



MINISTRY OF AVIATION SUPPLY

**EXPLOSIVES RESEARCH
AND DEVELOPMENT ESTABLISHMENT**

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**Proceedings of the
Symposium on
Sensitiveness and Safety of Initiators**

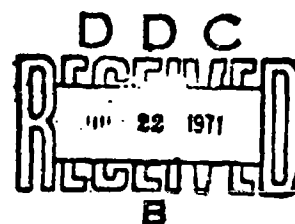
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**Editor
J M Jenkins**

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Symposium on
Sensitiveness and Safety of Initiators

17 April 1969
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Editor
J M Jenkins

Waltham Abbey
Essex

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CONTENTS

		Page No
Welcoming Address	L J Beilamy Director ERDE	1
Introduction	G W C Taylor	1
Present Status of Sensitiveness Testing	R M H Wyatt	1
Assessment of Anti-Static Materials	J F Sumner	6
Assessment of Hazards Associated with the storage and transport of wet initiatory compositions	R J E Williams T S Costain A T Thomas	10
Safety Certificates and Factory Safety Precautions	J V Griffiths R M H Wyatt	21
A Recent Incident with Lead Styphnate	R M Ferguson	27
The Explosive Reactivity of Metal Azides	P G Fox	33
New Data on the Electrostatic Sensitive- ness of Copper and Silver Azides	S Lamnevik	47
Summary	G W C Taylor	52

WELCOMING ADDRESS

A welcoming address was given by Dr L J Bellamy (D/ERDE) in which he extended a welcome to all visitors, especially those from overseas. He described the Symposium as a gathering of experts and friends, and hoped that all would benefit from the proceedings.

INTRODUCTION

THE CHAIRMAN (G W C TAYLOR)

I would like to define briefly the area in which ERDE work on primary explosives is concerned. Firstly there is the study of the preparation and properties of both well established and possible new types of explosive; this includes development of processes to production scale of manufacture.

Secondly, there is the study of sensitiveness, especially by development of appropriate tests and interpretation of results. This includes making recommendations with regard to Safety Certificates, and other advice on hazards.

Thirdly, there is a very broad area concerned with compatibility of primary explosives with other explosives and materials.

We consider that to be effective these activities require close collaboration with other research organisations, (in particular those concerned with design and functioning) and, equally important, is our contact with the production factories. The overall effort devoted to research on primary explosives is quite small in relation to the effort in production. Thus in this country alone the output of detonators and caps or primers is of the order of several millions per week. This is quite apart from the requirements for the more sophisticated and varied devices for military and special purposes and of course the problems of sensitiveness and safety which are peculiar to very sensitive explosives. Therefore we feel that it is not necessary to offer any excuses for arranging this symposium and we are very pleased that so many with direct responsibilities and experience in this field have been able to attend.

To define the area of discussion; we are concerned with the manufacture and handling up to and including loading of explosives in the most sensitive class usually described as primaries or initiators. We are excluding the hazards of filled stores which are not within the province of ERDE.

THE PRESENT STATUS OF SENSITIVENESS TESTING

R M H WYATT

I intend to present a short review of the sensitiveness testing of initiators particularly, as the Chairman has pointed out, in relation to the eventual production of the Safety Certificate, and in a wider context, the provision of useful information for the Ordnance Factories. The actual Safety Certificate of course comes up later in the day. Of the tests that are carried out, let us start first of all with the time honoured Rotter impact test which I think nearly everyone in this room knows about.

It has been agreed by a body called the Sensitiveness Collaboration Committee; a body composed of representatives of RARDE, AWRE, DCI, NOID, occasionally the Ordnance Board, and ourselves, that initiators are to be tested against standard RDX.

Just to make a short statement on results, the majority of initiatory compounds give an F of 1, of 10 or 20, where RDX equals 80. Now and again we get one up as high as 30, but the majority of them are 10 and 20.

The next test that is required by the Safety Certificate, is the Mallet Friction Test. In this instance we are concerned only with the boxwood mallet on anvils of hardwood, softwood and yorkstone, and in the majority of the compounds we are concerned with I'm afraid we get little discrimination, they will all give us a figure of 100, 100, 100, the majority firing on the very first strike.

