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Part III. (3) The Sensitiveness of Initiators to Friction. Temperature Coefficient

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Table 42. Emery paper on steel, load 6 lb.

velocity (ft./sec.)	5	6	7	8	9	10	11	12	13	14
initial angle (degrees from the vertical)	29	35	41	47	53	59	66	73	80	88
final angle (free swing)	27	32	38·5	44	49·5	55·5	62·5	69·5	75·5	84
final angle (rubbing friction)	20	25	32	37	41	47	53	60	66	75
percentage loss of velocity due to rubbing	—	10·0	16·6	14·7	17·6	16·6	14·6	12·0	12·0	10·0
actual energy loss at the rubbing surface (ft./lb.)	0·25	0·3	0·33	0·4	0·53	0·59	0·71	0·76	0·8	0·77

Table 43. Mild steel wheels, hard steel stationary surface

	ft./lb.
using 6 lb. load, average energy loss with explosive	0·15
using 6 lb. load, average energy loss in absence of explosive	0·28
using 40 lb. load, average energy loss with explosive	0·3
using 40 lb. load, average energy loss in absence of explosive	0·5

(3) THE SENSITIVENESS OF INITIATORS TO FRICTION. TEMPERATURE COEFFICIENT

By T. Nash, W. J. Powell and A. R. Ubbelohde

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[Plate 8]

In part III (2), a machine was described for subjecting explosives to grazing friction between a stationary and a moving surface, rubbing one over the other. By arranging Service initiators in a scale of increasing sensitiveness, it was shown that a different order was obtained: (*a*) when the rubbing surfaces were coated with standard emery paper, so that the friction was due to particles of hard grit; (*b*) when the rubbing surfaces were of steel; (*c*) when grit was introduced between steel surfaces.

Initiators such as mercury fulminate show much the same sensitiveness in all three cases, but others, such as Service azide, are notably more sensitive under the action of grit. The experiments described in this section were designed to give additional information on the nature of grit sensitiveness in particular, by investigating: (1) the effect of raising the temperature of the rubbing surfaces; (2) the deadening produced by wetting the explosive with various liquids.

The relative probability of initiation by grazing friction was determined for a range of velocities of the rubbing surface, as described in the part quoted above. Principal changes in determining grit sensitiveness were:

(i) Graded emery powder was mixed with the initiator which was then rubbed between steel surfaces. One reason for eliminating the use of paper was the uncertainty arising from the effect of heating or wetting on the standard emery paper.

(ii) An initiator balance (described below) was used to weigh out standard quantities of compositions for each test. These were sprinkled over a constant area of the steel on the tilting table through a small multiple sieve.

(iii) The temperature of the tilting table, and of the thin layer of powder on it was maintained by electric heaters, at various temperatures up to 300° C.

(iv) To investigate the deadening effect of liquids, drops or a fine spray were applied to the layer of composition. Liquids used included water and glycerine solutions with and without the addition of capillary active substances, and ethyl and butyl alcohols.

Principal results obtained were:

(i) *Effect of temperature on grit friction sensitiveness.* On heating, mercury fulminate, lead di-nitro-resorcinate (L.D.N.R.), lead styphnate, Service azide and A.S.A. show no definite increase in sensitiveness to friction between steel surfaces, with or without the admixture of grit. These results were in most cases confirmed up to 145° C; much above this temperature the heat sensitiveness of the initiators can lead to spontaneous ignition before the rubbing takes place.

A small increase in sensitiveness at 145° C was observed with the initiator 664 rubbed between steel surfaces. This was confirmed with a 664-grit mixture.

(ii) *Effect of wetting on grit sensitiveness.* Thorough wetting with water + glycerine solution or with ethyl or butyl alcohol largely deadened the sensitizing action of grit. Notable effects were observed even when the quantity of liquid was reduced to a very small amount by using a fine spray. The breaking of crystals in rubbing was substantially the same, e.g. in the case of Service azide, where the only effect of wetting was observed to be a small increase in the number of unbroken crystals.

From these results, it is concluded that:

(1) If the effect of rubbing initiators were merely to raise the overall temperature, till the decomposition induced led to self-heating and detonation, heating of the tilting table should provide some of the energy, and should result in a greater probability of detonation at the same velocity of rubbing.

