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Part III. (1) The Grit Sensitiveness of High Explosives

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phthalate was de-aerated by boiling with fragments of glass and cooling in vacuo before use. Figures given in table 28 show that under these conditions dibutyl phthalate behaves exactly like any other liquid whose boiling point lies below the detonation range, i.e. it first vaporizes and detonation then builds up in the vapour.

TABLE 28. EFFECT OF REDUCED PRESSURE ON THE INDUCTION PERIOD OF DEXTRINATED LEAD AZIDE IN DIBUTYL PHTHALATE. (BOILING POINT ABOUT 280° C)

313° C		321° C		335° C	
8·0	7·2	9·0	8·0	7·9	10·3
10·1	8·1	8·0	fail	9·2	8·5
8·0	8·6	8·3	8·2	7·8	8·2
7·8	7·6	6·5	fail	5·5	8·4
5·0	8·8	8·3	8·6	6·5	9·2
mean	7·9		8·1		8·1

Comparative values at normal pressures extracted from table 22, are: 313° C – 19·2 sec., 321° C – 4·2 sec.

DISCUSSION

The various experiments described make it clear that deflagration can be separated by experimental means from detonation, even with an initiator as prone to build up detonation as Service azide. Deflagration is a far milder form of energy release than detonation, even with cyclonite where the heat evolved per g. is some 3 or 4 times as large as for lead azide.

The results are of considerable interest in connexion with theoretical and practical problems. From the practical aspect, they support the view that separating grains of explosive by inert liquids which can absorb energy is one mode of desensitization, particularly when the liquids have a high boiling point.

The interesting new feature is that such phlegmatizers have far less effect on deflagration by self-heating, than on the build-up of real detonation. Build-up of real detonation is, apparently, much easier in a gaseous than in a liquid medium. The results probably explain why a low-boiling liquid such as water is not very effective in desensitizing Service azide.

This opens up the interesting practical possibility of phlegmatizing Service azide with a high-boiling liquid such as nujol or cresyl phosphate, for purposes of transport. When it is required to use the azide, the phlegmatizing liquid could be removed with some easily evaporated liquid with no solvent action on lead azide.

From the theoretical aspect, the results throw further light on the build-up of detonation, and emphasize its difference from deflagration by self-heating.

PART III

(1) THE GRIT SENSITIVENESS OF HIGH EXPLOSIVES

BY J. L. COPP AND A. R. UBBELOHDE

(*Report originally issued by the Armament Research Department* 18 *July* 1942)

Risks in handling various high explosives are enhanced if grit is present. Quantitative measurements of the enhanced sensitiveness, made by means of the Rotter impact machine, have included tests on the high explosives:

T.N.T., picric acid, tetryl, cyclonite and waxed cyclonite, and penta-erythritol tetranitrate (P.E.T.N.).

In addition to the standard Rotter test on the explosives as used in practice, experimental modifications tried include the admixture of controlled amounts of grit of varying hardness and size, to the high explosives. The effect has also been tried of confining the explosives between surfaces of tin or aluminium, in place of the usual brass and steel. Additional methods of calculating the probability of explosion have been used, to distinguish between initiation and propagation.

As a result of these experiments, a standard test has been specified for the grit sensitiveness of high explosives.

Sensitization by grit, as measured by the Figure of Insensitiveness (F.I.) on the Rotter machine under brass and steel confinement, does not appear to occur if the grit hardness is less than 4 on Moh's scale. With grit of hardness greater than 4, sensitization increases with increase in the weight percentage of grit.

Sensitization is normally greatest for the explosive with lowest F.I.; 1 % of various factory grits can lower the F.I. to a marked degree.

Confinement of cyclonite between surfaces of low melting metals lessens sensitization by grit, but enhances normal impact sensitiveness.

Comparison of the grit sensitiveness of cyclonite with that of waxed cyclonite suggests that the effect of the wax is to quench local 'self-heating'.

The results so far obtained on sensitization by grit can be explained in terms of the production of a number of 'hot spots' whose temperature in the case of cyclonite and P.E.T.N. appears to be around 750° K.

Introduction

In the Rotter impact test (cf. appendix II) a thin layer of explosive confined between two metal surfaces, usually brass and hardened steel, is subjected to a blow from a heavy falling weight. When partial or complete detonation occurs the gas evolved is collected, and the relative amounts produced with blows of increasing violence are used to measure the completeness of detonation. From inspection of samples, where no detonation has occurred as the result of the blow, it is clear that the explosive has been subjected both to normal impact, and to rubbing or pinching between metal surfaces. The brass in particular is deformed by the blow, and slides over the surface of hardened steel.

This type of mechanical action has analogies both with conditions which might arise in the handling and filling of high explosives, and with the results of 'setback' when a shell is fired. Figures of insensitiveness determined by the standard Rotter method thus give a valuable idea of the relative likelihood of unwanted explosions with various high explosives. They are required for assessing both factory and Service risks.

When the type of mechanical action on the explosive is changed, it is found that the order of insensitiveness in a list of high explosives can undergo striking changes. In particular, when a thin layer of explosive is subjected to impact between two blocks of hardened steel, in the test described by Taylor & Weale (1932), it is found that some compounds appear to be much less sensitive than in the Rotter test. No detectable sliding of metal occurs in Taylor & Weale's test. This suggests that compounds which undergo a marked increase in sensitiveness on changing from this test to the Rotter test are specially liable to the element of rubbing or pinching, which the Rotter test includes to a much greater degree.

In order to obtain a more fundamental measure of the influence of impact and friction in setting off explosives, it is essential to use tests in which the different kinds of mechanical action are segregated as far as possible. It is comparatively easy to subject the explosive to what may be termed 'pure impact' by using blocks of very hard steel and thin layers of explosive.

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

A method of measuring the relative sensitiveness of high explosives to friction by the addition of grit is quite distinct from the above in the type of mechanical action involved.

From a few results published by Muraour (1933 *b*) it can be inferred that certain explosives may be far more sensitized by the addition of grit than others, whose impact sensitiveness is of the same order. This suggests that the addition of grit might give some measure of the relative sensitiveness of various explosives to rubbing friction.

This present work includes systematic measurements of the enhanced sensitiveness of high explosives, including P.E.T.N., cyclonite, cyclonite/wax, tetryl, picric acid and T.N.T. on adding various kinds of grit. The data have been obtained using the Rotter impact machine. Standard procedure has been followed, except where modifications are indicated in the text.