Then we come to the Temperature of Ignition which for this type of explosive we use the smaller quantity of 0.05 grams heated at 5°C per minute. As far as we are concerned here it is largely a stability type of test.

Next we come to Electrostatic Spark Test. In the normal procedure for an unknown material one would subject it to the test where one uses sparks with energies of 4.5, 0.45 and 0.045 joules. I should also point out that all these tests are described in two documents which are being issued by, or have been issued by The Sensitiveness Collaboration Committee. That is the earlier one which is labelled "Safety Certificates Sensitiveness Tests" and, the current one which is called "Explosives Hazard Assessment". These tests are given in fair detail.

The explosives we are concerned with, of course, are regularly ignited by energies of 0.045 joules so in actual fact when we know it is an initiator compound we do not bother to do that test; and we go straight on to use energies of less than this figure. Normally we use capacitances of 300 and 500 pico farads charged to appropriate voltages to give us a couple of curves from which we can attempt to determine a minimum ignition energy using two metallic electrodes - for short we call it M/M - that is where one has an explosive laid out on an earthed metallic base, and a gramophone needle to which is attached the capacitor that you have charged is brought down towards it. This test has certain drawbacks in that it does not reproduce all of the conditions that are likely to occur in practice so we do another series of tests called R/M for short involving changing the base electrode to one of conducting rubber. A piece of conducting rubber is stuck to the base metal with conducting adhesive and the needle is used in the top half as before. This simulates the discharge that you get from the finger of a charged person because (a) you have turned one of the electrodes into a non-metallic one - (b) the resistance in the circuit on having this piece of conducting rubber, plus the conducting adhesive and the upper electrode approaching it, is very similar to the operative resistance of a spark from a charged person's finger. You have to carry this out with a variety of capacitances to determine a minimum capacitance for ignition and also a minimum energy at some optimum capacitance.

I think it would probably be worthwhile if I quote a few figures now. By and large with the explosives we are concerning ourselves today, figures of less than 30 micro joules are found for the M/M arrangement, and for the R/M we are involved with two groups - one where the minimum capacitance is less than 100 pico Farads and the energy is less than 20 micro joules, and another group in which the

minimum capacitance is 400/500 pico Farads and the energy in the region of 200 to 1,000 micro joules. You can see that both of these groups are well below the 0.02 joule sub-division of precaution.

Now these four tests are the statutory ones that we are concerned with on these explosives. The others, ie the Bickford Fuse and Train tests we do not need to consider as the response is predictable.

We do two other tests, usually as a matter of routine. They are both mechanical tests. The first is the one called the Ball and Disc Impact - which is a peculiar test really in that you only subject a part of the sample to impact. You lay out your material on top of a steel roller, and a brass disc of specified thickness is put on top of that and you gently place on top of the disc a drift which has a hemispherical end to it. A ball is dropped on to the drift. It is a peculiar test in that unlike most impact tests you only hit the middle of the sample.

This test has some value. It does give you some discrimination between the various types of primary explosives. Occasionally you do not get a particularly normal distribution with this impacting arrangement.

The second test that is done is the Emery Paper Friction test. This involves subjecting the explosive to a frictional action between two emery paper surfaces. This test is primarily a grit friction test but you can change the surfaces fairly readily and carry it out without the emery paper and do it between two relatively smooth steel surfaces. This gives you an idea of the effect of grit. Alternatively, you can change the metal of the fixed frictional surface to other metals in which you may be interested in the construction of your plant, steel, brass, or phosphor bronze. Unfortunately we cannot change the steel sliding block too readily as this is the part you have to impact with the steel pendulum bob.

We said that we normally get figures of Rotter impact of 10 and 20 and sometimes 30, but if you consider two compounds, firstly lead 2.4 DNR, which is relatively impact sensitive (and after all is the basis of a number of impact sensitive compositions) you get an F of I of 10. Lead Azide on the other hand rarely gives you a figure below 20 and on occasions you get values of 30. On that basis one would be keener, shall we say, if one could imagine that these two compounds were interchangeable, to use lead azide rather than LDNR. I do not suppose there is anybody in this room who would do that, and this really shows you that you cannot take F of I figures in isolation. We need to consider friction as well. We saw in the case of the mallet test this would give us no discrimination at all, we would get 100% ignitions every time. With the emery paper friction test, which gives us some idea of the relative sensitiveness to grit, we find a reversal in response. With service lead azide the velocity for 50% ignitions is about 4.5 feet per second, whereas the figure for lead 2.4 DNR is 7.3 feet/second, that is almost double. This serves to emphasise the point that in the examination of all explosives and propellants you must never take the result of one mechanical test in isolation but must look at the result of at least two of them.

