
Part II. (2) The Effect of Compression on the Sensitiveness of Initiators

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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 $25,600^{\circ}\text{C}$. 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.

Sensitiveness to heat was measured by determining the induction period at various temperatures, and also by evaluating threshold temperatures below which no detonation was observed for various masses of initiators.

Tests were also made to see how far the action of flame, and of percussion, could be correlated with the action of heat on these initiators.

Compression reduces the induction period in all cases, but the values of E and B (see text) are differently affected in the case of different initiators. Compression also lowers the threshold temperature below which a given mass of initiator will not detonate. Thus in all cases sensitiveness to heat is increased by compression.

On the other hand, compression lessens the sensitiveness of mercury fulminate to flash and percussion, corresponding with the well-known phenomenon of 'dead-pressing'. If anything, compression increases the sensitiveness of lead azide to flash and percussion.

A new detonation mechanism has been observed for both service and dextrinated lead azides.

The experimental results throw further light on the build-up of the detonation wave in explosives. When the volume of explosive 'primarily' involved in the sensitiveness phenomenon is small, as is usually the case for initiators, the mechanism of build-up differs from the 'self-heating' mechanism which may overtake it with larger volumes of explosive.

A simple explanation is suggested for the 'dead-pressing' of explosives, which is to be expected when 'self-heating' is the mechanism controlling the build-up of detonation.

INTRODUCTION

Attempts to place standard tests on the sensitiveness of initiators [cf. parts II (1), III (2) and IV] on a more scientific basis referred to work on loose powders. Experiments described in the present section were primarily carried out to extend the information to compressed initiators, using the sort of bulk densities encountered in practice. The results have thrown additional light on the well-known phenomenon of 'dead-pressing' of mercury fulminate, which is shown to involve a lessened sensitiveness to external stimulus, but which is accompanied by increased sensitiveness to uniform heating. In addition, the 'threshold curve' giving the relationship between mass of initiator, and the temperature at which it will detonate, has been explored in some detail, since it gives valuable information on the 'trigger mechanisms' which control the onset of detonation under various circumstances.

The low temperature at which the detonation of lead azide was observed under some circumstances points to unsuspected risks in its use.

EXPERIMENTAL METHODS

Description of the initiators used.

'Service' lead azide was used from current production. Two lots, bulk densities 1.94 and 1.98 respectively, were tested. The average size of the crystals was from 8 to 11×10^{-3} cm. long, and 3 to 5×10^{-3} cm. broad. A few crystal clusters were observed under the microscope, but generally the azide was in the form of good single crystals (cf. part II (1) and plate 5).

Powdered 'Service' azide. Samples were ground to powder behind a suitable screen, using a highly polished chromium plated steel mortar illustrated in figure 12. A pestle consisting of a highly polished steel ball bearing was used. Precautions were taken to earth pestle and mortar, and to avoid grit. Approximately 250 mg. at a time were ground to particles ranging from 1×10^{-4} cm. to about 25×10^{-5} cm. using a rolling action of the pestle to avoid percussion.

Dextrinated lead azide was a commercial sample from I.C.I. Ltd., bulk density 2.40 g./c.c.

Mercury fulminate. A single lot was used from current production. It contained a great variety of crystal sizes, from large crystals 40×10^{-3} cm. long to small crystals about 1.3×10^{-3} cm. long. An average size was about 16×10^{-3} cm. long $\times 10 \times 10^{-3}$ cm. across.

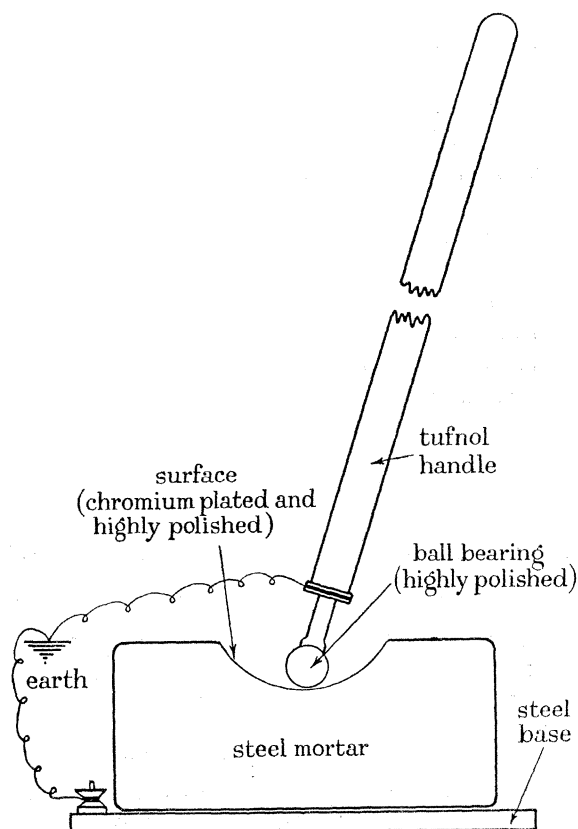


FIGURE 12. Polished chromium plated pestle and mortar for crushing lead azide.

Pressing methods

The initiators were weighed using the paper balance described in part III (3). A press was used with dead load up to 600 kg. on an area of about 0.25 sq.cm. The initiators were either pressed into no. 8 Briska aluminium detonator tubes (0.245 sq.cm. internal area of base, wall thickness of Al 0.038 cm.) or were prepared in the form of thin circular wafers 0.246 sq.cm. across for heat sensitiveness and 0.313 sq.cm. across for percussion sensitiveness. The wafers were from about 0.01 to 0.04 cm. thick according to the weights used. The thickness of the layers was measured with a (protected) micrometer depth gauge, and the bulk densities were calculated from the area and thickness, and the weights used. In the case of wafers, this gave a satisfactory measure of the density, but with initiators pressed into tubes special tests were made to allow for changes in the thickness of the metal after pressing.

Some practice was required before satisfactory wafers were obtained. The most important feature was to maintain a high state of polish on all the parts of the moulds and drifts in contact with the powder, and to use an aluminium sleeve (figure 13). Small quantities of 'Aquadag' were also used, and the state of the surface was inspected at intervals under the microscope.

