Part II. (1) Delay to Ignition and Its Temperature Coefficient

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PART II

(1) DELAY TO IGNITION AND ITS TEMPERATURE COEFFICIENT

By A. R. Ubbelohde

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[Plate 5]

In § (*a*), details are given of a method of determining the delay to ignition at various temperatures, for initiators. The heat sensitiveness of an initiator can be characterized by an equation

$$\log Y = E/4{\cdot}57\,T + B,$$

where Y is the induction period before ignition, E is the activation energy of the physico-chemical process controlling it, in kcal./mol., and B is a constant. T is the absolute temperature.

Values of E and B are listed for lead azide, mercury fulminate, basic lead di-nitroresorcinate (L.D.N.R.), lead styphnate and barium styphnate. From an extrapolation, ignition temperatures have been calculated corresponding with delays of 10^{-3} and 10^{-5} sec., to link these up with certain aspects of sensitiveness and detonation.

Experiments are described which show that initiators such as lead azide can be more or less permanently sensitized by heat treatment, and by photochemical action.

In § (*b*), experiments are described on the failure to detonate below a certain temperature, and on the ignition times, of lead azide, lead styphnate and mercury fulminate. The behaviour of mixed initiators, and of simple initiators admixed with inert diluents, has also been investigated. The results show that detonation is built up from the co-operation of a number of centres of reactivity.

It is shown that in the mixed composition 'A.S.A.' the lead styphnate plays the predominant role in the heat sensitiveness, improving the thermal pick-up and lessening the tendency of lead azide to fail to detonate on heating.

In § (*c*), X-ray measurements and determinations of the heat sensitiveness are described for Service and dextrin azides. It is shown that the grains of Service azide consist largely of single crystals, whereas the grains of dextrinated azide each contain about 10^6 crystallites. The lattice crystal structure in the two azides is the same.

With the samples investigated, the activation energy controlling the length of the induction period is about 41·3 kcal./mol. for Service azide and 23·4 kcal./mol. for dextrinated azide. The large difference between these values is correlated with the difference in initiating power of the two types of azide.

In § (*d*), sensitiveness to heat, percussion and friction are compared for Service and dextrin azides. General sensitiveness of Service azide is somewhat greater. Particular attention is drawn to the grit sensitiveness of Service azide.

(*a*) The delay to ignition and its temperature coefficient

Introduction

Two main variants have been proposed in routine tests for determining the heat sensitiveness of initiators. In the first routine test the explosive is heated up in a suitable container, starting from the cold, and using a controlled rate of rise of temperature. Ignition occurs above a limiting temperature. Provided a standard rate of heating is used, the *ignition temperatures* give information on the comparative sensitiveness of different explosives to heat.

In the second routine test, the container with explosive is suddenly plunged into a bath maintained at a constant temperature, and the time interval before ignition occurs is measured. As in a number of other reactions, this time interval or 'induction period' depends in a marked way on the temperature of the bath. For comparing the heat sensitiveness of explosives, it had proved convenient to choose the temperature at which the delay to ignition is 5 sec.

In the work described in the present section, with all the initiators yet investigated, it has been verified that the relation between the length of the induction period and the absolute temperature of the bath T can be expressed quite accurately by an Arrhenius equation of the type

$$\log Y = A/T + B. \tag{1}$$

A similar relationship has been found under rather different experimental conditions, as follows:

Activation energy of processes leading to detonation

lead azide—single crystals	Garner & Gomm (1931)
lead picrate—powder	Andreev (1934*b*)
mercury fulminate—powder	Narayana (1944)
—single crystals	Garner & Hailes (1933)
high explosives—melts	Andreev (1934*b*)
	Roginsky (1932)
	Roginsky & Andreev (1933)

Activation energy for thermal decomposition (not necessarily in detonation)

barium azide	Garner & Maggs (1939)

Although a greater number of experimental determinations is necessary to establish a complete ignition curve than to measure limiting temperatures using a steadily rising bath temperature, the complete ignition curve offers a number of advantages for comparing the sensitiveness of explosives to heat.

(i) In view of the linear form of equation (1) it is possible to obtain the line of closest fit to the experimental results by statistical calculations. Furthermore, the linear form of equation (1) permits extrapolation of results in either direction, with some confidence. This point is further discussed below.

(ii) From the coefficient A, the activation energy of the physico-chemical reaction controlling the induction period can be calculated. As a result, it is possible to obtain much more detailed information on the heat sensitiveness of initiators, and to correlate it with other properties, such as the sensitiveness to percussion (cf. Garner & Gomm (1931); Taylor & Weale (1932)).

Experimental details

The following briefly describes the set-up used: A mild-steel block, 3 in. diameter, 6 in. high, was maintained at a series of temperatures by varying the current through nichrome wire (approx. 40 Ω/230 V a.c.) wound on the outside of the block using alundum cement on thin asbestos paper as an insulating coating. In order to facilitate temperature control, the block was well lagged with asbestos cord, and rested on asbestos board.

An asbestos screen shielded the electrical fittings from undue radiation from the block, and from the effects of the explosions. The temperature was measured using a copper constantan thermocouple wedged into a thin hole near the axis. The e.m.f. of the couple was calibrated in the usual manner, at the melting point of ice and the boiling points of water, naphthalene, benzophenone and sulphur. Fluctuations in temperature did not as a rule exceed ±1° C.

Control of conditions of ignition

A bath of liquid metal filled an axial hole at the top end of the block. For temperatures considerably above 200° C, tinman's solder was used as the molten metal, but at lower temperatures, such as are required for mercury fulminate, Wood's metal was necessary. In order to obtain the most accurate determinations of ignition delays, it was essential to keep the axial hole sufficiently full by adding fresh solder from time to time. A little soya bean (or similar) oil and zinc chloride were added, to help to keep the surface clean. At the end of a day's use, the block was tipped to empty the molten metal. The hole was then reamered afresh at the beginning of a day's run, to remove any accumulations of oxide slag.

A little of the initiator whose ignition curve was to be determined was filled into a number of flat-bottomed aluminium no. 8 detonator sheaths, usually a dozen at a time. For most purposes, the quantity of initiator was judged by eye. Special experiments showed that the time of ignition was normally practically independent of the amount of substance taken, provided this exceeds a small lower limit, depending on the initiator and the temperature. At 5 sec. this lower limit was less than 0·003 g. for lead azide and in the neighbourhood of 0·003 g. for mercury fulminate (cf. Wohler & Martin (1917)). The induction period appeared to be more sensitive to the quantity of initiator used, towards the low temperature end of the ignition curve.