DISCUSSION

B H Newman

You quote in all of these tests the 50% point. I know experimentally it is easier to determine these, but from the safety aspects of handling initiators, generally speaking we are concerned with much lower probability of events than these. What have you done to determine these, and if you have determined them, do they come in the same order as the 50% points?

R M H Wyatt

Yes, the majority do come in the same order. The values of the standard deviations are similar over the whole range so they would then come in the same order. Largely I have given these 50 per cent figures today because they are a quick way of illustrating points about lead azide and LDNR. We also do a run down type of distribution particularly when we suspect non-normal distributions.

N Griffiths

There is some indication at the moment that the order of the 50% points is not the same as the order of the 0% points; at least in the case of secondary explosives I would like to suggest that perhaps the data you get out of these tests reflect more the tests themselves rather than the compositions.

E G Whitbread

What is meant by a 0% point? Presumably you do not mean a 0% point, you mean one in 100,000 or one in a million or something like that. Supposing you did define it as 1 in 10^5 , have you worked out how many tests you would have to carry out in order to get any sort of significance whatever? I think that you need something like 296,000 failures on the trot to have 95% confidence that you have a probability of fire of less than one in 100,000; so if your 0% is of the order of 1 in 10^5 then you are giving yourself an almost impossible job in testing and I strongly suspect that your 0% point is not 0% at all but something like 1 in 20 or 1 in 30.

E B Hancock

What about any possible hazard due to electrification of the explosive itself? You might expect a more insulating material to be worse than a more conductive one.

R M H Wyatt

I would think in the case of primary explosives that the majority of the present rules look after the electrification of those, and it is perfectly true that those which are of high resistance like lead styphnate electrify much more than the others. We did attempt to look at this from the point of view of whether the operations we carried out with dry styphnate were important from the point of view of drawing any charge from charged styphnate. I think by and large we came to the conclusion that the rules tend to look after this - particularly after it has been dried and you are doing this sort of half separation half sieving process through six funnels. There is a case where you obviously get a charge but the rules say you must leave it for half an hour or so and if you are working with a relatively high humidity this suffices.

Chairman

One often has hazards in mixing processes, for example mixing lead styphnate with graphite, which are rather greater than would be appreciated merely by taking the results on safety certificates. We also found this with some elastic pyrotechnics where it has been necessary to produce data during the mixing and during the curing process because one can get a situation where you get a high degree of hazard, a greater degree of sensitivity either electro static or mechanical at an intermediate stage before the mixing is complete.

J Wilby

Mr Rask might care to note in particular that although we use lead azide/graphite in CC detonators nowadays, we have considered silver azide/graphite for CC detonators for Sweden but abandoned that because we felt that the sensitisation by graphite of the silver azide was particularly pronounced.

ASSESSMENT OF ANTI-STATIC MATERIALS

J F SUMNER

I want to talk mainly about new developments in conducting polythene for use with initiator materials and initiator manufacturing practices. I feel I ought to mention first two other types of material that are important to the handling of initiators. These are floors and flooring materials and secondly, footwear and clothing. I will try and dismiss these two fairly briefly by saying that we are keeping abreast of recent developments in the trade as regards these materials. Floors and flooring materials; traditionally of course, for initiator manufacture these have been made of rubber which is made conducting by the addition of a fairly large amount of carbon black to avoid the development of electro-static charges. A number of plastics have appeared on the market recently and various firms have tried to incorporate carbon black in various ways into these materials. We are engaged on a programme of investigating these at the moment, studying them not just resistance-wise but actually developing electro-static charges in ways which are relevant to the electro-static hazard with initiators. Mr Cleves is studying these floors and we have tested several already.