Microscopic examination in polarized transmitted light of pressed wafers of lead azide, after wetting with methylene iodide, or phenyl diiodo-arsine, showed that a large proportion of the crystals in the loose powder remain comparatively unaltered in the compressed wafer, but were cemented together after pressing by a glassy amorphous powder presumably made up of azide crystals less than 10^{-4} cm. in size.

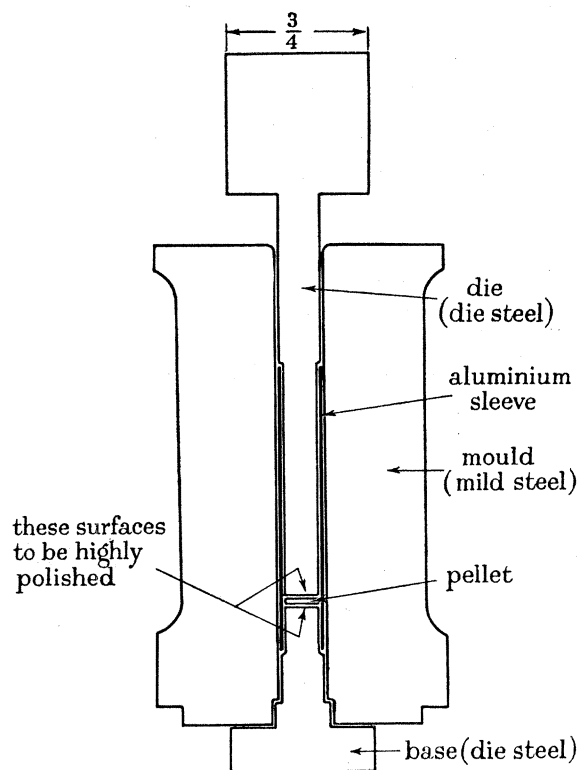


FIGURE 13. Mould and drift for pressing pellets of initiators.

(i) *Sensitiveness to percussion*

Comparative tests were made on layers of crystalline powder and on wafers of pressed initiators. 27 mg. of material was used for lead azide, and 17 mg. of mercury fulminate. The procedure of the test was as described in part IV except that a one-piece drift of hardened die steel was used in place of the composite drift incorporating a ball bearing (figure 14).

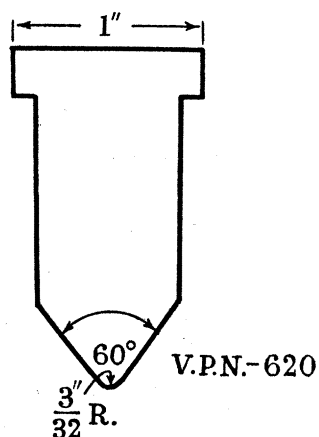


FIGURE 14. Die steel drift used in percussion tests. (Actual size.)

The lower brass disk between the initiator and the steel roller was also omitted, so that the initiator made direct contact with the steel surface on one side, and with the upper brass disk on the other.

Mercury fulminate. The effect of compression to a density of 3.5 g./c.c. (pressure 2300 kg./cm.²) is to desensitize this initiator to some extent.

Owing to the occurrence of partial detonations, not all the explosive is consumed in the ball and disk percussion test, and quantitative comparisons between loose and compressed fulminate are difficult, since they depend on the judgement of the operator.

To illustrate the effect of compression, the results have been classified by inspection of the roller bearings after the blow, as follows:

G = Complete detonation.

GP = Partial with most of the explosive consumed.

NP = Partial with faint but definite traces of some reaction.

N = No visible evidence of reaction.

With a 130 g. ball, the following were obtained in a total of 96 observations on each density of fulminate.

TABLE 14

height of fall (in.)	loose crystals density = 1.75 g./c.c.	pressed fulminate density = 3.5 g./c.c.
3	12 <i>G</i>	7 <i>G</i>
	17 <i>GP</i>	15 <i>GP</i>
	15 <i>NP</i>	22 <i>NP</i>
	4 <i>N</i>	4 <i>N</i>
3½	15 <i>G</i>	4 <i>G</i>
	14 <i>GP</i>	23 <i>GP</i>
	14 <i>NP</i>	21 <i>NP</i>
	5 <i>N</i>	—

Lead azide. This initiator does not give partials, which makes the percussion test more definite.

Comparisons indicate that compression to a density of 3.4 g./c.c. if anything may sensitize lead azide slightly, since the percentage of 'goes' for a given height of fall of ball increases by about 4 %.

The effect of powdering lead azide appears to be to sensitize it. At a height of 8½ in. (130 g. ball) powdering changes the probability of detonation from 50 to 70 %. The origin of this sensitization is being further investigated. It might be due to the somewhat lower bulk density of powdered azide (1.9 g./c.c.), though further compression to about 3.4 g./c.c. makes little difference to the percussion sensitiveness. Alternatively, the single crystals might be sensitized when they are broken.

On compressions of dextrinated azide to a density of 3.7 g./c.c. (pressure 2300 kg./cm.²) the probability of detonation increases by about 10 % at any height.

(ii) Sensitiveness to heat

Measurement of the induction periods were made by the methods described in part II (1) using a stopwatch reading to $\frac{1}{10}$ sec., and a temperature bath controlled to 0.25° C. In view of the probability scatter of the results, a more precise but more tedious method of timing

which had been devised was not used in the range of induction periods described below. Comparisons were made alternately on the loose and pressed initiators.