Section (*a*) describes to what extent the high explosives cyclonite, P.E.T.N. and tetryl are affected by grit percentage, grit hardness, and grit size. Section (*b*) gives data for various high explosives and proposes a specification for a standard test on grit sensitiveness. Section (*c*) describes special experiments and calculations to elucidate the mechanism of sensitization by grit. From these three sections of the report, some progress can be made in developing fundamental knowledge on the sensitiveness of explosives.

Sensitization by grit appears to be more closely related to the formation of local 'hot spots' than to other factors, such as crystal hardness of the explosive. An immediate practical application is summarized in § (*d*). Local contamination of explosives with grit appears to be inevitable in explosives factories, in some cases to a high degree. The effect of such contamination in increasing handling risks can be disturbingly large, e.g. in the case of P.E.T.N.

The bearing of the results about effect of wax on the sensitiveness of cyclonite and P.E.T.N. is also discussed in § (*d*).

Finally, the comparatively large number of impact tests which were required to obtain the results discussed in §§ (*a*), (*b*) and (*c*) have made it possible to give statistical estimates of probable errors in the determination of impact sensitiveness by the Rotter test (appendix II).

(*a*) The comparative grit sensitiveness of high explosives (with special reference to cyclonite and P.E.T.N.)

Experimental details

The general procedure for carrying out a determination of grit sensitiveness was as follows:

The high explosive was dried, when possible at 60° C in an air oven, and was then sieved through 100 mesh silk.

Samples of grit were powdered when necessary in order to limit the size range of particles; the coarser grit was used between two sieving ranges—e.g. between 100 and 200 mesh silk for the coarsest samples. The finer grit was segregated into size ranges by repeated settling of various fractions from suspension in water.

Before mixing-in with the high explosive, the grit was washed with acetone and benzene to remove any grease, and dried in an oven.

In order to secure as uniform mixing as possible the samples (approx. 2·0 g. explosive and 0·004 g. grit) were turned over and over with a glazed paper scoop for about 10 min. The mixtures with the more dilute proportions of grit were made up from about 10 % of a richer mixture, instead of from pure grit, so as to facilitate uniform dispersion.

The average size of the grit particles was determined by scattering these on a cross mesh graticule, and estimating the projected area of cross-section, using a microscope. Average values were obtained for twenty particles.

From this area, the average volume of the particles could be calculated assuming a cubical shape (marked departure from this shape was on the average observed only in the case of phosphor bronze, which was in the form of small plates). From the known density of the material, and the average volume, the actual number of particles in a given weight of mixture could be calculated from the weight percentage of grit.

This figure is important in the Rotter test, since the weight of explosive per brass cap is comparatively small. Constant weights of approximately 25 mg. were filled into each brass cap, using a counterpoised paper balance (cf. III (3)) for the weighings. In extreme cases it will be noted that sensitization was observed (cf. table 29) with as little as one particle of grit per cap filling, on the average.

Table 29. The grit sensitization of cyclonite

(F.I. = 64 based on picric acid = 100 and tetryl = 72)

grit	Moh's hardness	cross-section of grit particles (sq.mm.)	weight % grit	average number particles of grit/cap	area for standard curve	area for mixture curve	% sensitization*	F.I. of mixture P.A. = 100
carborundum	9	$1{\cdot}2\times10^{-2}$	1·0	60	—	3362	60	26
	9	$1{\cdot}2\times10^{-2}$	0·22	12	8270	4196	49	33
	9	$1{\cdot}2\times10^{-2}$	0·054	3	7976	6658	16	54
	9	$1{\cdot}2\times10^{-2}$	0·020	1	8646	7050	18	53
carborundum	9	$0{\cdot}15\times10^{-2}$	0·22	250	8960	4660	48	34
	9	$0{\cdot}15\times10^{-2}$	0·021	25	9352	8112	13	56
	9	$0{\cdot}15\times10^{-2}$	0·020	25	8534	6950	18	53
	9	$0{\cdot}15\times10^{-2}$	0·004	5	8678	8106	7	60
felspar	6	100–200 mesh	0·21	—	8264	3228	61	25
fluorite	4	$0{\cdot}7\times10^{-2}$	0·19	70	8826	7674	13	56
	4	$0{\cdot}7\times10^{-2}$	0·19	70	9062	7568	16	54
	4	$0{\cdot}7\times10^{-2}$	0·028	10	8901	9200	0	66
iron	4	$0{\cdot}20\times10^{-2}$	0·20	250	9349	8528	9	58
	4	$0{\cdot}20\times10^{-2}$	0·23	250	9162	8152	11	57
phosphorbronze	4	$2{\cdot}0\times10^{-2}$	0·19	2	8350	8748	0	67
	4	$2{\cdot}0\times10^{-2}$	2·64	26	8572	9222	0	69
rock salt	2	100–200 mesh	0·26	—	9162	8969	0	63

$$* \ \% \text{ sensitization} = 100\left\{1-\frac{\text{mixture area}}{\text{standard area}}\right\}.$$

With such small quantities of impurities, calculated on the basis of number or particles, accurate determinations of the enhanced sensitiveness could only be made by increasing the number of impact tests, particularly at the critical heights. When necessary, as many as sixteen impact tests on the mixture and sixteen on the comparison explosive, were carried out at each height, instead of the usual four. Some of the details are illustrated below (appendix I).

Volumes of gas evolved at various impacts were determined according to the standard procedure (see appendix II).

Estimation of the percentage sensitization by grit

The object of tests on grit sensitiveness is to determine what *additional* detonations are due to the presence of grit.

As mixtures are compared side by side with the original explosive, the percentage sensitization may be defined as (see below)

$$\text{percentage sensitization (P.S.G.)} = 100 \times \left(1 - \frac{\text{area for mixture}}{\text{area for standard}}\right).$$

An alternative definition based on the percentage increase in the number of initiations due to grit is described below.

Experimental results

Experiments were carried out in particular detail for cyclonite and P.E.T.N. and are given in tables 29 and 30.

Table 30. The grit sensitization of P.E.T.N.

(F.I. = 38. P.A. = 100. Tetryl = 72)

grit	Moh's hardness	cross-section of grit particles (sq.mm.)	weight % grit	average number of particles of grit/cap	area for standard curve	area for mixture curve	% sensitization	F.I. of mixture
carborundum	9	$1{\cdot}2 \times 10^{-2}$	1·0	60	—	—	66	12
	9	$1{\cdot}2 \times 10^{-2}$	0·22	12	5232	1866	64	14
	9	$1{\cdot}2 \times 10^{-2}$	0·05	3	5350	2922	45	21
hardened steel	8	$1{\cdot}6 \times 10^{-2}$	0·20	4	5304	2692	49	19
fluorite	4	$0{\cdot}7 \times 10^{-2}$	0·21	70	5308	3302	38	24
iron	4	$0{\cdot}2 \times 10^{-2}$	0·20	250	4914	5332	0	41 } 36 mea
	4	$0{\cdot}2 \times 10^{-2}$	0·20	250	6000	4750	21	30
	4	$0{\cdot}2 \times 10^{-2}$	0·20	250	5600	5620	0	38
phosphorbronze	4	$2{\cdot}0 \times 10^{-2}$	2·0	20	5404	4586	15	32

The following comments may be made on data in the tables.