Now, on the subject of footwear and clothing, again we have mainly conducting rubber shoes in initiator manufacture. We are quite happy with the conducting rubber shoes that are available. We would emphasise of course the importance of the use of a personnel test meter which can be used every time an operator goes into the workshop to assess his complete leakage circuit for getting rid of the electro-static hazard and reducing it to a satisfactory level. The normal value is 1 megohm as the maximum permissible resistance from hand to earth. I know the actual test is normally carried out on a metal plate but we would prefer to see it carried out through the floor as well, because this constitutes the whole system on which the operator is relying for his freedom from electro-static charges due to foot movements and certain other operations.

On the subject of clothing it has always been accepted that a close fitting cotton outer-garment, an overall, is satisfactory and that this forms an equi-potential system with the man. It is, of course, essential that the cotton outer-overall be in close contact with the skin of the wearer in order to achieve this effect, otherwise you are setting up a condenser. This was brought to our attention when we noticed that somebody was wearing a pullover under the overall. The pullover extended over the wrist - so that the overall was not in contact with the skin. We did some tests simulating this situation and measured the localised electro-static charge on the forearm of the cotton overall and found that it could easily be charged by friction with a safety screen. Imagine the operator working around the screen and just rubbing his/her forearm against the side of the screen. We found that this could easily be charged to 3 or 400 volts and we think that there is at least one instance where ignition has resulted from such a localised charge on the forearm of a cotton overall. They were obeying all the rules, they were wearing conducting footwear, standing on conducting flooring but, they still had this localised charge on their forearm which could result in an ignition. So we would emphasise that any cotton outer clothing should be in positive contact with the skin of the wearer in order to be sure that there is no electro-static charge to cause an ignition.

I would like to proceed now to the developments as regards conducting polythene. Many of the pieces of equipment used in initiator manufacture have traditionally been made of rubber and gutta-percha, both of which have been made conducting with the addition of carbon black. We find these days that the trade just is not interested in producing materials with these high loadings of carbon black in rubber and gutta-percha. Polythene, of course, is a very popular material as it

stands, it is reasonably cheap, it is very amenable to mass production. Conducting polythene as a raw material has now been fairly well established and those of you who have seen the exhibition will have seen some of the samples of satisfactory injection mouldings which are used as storage containers for use with initiator materials. Of course, these are used by the hundred or thousand and are from mouldings which are produced by ROF Chorley. The material incidentally is available as layflat film from which polythene bags can be made. The material at first did not weld but improvements have been made by slight modifications to the mix and you can now get quite a good weld in a conducting layflat film. The real problem arises when we want to make things like buchner funnels, buckets, dishes, trays and so on from conducting polythene. The material can be rolled out into flat sheet but when the trade has tried to put this on the market nobody has shown any real interest, at least in the vast quantities suited to mass production. We have been prodding at the trade here and there to see where we could meet them halfway, to effect a compromise. We now have a firm who are prepared to produce a few hundred feet of flat sheet 1/10" thick which we are going to try welding to certain shapes and we think this is feasible and probably suitable for producing small numbers of some of the types of component that are required.

Another process that has been suggested and that one of the Ordnance Factories is prepared to attempt in conductive polythene, is vacuum forming.

The level of electrical conduction is well above that necessary to eliminate all electro-static hazards with the material and provided we can solve the production problems, with the help of people who are experienced in the manipulation of these materials, I think we can look ahead to a brighter future in this respect.

Coming back to the sensitiveness problems of these materials, there is one aspect which we have recently been looking into ourselves, that is that Rigidex polythene when loaded up with carbon black does feel a bit hard to the touch and people quite naturally have asked us, is there not going to be a friction and impact hazard, a mechanical hazard due to the use of these materials? Many of you will have seen the demonstration where we took a friction test machine providing a similar load and velocity to our standard friction test for primary explosives. We have loaded up this old machine with conducting polythene surfaces and have rubbed lead azide and lead styphnate, two typical initiators, quite hard with them and have done several hundred tests without an ignition. The main purpose of this was to give people who handle these materials confidence in the use of these conducting polythenes which are rather hard to the touch. The softer versions of conducting polythene unfortunately do not have sufficient mechanical strength. This is why high density or Rigidex polythene, has found greater favour for injection mouldings. We hope in time it will prove suitable for other methods of fabrication.