In the no. 8 Briska aluminium detonator tubes used ($1\frac{3}{4}$ in. long, $\frac{1}{4}$ in. external diameter) 5 mg. of initiator gave a more or less uniform layer between two and three crystals thick over the bottom. Smaller quantities tended to cluster in islands after tapping. It was not found

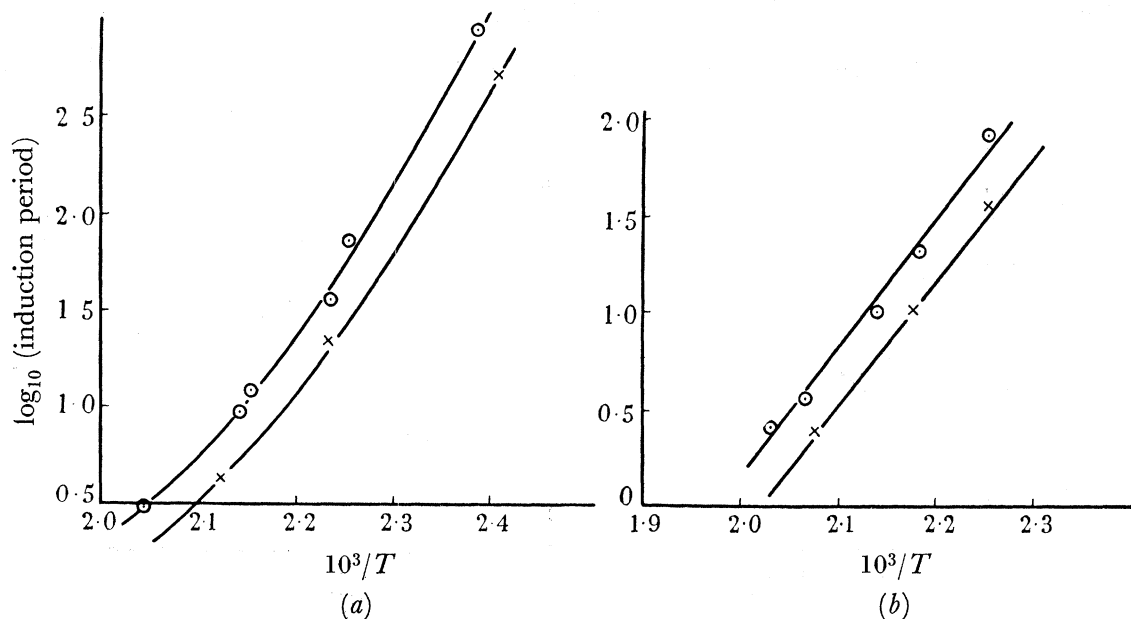


FIGURE 15. Effect of compression on induction period of mercury fulminate. (a) 20 mg.; (b) 9 mg. \circ loose, \times pressed (density 3.5 g./c.c.).

TABLE 15. SENSITIVENESS TO HEAT OF MERCURY FULMINE

Plots of $\log t$ against $1/T$ (cf. text)

induction period of loose crystals

mass (mg.)	activation energy (kcal./mol.)	'B' in equation $\log_{10} t = \frac{E}{4.57T} + B$
1	33.4	-14.38
2	33.4	-14.40
5	32.2	-13.86
9	29.2	-12.61
20	curve not linear (cf. figure 15)	

practicable to prepare wafers of less than 10 mg. but when these were dropped into the tubes much the same results were obtained as when the initiator was pressed *in situ*. Quantities smaller than 10 mg. were therefore pressed direct into the tubes.

The effect of compression of *mercury fulminate* to a density of 3.5 g./c.c. is to reduce the induction period to about half the value for loose fulminate, without changing the activation energy. Figure 15 illustrates the results for 9 and for 20 mg. As is shown from table 15, the induction period of loose fulminate changes slightly as the mass is increased, but pressing leads to much the same shortening whatever the mass compared (cf. figure 15, for the two masses).

From pressed fulminate the damage to the Al tubes on detonation is rather less than from loose fulminate.

The effect of compressing Service *lead azide* to a density of 3.4 g./c.c. is quite different from the effect on fulminate, since it leads to a reduction in activation energy from about 62 to about 40 kcal./mol. (figure 16). This difference between fulminate and azide is discussed below. The activation energy of powdered azide does not differ very much from that of the larger crystals (table 16), either in the loose or pressed form. It may be added that the activation energy of 62 kcal./mol. for loose Service azide as now determined is higher than for samples obtained in 1940 (part II (1) gives $E = 41.3$). This difference is being followed up.

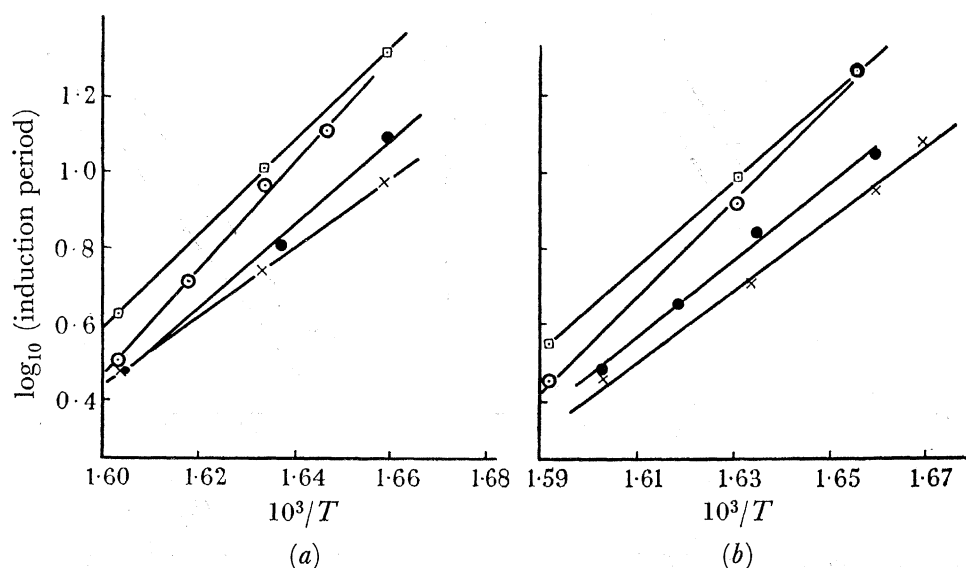


FIGURE 16. Effect of compression on induction period of lead azide. (a) 10 mg.; (b) 17 mg. \odot loose (density 1.98 g./c.c.), \times pressed (density 3.4 g./c.c.), \square crushed (density 1.9 g./c.c.) and \bullet pressed (density 2.6 g./c.c.).