1. *Details*

Column 1 describes the materials used as grit. The iron and phosphor bronze were filings from bulk material. The plate-like shape of the phosphor bronze particles has been referred to above, and may explain the small desensitization observed with the mixture.

The average volume of gas evolved per cap at any impact height is expressed as a percentage of the gas evolved for large heights. Areas under the curves are calculated as in appendix II. The ratio of the area for any explosive to the area for picric acid (taken as 100) gives the Figure of Insensitiveness (F.I.).

2. *Sensitization*

The percentage sensitization (P.S.G.) due to various admixtures can be seen from the penultimate column. Actual figures of insensitiveness are given in the last column, based on P.A. = 100 when tetryl = 72.

3. *Effect of grit hardness*

Grit with a hardness less than about 4 on Moh's scale is seen to have little effect on either cyclonite or P.E.T.N. Sensitization appears to increase to some extent with hardness, for values greater than 4. Thus the F.I. of cyclonite (64) is decreased by 11 units, through the presence of 1 particle/cap of carborundum, by 9 units, through the presence of 70 particles/cap of fluorite and is practically unaffected by 26 particles/cap of phosphor bronze.

A further illustration of the effect of hardness, which has a bearing on the mechanism of sensitization by grit, is obtained from special experiments with hardened steel particles as used for shot blasting. It will be seen from table 30 that whereas hard steel particles reduce the F.I. of P.E.T.N. from 38 to 19, filings of mild steel have little effect.

4. *Effect of grit percentage*

By increasing the weight percentage of grit, keeping the size constant, the average number of particles/cap in the impact test is increased. It will be seen that the percentage sensitization is in general increased, but not in proportion. Clearly the probability of initiation by impact does not depend in a simple way on the number of grit particles present. It is interesting to determine whether a lower limit of insensitiveness is reached with much larger amounts of grit.

Inspection of figure 30 shows that such a limit is reached with hard grit, and that the limiting F.I. depends on the size of the grit particles (curves II and III) as well as on the explosive. With 100 mesh carborundum P.E.T.N. is more sensitive than cyclonite (figure 30, curves I and II and tables 29 and 30).

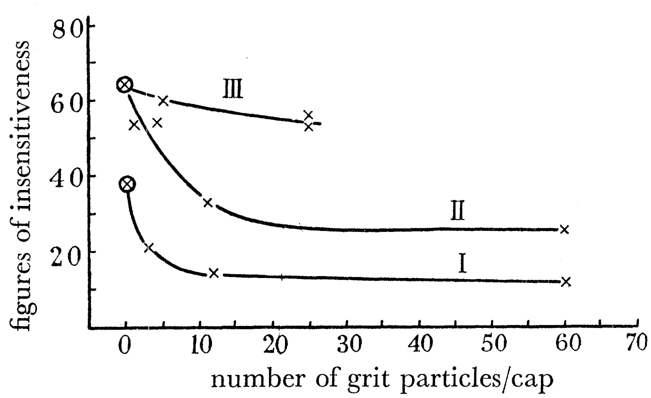

FIGURE 30. I, P.E.T.N.-CSi mixtures; II, cyclonite-CSi mixtures; III, cyclonite-fine CSi mixtures.

5. *Effect of grit size*

From the F.I.'s of mixtures of carborundum with cyclonite (table 29) it appears that coarser particles bring about greater sensitization.

Thus a mixture of cyclonite containing on the average 1 particle of coarse carborundum/25 mg. cyclonite has the same F.I. (53) as a mixture containing 25 particles of fine carborundum/25 mg. cyclonite (see also figure 30).

(*b*) STANDARD GRIT TEST ON HIGH EXPLOSIVES

The experiments with cyclonite and P.E.T.N. required the completion of some 25 impact curves, i.e. about 1500 impact tests.

A large number of experiments carried out with tetryl in connexion with a factory problem showed that grit percentages not exceeding 0·02 % by weight had little influence on the sensitiveness. It would not be possible to carry out experiments in the same detail with other high explosives.

In view of the above, a standard grit test has been devised, in which the nature, size and amount of grit have been selected so as to bring the less sensitive explosives on the scale, and also so as to give conditions more nearly representative of gross contamination.

Specification of a standard grit test

For gross contamination, 1 % by weight of carborundum, passing through 100 mesh but not through 200 mesh sieve to be uniformly mixed, using a paper scoop, with 99 % by weight of high explosive, sieved through 100 mesh silk.

Standard (Rotter test) brass caps to be filled with 25 mg. of the mixture, each, and to be subjected to the impact of a $2\frac{1}{2}$ or 5 kg. weight, alternating with caps filled with 25 mg. of high explosive without added grit. Sixteen blows on each type of filling to be used when the percentage detonation is around 50 %, and four caps at lower and higher impact heights.

(*a*) For calculating the percentage sensitization, based on gas evolution (P.S.G.), the percentage of the maximum gas is plotted against the impact height, according to standard Rotter method. The percentage sensitization is defined as

$$\text{P.S.G.} = 100 \times \left(1 - \frac{\text{area under mixture curve}}{\text{area under standard curve}}\right).$$

(*b*) For calculating the percentage initiation, compared with the maximum number of initiations possible (i.e. detonation of every cap), each cap giving a quantity of gas on impact greater than the experimental error, is to be counted as an initiation, irrespective of whether detonation is complete or partial.

The fraction of the number of impacts leading to detonation is plotted against the impact height and the percentage initiation by grit is defined as

$$\text{P.I.G.} = 100 \times \left(1 - \frac{\text{area under mixture curve}}{\text{area under standard curve}}\right).$$

As a subsidiary test, the P.S.G. and P.I.G. values may be conveniently determined using 0·2 % of grit by weight, as well as 1 %. All other details are the same.

Results are given in table 31.

