PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Part III. (4) Mechanical and Thermal Processes of Initiation

A. R. Ubbelohde

Phil. Trans. R. Soc. Lond. A 1948 **241**, 280-286
doi: 10.1098/rsta.1948.0019

greater than that of organic high explosives. Breaking of the crystals might be expected to have an effect of initiating detonation when the lattice energy is high (cf. I).

The deadening action of liquids might be due either to their lubricating effect, lessening mechanical breakage, or to their damping down of marginal initiation starting at one or two crystals. From the fact that lead azide is comparatively less desensitized than the other initiators, and is not easily wetted by the aqueous solutions tested, the lubricating effect would appear to be more important than the damping down of any detonation started locally. On the other hand, if only small quantities of liquid are sprayed on, the initiation which is observed at dry patches does not spread, giving evidence of the damping down of marginal initiation.

(4) MECHANICAL AND THERMAL PROCESSES OF INITIATION

By A. R. Ubbelohde

(*Report first issued by the Armament Research Department*, 26 *November* 1943)

The sensitiveness of initiators to mechanical action has been examined in relation to heat, for lead azide, mercury fulminate, and in some cases lead styphnate, in order to see how far mechanical action could be equated with local heating.

Previous information on *mechanical sensitiveness* has been extended by measuring friction sensitiveness with grit of varying hardness, and by varying the melting point and hardness of the rubbing surface. The percussion sensitiveness has been compared using as confining metals nickel and tin, as well as the brass normally used.

The relation between *sensitiveness to heat* and *sensitiveness to mechanical action* has been investigated by determining the percussion sensitiveness of initiators partly sensitized by heating, and also by studying the delay to ignition as a function of the quantity of initiator accessible to the growth of the detonation wave. In these tests, lead azide was found to build up to limiting detonation conditions in considerably smaller quantities than mercury fulminate.

It is found that grit does not appreciably sensitize initiators to friction unless it is harder than about 3·5 to 4 on Moh's scale, and unless the rubbing surfaces have a high hardness and melting point. It is confirmed that mercury fulminate is not appreciably sensitized by grit.

Percussion sensitiveness depends to some extent on the confining metal used, being rather lower for the metals of lower melting point.

Extension of previous observations confirms that if lead azide or mercury fulminate is heated during half the induction period at any one temperature, and then cooled, these heat sensitized initiators will detonate in approximately half the normal time at any other temperature. However, sensitization of initiators to heat in this way has only a secondary effect on their sensitiveness to percussion.

These observations together with previous work indicate the following relationships between mechanical and thermal sensitiveness.

(i) In *grit sensitiveness*, the mechanical action involves mainly the formation of 'hot spots' between the grit and a hard surface. These hot spots acting on the initiator generate the detonation wave more easily with lead azide than with mercury fulminate, so that lead azide is more sensitive to grit than mercury fulminate. Other mechanical effects may be present in a subordinate degree.

(ii) *Percussion sensitiveness* appears to be more complex, and may involve a tribo-chemical 'trigger' reaction as well as the formation of hot spots through friction. Tribo-chemical or other mechanical 'trigger reactions' are only indirectly related to the sensitiveness to heat since they involve a more direct transfer between mechanical energy and activation energy, than is involved if the mechanical energy is first converted into heat.

Introduction

Mechanisms of sensitiveness of initiators

All mechanisms of sensitiveness of explosives involve the release of free energy, by trigger mechanisms setting in train subsequent processes, which can under suitable conditions be integrated into a stable detonation wave.

The experiments described below give fresh information on two problems in the sensitiveness of initiators:

(i) which 'trigger mechanisms' are involved in mechanical operations, such as friction between smooth surfaces, grit friction or percussion;

(ii) how the energy released builds up into a detonation wave.

Possible trigger mechanisms with explosives

The first process of all in the change from (metastable) molecules of explosive to the final reaction products is conveniently graded according to the volume of explosive taking part. A plausible classification in decreasing order of such volumes includes

(*a*) *Sympathetic detonation*, which involves the simultaneous activation of comparatively large quantities of explosive by the pressure pulse, as the first process.

(*b*) *Rifle bullet impact*, which probably depends on the heating of a layer of explosive through stopping of the fragment or bullet, as the first process.

The dimensions of this layer are not known accurately, but its area is likely to be of the same order as that of the fragment or bullet itself.

(*c*) *Grit friction*. This involves the formation of 'hot spots' which heat layers of explosive of the same order of size or smaller than the grit particles. The decomposition of the explosive must liberate sufficient heat for 'self-heating' to set in and develop into detonation (cf. parts III (1), (2) and (3)).