TABLE 16								
E (kcal./mol.) (cf. figure 16)								
mass (mg.)	loose crystals		loose fragments		pressed crystals 2.6 g./c.c.		pressed crystals 3.4 g./c.c.	
	E	$-B$	E	$-B$	E	B	E	B
sensitiveness to heat of Service azide								
5	61.2	+21.0	61.2	+20.6	—	—	53.0	18.2
10	62.1	+21.3	56.7	19.3	49.4	16.9	39.3	13.3
17	57.1	+19.4	52.1	17.6	46.6	15.8	43.3	14.7
25	56.6	+19.2	—	—	—	—	—	—
dextrinated azide								
10	23.8	8.65	—	—	—	—	3.7 g./c.c.	
20	18.8	6.62	—	—	—	—	26.5	9.78
							23.8	8.65

With *dextrinated azide*, the effect of compression to a density of 3.7 g./c.c. is likewise to reduce the induction period. The scatter of results is rather large, but any change of E on compression does not exceed 5 kcal./mol. (cf. figure 17). The mean activation energy (21.3 kcal./mol.) agrees within experimental error with the value for other samples (part II (1)). Like Service azide, but unlike mercury fulminate, no difference in violence of detonation could be observed on compression.

Measurements of threshold temperatures

As previously recorded (part II (1)), below a certain temperature initiators 'fail' to detonate after the calculated induction period. This threshold temperature is a function of the mass of initiator present. With *lead azide*, the range of temperatures for 100 to 0 %

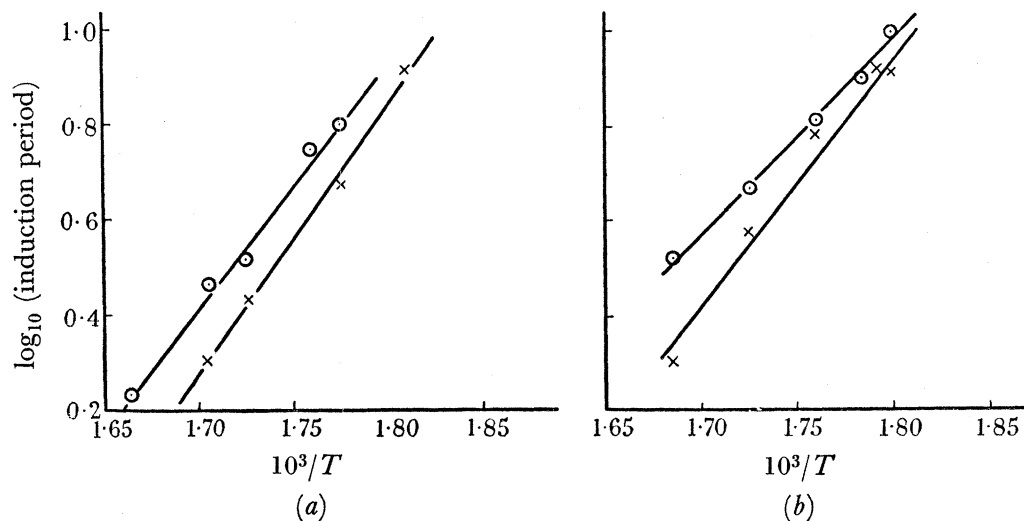


FIGURE 17. Effect of compression on induction period of lead azide (dextrinated). (a) 10 mg. \circ loose (density 2.4 g./c.c.); \times pressed (density 3.7 g./c.c.); E (loose) = 23.8 kcal./mol.; E (pressed) = 26.5 kcal./mol. (b) 20 mg. \circ loose; \times pressed; E (loose) = 18.8 kcal./mol.; E (pressed) = 23.8 kcal./mol.

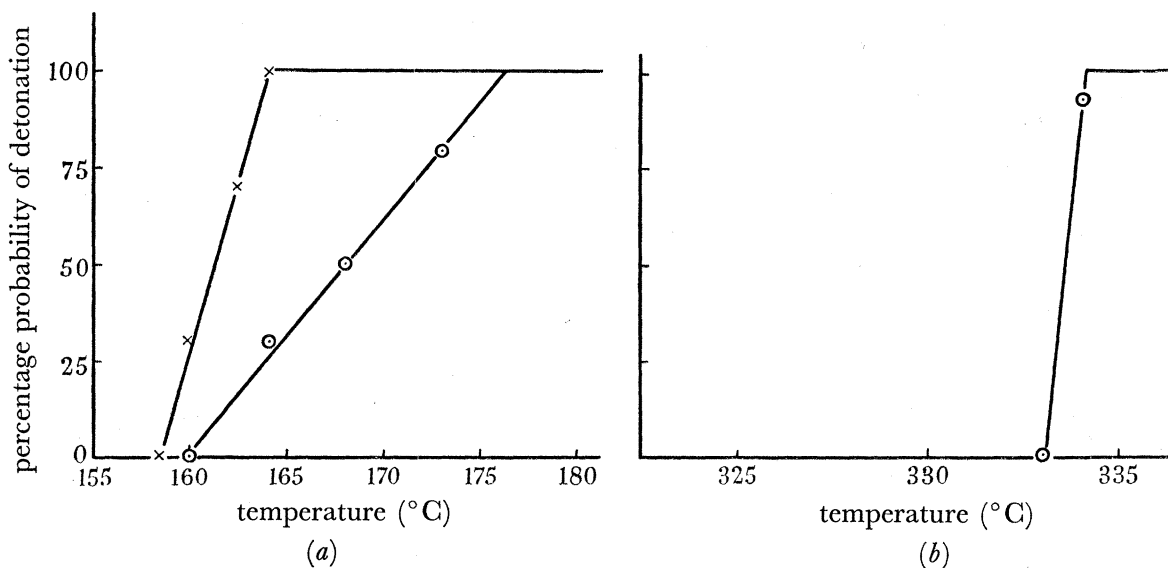


FIGURE 18. Breadth of threshold of detonation of mercury fulminate and lead azide. (a) Mercury fulminate (loose), \times 9 mg., \circ 5 mg. (b) Lead azide, 10 mg.

detonation is fairly narrow (figure 18), and threshold temperatures for various masses were determined within 1°C by searching for a bath temperature at which a proportion of failures was observed. With *mercury fulminate*, the range of temperatures for a given mass is rather broader. These ranges were determined in some detail with 5 and 9 mg. fulminate (figure 18) but in view of the labour required, the threshold for 50 % detonation

was estimated from measurements at a single temperature in the case of the other masses investigated.

With *dextrin azide*, the behaviour resembles that of mercury fulminate (figure 19). It was therefore necessary to determine the probability/temperature curve for a given mass, by using a series of temperatures. The 50% failure point was used as 'threshold temperature' for plotting as a function of the mass of initiator.