When the quantity of initiator had to be controlled more rigorously than can be estimated by eye, a filling plate device was used, similar to that used for filling initiators in factories (cf. p. 288).

A thin, flat plate of carefully smoothed brass or tinned iron was drilled with six holes of suitable diameter. This plate was pressed on to a flat Tufnol plate, and the holes were filled with the explosive to the level of the plate, using a long handled scoop for safety; the excess was removed by means of a rubber squeegee. On lifting the filling plate, six separate 'sandwiches' were obtained of the same thickness as the plate selected; these were brushed one by one on to a paper scoop, and transferred to detonator sheaths. The average weight delivered, and the deviations from the average, were determined by weighing the 'sandwiches' separately in a trial experiment.

Determination of the time to ignition

A detonator tube containing a filling was seized with long metal tongs and was plunged into the hole in the block containing molten metal. Sufficient metal was kept present to form an overflow pool round the tube when pressed in. The interval between the moment of insertion and the moment of detonation was timed with a stopwatch. Estimates from the thermal conductivity of aluminium, and the thickness of the detonator sheaths, showed that the time to reach a uniform temperature on the inside wall was of the order of 10^{-3} sec. The rate of heating up of the powdered explosive may be somewhat longer, but is probably less than the personal error in timing intervals of a few seconds, with a stopwatch reading to $\frac{1}{5}$ sec.

In order to eliminate accidental variations, the mean of twenty-four or more measurements of the induction period was taken at each temperature.

Figure 1 shows an ignition curve for crystalline lead azide (Service) (see also figure 2 and § (*c*) below).

In the case of lead azide and of mercury fulminate, the lines of closest fit for logarithmic equations of the type $\log Y = A/T + B$ (cf. figure 2) have been worked out by the method of least squares.

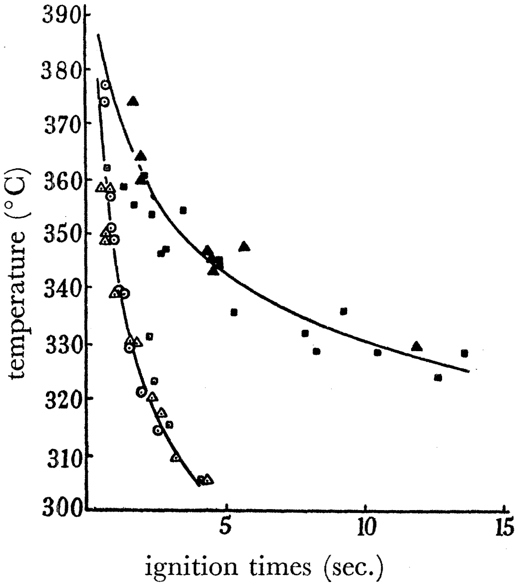

FIGURE 1. Ignition curves of Service and dextrin azides.
Service azide: ▲ lot 731, ■ lot 606. Dextrin azide: ⊙ lot D. 3, ⊡ lot A. 33, △ lot D. 783.

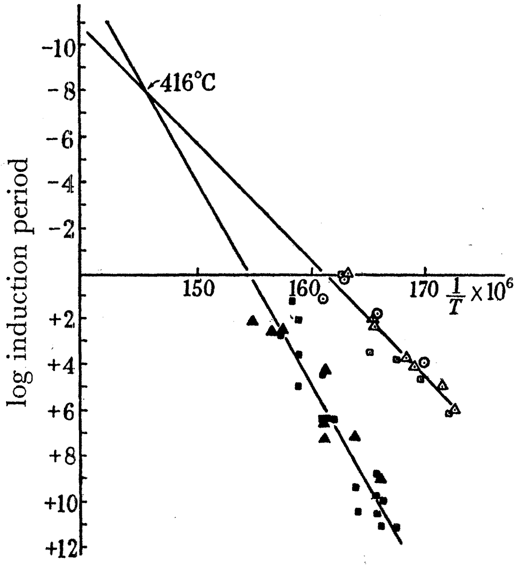

FIGURE 2. Logarithmic plot of ignition curves of Service and dextrin azides.
Service azide: ■ lot 606, ▲ lot 731. Dextrin azide: ⊙ lot D. 3, ⊡ lot A. 33, △ lot D. 783.

With the other initiators, the line of closest fit has been estimated graphically from a plot of $\log Y$ against $1/T$, using considerably fewer experimental determinations. Table 1 summarizes some of the data obtained at Swansea. The activation energy E in kcal./mol. is calculated from the equations

$$\log_{10} Y = E/4{\cdot}57\,T + B.$$

TABLE 1

initiator	activation energy (kcal./mol.) E	B	extrapolated ignition temperatures (°C) after delays of 5 sec.	10^{-3} sec.	10^{-5} sec.
lead azide (Service)	41·3	−13·97	343	551	735
mercury fulminate	25·3	−10·76	208	437	683
basic L.D.N.R.	22·9	− 7·90	308	747	1551
lead styphnate	61·6	−21·91	324	440	522
barium styphnate	35·4	−11·26	373	666	966
lead azide (dextrinated)	23·4	− 8·2	—	—	—

Note. Service azide consists of single crystals of PbN_6. Dextrinated azide contains rounded polycrystalline grains, cf. § (*c*) below.

Experiments on the sensitization of initiators by heat and photochemical action

In the above it was verified that when a small quantity of various initiators was maintained at a sufficiently high temperature, detonation normally occurred after a time Y sec. which can be related to the temperature of ignition $T°$ by the equation

$$\log Y = A/T + B,$$

where A and B are constants.

Obviously, during this induction period chemical reaction is occurring, which under favourable circumstances can build up a detonation wave. It was of interest to see whether chemical decomposition, produced either by thermal or photochemical means, insufficient to result in detonation, increased the subsequent heat sensitiveness of the initiator, i.e. whether the sensitization during the induction period had any permanence.

To test this point for thermal sensitization, constant amounts of Service azide were heated at a given temperature for a time insufficient to result in detonation. Each sample was rapidly chilled, stood, in some cases, for about an hour, and was then heated till detonation resulted at the temperature of test. The experimental data obtained are tabulated in table 2.

