and  $800^{\circ}C_{\cdot}$ , then it may be calculated that the crystal temperature immediately preceding detonation must be of the order of  $750^{\circ}C_{\cdot}$ 

#### DISCUSSION OF RESULTS

The theories which have been proposed to explain the process whereby the chemical reaction of thermal decomposition builds up to detonation have already been discussed, but the data presented in this thesis provide considerable material for criticism and amendment of some of these theories.

Whatever may be considered to be responsible for initiating the detonation of lead azide - heat, friction or shock wave - it is obvious that the result is merely a decomposition reaction, although one of high velocity. There seems little reason to suppose that simply because the reaction is fast and violent, it must necessarily involve some peculiar mechanism. If detonation is accepted as a chemical phenomenon, then chemical principles may be safely applied to its elucidation.

Compounds not ordinarily classed as explosives may be made to detonate under special temperature conditions. Potassium chlorate, for example, decomposes gently even when molten. Yet if droplets of KCl O<sub>3</sub> are allowed to fall on red hot glass in an enclosed space, a tiny explosion will occur as each droplet strikes the hot surface. Similarly, ammonium nitrate has been known to explode with tremendous violence when subjected to very high temperatures, as occurred in Oppau in 1921 when huge open stockpiles caught on fire, producing intense heat and subsequent explosion in what is ordinarily considered to be an insensitive compound.

Lead azide, too, will decompose non-violently on heating, if the temperature of heating is maintained below a certain critical value. Unless this temperature is exceeded, lead azide might be classed as a thermally insensitive compound.

Sutton (45) has considered the difficulty of classification of compounds into explosive or non-explosive types. He affirms that although explosive compounds and mixtures may be "designed" on a theoretical basis to give a maximum product of heat evolved multiplied by volume of gases produced (which gives a measure of "explosive power") yet the final determination of stability, sensitivity and power must be made experimentally. While thermochemical instability is a necessary condition for a compound to be explosive, it is by no means a sufficient one, and no present theory can guarantee the prediction that a given compound will be an explosive. There is evidence, however, that rate and temperature of heating are important factors.

It would seem that friction and steady compression, as produced by impact, might be held responsible for the production of local hot spots of sufficient temperature to initiate a violent decomposition. The addition of grit particles is known to produce an initiator more sensitive to friction, which might well be the result of greater local

heating by friction between the grits and the particles of detonating compound. The relative hardness of the particles added is found to be an important factor in determining the extent of the increase in sensitivity. Some initiators are more amenable than others to such an enhanced sensitivity, and, it is possible that the crystal hardness of the initiator concerned may be the determining factor.

The fact that, according to most workers, the inducperiods leading to detonation are variable at a constant temperature, has lead to many theories involving probability considerations -- the collision of chains, whether energy or material, the simultaneous decomposition of adjacent molecules of reactant -- all such coincidences which would be capable of producing very local concentrations of energy, thus increasing the reaction rate locally to explosive velocity.

The detonation of lead azide has been thus explained, but the present investigation demonstrates that the induction period need not be widely variable, providing sufficient care be taken to ensure that the controlling factors are truly constant. There is not sufficient evidence available to suggest reasons for the widely variable induction periods reported by Ubblehode (41) for lead azide, for example, but one must assume that he has neglected to give adequate attention to some experimental conditions. The data given in Table I showed that the induction period can be kept constant within about 5%, which represents a reasonable error in view of the short times involved, and the consequent difficulty of measuring these times with greater accuracy in the absence of an automatic precision timing device. An automatic voltage regulator would also increase the constancy of the observed induction period by preventing minor fluctuations in temperature.

Close duplication of induction periods should not be possible if detonation depended upon the chance of a "binary event", as has been postulated, or upon the chance of a chain collision. Such chance occurrences would be certain to produce a much more random distribution of reaction times. That such a random distribution does occur with impact measurements suggests that additional factors are involved in these experiments, such as the reproducibility of the sample itself, its crystal sizes and shapes, distribution of the charge on the impact anvil, etc.