Table 31. Standard grit tests

Mixtures contain known percentages of 100 to 200 mesh carborundum of average particle cross-section $1{\cdot}2 \times 10^{-2}$ sq.mm.

explosive in order of decreasing F.I.	F.I. of explosive (tetryl = 72)	number of grit particles/cap	P.S.G. % gas sensitization (A)	P.I.G. % initiation sensitization (B)
T.N.T.	120	60	—	69
cyclonite/wax	100	60	—	57
picric acid	100	60	—	67
cyclonite	64	60	60	61
P.E.T.N.	38	60	68	68
tetryl	72	12	23	48
cyclonite	64	12	49	52
P.E.T.N.	38	12	64	66

The following comments may be made on the results in this table.

(i) By plotting the F.I. of an explosive against its percentage sensitization in the standard grit test (figure 31), it can be seen that sensitization by grit follows the same sequence as sensitiveness to impact in the usual Rotter test. One or two other high explosives were tested, and only one marked anomaly was observed.

(ii) Closer inspection of individual impact data shows that the extent to which the explosion is propagated is a characteristic of the explosive. With P.E.T.N. and cyclonite, each additional detonation, due to grit, gives the whole volume of gas corresponding with 100 % ignition. Thus, with these two explosives, when sensitization by grit occurs, propagation is complete (P.S.G. = P.I.G. within experimental error).

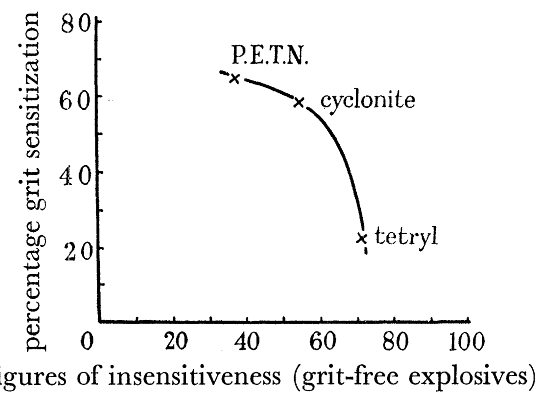

FIGURE 31. 0·2 % carborundum-explosive mixtures.

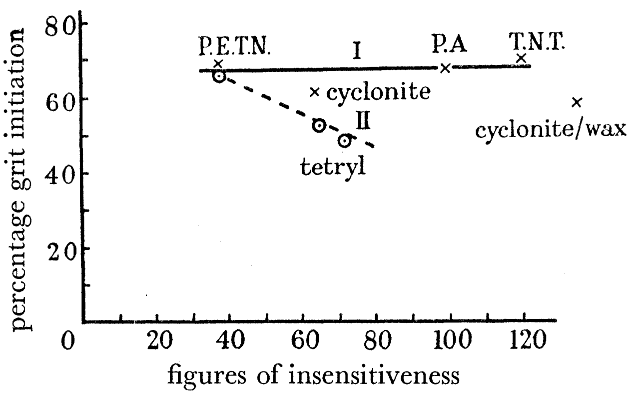

FIGURE 32. I, 1 % carborundum-explosive mixtures; II, 0·2 % carborundum-explosive mixtures.

With tetryl the increase in the *number* of partials, due to grit, is practically the same as the increase in the number of total 'goes' with cyclonite (appendix I). Propagation is, however, incomplete with tetryl at low impact heights, so that the percentage increase in volume of gases, due to grit, is therefore smaller with tetryl than with cyclonite (P.I.G. > P.S.G.).

This distinction in behaviour under the action of grit can be seen from a typical record of impact data (see appendix I) and also from detailed consideration of the percentage initiation due to grit (P.I.G.).

P.I.G. values are plotted against F.I. values in figure 32; it can be seen that with 1 % carborundum these values are practically independent of the F.I. of the explosive. This means that the area of the 'initiations curve' for the mixture with grit must be proportional to the area of the curve for the standard explosive. Algebraically it follows that the average probability of additional initiations by grit is directly proportional to the average probability of initiation without grit. Presumably similar mechanisms are involved.

The additional falling off observed on comparing figure 31 with figure 32 is due to the fact that the less sensitive high explosives also propagate less well. A compact presentation of this fact is obtained from the extent to which the percentage sensitization (P.S.G.) figures fall below the percentage initiation (P.I.G.) in table 31. When the two figures are identical, propagation is practically complete under the conditions of confinement of the standard test. When the P.S.G. falls below the P.I.G. propagation is less complete.

(*c*) Mechanism of sensitization by grit

Probability of initiation by grit

In order to discuss the mechanism of sensitization, the simplifying assumption may be made that caps containing a mixture of grit and explosive, which detonate as the result of impact may be separated into two distinct groups, each with a distinct mechanism of initiation: (*a*) caps detonating through true 'impact'; (*b*) caps detonating due to the presence of contaminating grit.

When the amount of grit is not too large, it may be assumed not only that (*a*) and (*b*) are independent mechanisms, but that the probability of detonations occurring through mechanism (*a*) is the same when (*b*) is operative, as in the absence of grit. Probability considerations may be developed as follows:

If M is the total number of impacts, N the total number of initiations (partial or complete), N_A the number of mechanism (*a*), $N_B = (N - N_A)$ by mechanism (*b*). Since when (*b*) is operative the event cannot count in the probability of detonating by mechanism (*a*), the probability of (*a*), $P_a = N_A/(M - N_B)$, and the probability $P_b = N_B/(M - N_A)$.

Table 32. Percentage probability of initiation by grit at various impact heights

(Explosive mixtures containing 1·0 and 0·2 % of carborundum grit)

wt. % of grit (explosive)	momentum of impact (mass × impact height (kg. × cm.)) ... 125	150	250	375	500	750
2½ kg. wt.						
P.E.T.N. (1 %)	62·5	(70)	100	100	100	100
P.E.T.N. (0·2 %)	62·5	(70)	100	100	100	100
cyclonite (1·0 %)	0	—	100	100	100	100
cyclonite (0·2 %)	0	—	66·6	100	100	100
tetryl (0·2 %)	0	—	50	82	100	100
5 kg. wt.						
P.A. (1·0 %)	0	0	(28)	(66·6)	100	100
T.N.T. (1·0 %)	0	0	(28)	(66·6)	100	100
cyclonite/wax (1·0 %)	0	0	0	(43)	88	100

Note 1. The probability of grit initiation at any impact height is calculated from the number of additional detonations, expressed as a percentage value of the number of blows.

Note 2. Bracketed values were interpolated from the straight line graphs of figure 33.

P_a can be estimated from a separate experiment, relating the number of detonations N_A in the absence of grit, due to mechanism (*a*), at the same impact height, to the number of impacts, i.e. $P_a = N_A/M'$. By rearrangement, it can be seen that the probability of initiation by grit, at various impact heights, may be calculated from the equations

$$1/P_b = M/N_b - N_A/N_B, \quad 1/P_a = M'/N'_a = M/N_A - N_B/N_A, \quad N = N_A + N_B.$$

For convenience probabilities are expressed as a percentage.