Although at the moment we are concentrating on vacuum forming and welding for the fabrication of these new shapes we may have to think in rather wider terms for some requirements.

DISCUSSION

Chairman

Should the floor be earthed or should it be a floating conductor?

J F Sumner

Originally, all the booklets - British Standard booklets on the subject - and most of the reports and literature which appeared on this, indicated that floors should be earthed. However, some 10-12 years ago literature in relation to anti-static floors for use in hospitals suggested that there is no need to have such a floor earthed. This we do not agree with ourselves; my own philosophy on this is that you must have everything at the same potential and if you have a small section of conducting or anti-static floor which is not definitely earthed it is possible to charge this section of flooring up by several people walking over it, by somebody carrying out an operation such as wiping a window or wiping the dust from a safety screen which may have collected it over the weekend. In doing so they develop a charge on themselves and the only safe thing is to get this away to earth through the footwear and flooring. If you are going to leave a charge on a section of flooring and a second person steps on to it and handles an initiator through which the charge might then be dissipated, then sooner or later somebody is going to blow themselves up. This is particularly the case with a small section of flooring and we do know of instances where only small sections of conducting flooring have been laid. It might be a room as large as this for instance with just one small bench where a person has to insert an igniter into a weapon or to just load an igniter into a fuze assembly. All the other operations are considered safe so a small piece only of conducting flooring is provided, perhaps one or two square yards at the most, for this one single operation. All these operations tend to be very stereotyped and one can usually say "only in this place can a person handle a bare explosive or a bare igniter, so that we can make him safe and forget about everybody else". This I think is reasonable, providing you earth that section of the flooring, but I think it is a big mistake to leave that section of flooring insulated because it is a conductor.

I would like to emphasise the actual value of a personnel test meter because it does test your complete system whatever it happens to be whether it is bare feet or conducting shoes, or conducting overshoes. The essential thing is to establish a complete conducting path from the body of the operator right through to earth and this test can be done on a daily basis by a personnel test meter at the entrance to the workshop.

Chairman

This question of footwear is important. In India it was found that an explosion occurred when a particular foreman came into the shop. It turned out that he was the only one who wore boots - the other operatives were barefoot.

A T Thomas

What is the importance of surface cleanliness of the conducting flooring; at Woolwich our water is loaded with calcium carbonate, would it have any effect?

J F Sumner

I do not think that calcium carbonate deposited on the floor from the hard water in this area is likely to make the surface any less anti-static than by using pure water. Any chloride in solution would, of course, tend to help contact leakage. If you have two conducting rubber or polythene surfaces in contact then the contact resistance between these surfaces is quite high unless you have some ionic material on the surface, and this is where chlorides do help. They also help, of course, by absorption of moisture and the maintenance of the fairly high relative humidity we mentioned.

N Griffiths

Is it important to get the floor free from dust?

J F Sumner

This is important because a lot of dust that we get on floors is fluff from clothing and silica dust. Silica is one of the easiest materials to give rise to an electro-static charge.

L D Cole (submitted after Symposium)

Caution should be used in accepting the idea of a "floating earth" system. This is all very well in itself and I believe it is often used in hospitals. However for our use in a laboratory and plant it does not appear very practical. The piped services are insulated from the floating earth and hence any charge developed would be released by an operator touching a steam or water valve.

J F Sumner

It is safer to dissipate any charge arising on a person, through his footwear to earth. If he acquires a charge while standing on an unearthed floor, whether this is conducting or not, he can discharge when he touches an earthed object with his hand. This could be a service pipe or valve, or even an earthed vessel, maybe containing sensitive material.

ASSESSMENT OF HAZARDS ASSOCIATED WITH THE STORAGE AND TRANSPORT OF WET INITIATORY EXPLOSIVES

R J E WILLIAMS T S COSTAIN A T THOMAS

Little is known about the sensitiveness of initiators wetted with water. Some experimental data obtained by a simple test devised to provide information on the ease of ignition of wet initiators is presented. When analysing the test results there are two important questions

- 1 The safety aspects of bulk transport of initiators wetted with water, and
- 2 The hazard associated with the handling of wet lead styphnate.