It is impossible to state definitely that the variation of induction periods for mercury fulminate, silver oxalate, lead picrate and other detonators could be similarly reduced with careful manipulation, but there is no reason to believe otherwise. For the thermal detonation of lead azide, at least, theories involving probability as a major causal factor would seem to be denied.

Garner has suggested that in lead azide decomposition, the reaction is confined initially to the crystal

surfaces, where lead nuclei are formed, the subsequent decomposition reaction occurring at the lead-lead azide interfaces. Ubbelohde logically extended this idea to explain the higher heat sensitivity of dextrin azide, assuming that since the surface/weight ratio is there increased by a factor of approximately 10<sup>6</sup>, the reaction should be more rapid. This theory fails completely to explain the effect of wetting both service and dextrin azide samples with phthalate before heating (see Tables VII, VIII and X). The two types then show almost identical properties of minimum detonation temperature and length of induction period. Yet. the wetting by phthalate cannot change the amount of interface upon which reaction can occur. Even if the phthalate succeeded in penetrating through the particles of dextrin azide. separating the crystallites of each agglomerate particle from one another, the destrin azide would still have the much larger surface/weight ratio that it had in the dry state, and hence on the basis of the interface reaction theory it should preserve its properties despite the wetting. Since phthalate does markedly change the thermal detonation properties of dextrin azide, it must be assumed that the large surface offered by the crystallites is not an important factor. It follows, too, that the surface of service azide, as far as affording a reaction area is concerned, is not a major factor in its detonation.

The fact that phthalate changes the detonation

characteristics of dextrin azide may be explained on the basis of the data given in Tables IV, V and VI. When service or dextrin azide was detonated in glass capillaries, it was shown that the minimum detonation temperature increased with the increase of surface/volume ratio of the sample as a whole. If the reaction takes place at the temperature of the surrounding bath. increasing this ratio should facilitate detonation by increasing the rate at which heat is conducted from the bath to the initially cool But the reverse effect occurs - the minimum desample tonation temperature is raised, not lowered. It is possible, then, that heat is being conducted in the opposite direction, from the sample to the bath, which would occur only if the charge were at a higher temperature than its Self-heating of the sample during the presurroundings. detonation decomposition is at once suggested.

A similar increase of the minimum detonation temperature was produced by compressing the charges before detonation. The "packing" thus produced should improve the thermal contact between the particles of the samples, which should, in turn, facilitate conduction of internal heat away from the decomposing azide. Thus, a higher bath temperature should be necessary to produce detonation, and this is found to be true; the minimum detonation temperatures of the charges are increased by 5°C. for service azide, and 15°C. for dextrin azide. On returning to the effect of wetting by phthalate (Tables VII and VIII), it is found that this treatment is effective in raising the minimum detonation temperature of service azide about  $5^{\circ}$ C., and of dextrin azide by as much as  $40^{\circ}$ C. Again it can be assumed that the effect is produced by increasing the inter-particle thermal conductivity of the samples.

The lower minimum detonation temperature of untreated dextrin azide can be explained solely on the basis of conductivity. Crystallographically, the two forms of lead azide have been shown to be identical, hence it is necessary to explain their different properties on the basis of a physical difference. Examination of the two forms under the microscope shows service azide to consist of fairly uniform and well-shaped rhombic crystals, which would pack closely and evenly in bulk. Dextrin azide, on the other hand, is made up of rough uneven "prickly" particles or agglomerates, which would pack poorly and loosely, affording comparatively poorer thermal contact between the particles. Compression and wetting by phthalate should both improve the thermal conductivity of dextrin azide markedly, the former by crushing and packing the particles together, the latter by providing a conduction medium between them. Service azide, which is naturally fairly closely packed, is not affected so considerably by these treatments.

This explanation based on thermal conductivity is further confirmed by examination of the data for the service-dextrin azide mixtures (Tables XVIII and XX). Here it was shown that the mixture with the highest minimum detonation temperature (75% service azide) was the one with the lowest packing density. That is, this mixture packed more closely than any other, better even than pure service Although the differences in relative denazide itself. sities are not great, it has been shown that thermal conductivity is quite sensitive to packing density (46). As a result, the 75% service azide mixture should have a thermal conductivity superior to the others, and hence requires a higher bath temperature to bring about detonation.