TABLE 2. THE EFFECT OF THERMAL SENSITIZATION OF LEAD AZIDE ON SUBSEQUENT IGNITION TIMES

temperature (°C)	preheating time (sec.)	subsequent time to ignition of sensitized azide (sec.)	total heating time (sec.)	one stage time to ignition (sec.)
330	3	4	7	6·6
324	7	—	13	11·5

On comparing the times to ignition of normal and preheated lead azide, it is obvious that lead azide is more or less permanently sensitized by the first heat treatment, the activation as measured by ignition times being approximately additive. Experiments to determine whether the heat treated crystals slowly revert to normal have not yet given conclusive results.

Brief reference to an analogous behaviour in the case of silver acetylide has been made by Muraour (1933*a*).

Photochemical activation of initiators

During the course of the above experiments it was observed that lead azide darkened on standing in the light. This indicates a photochemically induced decomposition which may alter the thermal sensitiveness of the initiator. The possibility that photochemical sensitization of initiators can occur was tested by exposing Service azide, dextrinated azide, and mercury fulminate to direct sunlight for a number of hours. The induction periods of these exposed initiators are tabulated in table 3.

Table 3. Photochemical sensitization of lead azide

temperature (°C)	normal induction period (sec.)	induction period of exposed azide (sec.)
373	1·6	0·9
361	1·8	1·3
347	4·4	2·9

Thus irradiation of Service azide results in a sensitization which is reflected in the shorter induction periods; irradiation has little effect on the energies of activation as determined graphically. Presumably it leads to the same kind of sensitization of the crystals as the heat treatment.

Dextrin azide

Irradiation of dextrin azide had no detectable effect on the thermal induction periods, though it increased the percentage of ignitions at 301° C from 0 to 30 %. This difference from Service azide may be partly due to a different mechanism of ignition for dextrin azide, as is discussed in § (*c*) below.

Mercury fulminate

Irradiation of mercury fulminate likewise shortened the induction periods though the sensitization produced is small.

Table 4. Photochemical sensitization of mercury fulminate

temperature (°C)	normal induction period (sec.)	induction period of exposed initiator (sec.)
197	7·0	6·3
181	22·2	19·7

These results showed that it is possible to sensitize initiators more or less permanently (by thermal and photochemical means). The mechanism of sensitization must be to produce regions of instability in the crystals, which facilitate subsequent decomposition. This suggests experiments to link up the thermal sensitization with sensitization to impact, and also to determine how long it persists in the crystals. These are further discussed in subsequent pages.

On the calculation of activation energies from observed induction periods

Calculation of the above values of E may be affected by the fact that samples may not heat up quite instantaneously in the method described.

If the samples take an appreciable time to heat up, the measured induction period will be longer than the true value at the same temperature. The activation energy is calculated from the slope of the logarithmic curve, i.e.

$$d\log Y/dT = -E/4{\cdot}57\,T^2.$$

Substituting $Y = Y_0 + K$, where K is the (constant) heating-up interval, and transforming

$$\frac{1}{(Y_0+K)}\frac{dY}{dT} = -E/4{\cdot}57\,T^2.$$

The value obtained for E when $Y_0 \gg K$, as has been assumed, is clearly larger than if K is an appreciable fraction of Y_0. It is unlikely, however, that K exceeds 0·1 sec. so that any error in E from this cause is small.

In calculating the line of closest fit, only those experimental induction periods are selected which lie between 1 and about 15 sec. For times shorter than 1 sec., the errors of timing are too large, and for times longer than about 15 sec. the duration is usually too sensitive to small uncertainties in determining the temperature of the metal bath. Shorter and longer times have, however, been plotted on the smoothed curve calculated from this limited range, and show good general agreement.

(*b*) Mechanism of detonation and failure. Behaviour of mixed initiators

When initiators are heated at a sufficiently high temperature, detonation normally occurs after a short induction period, which can be related to the corresponding temperature of ignition by the linear expression

$$\log Y = A/T + B$$

as shown in § (*a*) above.

Further experimental observations are described below, which have a bearing on the way in which detonation is built up by the co-operative action of a number of local reaction centres.

As the ignition temperatures were lowered, it was found that the behaviour of individual samples could be divided into two distinct groups.

(i) Samples which detonated after an induction period of magnitude equal to the value of Y calculated from the appropriate equation, allowing for statistical scattering.

(ii) Samples which failed to detonate even after extremely long times of heating. These may be referred to as 'failures'.

When the ignition temperature was lowered the percentage of 'failures' increased throughout a short temperature interval from 'ignition in all cases' to 'ignition in no case'.

The main features of this 'failure' phenomenon are conveniently described under the following heads:

(1) The quantity of the initiator may affect the length of the induction periods, and the percentage of failures.

(2) With constant amount of initiator, temperature T affects the percentage of failures for simple initiators.

(3) Dilution with inert material separates the grains, and affects the percentage of 'failures'.

(4) The failure of mixed initiators to detonate has also been investigated.

The main conclusions drawn from the results have a bearing on theories of the mechanism of building up to detonation on heating. They have also a direct practical bearing on the sensitiveness of initiators to flame and to impact. The 'failure' results obtained for mixed initiators give new information on the behaviour of compositions such as A.S.A. and 664, and demonstrate the value of constituents such as lead styphnate in improving the 'pick up' of lead azide in A.S.A. mixtures.

(1) *The dependence of induction periods and percentage failures on the mass of initiator used*

Using the experimental method described in § (*a*), data have been obtained for Service azide, mercury fulminate and lead styphnate. The results are set out in table 5.

TABLE 5. THE EFFECT OF AMOUNT OF INITIATOR ON THE INDUCTION PERIOD AND ON FAILURES

temperature (°C)	induction period (sec.)	induction period (sec.)
Service azide	smaller amount of 0·007 g.	larger amount of 0·02 g.
350	1·2	1·4
340	2·6	2·8
333	5·4	5·5
329	no ignition	7·7 (100 %)
319	no ignition	23·1 (100 %)
mercury fulminate	smaller amount of 0·005 g.	larger amount of 0·02 g.
202	3·0	3·0
190	8·2	6·6
184	18·5	13·7
lead styphnate	smaller amount of 0·007 g.	larger amount of 0·02 g.
300	14·9 (100 %)	14·0 (100 %)
290	45·5 (75 % ignitions)	42·7 (100 %)

From this table the following conclusions may be drawn.