For all three initiators the threshold is lowered by compression, but in varying degree. Figure 20 shows the direct plot for both azide and fulminate and figure 21 for dextrinated azide.

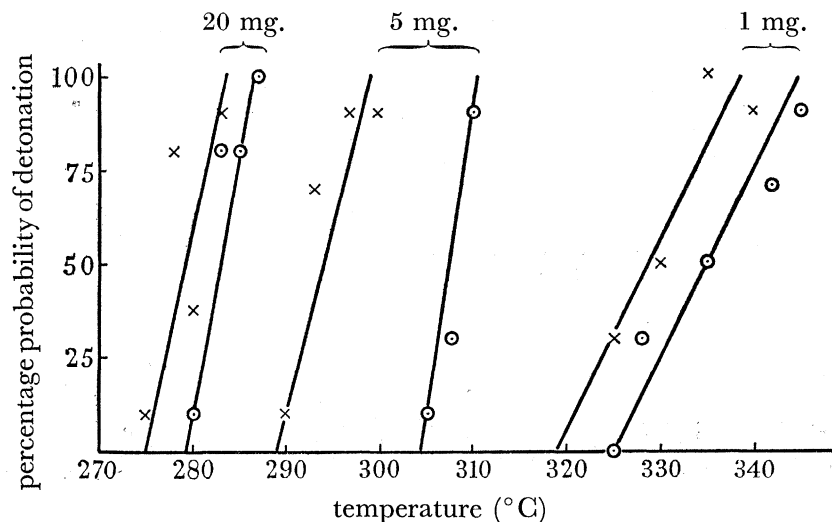


FIGURE 19. Breadth of threshold for various masses of dextrinated lead azide.
 ○ loose (density 2.4 g./c.c.); × pressed (density 3.7 g./c.c.).

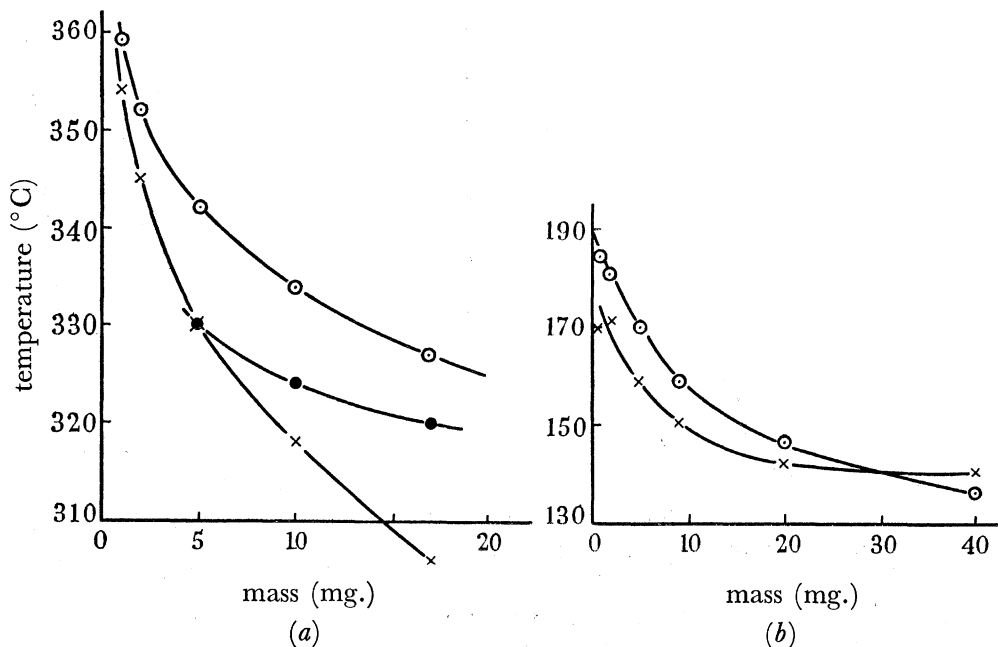


FIGURE 20. Effect of density on threshold temperatures of lead azide and mercury fulminate.
 (a) Lead azide: ○ loose crystals (B.D. 1.98 g./c.c.); × pressed (density 3.4 g./c.c.); ● powdered (1.9 g./c.c.). (b) Mercury fulminate: ○ loose crystals (B.D. 1.75 g./c.c.); × pressed (density 3.5 g./c.c.).

Breadth of threshold. The effect of mass on the breadth of threshold could not be conveniently investigated with lead azide, owing to the narrow range of temperatures involved. Data for 5 and 9 mg. of mercury fulminate are illustrated in figure 18. It will be noted that the breadth of threshold becomes narrower as the mass of explosive increases. A similar observation was made in the case of dextrinated azide—figure 19.

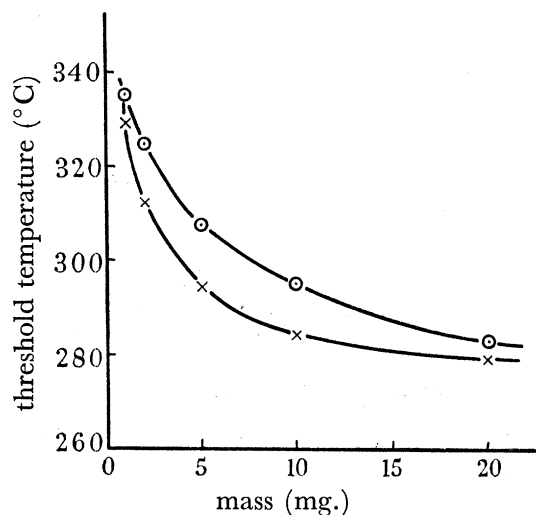


FIGURE 21. Effect of density on threshold temperatures of dextrinated lead azide.
 ○ Loose crystals (density 2.4 g./c.c.); × pressed crystals (density 3.7 g./c.c.).