Since no such effect is observed as a general rule, the conclusion is that the friction sensitiveness cannot be represented as due to an overall heating.

Initiation by friction may be due to the formation of a few local hot spots, or to shearing of the crystals, but if these effects are operative, the conclusion is that they do not show a marked temperature coefficient within the range of the present experiments.

(2) Wetting of the initiator crystals does not appear to lessen the gross breakage sufficiently to account for the observed desensitization. The observed deadening must be due either to the prevention of local hot spots, or to the damping down on propagation from marginal initiation.

Experimental methods

In addition to the details described in III (2), the following may be mentioned.

(*a*) *Handling and weighing of the samples.* In spite of its convenience and safety, the use of grit in the form of standard emery paper is open to objection. Even for the 'standard' E.P. test, there is no guarantee that a manufacturer will continue to use the same backing and binding for the emery over a period of years.

This difficulty might, to some extent, be overcome by standardizing the paper at intervals with a standard initiator such as mercury fulminate.

For the experiments described in this section it was, however, necessary to wet and to heat the emery, and the uncertainties introduced by the paper backing might have altogether vitiated any conclusions.

It was therefore decided to mix emery powder of known fineness (average diameter of particles 3×10^{-3} cm.) with the various initiators under test, and to sprinkle the compositions on to a steel surface for the friction tests. A quadruple sieve of 30 mesh silk was used for sprinkling. Compositions containing grit are more dangerous to handle than usual; they could not be transferred by the felt pad method, since this might lead to the sorting out of one or other of the components. Weighing on a laboratory balance is both dangerous and tedious and the filling plate method of obtaining small reproducible quantities was inadvisable in view of the friction sensitiveness due to the added grit.

A small balance made of glazed paper was devised which is most convenient for handling these compositions. Figure 43, plate 8, gives the general set-up and illustrates the method of catching the sample after it has been weighed and tipped down the paper chute. The weight of the sample can be controlled by adjusting the size of the paper counterpoise stuck on the back of the moving balance part. Normally 5 mg. was used, and special tests showed successive weights of 0·0050, 0·0050, 0·0052 g. for one balance. The small scoop *B* shown resting on the table is used for transferring lead azide from the stock *A* to the balance, until it just tips over.

Even in the case of rapid work the accuracy was ±5 %. The balance was used behind an explosive screen, with the usual precautions in handling initiators. It was transferred to a beaker of destroying solution when it became seriously contaminated.

Mixtures containing grit were prepared with a camel hair brush, and contained about one particle of carborundum for every three of azide, styphnate or fulminate.

(*b*) *Control of temperature*. A flat mica-insulated coil was sandwiched between the tilting table and a thin steel plate on which the steel strip was held. A resistance in series was varied to give required temperatures. 20 min. was required to reach a steady state at 140° C and about 30 min. for 240° C.

A number of precautions were taken to ensure that rubbing took place with the initiator at the temperature of measurement.

(i) To measure the temperature of the hot plate on the tilting table, a thermometer was used with its bulb surrounded by Woods' metal, forming a pool on the heated surface. This temperature was checked by inserting a thermocouple into one of the clamps, and also with a thermocouple attached to a small metal proof plane resting on the flat surface. It was confirmed that no large gradients were present in the immediate neighbourhood of the heated friction surface.

(ii) The wheel was normally used cold, since its time of contact with any small portion of the hot striking surface would not exceed 10^{-3} sec. Confirmatory experiments were, however, carried out with the wheel heated.

These involved considerably more difficult manipulation, since it was necessary to control the temperature of the wheel, and also to correct for the thermal expansion of the pendulum arm, to ensure that the length of strike in the hot was the same as in the cold. Longer strikes would have given a spurious increase in sensitiveness.

The results of these confirmatory experiments with hot wheels confirmed the conclusion from more numerous experiments with cold wheels, that the temperature coefficient of friction-sensitiveness was small.

(iii) When the hot plate had reached a steady temperature, the initiator powder was sprinkled on to it and was allowed to heat up whilst the template was removed, leaving an oblong area of about $\frac{1}{2}\times\frac{3}{4}$ in. of mixture. 5 mg. gave a layer not more than one crystal thick. The wheel was then lifted, and the strike followed approximately 7 sec. after sprinkling.