Service azide

Variation in the amount of Service azide between the limits of 0·007 and 0·02 g. had no appreciable effect on the observed induction periods. Down to 0·007 g. at least, it is clear that the constants A and B in the equation $\log Y = A/T+B$ are independent of the amount of azide used. The incidence of 'failures' with 0·007 g. of azide at temperatures at which 0·02 g. of azide continues to detonate, showed that the amount of azide used determined the temperature at which failures begin, even when the constants 'A' and 'B' remain unaffected. There is thus a further condition for detonation, which involves both mass and temperature, and which is not expressed in the above equation.

Mercury fulminate

No 'failures' were recorded with this initiator, even at temperatures which corresponded to induction periods of several minutes' duration, so that the effect of amount on the percentage of failures has not been recorded. The amount of fulminate used had, however, an effect on the length of the observed induction periods, especially at low temperatures, when with decreasing amounts of fulminate the times to ignition increase. The constants 'A' and 'B' for mercury fulminate refer to experiments where sufficient initiator has been used to give induction periods independent of further increases of the quantity.

Lead styphnate

The behaviour of lead styphnate appeared to be intermediate between that of lead azide and lead fulminate.

From the above results it is clearly necessary to specify the amount of initiator to which any series of experiments relates. When this amount exceeds a small lower limit the induction period becomes less and less dependent on the amount of initiator. For smaller quantities of initiator the heat sensitiveness, as characterized by the induction periods and by percentage of 'failures', may depend on the amount of initiator used.

(2) *Relationship between the percentage of ignitions and temperature*

Using constant mass of initiator per filling, it has been found that as the ignition temperature is lowered, an increasing proportion of samples fails to build up to detonation if maintained at constant temperature. The change over from 100 to 0 % ignitions takes place over a short temperature interval, the limits of which are moved to higher temperatures by decreasing the amount of initiator used per filling. The temperature limits are tabulated below and the experimental data for Service azide, dextrin azide and lead styphnate are plotted in figure 3. In the region of temperature intermediate between the limits in table 6 the remarkable difference in behaviour between samples of equal weight, some of which build up to detonation and some of which fail to detonate, cannot be attributed to any very obvious differences of a chemical or physical nature. The most likely point of difference between samples, which behave so differently to thermal activation, is in the geometrical location of individual centres of chemical activity. It may be suggested that, in the powder, various crystallites are decomposing at more or less steady rates, once their decomposition has begun. In the case of samples of lead azide which fail to detonate, the fact that chemical decomposition has occurred can be clearly detected under the microscope by the blackening of the crystals, produced by the heating process. Detonation will not occur, apparently,

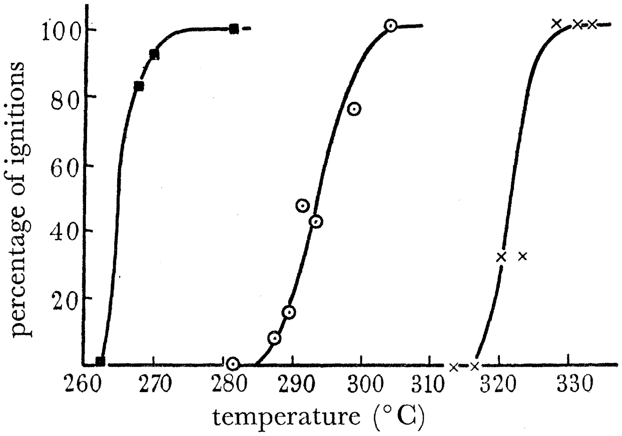

FIGURE 3. Percentage failure-temperature curves for simple initiators.
■ lead styphnate (0·01 g.); ⊙ dextrin azide (0·01 g.); × Service azide (0·02 g.).

TABLE 6. PERCENTAGE IGNITION. TEMPERATURE LIMITS FOR 100 AND 0 % IGNITIONS

initiator	amount (g.)	0 % ignitions below (° C)	100 % ignition above (° C)
Service azide	0·02	316	326
dextrin azide	0·01	285	305
lead styphnate (I.C.I.)	0·01	260	273

unless the energy liberated by chemical action within any given volume is sufficient to build up a detonation wave. If this view is justified, then dilution of an initiator with inert material, which decreases the amount of energy available in any specified volume, should appreciably modify the above limits of temperature for 100 and 0 % ignitions.

(3) *The dilution of initiators with inert materials*

(*a*) *Constant bulk of composition*

Owing to its use in certain compositions, powdered glass was used as diluent, to diminish co-operative action between the crystals of an initiator. The results plotted in figure 4 show the temperature dependence of the percentage ignitions of mixtures of lead azide (Service) and powdered glass (400 mesh). The total bulk of mixture was kept constant by using a filling plate device. It will be noted that as the dilution is increased, the failures set in sooner.

From these results alone, it would not be clear whether the increase in the percentage of failures at a given temperature, which is observed as dilution increased, is due to a decrease in the mass of azide, or to the effect of the inert diluent in separating the azide grains from one another.

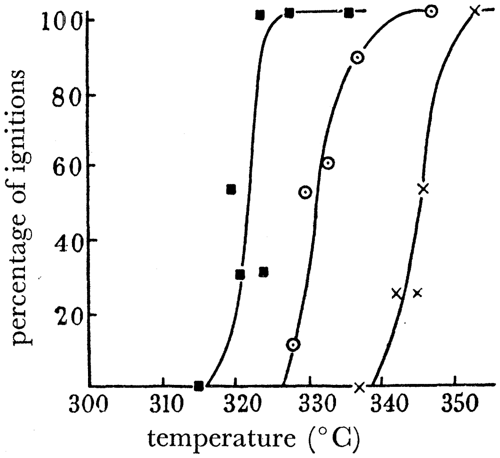

Figure 4. Effect of inert diluent on failure of Service azide, constant bulk of material.
■ 0·02 g. azide; ⊙ 0·005 g. azide + 0·004 g. glass; × 0·002 g. azide + 0·007 g. glass.

(*b*) *Constant mass of azide*

In order to discover whether the separation factor has an effect on the percentage of ignitions, an investigation of the percentage of ignition of glass-azide mixtures was carried out at constant temperature, in which the amount of azide was constant, but the degree of dilution was varied. Results are given in table 7.