Figure 33 depicts these results graphically.

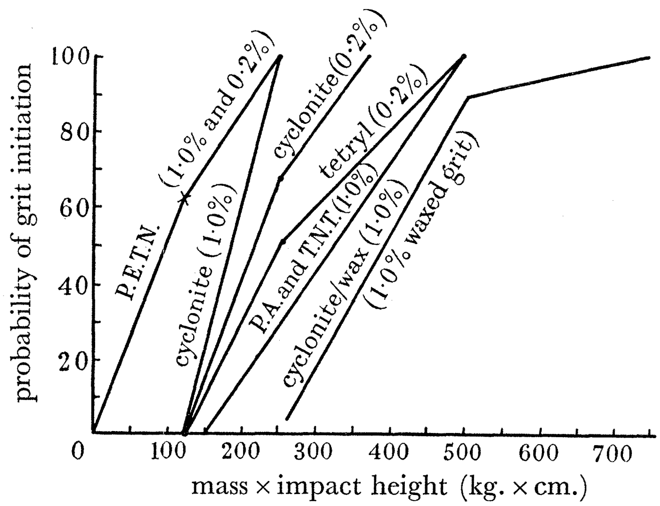

FIGURE 33. Carborundum mixtures.

Formation of 'hot spots' due to grit

Amongst the various explanations of sensitization by grit to be considered, it may be that the grit interacts with the (hard) crystals of the explosive, or alternately, that the grit interacts with the polished surface of hardened steel of the anvil pip, over which the explosive is confined.

Information on the relative hardness of various crystals of explosives is not available. For various reasons (cf. part I) it seems unlikely that the hardness of these crystals has a major influence on sensitization by grit.

In the present section, only the implications of action on the surface of the anvil will be dealt with. As the result of rubbing, local 'hot spots' may be formed around the particles of grit, and may persist for a time comparable with the time required to destroy the momentum of the falling weight. When these hot spots can produce sufficient thermal decomposition of the explosive, the energy liberated may initiate 'self-heating' and detonation of the charge may be expected to spread outwards from the hot spot.

On this basis, it must be assumed that increasing the impact height alters the time/temperature characteristics of the hot spots, so as to increase the probability of detonation, as indicated by the results in table 32.

This hypothesis as to the origin of grit sensitiveness can be checked in a number of ways.

(i) Calculations from the known equations of thermal decomposition for cyclonite and P.E.T.N. must give time and temperature characteristics which are physically reasonable.

(ii) By covering the surface of the anvils with a low melting metal, the maximum hot spot temperature should be lowered, owing to the absorption of heat as latent heat of fusion. The probability of initiation by grit at a given impact height should be correspondingly lessened. This has been checked experimentally, as is shown below.

(1) *Calculations of temperature-time characteristics of 'hot spots' due to grit*

Only brief outlines of these calculations can be given in the present paper.

(*a*) Calculation of the duration of impact from the height of fall of the weight, its calculated striking velocity V, its experimentally observed rebound velocity v, its mass M, and the yield point of brass.

The simplifying assumption on which this calculation is based is that the decelerating force acting on the weight is of the order of the yield point of brass, multiplied by the area of the brass cap on which this force acts, say total force F.

Thus $F\gamma = m(V+v)$, since, if γ is the duration of impact, the impulse is $F\gamma$ and the momentum change is $m(V+v)$. (Yield point of brass = 47 kg./sq.mm.; area of cap = 0·46 sq.cm.)

Using observed rebound velocities, these assumptions lead to the following durations of impact for $2\frac{1}{2}$ kg. weight falling from a height H, on to the drift of the Rotter machine, neglecting any small correction due to movement of the drift.

TABLE 33. CALCULATED DURATIONS OF IMPACT AT VARIOUS IMPACT HEIGHTS

height of fall (cm.)	50	100	150	200
duration (sec.)	$5{\cdot}0\times10^{-4}$	$7{\cdot}5\times10^{-4}$	$9{\cdot}1\times10^{-4}$	$10{\cdot}7\times10^{-4}$

Times of the same order have been observed and calculated for the impact of steel balls on steel (Bowden & Tabor 1941). With lead on lead, the duration of impact is about three times that of steel on steel.

(*b*) Calculation of the extent of thermal decomposition for actions of this order of duration.

From recent measurements it has been established that the thermal decompositions of both cyclonite and P.E.T.N. follow a unimolecular law, such that the fraction α decomposed is related to the velocity constant K_T at $T°$ K by the equation

$$K_T = \frac{1}{t}\ln\frac{1}{(1-\alpha)}.$$

Furthermore, $$K_T = 10^{13}\exp\left[-\frac{34{,}500}{RT}\right] \text{ for cyclonite,}$$

and $$K_T = 10^{12}\exp\left[-\frac{28{,}400}{RT}\right] \text{ for P.E.T.N.}$$

From these equations, the following fractional decompositions are calculated for the two explosives, for durations of impact of the order indicated.

Although it is not known what fraction α of the explosive must decompose to give initiation by self-heating it can be seen that with the durations assumed, plausible values for the temperatures of the hot spots lie between 700 and 800° K for P.E.T.N. and a similar but somewhat higher range for cyclonite.

TABLE 34

(°K)	5×10^{-4} sec.	$7{\cdot}5\times10^{-4}$ sec.	$10{\cdot}0\times10^{-4}$ sec.
Fraction α of cyclonite decomposed during interval γ, in the small region around each grit particle, raised to the temperature of the hot spot			
500	0	0	0
600	0·0005	0·0010	0·003
700	0·11	0·15	0·20
800	0·9	0·97	0·99
1000	1	1	1
Fraction α of P.E.T.N. decomposed during interval γ			
600	0·045	0·07	0·088
700	0·54	0·66	0·79
800	1·0	1·0	1·0

Note. α is the fractional decomposition of small amounts of explosive which are in the immediate vicinity of the grit hot spots and which may be assumed to be at the same temperature.

A further check can be based on the relative probability of initiation of P.E.T.N. and cyclonite, as obtained from the experimental data (table 32), at low impact heights; this is also in reasonable agreement. Calculations would take too much space to give in detail, but it can be shown that $1220^\circ\,\mathrm{K} > T > 590^\circ\,\mathrm{K}$, on the basis of reasonable physico-chemical assumptions about the extent of decomposition required for self-heating, sufficient to lead to detonation.