From experiments on the sprinkling of yellow mercuric iodide (transition point to red $HgI_2 = 128°$ C) it was inferred that a layer one crystal thick would reach the temperature of the hot plate within 1 sec.

A further check was to sprinkle the HgI_2 on mica and to lower this on to the hot plate. It was estimated that the thermal conductivity of mica was about one-quarter that of lead azide and it was found that layers of mica 0·01 cm. thick transmitted sufficient heat with the plate at 160° C to change the yellow to red within 2 sec. Since the lead azide crystals themselves are only 0·002 cm. thick, it may be assumed that they had reached substantially the temperature of the hot plate, before the strike took place. Any small lag would not affect the conclusions reached below.

(*c*) *Wetting of the compositions*. Experiments on the deadening action of various liquids were carried out by first sprinkling 5 mg. of the composition with admixed grit on the friction surface of the tilting table, and then adding one drop of liquid. When less was required, the composition was sprayed during a measured interval with a very fine spray given at constant pressure, and the weight of liquid delivered during this interval was separately determined. (Wt. deposited/unit area in 10 sec. $1{\cdot}15 \times 10^{-4}$ g.)

A point of practical importance in the desensitization to grit friction, by the use of water and other liquids, is the rate at which the composition is wetted.

In the friction tests, the layer of composition is so thin that it is wetted rapidly during spraying. Water + glycerin was used in most of the tests, to slow down evaporation from thin layers, but pure water is as effective before it evaporates.

It was of interest to determine whether desensitization was improved by the addition of capillary active substances. Turkey red oil gave an insoluble lead salt, and was therefore less suitable for subsequent chemical destruction and the composition, than saponin or 'perminal' (essentially the sodium salt of an isopropyl naphthalene sulphonic acid).

The wetting of lead styphnate in bulk was found to be accelerated by both saponin and perminal; the wetting of lead azide is more difficult, but accelerated wetting by aqueous solutions was observed after adding 0·1 % perminal.

Little difference was found in sensitiveness to grit friction when these surface active solutions were used for spraying, instead of water or water + glycerin. This is probably due to the fact that thin layers of composition are in any case very rapidly wetted.

To investigate this point, the active ingredient from solid perminal was extracted with acetone, and recovered by evaporation. Tubes of gutta-percha and of glass (0·6 and 0·3 cm. diameter respectively) were filled with 3 cm. of initiator. The bottom was placed in the aqueous solution, and the time for the solution to creep up to the top was measured. Comparative tests show that the rate of creep through lead styphnate is accelerated some five-fold in glass by the addition of 0·1 % by weight of the active ingredient of perminal to the glycerin + water solution. Similar acceleration is observed in the case of azide. With gutta-percha tubes no creep occurs without perminal.

The practical conclusion is that this addition facilitates the desensitization of azide and styphnate to grit, even in bulk, by speeding up wetting.

(*d*) *Preparation of steel surfaces for grit friction tests*. (i) It was found that the tests made using the same surface continuously either on the wheel or plate, or both, for a number of strikes, were unreliable, whenever grit was used, owing to the fact that the roughness increased progressively.

(ii) The wheel must in all cases be smoother than the plate, since otherwise the composition is merely brushed off the smoother surface, and a low sensitiveness observed. For example, with emery paper on the wheel, and roughened steel on the table, lead azide is less sensitive than with a smooth steel wheel and roughened steel on the table, though generally azide is very sensitive to grit.

In view of these observations, the only satisfactory method found was to turn the wheel through a small angle after each strike, and also to renew the plate surface after each strike, if grit was present in the composition under test.

Plate surfaces for use with mixtures with grit. Strips of thin tinplate $1\frac{1}{2}$ in. wide were cut and de-tinned by immersion in a solution of 20 g./l. Sb_2O_3 in concentrated HCl. They were cleaned and kept in a desiccator until wanted for use. After each strike the steel strip was pulled along to expose a fresh surface. Sections that were not quite flat had to be rejected, or the results were markedly affected.

All the grit mixture results quoted below were obtained, using strips of steel prepared as described.

Mixtures without grit. In view of the smaller wear in the absence of grit, it was possible to use a quicker and more reliable method, with hardened roughened steel on the table, carefully levelled once for the whole run, and a smooth steel wheel. In the absence of grit it was not necessary to change the surface of the hardened steel.