(*d*) *Action of heat*. When initiators are heated, there is evidence that reaction centres are formed in the crystals, which may involve only a few molecules at first. Decomposition branches from these centres, and detonation ensues when the energy released at various parts of the mass of crystals can build up into a detonation wave. Once the detonation wave is formed, it propagates through adjoining layers of initiator, by a mechanism analogous with (*a*) (cf. part I).

(*e*) *Tribo-chemical action*. Types of sensitiveness are known in which it is difficult or impossible to ascribe the formation of the first reaction centres to random molecular motion (i.e. to the action of heat). In such cases the trigger mechanism has been termed 'tribo-chemical'. The suggestion is that a few chemical bonds are activated by some direct mechanical action, such as the breaking of crystals. Unfortunately most of the evidence is of a negative character.

Tribo-chemical action has been assumed by Taylor & Weale (1932) to explain their results on impact sensitiveness. Some kind of mechanical action may also be operative in the Rotter impact test, and in the percussion test (cf. part IV). Owing to the difficulty of standardizing direct mechanical action on crystals, details of tribo-chemical action are difficult to place on a firm experimental footing.

The bearing of these mechanisms on the sensitiveness of initiators can be discussed in the light of the following experimental results.

Experiments on friction sensitiveness

For these experiments grit of size between 100 and 200 mesh was mixed with the various initiators listed in tables 45 and 46, and rubbed between the surface indicated, in the friction machine (cf. part III (2)).

Preliminary experiments (cf. table 46) showed that with the size of grit used limiting sensitization was obtained for addition of 10 %. This quantity was mixed with the initiators in table 45, using a paper scoop to turn the mixture over and over.

Handling of the sensitive compositions was made possible using previously described techniques. Ten trials at each of ten velocities from 5 to 14 ft./sec. were summed. The results are recorded in table 45.

Table 45. Effect of grit hardness on friction sensitiveness of initiators. Percentage initiations in a standard run (cf. part III (2))

10 % added grit of size between 100 and 200 mesh

initiator	no grit (%)	hardness 2 KCl (%)	hardness 3 calcite (%)	hardness 4 fluorite (%)	hardness 9 carborundum (%)
A. Rubbing surfaces on wheel and table: papier mâché					
Service azide	0	—	—	1	0
I.C.I. styphnate	0	—	—	0	0
mercury fulminate	0	—	—	0	0
B. Rubbing surfaces: brass on wheel, papier mâché on table					
Service azide	—	—	—	—	1
C. Rubbing surfaces: brass on wheel, graphitized bakelite 'C' on table					
Service azide	—	—	—	—	0
D. Rubbing surfaces: aluminium on wheel and table					
Service azide	0	—	—	—	2
lead styphnate	0	—	—	—	2
mercury fulminate	(attacks Al)	—	—	—	—
E. Rubbing surfaces: tinned steel on wheel and table. Thickness of fusible layer of tin 0·001 in.					
Service azide	4	—	—	5	30
lead styphnate	1	—	—	3	28
mercury fulminate	3	—	—	—	3
F. Rubbing surfaces: plain mild steel on wheel and table					
Service azide	0	1	3 (4 % with strontium sulphate)	43	99
lead styphnate	0	—	7	17	77
mercury fulminate	56	—	59	59	37

Table 46. Friction sensitiveness of initiators (effect of grit percentage). Effect of varying percentage of grit on friction sensitiveness of Service azide

Added grit: carborundum (between 100 and 200 mesh). 9 mg. charges

grit (%)	none	2	5	10
sensitiveness (%)	0	35	86	99

From the observed relations between friction and detonation, it can be concluded that

(i) No appreciable sensitiveness is observed except towards the bottom right-hand of table 45, i.e. for grit of hardness about 4 and over, and for surfaces of mild steel. Mercury fulminate is not sensitized by grit.

(ii) The fact that even hard grit such as carborundum has no marked effect on the initiators, under the conditions of the test, until hard surfaces are likewise present, supports the previous conclusion that grit acts on hard surfaces by forming hot spots of a sufficiently high temperature to activate grains of initiator in the neighbourhood (cf. part III (1)).

(iii) The fact that lead azide is markedly more grit sensitive than fulminate appears to be due to its superior 'pick up' from the decomposition of individual grains, in building up detonation.

Evidence on this property is given below (cf. part II (2)). It is of importance in applications of initiators.

(iv) The partial quenching of hot spots by a surface layer of tin 0·001 in. thick is of interest. If the order of magnitude of the heated regions were many powers of 10 less than 0·001 in., complete quenching would be expected.

Experiments on percussion sensitiveness

In order to determine how far percussion sensitiveness in the ball and disk machine (part IV) might arise from hot spots, tests have been made with confining surfaces of nickel and tin, as well as with the brass disks usually employed. In these experiments disks of nickel or tin 0·001 in. thick were placed between the usual brass disks, so as to sandwich the layer of initiator.