'Slow' mechanism of detonation of lead azide. Around the threshold temperature, the 'normal' detonation mechanism, which is controlled by a process with activation energy 62 kcal./mol., fails to operate. But in the case of lead azide, a second much slower mechanism has been observed to 'take over' in a number of cases. These observations can be illustrated from data recorded with 10 mg. loose azide at 334° C (the nominal threshold temperature). Successive induction periods were, in sec.: 12.5, (58.0), 12.2, 12.5, (74.3), 12.8, (16.4), 13.6, (90.0), 12.0, 13.6, 13.1, (58.0), 13.0, failure, and so on.

In this series, the mean value of 12.8 sec. obtained from the figures not in brackets agrees with the Arrhenius curve for the normal process. But it will be seen that a second group of much longer times (in brackets) and one failure to detonate, were also observed.

Naturally, these longer times are only observed around the threshold, since at higher temperatures the normal mechanism never fails to detonate the mass before the slower mechanism can take over.

Measurements of the ultra-rapid detonation of lead azide

Over the range of temperatures measured (310 to 350° C) the induction period 'Y' for the normal detonation process of lead azide occupies several seconds, and gives an Arrhenius plot of $\log Y$ against the reciprocal of the absolute temperature.

But in addition to this 'normal process', a proportion of the samples (particularly in the case of pressed lead azide) detonate practically instantaneously on plunging into the temperature bath. This behaviour appears to be associated with a mechanism of build-up of detonation in lead azide which has been sensitized in some way. Up to the present, it has been observed at temperatures as low as 230° C with 5 mg. material, at which the 'normal process' fails completely. The sensitization involved is being further investigated.

The incidence of this abnormal 'instantaneous' detonation was observed in about 20 out of 700 tests, with Service azide. The same phenomenon was observed in 14 out of 500 tests with loose and pressed dextrinated azide.

Measurements of sensitiveness to heat after percussion

In order to throw further light on the mechanism of percussion sensitiveness, samples of lead azide which had failed to detonate in the ball and disk test (cf. part IV) were tested to see if their sensitiveness to heat had been increased as a result of the blow. The decrease of induction period observed for such samples did not exceed that due merely to the estimated compression of the powder by the blow, but the number investigated was rather too small to confirm this fully.

(iii) *Sensitiveness to flash*

Qualitative tests were made to compare the 'pick-up' from a flash, under various physical conditions.

The flash was produced from 15 cm. of Bickford fuse mounted vertically about 0.5 cm. above a layer of the initiator, supported on a steel roller bearing (figure 22).

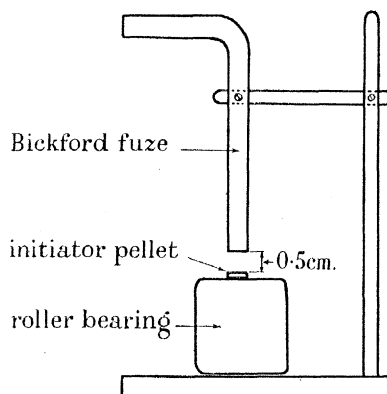


FIGURE 22. Apparatus for observing sensitiveness to flash of initiators.

Three physical conditions of the initiator were compared for noise and damage with loose powder under the same conditions.

- (a) Unconfined pressed wafers.
- (b) Pressed in copper 5 g. caps $\frac{3}{16}$ in. high.
- (c) Pressed in $\frac{1}{2}$ in. Al tubes (no. 8 Briska cut short).

In these three cases with *lead azide*, no distinction could be made between the violence of detonation on igniting the Bickford.

With *mercury fulminate* (a) unconfined heaps up to 50 mg. failed to detonate from the Bickford flash; (b) 50 mg. loose powder occasionally detonated when present in copper caps, but pressed wafers never did; (c) with the more complete confinement of the $\frac{1}{2}$ in. Al tubes, detonation could be obtained both with loose and with pressed wafers, but the violence of damage was always much greater with the loose powder.

This qualitative difference between azide and fulminate in their response to a flash, when compressed, corresponds with the phenomenon of 'dead-pressing' of fulminate.

DISCUSSION

(i) *Examination of the self-heating mechanism applied to initiators*

As has been previously pointed out (part II (1)), it is highly unlikely that the detonation of initiators in small quantities occurs by the 'self-heating' process discussed for high explosives by Rideal & Robertson (1944). The present series of results permit a quantitative analysis of the phenomena over a wide range of temperatures.

According to Frank-Kamenetsky, the necessary condition for detonation by self-heating of an infinite slab of explosive is $P > 0.88$, where

$$P = (d^2W/k) A e^{-E/RT_0} \cdot (E/RT_0^2) > 0.88. \quad (1)$$

In equation (1) $2d$ = thickness of layer,

W = heat of reaction per unit volume,

k = thermal conductivity of the explosive,

$A e^{-E/RT_0}$ = rate of decomposition,

E = activation energy controlling the rate of decomposition,

T_0 = initial temperature before 'self-heating' is appreciable.

In attempting to apply this equation to initiators, the two physicochemical quantities about which least is known are the thermal conductivity k , and the constant A .

The cylindrical wafers of initiator actually used are only $\frac{1}{4}$ in. diameter, so that the above condition for detonation of an infinite slab is more favourable to self-heating than that which actually applies in practice. Probably for the practical case $P > 3$, but since the aim is to test whether self-heating can account for the thermal detonation of initiators, the most favourable case of $P > 0.88$ is plotted in figure 23.