The main results are summarized in table 44.

Table 44. Temperature coefficient of friction sensitiveness

initiator	temperature (°C)	% ignitions	conditions
Service azide	18	89	10 % fine carborundum.
	135	90	Smooth steel on steel
lead styphnate	18	4	20 % fine carborundum.
	135	5	Smooth steel on steel
A.S.A.	18	49	20 % fine carborundum.
	135	49	Smooth steel on steel
664	18	11	10 % fine carborundum.
	135	24	Smooth steel on steel
mercury fulminate	18	50	smooth steel on steel (no grit)
	145	47	
664	18	67	smooth steel on steel (no grit)
	145	92	
L.D.N.R. lot 14	18	45	steel on hardened, roughened
	155	45	spring steel (no grit)
mercury fulminate	18	82	steel on hardened, roughened
	100	76	spring steel (no grit)

Additional experimental results were as follows:

(A) *Temperature coefficient of friction sensitiveness*

The following notes record additional observations on the various substances.

Service azide

(i) In the absence of grit, no ignitions were observed at 14 ft./sec. in thirty trials at 20, 150 and 200° C showing that no marked increase in friction sensitiveness had occurred up to this temperature.

In a further series of 140 trials at intervals of 50 up to 300° C, using a smooth steel wheel and a roughened (de-tinned) steel strip, only nine detonations were observed in all, and their distribution did not indicate any definite temperature coefficient.

Around 300° C 'browning' of the azide and in some cases spontaneous ignitions were observed before the wheel could be released, but this was not accompanied with increased sensitiveness to rubbing.

(ii) With added grit (10 % by weight of 300 mesh carborundum) wheel and strip surfaces renewed at every stroke.

	velocity (ft./sec.) ...	5	6	7
ignitions in 10 trials	18° C	4	5	10
	136° C	4	6	10

These trials again did not indicate any marked temperature coefficient for grit friction. Preliminary trials with emery *paper* at 190° C showed a small increase in sensitiveness compared with room temperature, but this was probably due to hardening of the paper backing on heating.

Lead styphnate (commercial sample)

(i) In the absence of grit a series of fifty trials at 14 ft./sec. at 30° C intervals up to 210° C showed no marked increase in friction sensitiveness with rise in temperature.

(ii) With added grit (20 % by weight of 300 mesh carborundum).

	velocity (ft./sec.) ...	13	14
ignitions in 10 trials	18° C	0	4
	135° C	0	5

These trials again failed to show a marked temperature coefficient of grit sensitiveness.

Preheated lead styphnate (commercial sample)

In view of the loss of water of crystallization by lead styphnate when heated in air around 130° C, tests were carried out to verify whether samples after preheating and cooling were appreciably sensitized to the action of grit.

A sample of lead styphnate heated 15 min. to 200° C and cooled, was permanently lighter in colour. On mixing with 10 % by weight of 100 to 200 mesh carborundum and comparing with the original sample mixed with grit, no sensitization was observed in eighty trials.

Similarly, a sample of lead styphnate heated 6 hr. at 55 to 57° C and cooled showed the same sensitiveness to grit as the original sample, in forty trials.

A.S.A.

(i) Without added grit, no marked sensitization was observed on rubbing by aluminium surfaces at 100° C (forty trials in all).

	velocity (ft./sec.) ...	14	14
ignitions in 10 trials	18° C	0	5
	100° C	1	5

(ii) With 20 % 100 to 200 mesh carborundum by weight.

	velocity ft./sec. ...	6	7	8	9	10	11	12	13	14
ignitions in 10 trials	18° C	(0)	1	1	5	4	8	10	(10)	(10)
	135° C	0	2	2	7	6	8	7	9	8

In this case again no marked temperature coefficient was observed for grit friction, for a rise of 117° C.

Basic L.D.N.R.

Without added grit.

		8	9	10	11	12	13	14
velocity (ft./sec.)	...	8	9	10	11	12	13	14
ignitions in 10 trials	18° C	0	2	7	8	8	10	(10)
	135° C	2	3	4	8	10	8	10

The conclusion is that no marked temperature coefficient could be observed.

Mercury fulminate

Without added grit.