Table 7. The dependence of percentage of ignitions on dilution

Temperature = 338° C. Mass of azide throughout = 0·007 g.

wt. fraction of glass	induction period of mixture (sec.)	induction period for 0·007 g. azide (sec.)	percentage ignitions
0·00	2·6	2·6	100
0·53	7·6	2·6	80
0·77	14·0	2·6	30
0·81	16·0	2·6	12

These results, which are plotted in figure 5, show clearly that with increasing separation of the crystals, the percentage of ignitions of glass-azide mixtures at constant temperature decreases. They also demonstrate that with increasing dilution, the mean induction period of those mixtures which build up to detonation increases as the dilution increases.

Data have also been obtained on the effect of inert diluents on the induction periods for lead styphnate. Admixture with up to 30 % of graphite does not appreciably modify the ignition curve of lead styphnate. The temperature-'failure' relationship for graphitized lead styphnate mixtures has not, as yet, been fully investigated.

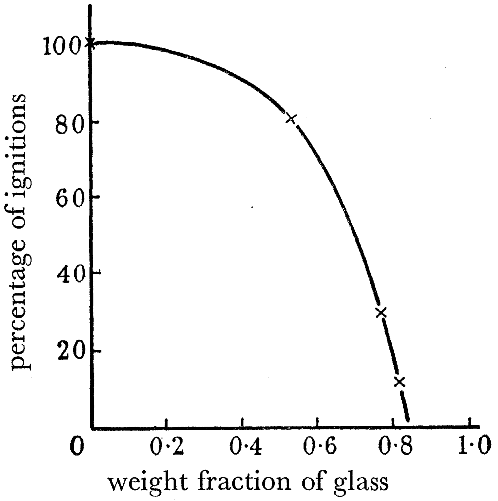

FIGURE 5. Effect of inert diluent on failure of Service azide, constant weight of material (0·007 g. at 338° C).

Further data on the effect of diluents are available from a comparison of mercury fulminate with the composite initiator (fulminate, antimony sulphide and potassium chlorate) 664, although in this case the diluent is not strictly inert. It was found that at all temperatures the induction periods for 664 are greater than those for pure mercury fulminate, this difference increasing as the temperature decreases. The calculated energies of activation for these two initiators are, however, practically identical.

$$E\,(\text{mercury fulminate}) = 25{\cdot}1\,\text{kcal.}\quad E(6\text{–}6\text{–}4) = 26{\cdot}6\,\text{kcal.}$$

Again, at quite low temperatures, the amount of 664 used must be increased above its normal value in order to get it to detonate. The violence of the detonation of both mercury fulminate and 664, at temperatures which correspond to induction times of the order of a few minutes, was noticeably less than their violence at higher temperatures, a fact which points to a slow thermal decomposition of the mercury fulminate during the induction period.

In view of the marked dependence of the length of the induction periods of mercury fulminate on its amount (see p. 211) it would not be evident from the above experiments whether the longer induction periods for 664 result from the smaller amount of fulminate, or from dilution. This point was settled by increasing the amount of 664 so that its fulminate content was equal to the amount of fulminate normally used in ignition experiments. Even with amounts of 664 containing the same weight of fulminate as used with this substance alone, longer times were obtained, showing that dilution increases the induction period.

Table 8. Dependence of induction period on dilution

Weight of fulminate 0·02 g. Weight of 664 0·06 g.

temperature (°C)	induction period pure fulminate (sec.)	induction period 664 (sec.)
193	5·7	9·3
183	14·4	20·7

The main conclusions from these experiments with inert diluents have special reference to Service azide. With this material it is clear that separation of individual azide crystals can prevent the setting up of a detonation wave, even though thermal decomposition proceeds normally. Thus, even with lead azide, detonation only results through the co-operation of a number of reactive centres. Both the incidence of detonation and the magnitude of the induction period depend on this co-operation.

(4) *Behaviour of mixed initiators*

In this section the induction time-temperature relationships and the failure of A.S.A. mixtures to detonate are described, and are contrasted with the corresponding data for the simple initiators composing the mixtures, i.e. lead azide and lead styphnate. The aluminium in A.S.A. probably does not react during the induction period.

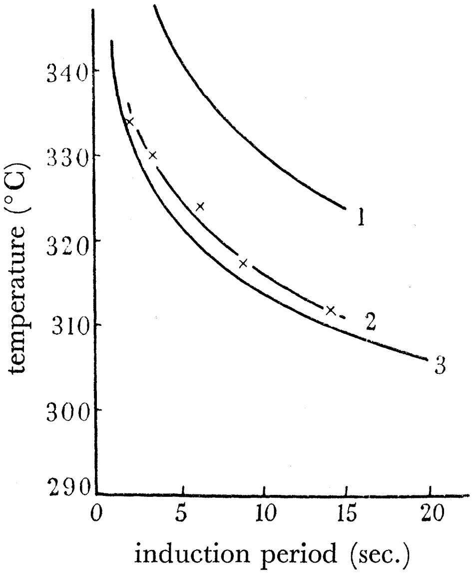

Figure 6. Ignition curve for Service A.S.A. and its components. 1, Service azide; 2, Service A.S.A.; 3, lead styphnate.

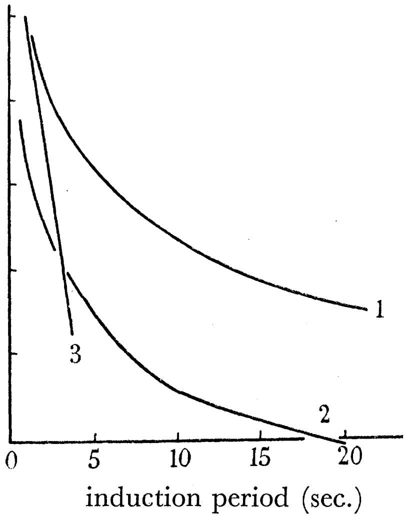

Figure 7. Ignition curve for commercial A.S.A. and its components. 1, lead styphnate; 2, A.S.A. (dextrin azide); 3, dextrin azide.

The induction period-temperature relationships for Service A.S.A. (crystalline azide, styphnate, aluminium), commercial A.S.A. (dextrinated azide, styphnate and aluminium) and for the three simple initiators concerned, may best be represented graphically as in figures 6 and 7).