(2) *Experiments with skins of low melting metals on the anvil*

The temperature of grit hot spots has an upper limit which is determined by the melting point of the metal surface, on which the grit impinges. This fact makes it possible to control the maximum temperature of grit hot spots by using metal foil to confine the explosive in the Rotter impact test. The following table describes experiments on the grit sensitization of cyclonite using 0·2 % of carborundum grit, the explosive being confined between disks of aluminium or of tinfoil 0·001 in. thick.

An unexpected result discovered in these experiments is that metals such as aluminium, and especially tin, greatly increase the ordinary impact sensitiveness of cyclonite in the absence of grit. The implications of this observation for the mechanism of impact sensitiveness are being followed up.

For the purpose of this report, the essential point to note is that added grit fails to lead to an increase in the percentage initiation when tin is used for confining the explosive.

TABLE 35. EFFECT OF LOW MELTING METALS ON SENSITIZATION BY GRIT

confinement of explosive	standard initiation area	mixture initiation area	P.I.G. (%)	m.p. of metal confining surfaces (°K)
normal (brass/steel)	8250	4000	51	1700
between Al disks	7750	5125	34	931
between Sn disks	3000	3000	0	505

The conclusion from the calculations and experiments described in § (c) thus support the hypothesis that grit forms hot spots which lead to initiation through thermal decomposition and self-heating. The use of low melting alloys to coat metal surfaces cannot, however, be recommended as a precaution against grit sensitiveness, without further experiments, since the ordinary impact sensitiveness may be enhanced, as above.

(*d*) Sensitiveness of cyclonite contaminated with factory grits

Using the methods described above, the sensitization of cyclonite by various factory grits has been investigated. These grits included sweepings from cleanways, coal dust from plant, and from the dust extractors, sweepings from the expense magazines and dust from the cements and bricks used.

On mixing cyclonite with quite small percentages of factory grits, marked increases in impact sensitiveness are observed.

Mixtures of cyclonite with 1 % of some of these dusts have figures of insensitiveness of the order of 20, a figure which is but little larger than that of Service azide.

Microscopic inspection shows that these dusts consist of crystalline particles, probably hard silicates, mixed with other impurities in some cases.

Discussion

The main experimental results described in this section may be summarized as follows:

(*a*) Added grit enhances the impact sensitiveness of high explosives, confined between brass and steel, but only when the hardness of the grit is about 4 or over on Moh's scale. If the crystals of explosive should themselves be of this order of hardness, this conclusion may need modification. Size of grit is important, and with the coarser samples one particle can suffice to initiate the whole charge.

(*b*) The increased reaction at a given impact height, when grit is added, is evidently due to a statistical increase in the number of initiations, which appear to be propagated to much the same extent (possibly by the same mechanism) as in the absence of grit.

(*c*) With P.E.T.N. and cyclonite each additional initiation due to grit leads to a 'complete' detonation of the contents of the cap. With tetryl, picric acid, and T.N.T., on the other hand, each additional initiation normally leads only to a 'partial'. In consequence, the effect of grit on the F.I., when determined in the standard manner from the percentage gas evolved at various heights, is much greater with P.E.T.N. and cyclonite than with, say, tetryl or T.N.T.

(*d*) Following the hypothesis that the action of hard grit under impact is to form local hot spots in the explosive, which produce detonation if the thermal reaction is sufficient to lead to self-heating, experiments have been carried out with thin foils of metals of low melting point covering the brass and steel. With cyclonite confined by pure tin, added grit fails to increase the initiation sensitiveness. With cyclonite confined by aluminium, some increase in initiation is observed, though not so much as with brass and steel confinement.

These results suggest that the temperature of such hot spots lies around 700° K with cyclonite and P.E.T.N. Theoretical calculations based on experiments on thermal decomposition confirm that such a temperature gives a reasonable picture of initiations due to added grit.

(*e*) The use of low melting metals such as aluminium and especially tin appears to sensitize cyclonite and other explosives to normal impact, although the formation of additional hot spots due to grit is prevented.

(*f*) Various samples of grit from factories are capable of sensitizing cyclonite to a marked degree. When perfectly free from grit, cyclonite is not much more sensitive than tetryl.

(*g*) In addition to these experimental results, the large number of standard areas determined for P.E.T.N., cyclonite, and tetryl permits statistical calculation of probable errors in F.I. figures. It is found that these errors do not exceed 1 %, provided at least 16 tests are made at each impact height where the probability of detonation is changing rapidly.

The results described are of interest in two ways. In the first place they give quantitative evidence of the grave handling risks introduced by grit, particularly when the explosives propagate well, as in the case of cyclonite and P.E.T.N. Secondly, they indicate that when explosives are apparently less sensitive to grit, this may in part be due to poorer 'pick up' or less self-heating.

The mechanism of phlegmatization

This second point is of very considerable interest in view of the various attempts which have been made to phlegmatize explosives, including cyclonite and P.E.T.N. Using the technique described in this section, it is possible by adding grit to determine whether the desensitizing action of waxes lessens the number of initiations, by 'lubricating' the crystals, or whether it merely damps down propagation.

Tests have been made on cyclonite with 9 % beeswax to obtain information on the mechanism of desensitization. The composition was crushed in a glass mortar but not sieved. 1 % of carborundum (100 mesh) was added. A large increase in the number of initiations was observed, but in no case did these lead to complete detonation. The F.I. could not be calculated, but the percentage initiation of cyclonite/wax mixed with 1 % grit was 57 % (P.I.G.).

TABLE 36. RESULTS ILLUSTRATING 'PARTIALS' PRODUCED BY 1 % CARBORUNDUM (100 MESH) ON CYCLONITE/WAX

	impact heights in cm. (5 kg. wt.)					
standard	50	100	150	200	250	300
cyclonite/wax	0	0	0 3·0	2·0 2·0	0 1·0	3·5
(no grit),	0	0	0 0	0 0	0 3·0	3·0
c.c. gas/cap	0	0	0 0	1·0 0	2·0 2·0	3·0
	0	0	0 0	3·0 0	0 2·0	3·0
	0	0	—	—	—	—
	no complete detonation at maximum height (F.I. > 120)					
cyclonite/wax	0	4·0 4·0	4·0 4·0	3·0 3·0	2·0 3·0	6·0
with 1 % grit,	0	2·0 4·0	5·0 6·0	5·0 4·0	5·0 6·0	3·0
c.c. gas/cap	0	3·0 4·0	3·0 3·0	3·0 4·0	4·0 3·0	7·0
	0	3·0 0	4·0 2·0	3·0 3·0	4·0 3·0	7·0

Detonation is probably never complete, even at maximum height, though the mixture has an initiation sensitiveness figure (P.I.G.) of 57 %.