If the decomposition reaction could produce detonation while the sample was at bath temperature, the induction period of mixtures should be governed only by the induction period required for the more sensitive component, in this case dextrin azide. That is, an 80% mixture should detonate in 6 seconds at 320°C., the time required for dextrin azide to detonate at that temperature. However, the 80% mixture requires about 40 seconds to detonate at 320°C., and it must be assumed that that time is required before the temperature of the sample as a whole is sufficiently high to produce a decomposition rate of explosive velocity and violence.

The self-heating effect is also evident in the detonation of single crystals, where it is shown (Table XXV) that the larger crystals have a lower minimum detonation temperature. These crystals with the larger cross-sectional area, should not dissipate the heat produced by the predetonation dec omposition to the surrounding air and the supporting boat as rapidly as the smaller crystals. Hence a lower furnace temperature should be required to enable the temperature of the larger crystals to become sufficiently high for the reaction to attain detonation.

As stated in the work with single crystals (pp.74 and 75) a distinct swelling of the crystal invariably precedes its detonation. An increase of comparable amount in crystal size occurs when the temperature of the crystal is raised from that of the room to the bath temperature of  $300^{\circ}$ C. or over. The abrupt swelling prior to detonation suggests a sudden rise in crystal temperature, which could only be produced by heat within the crystal itself. Calculations show that a temperature of about  $750^{\circ}$ C. would be required to produce the observed expansion, and at such a temperature, the decomposition of lead azide should be sufficiently rapid to produce a reaction of explosive violence.

With self-heating playing such an important part in the detonation of lead azide, the validity of the equation

 $\ln t = \frac{E}{RT} + B$ 

must be questioned as a means of determining the activation energy, E, of detonation, It has been shown (Table X) that the low apparent activation energy (10.6 Kcal.) for untreated dextrin azide may be increased by wetting with phthalate to a much higher value, closely approximating that for service azide. Since phthalate only serves to change the physical characteristics of the system, the value of the activation energy obtained by this equation cannot be a true measure of the activation energy of the If all that is required to produce chemical reaction. detonation in lead azide is the addition of an amount of heat equal to the activation energy, all mixtures of service and dextrin azide should detonate after the same induction period, since the form which has the lower activation energy should detonate first (thereby detonating the whole mixture) regardless of the quantity in which This, however, is not true, desthat form was present. pite the fact that according to the equation, the induction period is the only variable at a given temperature. and hence all the mixtures should show induction periods equal to that for dextrin azide.

It remains to discuss the nature of the sensitization effect produced by pre-heating lead azide. This effect is readily produced in service azide (pp43 - 48), produced with difficulty in dextrin azide (pp 49 - 50) but readily in phthalated dextrin azide (p.50), and very slightly, if at all in single large crystals of lead azide. The
sensitization is apparently permanent (Table XV) and not changed by slow cooling (Table XVI) after the pre-heating process.

At first glance, the sensitization effect would seem to be due to the presence of a catalyst or unstable intermediate produced during the pre-detonation decomposition reaction. Closer examination of the data presented here, however, indicates that it cannot be due to such a catalytic effect.

There is a limit to the sensitization effect, as clearly shown in Table XII, where the samples were preheated below the minimum detonation temperature. If the pre-heating is continued for longer than 120 seconds at 310°C., the sensitization decreases, i. e., the second induction period required to produce detonation at 320°C. becomes increasingly longer. This limit is also apparent when service azide is pre-heated above the minimum detonation temperature (Tables XI and XIII). At 320°C... where a single induction period of about 50 seconds is required to produce detonation, the charge may be pre-heated to within 1 or 2 seconds of detonation, and then quenched, but on a second heating about 20 seconds are still required to produce detonation at the same temperature. This fact suggests two things: (1) that a sample within 1 or 2 seconds of detonation is much different after it is quenched than before, the difference probably being due to its having lost by quenching the high temperature produced by

self-heating, and (2) that sensitization is not a necessary prerequisite for detonation but may be merely a subsidiary effect resulting from the pre-detonation decomposition. This second point is also supported by the fact that dextrin azide and single crystals of pure lead azide could not be sensitized by pre-heating above their minimum detonation temperatures, although detonation could be produced at those temperatures. Sensitization beyond the limit observed, if it does occur, must occur immediately prior to detonation. According to the data in Table XIII, however, this seems unlikely, for the sensitization effect seems to have reached a constant limit some seconds before detonation should be expected.