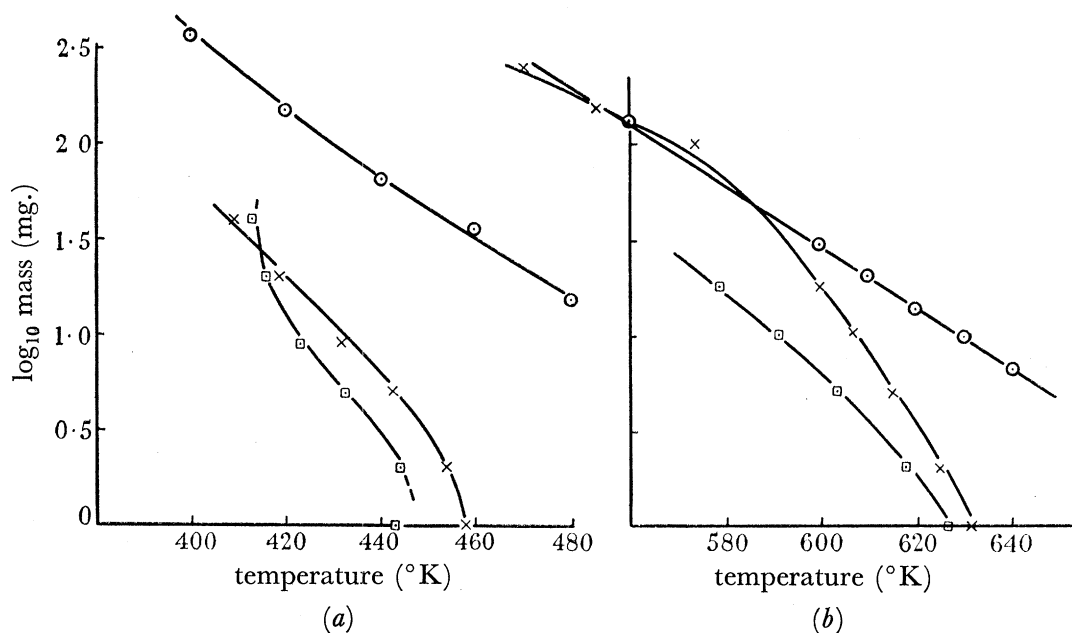


FIGURE 23. Theoretical and observed curves showing \log (mass) and threshold temperatures. (a) Mercury fulminate: \odot theoretical, \times loose and \square pressed (obs.). (b) Lead azide: \odot theoretical curve ($f = 1$), \times loose crystals (obs.) and \square pressed azide (obs.).

By comparison with other lead salts, k is of the order 1×10^{-3} c.g.s. units, but until direct measurements are available on loose and pressed initiators, we must write $k = f \times 10^{-3}$ c.g.s. units, where the factor f may range over several units, and is likely to be greater when the azide is compressed.

To evaluate A , we follow Rideal & Robertson (1944) and assume a first order reaction controlling decomposition and a half life only twice the induction period t , i.e.

$$A e^{-E/RT} / \log_e 2 = \frac{1}{2}t.$$

For lead azide, when $T = 624^\circ \text{K}$, $t = 3.2 \text{ sec.}$, $E = 61.2 \text{ kcal./mol.}$ for 5 mg.

Then $A = 0.1083 \times e^{49.3} = 2.79 \times 10^{20}$ and the Frank-Kamenetsky condition becomes

$$P = \frac{d^2 W}{k} \left[0.1083 e^{49.3} \times \exp \left(-\frac{61,200}{1.99 T_0} \right) \right] \frac{61,200}{R T_0^2} > 0.88,$$

where T_0 is the bath temperature.

But if m is the mass of azide in mg., since the area of cross-section of the tubes is 0.246 sq.cm. and the bulk density of loose azide is 1.98 g./c.c. ,

$$d = \frac{m \times 10^{-3}}{0.246 \times 1.98 \times 2} \text{ cm.}$$

$W = 721 \text{ cal./c.c.}$ (cf. p. 286). Taking the factor f as unity in the thermal conductivity this gives as the equation relating the bath temperature with the mass for the threshold of detonation

$$m = B T_0 e^{-N}, \quad (2)$$

where $B = 1.87 \times 10^{-2}$ and $N = 24.65(1 - 624/T_0)$.

Equation (2) gives the following values for lead azide:

TABLE 17

temperature (°K)	m (mg.)	$\log_{10} m$
560	129.8	2.1133
600	29.97	1.4767
610	20.05	1.3021
620	13.60	1.1335
630	9.327	0.9697
640	6.471	0.8110

These values are plotted to give a theoretical 'self-heating threshold curve' in figure 23. If the assumptions about f or A are numerically incorrect, this will lead to a displacement of this curve, which is likely to be upwards.

When the bulk density is increased, this affects W , and the thermal conductivity k . It also affects the relation between d and m . No attempt is made to draw the curve for the higher bulk density, pending measurements of thermal conductivity of loose and pressed azide.

For *mercury fulminate* k is taken the same as for lead azide, pending actual measurements.

At 221°C , 5 mg. detonate in 2.3 sec. and $E = 32.2 \text{ kcal./mol.}$ Making the same assumption about the reaction velocity as for azide, $A = 0.1507 \times e^{32.7} = 2.44 \times 10^{13}$ and with a bulk density of 1.75 g./c.c. and a heat of reaction $W = 717.4 \text{ cal./c.c.}$ (cf. p. 286.)

$$m = B T_0 e^{-N},$$

where $B = 1.933 \times 10^{-2}$ and $N = 16.35(1 - 494/T_0)$.

This gives the theoretical curve for the threshold for self-heating to detonation of fulminate plotted in figure 23.

TABLE 18

temperature (°K)	m (mg.)	$\log_{10} m$
400	360.2	2.5566
420	144.7	2.1607
440	63.28	1.8013
460	29.88	1.5450
480	15.01	1.1762
500	7.916	0.8985
520	4.432	0.6466
540	2.602	0.4153

As in the case of lead azide, this curve may be displaced parallel to itself on account of incorrect numerical assumptions, and will also be displaced when the bulk density changes.

For 10 mg. dextrinated lead azide, when $T = 579^\circ \text{K}$, $t = 3.3 \text{ sec.}$, $E = 24,100 \text{ cal./mol.}$

Hence $A = 0.1050 \exp(20.91) = 1.258 \times 10^8$.

$$P = \frac{d^2W}{K} \left[0.1050 e^{20.91} \times \exp\left(-\frac{24,100}{1.99T_0}\right) \right] \times \frac{24,100}{1.99T_0^2} > 0.88,$$

where T_0 is the bath temperature.

Now, area of pellet = 0.246 sq. cm. , and bulk density of dextrinated lead azide = 2.4 g./c.c. , so

$$2d = \frac{m \times 10^{-3}}{0.246 \times 2.4} \text{ cm.},$$

where m is the mass of azide in mg. In the absence of direct experiments and in view of the similar crystal structure, W is calculated on the basis of the bulk density and Garner's value for lead azide crystals; i.e. $W = 874 \text{ cal./c.c.}$ (cf. p. 286) and taking $f = 1$ in the thermal conductivity this gives, as the equation relating the bath temperature with the mass for the threshold of detonation, by self-heating mechanism

$$m = BT_0 e^{-N}, \quad (2.1)$$

where $B = 3.323 \times 10^{-2}$ and $N = 10.45(1 - 579/T_0)$.