Visual inspection of the crushed cyclonite/wax showed that some of the small crystals were not covered with wax; initiation by grit might have occurred at these points, particularly since as much as 1 % was present (60 grit particles/cap). To lessen this uncertainty, the carborundum itself was coated with beeswax (28 % by wt.) in the hot and the mass was powdered at the temperature of solid CO_2. This waxed carborundum was mixed with the cyclonite/wax. The percentage increase in initiation sensitiveness (47 %) was, however, much the same as that produced by 1 % of unwaxed grit.

Inspection of the data in table 36 and of figure 33 makes it clear that the wax both lessens the number of (detectable) initiations for a given momentum dissipated on impact, and also that the presence of the wax damps down the *probability of propagation* by self-heating, in a marked degree. The wax acts as phlegmatizer, since the cyclonite/wax gives partials.

A corollary of this view of the mechanism of phlegmatization by the quenching of local heat centres, is that the crystals separated by films of wax must not be too large, since if any one of them decomposes through the action of a local hot spot, the magnitude of the heat of reaction liberated, before a quenching film of wax is reached, will be proportional to the size of the crystal. Large crystals on this view are primarily harmful in enlarging the regions of chemically pure explosive, and it is not necessary (though not contradictory) to postulate that they are unusually sensitive when crushed.

In conclusion it may be noted that all the cases of sensitization by grit, described in this section, can be explained in terms of the thermal reaction of high explosives, and their propagation by self-heating. If this conclusion is supported by further work, the grit sensitiveness of high explosives may well be the simplest type of sensitiveness to explain in terms of the fundamental thermal properties of the compounds.

The increased sensitization to normal impact, which is observed when the confinement is changed from brass + steel to tin, is one of many indications that impact sensitiveness involves other factors, and is more complex than grit sensitiveness. This aspect of the work is being followed up.

A further noteworthy feature, deserving investigation, is the sensitization of P.E.T.N. by grit. From figure 30, the limiting F.I. with 1 % carborundum is 12, a value which is below the nominal F.I. of lead azide. Preliminary tests on cyclonite and P.E.T.N. with percussion and friction machines (parts IV and III (2)) suggest that under the lighter confinement in these two tests the sensitizing action of grit is less marked.

Appendix I

Statistical aspects of the impact test

Detailed analysis, which need not be reproduced, shows (i) as might be expected on mathematical grounds, the mean deviation $|\overline{\Delta p}|$ in percentage gas per cap is greatest where this percentage is changing most rapidly with impact height; (ii) the probable error in the mean values of p according to standard probability theory is $\frac{0{\cdot}85\,|\overline{\Delta p}|}{\sqrt{n}}$, where n is the number of observations at the impact height under consideration. These probable errors in the means range from 2·5 to 9 %.

Up to sixteen caps ($n = 4$) have been tested at impact heights near 50 % detonation, instead of the prescribed four ($n = 2$), to allow for observation (i) above.

(iii) From the probable errors in the p values at each impact height, the random error in A can be calculated. If all the p values deviated in the same direction the probable error in A would be merely proportional to $\Sigma|\Delta p|$. This is however unlikely, and following the usual theory, the random error in A, due to random errors in p, will be nearer the value

$$\Delta A_{\text{mean}} = -\frac{20 \times 0{\cdot}85\,\overline{\Sigma_1^5\,\Delta p_m}}{\sqrt{5}}.$$

Table 37. Specimen results with grit on P.E.T.N., cyclonite and tetryl

	standard P.E.T.N.					0·22 % carborundum-P.E.T.N. mixture				
ht. of fall (cm.) …	50	100	150	200	250	50	100	150	200	250
c.c. gas/cap	0, 0	0, 0	12·5, 11·0, 13·5, 12·5	13·5, 14·0, 14·5	14·0	13·0, 0	13·0, 12·5	13·0, 12·5, 0, 13·0	13·5, 12·5, 12·5	12·5
	0, 0	12·5, 0	13·0, 11·5, 0	14·0, 14·0, 14·0	14·0	12·5, 12·0	12·5, 11·5	13·5, 13·0, 13·0	13·0, 13·0, 13·5	13·5
	0, 0	0, 0	13·0, 13·5, 14·0, 14·0	13·5, 14·0, 0	14·0	12·5, 0	11·5, 14·0	13·0, 13·0, 12·0, 12·0	13·5, 12·5, 13·5	12·5
	0, 0	13·5, 13·5	0, 13·5, 13·5, 0	14·0, 0, 14·5	14·0	0, 13·5	13·5, 12·5	14·0, 13·0, 12·0, 13·5	12·5, 13·0, 12·5	13·0
gas/4 caps	0	19·7	38·9	46·8	56·0	31·7	50·5	48·5	51·8	51·5
% gas	0	35·3	69·5	83·6	100	61·6	98·1	94·2	100	100
% initiation	0	37·5	75·0	83·3	100	62·5	100	93·8	100	100

Standard gas area = 5232 sq.mm.
Mixture gas area = 1866 sq.mm. } F.I. of mixture = 16.

% sensitization (gas) = 64.
P.I.S. = 66 %.

Note absence of partials, with and without grit.

	standard cyclonite						0·22 % carborundum-cyclonite mixture			
ht. of fall (cm.) …	50	100	150	200	250	300	50	100	150	200
c.c. gas/cap	0, 0	0, 0	0, 0	14·0, 0	14·0, 13·0	13·0, 14·0	0, 0	0, 12·5	14·0, 14·0	14·0, 13·0
	0, 0	0, 0	0, 0	0, 0	14·0, 14·0	14·0, 13·5	0, 0	13·0, 0	13·5, 14·0	13·5, 13·0
	0, 0	0, 0	0, 0	0, 12·5	13·5, 14·0	14·0, 14·0	0, 0	0, 14·5	14·5, 14·0	14·0, 14·0
	0, 0	0, 0	0, 0	0, 14·0	14·0, 14·5	14·5, 14·0	0, 0	13·5, 0	13·5, 13·5	13·0, 12·0
gas/4 caps	0	0	0	20·2	55·5	55·5	0	26·7	55·5	53·25
% gas	0	0	0	36·5	100	100	0	48·2	100	100
% initiation	0	0	0	37·5	100	100	0	50	100	100

Standard gas area = 8270 sq.mm.
Mixture gas area = 4196 sq.mm. } F.I. of mixture = 31.

% sensitization (gas) = 49.
P.I.S. = 52 %.