Evidence to refute the catalytic theory of sensitization is given in Tables XXIII and XXIV, and in Fig. VIII. Here it was shown that the activation energy of the preheating reaction is essentially the same as the activation energy for the detonation of sensitized service azide. In general, the effect of the addition of a catalyst to a reaction is to reduce the activation energy required for the reaction, thus permitting the reaction to proceed more rapidly or at lower temperatures. If a catalyst is produced by pre-heating, it would be logical to expect that the activation energy for the second part of the reaction (the detonation of the sensitized product) should be appreciably less than the activation energy required for the initial

part of the reaction during which the catalyst should be produced. Such a lowering of activation energy should be observed whether the catalytic effect is produced by an unstable intermediate, the presence of catalytic by-products, or the presence of reaction nuclei. Since this lowering of the activation energy is not noticeable here, it can be assumed that **the** detonation reaction of lead azide is not catalyzed.

Samples heated to within 1 or 2 seconds of detonation (Table XIII) still require, after quenching, a considerable heating period to produce detonation, although they are certainly sensitized. Catalytic conditions produced by the first heating would not be disturbed by quenching, and the samples should be expected to detonate after a second heating of only 1 or 2 seconds. It is difficult to explain this phenomenon unless self-heating is assumed. The second heating period is then required to reproduce, by selfheating, the internal temperature that existed at the time the sample was quenched.

Nevertheless, pre-heating of lead azide does shorten the induction period required for detonation. It has been shown that pre-heating does not produce any crystallographic change nor any chemical change exceeding 5%. A darkening of the crystal is, however, very evident, apparently as a result of lead deposits, which have been converted in the presente of air to lead oxide. If the surface changes are sufficient to affect the inter-crystal conductivity, a change in induction period may be expected. If the change is merely one of conductivity, producing a detorator comparable with dextrin azide, wetting with butyl phthalate should restore the sensitized azide to its normal untreated condition. This was shown to be possible by the data in Table XVII, where it was demonstrated that service azide samples pre-heated at  $310^{\circ}$ C. for periods above and below the time required to produce the maximum sensitization had their induction periods completely restored on subsequent wetting with phthalate. The induction periods of samples pre-heated above the minimum detonation temperature were also similarly restored.

It seems apparent then, that the sensitization resulting from pre-heating is due merely to surface changes in the form of an oxide layer and a roughening, which impair the inter-crystal conductivity of the material sufficiently to yield a product requiring less time to reach detonation through self-heating, since the reaction heat is less readily dissipated to the surroundings.

The fact that there is a definite limit to the extent of sensitization possible by pre-heating (Table XII), and that further heating desensitizes surface azide, suggests that there are two opposing factors introduced by pre-heating, one of these shortening the induction period, the other increasing it, as well as increasing the minimum detonation temperature. This second factor becomes more

important as pre-heating is continued, as for example, beyond 120 seconds at 310°C. (Table XII). The desensitizing effect may be the result of microscopic or sub-microscopic fissures being produced in the service azide crystals, thus increasing the surface/volume ratio, and preventing the accumulation of heat in the crystal mass. If this effect becomes important only on prolonged heating, then it would tend to limit the amount of sensitization possible by preheating for long periods below the minimum detonation temperature.

It must be admitted that the relation between the minimum detonation temperature and the length of the induction period is not yet clear. Where the differences in both are large, as in comparisons of dextrin and service azide, the explanations offered are quite plausible, and the differences may be nearly nullified by such treatments as wetting with phthalate. Nevertheless, it cannot yet be fully explained why the minimum detonation temperature of dextrin azide is readily increased by pre-heating, while that for service azide is only slightly changed despite a considerable decrease of induction period. The answer may be found in some interfering influence due to the effect of the decomposition products of the dextrin itself, as previously suggested.