Steel wheel on hardened scored spring steel plate. Test in hot bracketed between two tests in cold, of which the mean was taken.

velocity (ft./sec.)	...	4	5	6	7	8	9
ignitions in 10 trials	18° C	0	2	4	7	9	10
	100° C	1	2	2	3	9	10

A confirmatory series at 145° with smooth steel on steel verified the absence of marked temperature coefficient, under somewhat different conditions.

velocity (ft./sec.)	...	8	9	10	11	12
ignitions in 10 trials	18° C	1	4	8	7	10
	145° C	0	3	8	7	9

664

This is the only initiator for which a temperature coefficient of friction sensitiveness was definitely observed.

Smooth steel on steel

velocity (ft./sec.)	...	5	6	7	8	9	10	11	12	13	14
ignitions in 10 trials	18° C	1	4	4	9	6	8	9	6	10	10
	145° C	7	7	8	10	(10)	(10)	—	—	—	—

(B) *Effect of liquids on grit friction*

In these experiments, the initiators were mixed with 10% by weight of 100 to 200 mesh carborundum, and 9·5 mg. were sprinkled on to a plate of hardened spring steel, scored across, and then moistened with a densensitizing agent. The action of liquids led to marked desensitization more particularly in the case of fulminate and styphnate. All the trials were carried out at a rubbing velocity of 14 ft./sec. to obtain sufficient ignitions.

Mercury fulminate

desensitization	number of ignitions at 14 ft./sec.
without desensitizer	10/10
sprayed 20 sec. with water or with 20% glycerin solution	2/10
do. with additional 0·1% 'perminal'	2/10
one drop of ethyl alcohol	0/10

('Perminal' is the sodium salt of isopropyl naphthalene sulphonic acid.)

Larger quantities of 20% glycerin + water led to complete desensitization at 14 ft./sec. The alcohol was not sprayed, owing to rapid evaporation, but one drop is considerably more than the amount of liquid delivered by a 20 sec. spray.

Lead styphnate

desensitization	number of ignitions at 14 ft./sec.
without desensitizer	10/10
sprayed 10 sec. with water or with 20 % glycerin solution	6/10
do. with 0·1 % perminal	6/10
do. with 0·1 % turkey red oil	5/10
one drop of ethyl alcohol	0/10

Larger quantities of water or 20 % glycerin solution led to complete desensitization up to velocities of 14 ft./sec.

Service azide

desensitization	number of ignitions at 14 ft./sec.
without desensitizer	10/10
sprayed 10 sec. with water or with 20 % glycerin solution	6/10
do. + 0·1 % perminal	8/10
do. + 0·1 % turkey red oil	5/10
one drop ethyl alcohol	1/10
20 sec. spray butyl alcohol	6/10
one drop butyl alcohol	0/10

Discussion

(*a*) In all cases the fluids minimize the action of grit, though the proportionate effect is markedly less for Service azide than for the other two initiators investigated. This difference may be associated with the fact that lead azide is not easily wetted by the aqueous solutions tried.

(*b*) *Mechanism of sensitiveness to grit friction.* The fact that no large temperature coefficient has been observed for grit friction is most simply accounted for by assuming that the action of friction in giving rise to detonation is mechanical, rather than thermal. It has been shown (cf. Bowden & Tabor 1942) that no large temperature coefficient is associated with mechanical friction.

Further support for this assumption is derived from the experiments on Service azide around 300° C. At this temperature, during the inevitable delay after sprinkling the initiator, and before the wheel can be released, the crystals went visibly brown, and in some cases spontaneous ignition was observed. Previous experiments in part II (1) have shown that lead azide is sensitized to heat when it is maintained at 300° C for some time. Since it is not noticeably sensitized to friction, initiation by heat appears to follow a different mechanism from initiation by friction.

The assumption that the primary action of grit is mechanical rather than thermal cannot be regarded as completely proved by the present experiments, but it can be stated that if the action of grit is to favour hot spots, as appears to be the case with high explosives (part III (1)), then the temperature of these hot spots must be so high that 100° rise in the starting temperature makes little difference. (See also III (4).)

This suggested sensitiveness of some initiators to mechanical action in the strict sense as distinct from the sensitiveness to hot spots produced by mechanical action might be associated with the fact that the majority of them are salts, whose lattice energy is very considerably 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.