Values of the activation energies of these mixed initiators calculated from the results are given below.

TABLE 9. ACTIVATION ENERGIES IN MIXED INITIATORS

composite activation energy	constituents	activation energy
Service A.S.A. 62·6 kcal.	Service azide	41·3 kcal.
	styphnate	61·6 kcal.
commercial A.S.A. 57·9 kcal.	dextrinated azide	23·4 kcal.
	styphnate	61·6 kcal.

Thus, though the induction period-temperature curves for A.S.A. mixtures lie between those for the two simple initiator components, their calculated energies of activation are of the same order as that for the *lead styphnate* component. This shows that in the build-up of detonation of A.S.A., the lead styphnate plays a dominant part in determining the rate of the processes leading to detonation, independently of whether Service or dextrin azide is the other component.

The temperature-failure curves for these mixed initiators are likewise of interest. They show that the addition of lead styphnate to lead azide prolongs the 'pick-up' of lead azide towards lower temperature. Especially is this the case with A.S.A. which contains Service lead azide (cf. figures 8 and 9).

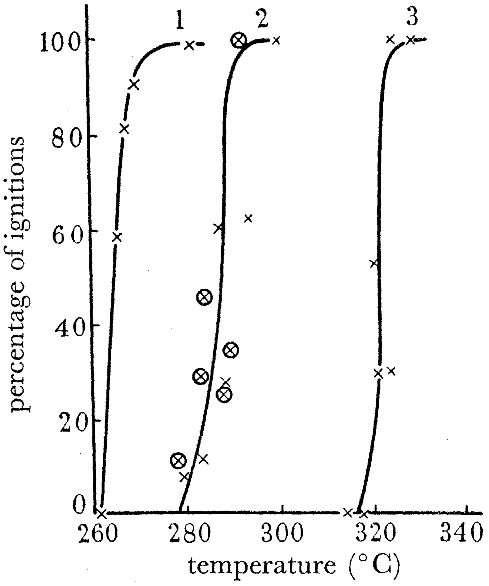

FIGURE 8. Temperature-failure curves for Service A.S.A. and its components. 1, lead styphnate (0·01 g.); 2, Service A.S.A. (0·01 g.); 3, Service azide (0·02 g.).

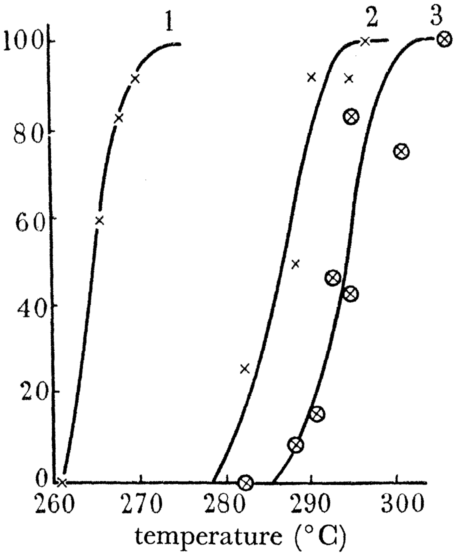

FIGURE 9. Temperature-failure curves for commercial A.S.A. and its components. 1, lead styphnate (0·01 g.); 2, A.S.A. (commercial components); 3, dextrin azide (0·01 g.).

Thus admixture of lead styphnate with lead azide extends to lower temperatures the range over which 100 % ignitions of lead azide occur, as a result of thermal activation. Considering only the azide constituent, this effect of admixture with lead styphnate produces the opposite result to admixture with inert materials.

The conclusion drawn from both the activation energies and the failure curves for A.S.A. is that the addition of lead styphnate improves the 'pick-up' of lead azide and extends its temperature range for detonation.

TABLE 10. TEMPERATURE LIMITS FOR 0 AND 100 % IGNITIONS, MIXED INITIATORS (see also figures 8 and 9)

Amount of initiator: approx. 0·01 g.

initiator	0 % ignitions below temperature (° C)	100 % ignitions above temperature (° C)
lead styphnate	262	271
Service azide	326	328
A.S.A. (Service)	275	296
lead styphnate	262	271
dextrin azide	283	304
A.S.A. (commercial)	270	296

(*c*) HEAT SENSITIVENESS AND STRUCTURE OF LEAD AZIDE (SERVICE AND DEXTRIN AZIDE)

Two main methods are currently used in manufacturing lead azide. In the case of Service azide, the risks in handling the product are minimized by manufacturing crystals of carefully controlled size, and by maintaining conditions during precipitation so that the occurrence of twinned crystals and feathery growths is reduced to a minimum. In the case of commercial lead azide, twinning and feathery growths are avoided by precipitating the lead azide in the presence of dextrin. About 3 to 5 % of dextrin by weight is co-precipitated with the lead azide.

The object of this section is to describe the marked difference in heat sensitiveness of lead azide manufactured in these two ways, and to correlate it with other properties of the initiators. From X-ray measurements, it is shown that lead azide is crystallographically identical in the Service and dextrinated products. An important difference is that the grains of initiator are single crystals in Service azide, and an agglomerate of fine crystallites in the dextrinated material.

From measurements of the ignition delay at different temperatures, it is shown that the ignition of Service azide is dependent on a mechanism with an activation energy of about 41·3 kcal. whereas dextrin azide requires a much lower activation energy, about 23·4 kcal./mol.

Some of the consequences of this difference are discussed in relation to the pick-up and initiating power of the two products.

Experimental details and results

X-ray investigations of structure

Figure 10, plate 5, shows photomicrographs of the two products. It will be noted that the grain size is about $0{\cdot}5 \times 10^{-2}$ cm. in both cases, but that the dextrinated grains are rounded. A few twins will be noted in the Service sample, in addition to well formed single crystals.

From the photomicrographs alone, it would not be clear as to what is responsible for the rounding in dextrin azide. More detailed information is given by X-ray photographs. Good film records are rather difficult to obtain, on account of the high absorption of lead salts. The pictures shown in figure 11, plate 5, were obtained using the powerful X-ray beam of Ni-filtered Cu $K\alpha$ radiation obtained from a 50 kW tube, loaned by courtesy of the late Sir William Bragg, P.R.S. The samples were spread in single layers of grains on cellophane and moistened with a solution of cellulose nitrate to fix the grains in position. Flat layers of lead azide formed in this way were mounted perpendicular to the X-ray beam to have the minimum absorption, and were oscillated through an angle of about $7\frac{1}{2}°$ on either side of the perpendicular during an exposure. The X-ray beam was collimated with a vertical slit system. Films obtained in this way, after about 15 min. exposure, show two main features (figures 11 *a* and *b*). (The films have been turned through 90° for convenience.)