Results plotted in figure 44 *a* and *b* (table 47) indicate that the sensitiveness to percussion of Service azide decreases in the order

	nickel	>	brass	>	tin
m.p.	1455° C		950° C		231·9° C

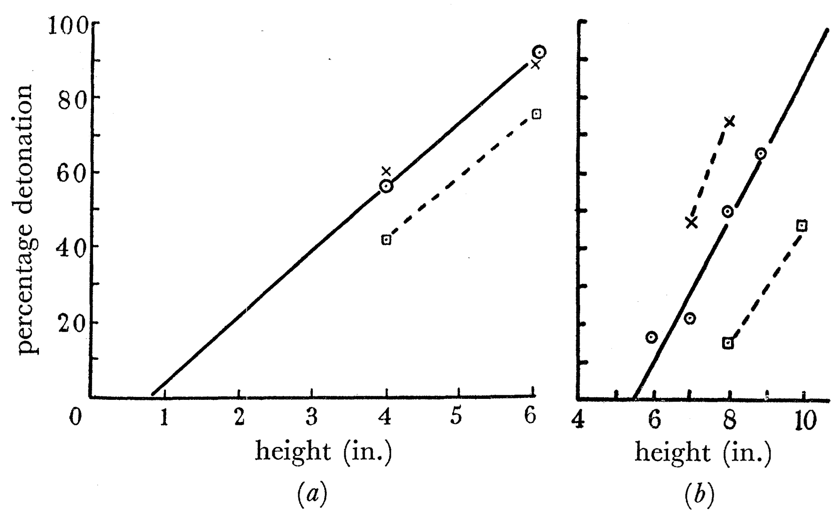

FIGURE 44. Effect of confining metal on percussion sensitiveness. *a*, Mercury fulminate; *b*, lead azide. ☐ Tin foil points, × nickel foil points, ⊙ brass confinement.

Table 47. Percussion sensitiveness of initiators (effect of confining metals)

Height of fall for 50 % detonation

initiator	brass + brass (in.)	confinement brass + tin foil (in.)	brass + nickel foil (in.)
Service azide, 255 g. weight	8	10·5	7
mercury fulminate	3·6	4·5	3·4

This order suggests that the lowered melting point of the confining surface of tin may be a contributory factor in leading to desensitization in these tests by 'quenching' hot spots.

The small increase in sensitization of lead azide by nickel foil may likewise be due to the higher melting point of nickel.

An alternative explanation of the results would be that the hardness of the confining disks determines the degree of sensitization. Although the hardness of bulk nickel is slightly lower than that of brass (brass disk D.P. hardness = 165) it has not been feasible to eliminate the possibility that these electrodeposited thin films of nickel are considerably harder. Comparative results with fulminate (figure 44*a*) and azide (figure 44*b*) under nickel foil confinement are, however, against this possibility.

Other evidence (see below) indicates that the sensitiveness to percussion is not simply linked with the sensitiveness to heat, and probably involves more than one process of activation.

Experiments on sensitization by heat in relation to sensitization by mechanical shock

(*a*) *Permanent sensitization of initiators by heat.* Previous observations (part II (1)) on the permanent sensitization of initiators by heat have been confirmed by the more extensive data recorded in table 48.

Table 48. Effect of pre-heating on delay to ignition

Service azide

temperature (°K)	temperature (°C)	average delay to ignition (single heating) (sec.)	delay after heating during half the induction period at 333·0° C for 10 sec. (sec.)
606·4	333·0	20·0	10·0
607·4	334·3	16·3	8·4
609·9	336·8	12·6	7·1
612·1	339·0	10·5	6·1
614·6	341·5	8·2	4·4

Mercury fulminate

temperature (°K)	temperature (°C)	average delay to ignition (single heating) (sec.)	delay after heating during half the induction period at 192·5° C for 10 sec. (sec.)
465·6	192·5	20·4	13·2
467·0	193·9	18·6	10·9
471·3	198·2	14·5	8·4
			(after heating during half the induction period at 186°)
459·1	186	30·0	15·0
469·1	196	16·0	8·1

The average (for 24 measurements) of the induction period preceding detonation is given for a series of temperatures in the second column of table 48.

Similar samples were heated during half the induction period at 333° C, and were then allowed to cool.

On re-heating at a number of different temperatures, the delays with these heat sensitized samples (3rd column of table 48) were slightly greater than half the induction period at the temperature of second heating, i.e. data in column 2 are somewhat less than twice those of column 3. This showed that the sensitization by heat was to some extent permanent. Since the azide is coloured by heating, the sensitization is probably associated with the production of lead atoms at favoured portions of the azide crystals.