Further elucidation of the relation might be found by experiments with a range of crystal sizes of service

azide, carefully screened and detonated in bulk. Some useful data might be obtained by detonating such bulk samples in vacuo.

It seems evident from the available data that thermal detonation of lead azide arises from self-heating due to ineffective dissipation of the heat from the decomposition reaction. The temperature of the reactant material is raised to such an extent that the reaction is accelerated to explosive velocity, aided by the fact that the rate of dissipation of heat is linearly related to the temperature gradient between the sample and its surrounding bath, while the reaction rate is logarithmically dependent on the temperature of the sample. Crystal strains, and other such influences may be neglected. A simple chemical explanation suffices to explain the detonation phenomenon, modified by a temperature influence, produced by self-heating which is dependent upon the thermal conductivity of the bulk charge.

## SUMMARY

It was shown that the minimum detonation temperature of given batches of dextrin and service azide were sharply critical (within  $1^{\circ}C.$ ), with values of about  $275^{\circ}C.$ for dextrin azide, and  $315^{\circ}C.$  for service azide. These could be raised considerably by increasing the surface/ volume ratio of the charge in its container, as well as by compressing or wetting the charge with phthalate before detonation.

The induction periods for dextrin and service azides at a given temperature were found to be reproducible within experimental error (about 5%).

Dextrin and service azides, when wetted with phthalate, were found to have similar properties, the differences in their minimum detonation temperatures and induction periods over a range of temperatures being nearly nullified by this treatment.

The sensitization of service azide by pre-heating was confirmed, and the effect found to be permanent. It was shown that a definite limit to this sensitization exists when the samples are pre-heated below the minimum detonation temperature, and a similar limit probably exists on pre-heating above the minimum detonation temperature. The sensitization effect is nullified by wetting pre-heated samples with phthalate before heating to detonation.

Data obtained by detonating mixtures of dextrin

and service azide show that, although dextrin azide is much more thermally sensitive when alone, mixtures containing 70% service azide or more show a sharp change to service azide properties. The mixtures are apparently not detonated by the dextrin azide which they contain, as might have been expected. The mixture (75% service azide) having the highest minimum detonation temperature was shown to be the mixture with the lowest bulk density.

The activation energy of detonation of sensitized service azide was shown to be slightly larger than the activation energy of the pre-heating reaction which produces sensitization.

Minimum detonation temperature of single large crystals was shown to increase with crystal size, and to be fairly critical for a given crystal size. The induction periods for single crystals at a given temperature were found to be fairly reproducible. Measurement of thermal expansion preceding detonation of single crystals indicates that self-heating may raise the crystal temperature to about 750°C.

The above data have been interpreted as showing that thermal detonation of lead azide may result from self-heating of the initiator, the heat of the pre-detonation decomposition not being efficiently dissipated from the material.

The evidence presented in this thesis, while not

presuming to be final, certainly suggests that self-heating of lead azide is a major factor to be considered in its thermal detonation. It offers a much simpler explanation for a chemical reaction, the peculiarities of which have tended in latter years, to yield many unusual and complex theories in attempts to elucidate its mechanism.

## CLAIMS TO ORIGINAL RESEARCH

1. Improvement of apparatus and technique for thermal detonation of initiators.

2. Design of apparatus and development of technique for detonation of single lead azide crystals under a micro-scope.

3. Extension of thermal detonation data for dextrin and service azides over a large temperature range.

4. Investigation of the limit of sensitization of service azide by pre-heating, and of the duration of the sensitization.

5. Investigation of the thermal detonation properties of mixtures of dextrin and service azides.

6. Determination of the activation energies of the preheating reaction and of the detonation of pre-heated service azide.

7. Investigation of the effect of surface/volume ratio, compression, and wetting by phthalate on the thermal detonation properties of dextrin and service azides.

8. Elucidation of the mechanism of the thermal detonation of læad azide, and of the sensitization of service azide by pre-heating.

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