(1) The powder rings have identical positions in the case of Service and dextrinated azide, showing that the samples are crystallographically identical.

(2) Service azide gave rings made up of discrete black specks whose size indicates that the single crystals in the powder were of the same magnitude as the grains of initiator. Coupled with the appearance of the photomicrographs, this definitely showed that in Service azide each of the initiator grains is generally a single crystal.

Dextrin azide on the other hand gave fine powder rings, which showed neither speck structure, nor appreciable broadening at the equator. This means that the grains of initiator were made up of fine crystallites whose size must be of the order of 10^{-4} to 10^{-5} cm. (cf. Wiedmann & Freyer (1940)).

If the average size of these crystallites is taken as about 5×10^{-5} cm. and the average size of a grain of initiator as 5×10^{-3} cm., there are roughly 10^6 of these crystallites per grain of dextrin azide.

Heat sensitiveness

The tendency to failures has been described in § (*b*) and only the ignition curves will be dealt with here. Plots of experimental induction periods compared with the curve of closest fit, are shown in figure 1 for various batches of azide. It will be seen that the ignition curve of Service and dextrinated azides are entirely different. At low temperatures, the time to ignition of the dextrinated sample is considerably shorter. The usual logarithmic plots are also given in figure 2 to show the sort of concordance obtained between different samples.

Table 11 presents data calculated by the method of least squares for a number of batches of azide manufactured in the two ways.

TABLE 11. IGNITION DATA FOR LEAD AZIDE

initiator	activation energy E (kcal./mol.)	B
Service azide	41·3	−13·97
dextrin azide	23·4	− 8·2

Experiments described in § (*c*) were carried out with the collaboration of Mr J. L. Copp and Miss J. Muir.

(*d*) FURTHER TESTS ON THE SENSITIVENESS OF LEAD AZIDE IN RELATION TO STRUCTURE (SERVICE AND DEXTRIN AZIDES)

The grains of Service azide are normally single crystals, whereas in dextrin azide each grain contains approximately 10^6 crystallites. This difference in structure of the grains may be expected to lead to differences in sensitiveness of the initiators.

The present section briefly records experiments to compare the sensitiveness of Service and dextrin azides, from various aspects.

Results show that:

(1) Dextrin azide is markedly more sensitive to heat, but only below about 416° C. Above this temperature Service azide is more sensitive.

From the above E and B constants, calculated delays at various temperatures would be:

TABLE 12. IGNITION DELAYS IN SEC.

temperature (° C)	Service azide	dextrin azide
300	(63)	(5)
330	10·5	2·0
360	2·0	0·8
390	0·46	0·3
420	0·12	0·16

The conclusion is that on exposure to comparatively low temperatures for fairly long intervals, dextrin azide is more sensitive to heat; extrapolation of the ignition data shows that at high temperatures Service azide 'picks up' to detonation in much shorter times.

(2) Both azides show about the same sensitiveness to percussion, in the ball and disk machine (cf. part IV).

(3) Service azide is markedly more sensitive to grit friction, both when rubbed between emery paper in a friction machine (part III (2)) and when mixed with emery powder and subjected to percussion in the ball and disk machine (part IV).

TABLE 13. EFFECT OF GRIT ON PERCUSSION SENSITIVENESS OF LEAD AZIDE (PERCENTAGE IGNITIONS)

Weight of ball 9 oz.

impact oz. in.	Service azide	Service azide plus 9 % emery	dextrin azide	dextrin azide plus 9 % emery
31	(2 %)	44 %	(2 %)	10 %
40	3 %	46 %	3 %	10 %

It will be seen that although dextrin azide is slightly sensitized by the admixture of emery, the sensitiveness of Service azide is increased to a remarkable extent.

Variations of climatic conditions (relative humidity 0 to 95 %) for both Service and dextrin azides did not appear to affect the sensitiveness to grit friction within the range of conditions indicated.

The contrast between the relative sensitiveness to heat, percussion and friction of dextrin and Service azides makes it unlikely that detonation depends on the same mechanism of activation in the various tests for sensitiveness. This point is again referred to in subsequent pages.

Preliminary tests showed that approximately the same proportion of ignitions was obtained under various conditions of impact, with different batches of Service and dextrin azides.

A more exhaustive and detailed comparison was also made between one batch of Service and one batch of dextrin azide, both considered to represent fair average products.

The impact figures for 50 % detonation using 50 trials at each of various heights, and a 9 oz. ball were

$$54\,\text{ft.lb.} \times 10^{-2} \text{ for Service azide,}$$
$$69\,\text{ft.lb.} \times 10^{-2} \text{ for dextrin azide.}$$

The sensitiveness of Service azide appears to increase rather more steeply with increased heights of fall, than in the case of dextrin azide.

Discussion

The results described in § (*a*) may be compared with data reported by previous workers (Garner & Gomm 1931; Taylor & Weale 1932; Wohler & Martin 1917; Muraour 1934; Garner & Hailes 1933). There is general agreement about the form of the temperature-induction period relationship, which has now been extended to a number of initiators not previously quoted in the literature. The experimental procedures in the present investigations differ, however, in some important details, from the work quoted above. For example, the results of Garner & Gomm were obtained with single crystals from 2 to 5 mg. in mass whereas the present data refer to a polycrystalline powder (see § (*c*)) in which the total mass of material is around 3 mg. but the individual crystals (in the case of Service azide) have masses of around 0·0005 mg.

The small masses used, and the spread of crystals of initiator in a thin layer at the bottom of the aluminium detonator sheath, minimize any tendency to 'self-heating' resulting from the thermal decomposition of the explosive, i.e. the explosive remains very approximately at the temperature of the bath right up to detonation. Again, detonation clearly involves some sort of co-operative action between the single crystals of initiator in the present experiments.