Note absence of partials, with and without grit.

	standard tetryl							0·22 % carborundum-tetryl mixture						
ht. of fall (cm.) …	50	100	150	200	250	300	330	50	100	150	200	250	300	330
c.c. gas/cap	0	0, 0	12·0, 0, 1·0	0, 0	16·0, 17·0	18·5, 18·0	18·5	0	0, 3·0	11·0, 10·0, 5·0	100, 8·0	8·0, 17·0	15·0, 13·0	17·0
	0	0, 0	9·0, 0, 9·0	0, 3·0	0, 19·0	19·5, 19·0	18·0	0	7·5, 0	0, 5·0, 9·0	13·0, 14·0	12·0, 13·0	17·0, 16·0	18·0
	0	0, 0	0, 0, 0	14·0, 16·0	0, 1·0	1·0, 16·0	20·0	0	5·0, 6·0	7·0, 8·0, 12·0	6·0, 18·0	15·0, 6·0	9·0, 17·0	18·0
	0	0, 0	0, 0, 0	3·0, 0	18·0, 0	16·0, 18·0	20·0	0	0, 0	0, 6·0, 9·0	10·0, 12·0	14·0, 19·0	17·0, 16·0	19·0
gas/4 caps	0	0	10·33	18·0	35·5	63·0	76·5	0	10·7	27·3	45·5	52·0	60·0	72·0
% gas	0	0	13·5	23·2	46·4	82·4	100	0	14·9	38·0	63·0	72·2	83·3	100
% initiation	0	0	33·3	50·0	62·5	100	100	0	50·0	83·3	100	100	100	100

Standard gas area = 9560 sq.mm.
Mixture gas area = 7338 sq.mm. } F.I. of mixture = 54.

% sensitization (gas) = 24.
P.I.S. = 48 %.

Note partials, increased in number by grit.

If the number of impact heights were very large, instead of only 6, this equation would be exact.

Inserting figures from the data available:

For tetryl $$\Delta A(\text{mean}) = \frac{20}{2\cdot 24} \times 0\cdot 85\,(19\cdot 9) = 150\,\text{sq.mm.}$$

For P.E.T.N. $$\Delta A(\text{mean}) = \frac{20}{2\cdot 24} \times 0\cdot 85\,(18\cdot 9) = 144\,\text{sq.mm.}$$

Comparison of these random errors within any one series of impacts with the mean deviation ΔA (table 38) over a large number of series shows that systematic variations from one series to another due to anvils, etc., are somewhat larger than random errors introduced through insufficient observations at each impact height.

The conclusion is that, provided the number of determinations around the 50 % value is not less than sixteen, no additional accuracy will be secured in figures of insensitiveness, by increasing the number of impact tests, in view of systematic variations from anvil to anvil. The probable error in a F.I. figure based on single series of tests, using the technique recorded in this report, is thus of the order ± 1 %. Systematic errors additional to this would tend to cancel out on dividing by the standard area.

Table 38. Mean deviations in standard impact area

explosive	sq.mm.
tetryl	350
cyclonite	341
P.E.T.N.	280

Appendix II

Evaluation of Figure of Insensitiveness in the standard impact test

In the standard determination of the Figure of Insensitiveness by the Rotter method, a fixed quantity of high explosive is subjected to the impact of a weight falling from a series of heights. The extent to which explosives may detonate is measured by the volume of gases evolved as a result of decomposition due to the impact.

To calculate a Figure of Insensitiveness, impact tests are made alternately on two explosives A and B, one of which serves as standard. From the mean value (usually based on 4 caps) for the maximum gas obtainable at greater heights, and the mean value of the gas actually obtained at lower heights, the percentage detonation at these lower heights is calculated.

A plot is made of the percentage detonation against height of fall of the weight, and the area between the curve and the Y axis is taken as a measure of the insensitiveness.

Convenient co-ordinates, which are used in determining the areas in the tables, are

$$X,\quad 50\,\text{cm. height} \equiv 20\,\text{mm.}$$

and $$Y,\quad 10\,\%\ \text{detonation} \equiv 10\,\text{mm.}$$

On this basis, F.I. = const. × area under curve; the constant is determined by putting the F.I. of picric acid ≡ 100.

Thus, if the ordinates are as follows,

height of fall (cm.)	...	50	100	150	200	250	300
percentage detonation (from gas evolved/maximum gas obtainable)		p_1	p_2	p_3	p_4	p_5	100

the area from which the insensitiveness is calculated is

$$A = 12{,}000 - \left(\frac{p_1}{2} + \frac{p_1+p_2}{2} + \frac{p_2+p_3}{2} + \frac{p_3+p_4}{2} + \frac{p_4+p_5}{2} + \frac{p_5+100}{2}\right) 20$$

$$= 11{,}000 - 20\,\Sigma_1^5 p.$$

The probable error in such a calculated area is

$$\overline{\Delta A} = -20\overline{\Delta\Sigma_1^5 p}.$$

(In grit sensitiveness determinations, the above remarks apply directly to the P.S.G. values. As previously explained, P.I.G. figures are obtained by calculating the percentage increase of initiations. This does not affect the probability argument.)

With the data available from the experiments reported, it can be tested how far the deviation in experimentally observed areas can be ascribed to chance errors within a single determination of F.I., and how far systematic variations such as changes from one anvil to another can affect the sensitiveness.

Within any one series of impact tests, systematic variations such as anvil hardness may be assumed constant, so that only random errors need be considered.

Random errors at any one impact height will be given by the mean value of Δp, where

$$\Delta p = \frac{\text{c.c. gas/cap} - \text{average c.c./cap}}{\text{maximum c.c./cap}} \times 100$$

and according to probability rules the probable error in $(\Delta p)_{\text{mean}}$ will be $\frac{0{\cdot}85\,|\overline{\Delta p}\,|}{\sqrt{n}}$, where n is the number of determinations.

(2) THE SENSITIVENESS OF INITIATORS TO FRICTION. APPARATUS FOR MEASURING RELATIVE SENSITIVENESS TO GRAZING FRICTION WITH OR WITHOUT GRIT

By S. E. Napier, W. J. Powell and A. R. Ubbelohde

(*Report first issued by the Armament Research Department*, 11 *August* 1942)

[Plates 6 and 7]

Apparatus is described for subjecting explosive compositions to grazing friction between surfaces of various materials, which can be made to move at various relative velocities up to about 15 ft./sec. Conditions for obtaining reproducible results are detailed.

Tests on a number of initiators by means of this apparatus give an order of relative sensitiveness to rubbing between smooth surfaces of steel. When the rubbing occurs in the presence of grit, it is found that certain initiators such as lead azide and lead styphnate have their sensitiveness notably enhanced compared with others, such as mercury fulminate.

Photomicrographs of the explosives after rubbing show very considerable break-up of the crystals even when no detonation has occurred.