Table 49. Percussion sensitiveness of initiators (effect of preheating, figure 44)

initiator	extent of preheating	effect on sensitiveness (height for 50 % detonation) (in.)	
mercury fulminate	none	4·4	(130 g. ball)
	50 % of induction period at 193° C	5·6	
lead azide	none	9·7	(254·8 g. ball)
	50 % of induction period at 332° C	8·2	

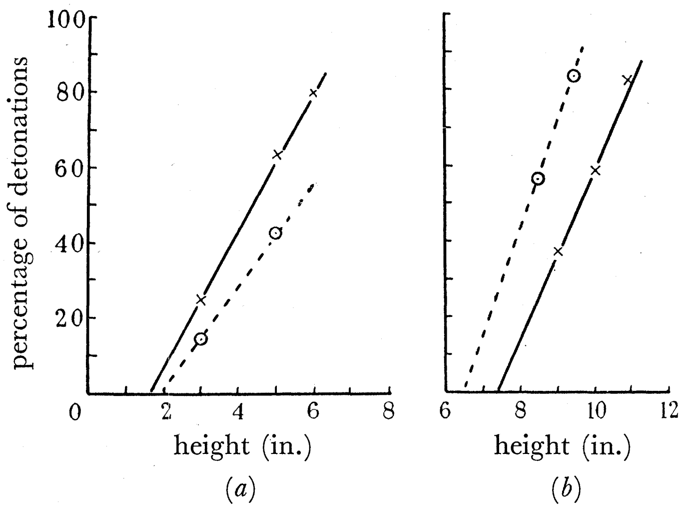

Figure 45. Percussion sensitiveness of heat treated samples. (*a*) Mercury fulminate; (*b*) lead azide. × Normal, ⊙ heated for 10 sec.

It was of considerable interest to see how far this permanent sensitization to further heating affected the sensitiveness to mechanical shock.

Tests were limited by the precautions necessary in handling lead azide and mercury fulminate, after they have been sensitized by heat. Results are given in table 49. They show that whereas mercury fulminate is desensitized to percussion by heat treatment, lead azide is somewhat sensitized (cf. figures 45 *a* and *b*). With both initiators the effects of heat treatment on percussion sensitiveness are comparatively small. Experiments showed similar behaviour of friction sensitiveness, which is not increased by heat treatment of the initiators.

(*b*) *Build-up of detonation as a function of quantity of initiator.* Previously described experiments (parts II (1) and (2)) on the detonation of mercury fulminate and lead azide were extended by measuring the induction periods for quantities from 2 to 12 mg. It was found that although the linear relationship between $\log t$ and $1/T$ holds for all quantities, the values of E increase with decreasing amounts of fulminate. It appears that detonation 'builds up' in a mass $12 > m > 2$ mg. (cf. part II (3)).

For lead azide, all the points for the different masses lie on the same straight line, i.e. down to 3 mg. at least, the activation energy does not depend on the bulk taken, and detonation 'builds up' in a mass $3 > m$ mg.

With a bulk-density of 4·4, a uniform layer of initiator at the bottom of a no. 8 Briska detonator tube has a thickness of about 10^{-3} cm./mg.

It is very unlikely that the 'build-up' is conditioned by any self-heating mechanism in view of the small thickness of the layers involved, and also in view of the fact that sensitization persists on cooling and then re-heating.

Discussion

(i) The greater volume of initiator required for 'build-up' with mercury fulminate gives some explanation why mercury fulminate is much less sensitive to grit than lead azide. From the experimental conditions, the hot spots formed by rubbing grit on a hard surface are very local. Unless detonation can build up from a very small local disturbance, no special sensitization by grit is to be expected.

Two interesting points arise. In the first place, the usefulness of Service azide lies precisely in the fact that it builds up to complete detonation in very small volumes. Any attempt to preserve this property of an initiator has almost inevitably the concomitant of a high grit sensitiveness, if the proposed theory of grit sensitiveness is correct. Secondly the heat of explosion/g. of lead azide and mercury fulminate are stated to be (Escales & Stettbacher 1917)

mercury fulminate 410 cal./g. lead azide 364 cal./g.

so that the better build-up with lead azide must be due to the chain mechanism of its decomposition, and not to a greater heat of reaction.

(ii) The results for the percussion sensitiveness of lead azide could be explained if, say 20 % of the detonations on percussion started from thermal hot spots, and the rest from a mechanical process not affected by preheating of the crystals. This would agree with the observations that heat-sensitized azide gives only a comparatively small increase in percussion sensitiveness. Sensitized fulminate (which would not pick up easily from thermal hot spots) is actually desensitized by preheating.

The description of this mechanical process of initiation as 'tribo-chemical' must be regarded as a mere change of words, until mechanical effects on the crystals can be measured quantitatively.