Equation (2.1) gives the following values for dextrinated lead azide:

TABLE 19

temperature (°K)	m (mg.)	$\log_{10} m$
520	56.59	1.7528
540	38.22	1.5823
560	26.54	1.4244
580	18.93	1.2773
600	13.85	1.1413
620	10.34	1.0143

These curves are plotted to give a theoretical 'self-heating' curve in figure 24. Curves for Service azide are also given for comparison.

(ii) *Comparison of self-heating thresholds with experimental data for initiators*

Comparison may be made with the experimental threshold temperatures for the detonation of various masses, which are plotted in figures 23 and 24 for both loose and pressed initiators.

It will be seen that in the case of lead azide, the threshold for *large masses*, agrees with the self-heating curve. The exact agreement must to some extent be regarded as fortuitous, until thermal conductivity data are available. But the fact that for large masses the experimental curve assumes the same slope as the self-heating curve suggests that this mechanism of detonation takes over when the amount of initiator is large. On the other hand, for small

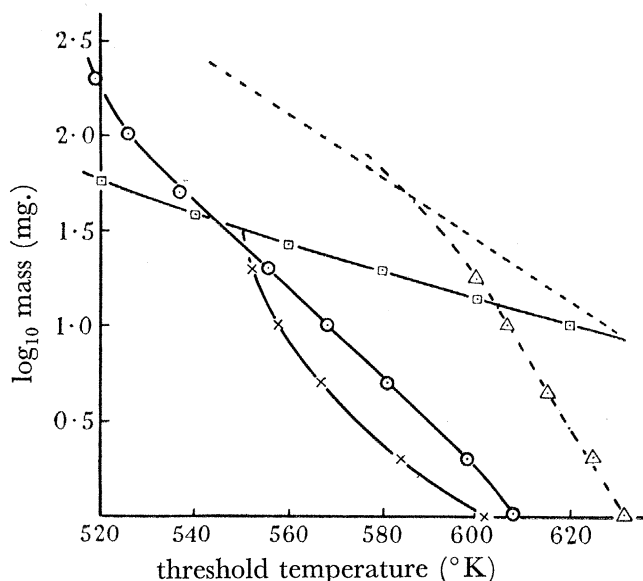


FIGURE 24. Theoretical and observed curves showing log mass and threshold temperatures of dextrinated lead azide. \square Theoretical curve ($f = 1$); \circ loose (obs.); \times pressed (obs.). Comparison curves for Service azide --- theoretical; - · - · - practical.

masses of initiator, the observed threshold temperature falls away more and more below the self-heating value. Since the curve is logarithmic, this indicates quite clearly that *small masses of initiator, when heated, detonate well below the self-heating threshold temperature, and cannot involve self-heating as the controlling mechanism.* This behaviour is also shown by dextrinated azide. Unlike service azide, the experimental curve shows no signs of bending over to the self-heating slope at the upper end of the range of masses investigated (1 to 200 mg.). This may be because the much smaller activation energy of dextrin azide prolongs the mechanism of initiation which applies to small masses. The self-heating mechanism will only become operative when it requires shorter times than the mechanism applying for small masses.

Similar remarks apply to mercury fulminate, where the slope of the experimental curve approximates to that of the self-heating threshold curve for large masses, but not for small masses. Since the characteristic difference between initiators and high explosives lies in the much smaller minimum volume of initiators which will detonate (cf. part III (4)), it can be said that the sensitiveness of initiators does not normally involve self-heating as the mechanism controlling the onset of detonation.

Comparison of pick-up sensitiveness of Service and dextrinated azides

As was stated above, with dextrinated azide the threshold region for detonation occurs over several degrees of temperature, compared with a spread of only one or two degrees for Service azide. A similar evidence of statistical spread is shown in individual measurements of the induction period. When temperatures are selected so as to give induction periods of about the same duration, table 20 gives the comparative fluctuations observed.

TABLE 20

Service azide, 10 mg.					dextrinated lead azide, 10 mg.						
350° C	3.0	2.9	3.3	3.0	3.5	300° C	3.4	4.9	3.7	3.7	2.9
	3.2	3.3	3.4	3.1	3.0		3.4	3.1	3.3	3.2	3.1
	mean				3.2		mean				3.5
	max. error				± 0.3		max. error				+ 1.4 - 0.6

This difference is probably due to the superior pick-up of Service azide compared with dextrinated azide.

The *threshold temperatures* for dextrinated azide lie below those for Service azide throughout the region of temperatures investigated, but the curves may cross outside this region. As has been previously pointed out (part II (1)), the temperatures corresponding with pick-up sensitiveness lie above the inversion point of about 400° C, above which induction periods for Service azide are shorter than for dextrinated azide. Allowance for this crossing over must be made before attempting to correlate pick-up with sensitiveness to heat.

The fact that *compression increases sensitiveness* to percussion and heat is in contrast with a number of high explosives which are less sensitive at higher densities, and appears to be associated with the special pick-up mechanism of initiators.

It is of interest to note that the Frank-Kamenetsky relation between threshold temperature and mass, may be written in the form

$$m = 2a \sqrt{\left(\frac{k\rho}{AW_0} \cdot e^{E/RT} \frac{RT_0^2}{E} \cdot 0.88 \right)},$$

where a = area of cross-section of the tube, ρ = density of pellet, and W_0 = heat/unit mass.

Since the value of k is almost certainly increased by increasing the density, an increase in density should normally *raise* m for the same T_0 , if the self-heating mechanism operates.

This is the opposite to the effect observed in practice (see figures 23 and 24) for compression of the lead azides, and is further evidence for their special pick-up mechanism. It is, however, in line with the 'dead-pressing' observed with high explosives, where detonation almost certainly involves the self-heating process. According to the above equation, in a given sensitiveness test, the mass of explosive in the 'hot spot' must be increased to ensure detonation when the density is increased. This agrees with the well-known desensitization of high explosives on compression, and with the desensitization of mercury fulminate on 'dead-pressing'. [For an alternative explanation of 'dead-pressing' see Andreev (1941).]