Section (*a*) suggests that since the activation energies controlling detonation in the *polycrystalline powder* are much the same as for the slow decomposition of single crystals of lead azide (47·6 kcal./mol. Garner & Gomm 1931) and mercury fulminate (29·4 kcal./mol. Taylor & Weale 1932) detonation is rendered more probable as a result of the slow decomposition. The sensitization of the crystals by pre-heating and cooling, and by exposure to light, are further evidence for this increased probability of detonation in partly decomposed crystals. Since the heat of decomposition has been dissipated in the pre-heating experiments, this gives further support to the view that the co-operative action leading to detonation is not merely 'self-heating'.

In order to visualize what happens in a detonation wave, it may be noted that with a detonation front travelling at 5×10^5 cm./sec., a single crystal of initiator such as lead azide of size 5×10^{-3} cm. as in the samples used, is traversed by the wave front in 10^{-8} sec. With the activation energies measured, the temperatures for delays of 10^{-5} sec. and 10^{-3} sec. have been calculated, in table 1, in order to illustrate how initiators with high activation energy such as lead azide and lead styphnate are likely to 'pick-up' in a shorter distance, from a detonation wave of given temperature, than initiators such as mercury fulminate. These calculations should not be regarded as more than illustrative, as a considerable extrapolation is involved.

Section (*b*) describes further experiments designed to elucidate the co-operative build-up of detonation from reaction centres which probably are located on different single crystals. The experiments on detonation and 'failure' indicate that detonation is not merely a culmination of decomposition, but that it involves the onset of a new regime which may or may not succeed in establishing itself after sufficient thermal decomposition has occurred to sensitize the crystals. Separation of the grains by inert material lessens the probability of successful co-operation, and when two initiators are mixed the crystals with highest activation energy appear to control the onset of detonation.

The statistics of detonation have been discussed (Andreev & Chariton 1934; Muraour 1934) on the basis of rather limited experimental evidence. Although the experiments in the present section extend the information available, rather more data are required to make real theoretical progress. It may again be noted that the observations of Garner & Gomm on single crystals are rather different from the present experiments which involve crystals of much smaller mass.

Section (*c*) describes an unexpected difference which was discovered between the onset of detonation in Service azide, which consists of small single crystals, and in dextrinated lead azide in which the grains consist of aggregates of crystals even smaller in size. X-ray powder photographs show that the crystal structure is the same in dextrinated azide as in single crystals of Service azide (Miles 1931; Sutton 1934). In spite of this, the activation energy controlling the onset of detonation is markedly lower for dextrinated azide.

Presumably this is associated with the much larger internal surface of the crystallites in dextrinated azide. From the X-ray data given,

$$\frac{\text{Surface of crystals per grain of dextrin azide}}{\text{Surface of crystal per grain of Service azide}} = \frac{(5\times10^{-5})^2\times10^6}{(5\times10^{-3})^2} = 100.$$

Although the precise nature of the two mechanisms of decomposition in Service and dextrin azide is not yet elucidated, the results of § (*b*) suggest that detonation will only be set up when a sufficient number of reaction centres in close juxtaposition are activated simultaneously. It seems likely that these reaction centres are formed on the surface of the crystals. The close approach of neighbouring crystallites in a single grain of dextrin azide (corresponding with a high density of packing), and possibly the influence of adsorbed dextrin on the activation energy required by surface decomposition, may explain why this initiator ignites more easily at low temperatures, than Service lead azide. Reference may be made in this connexion to the theories of Mott (1939) on the decomposition of metallic azides.

The heat pick-up of Service and dextrin azide is very different. At low temperatures, dextrin azide ignites more readily. By extrapolating the logarithmic ignition curves (cf. § (*c*)) it can be shown that above about 416° C (cf. figure 2) the ignition delays will be shorter for Service azide, so that at temperatures above this the heat sensitiveness is reversed. This must affect the comparative behaviour of Service and dextrin azides when used in a detonator.

In order to calculate how this factor influences the propagation of detonation, a velocity of 5000 m./sec. may be assumed for the detonation wave front. This means that a grain of initiator of 5×10^{-3} cm. is traversed by the wave front in about 10^{-8} sec. The activation energy controlling build-up of detonation may increase at the higher temperatures and higher pressures prevalent in the detonation wave. But so far as the activation energies of 41·3 and 23·4 kcal./mol. respectively, can still be used to compare the behaviour of Service and dextrin azides just in front of the detonation wave, it can be calculated that the temperature required to give a delay of 10^{-7} sec. for Service azide is about 800° C, whereas for dextrin azide the temperature is of the order of 4000° C. For a delay of 10^{-8} sec. these temperatures would be about 1500° and 25,600° C. It follows that the rate of pressure rise in front of the detonation wave will be steeper in the case of Service azide, since the chemical energy is released much more speedily.

If the delay to ignition really remains as large as calculated, in the case of dextrin azide, the whole pressure-time curve of the detonation wave would be modified, since the chemical energy would not be released in a time small compared with the rate of traverse of the crystals by the detonation wave front. The peak pressure should be smaller, and the duration longer.

This conclusion can probably be related to the markedly inferior initiating power of dextrin azide, when used in place of Service azide in standard fuse designs. Good initiating power appears to be associated with a steep rise to maximum pressure in the detonation wave front.

The marked difference in heat sensitiveness of Service and dextrin azide, together with their close chemical similarity, makes a comparison of other sensitiveness tests for these two initiators of particular interest. Knowledge of the activation energy for heat sensitiveness makes it possible to determine how far other sensitiveness tests merely involve the production of local hot spots, by mechanical means, and how far other activation mechanisms are operative. This aspect of heat sensitiveness is briefly described in § (*d*) and is referred to more fully in part III (4).

A point of considerable practical importance, which emerges from the experiments described, relates to the effect of grit on Service azide.

A point of theoretical interest arises from the fact that dextrin azide is more sensitive to heat below 416° C, so that if the action of grit friction is to be explained by the production of local 'hot spots' these must involve temperatures considerably above 416° C in the case of lead azide.

(2) THE EFFECT OF COMPRESSION ON THE SENSITIVENESS OF INITIATORS

By A. R. Ubbelohde and P. Woodward

(*Report first submitted by the Armament Research Department, January* 1945)

The sensitiveness of the following initiators has been compared when used loose, and when compressed up to 2300 kg./cm.

Crystalline Service azide (crystals 75×10^{-4} cm.).
Powdered Service azide (fragments 1 to 25×10^{-4} cm.).
Dextrinated lead azide.
Mercury fulminate.