SAFETY ASPECTS OF THE BULK TRANSPORT OF INITIATORS WETTED WITH WATER

In this country the transport of lead azide in bulk is prohibited, and the various types of lead azide are manufactured on site at the filling factories. Certain authorised initiators such as lead styphnate, barium styphnate, lead dinitroresorcinat, mercury fulminate, and tetrazene are permitted to be transported in bulk when wetted with water and packed in a special manner. Conversely it is the practice in the United States to transport wet lead azide in bulk, while in some cases it is preferred to manufacture lead styphnate on site at the filling factories. This difference in procedure, together with the need to know whether new ERDE initiator compositions are safe to transport under water, prompted this investigation.

The novelty of the test lies in the use of miniature detonators and igniters, which are based on the ease with which controlled amounts of initiator compositions can be placed on the bridgewires of standard ICI fuseheads, giving reproducible sources of small explosive stimuli. Miniature lead azide detonators were prepared by dipping bare fuseheads into a suspension of finely divided lead azide in nitrocellulose lacquer. One dip gave an explosive bead weighing 5 to 7 mg and a further dip gave a bead weighing 14 to 16 mg. Also single and double dipped lead styphnate igniters were prepared from a suspension of lead styphnate in nitrocellulose lacquer.

Fig 1 shows the test apparatus.

The initiator and water were placed in a polythene container 75 mm long by 23 mm internal diameter. A fusehead was lowered into the explosive slurry and the container placed on a 1½ mm lead witness plate seated on a backing block. The fusehead was fired with a 1½ volt dry cell. In the first series of tests 1 g of initiator was placed in the container and thoroughly wetted with 1 g of water, or with 50/50 alcohol/water. This mixture is used in the United States to avoid freezing of the liquid during transport. The wet initiator stood 1 to 2 mm above the bottom of the container with an approximately equal volume of free liquid on top. A 7 mg lead azide fusehead detonator was lowered through the liquid layer into the explosive slurry but not quite touching the bottom of the container. The fusehead was fired, and when detonation of the acceptor occurred a 25 mm disc was punched from the witness plate. When no ignition of the acceptor occurred a small dent was made in the witness plate by the force of the miniature detonator alone.

The results of this first series of tests are shown in Table 1.

TABLE 1
RESULTS OF TESTS

Explosives Tested	Number of Detonations in five tests	
	Under Water	Under 50/50 Alcohol/Water
SL AZIDE N ₃ Value ~96.5% Basic Lead Carbonate ~ 2.5%	5	Not tested
RD 1343 LEAD AZIDE N ₃ Value ~96.5% - 0.3% Basic Lead Azide - 1.0%	5	5
RD 1333 LEAD AZIDE N ₃ Value ~97.0% LCMC - 1.0%	0	0
RD 1352 DEXTRINATED N ₃ Value ~94.5%	0	Not tested
ICI DEXTRINATED N ₃ Value ~93.0%	0	0
RD 1336 PURE SILVER AZIDE N ₃ Value ~99.5%	0	0
RD 1303 PURE LEAD STYPHNATE	0	0
RD 1337 PURE LEAD 2.4 DNR	0	Not tested
RD 1357 PURE TETRAZENE	0	Not tested

Only the service lead azide and lead azide RD 1343 were ignited to detonation. The relatively powerful impulse delivered by the miniature detonator failed to ignite the other lead azide types, silver azide RD 1336, lead styphnate RD 1303, lead 2:4 dinitroresorcinat RD 1337, and tetrazene RD 1357. All these compositions when dry are known to be very sensitive to shock. Nevertheless, the test is sufficiently discerning to distinguish between the different types of lead azide and indicates that it is inadvisable to transport service lead azide or RD 1343 in bulk even when completely wetted with water. An ERDE technical Memorandum No 1/M/69 has been issued covering the work up to this point.

Further tests using increased mass, and greater impulse on increased mass to see whether ignitions could be obtained, were carried out on the compositions which failed to respond to the stimulus.

Table 2 gives the results.

TABLE 2
50 PER CENT WATER - WET INITIATORS

Initiator	Dry Weight g	Number of Detonations in five tests	
		Single Dip 7 mg Lead Azide Fusehead	Double Dip 15 mg Lead Azide Fusehead
RD 1333 LEAD AZIDE	2	5	Not done
RD 1336 SILVER AZIDE	2	5	Not done
RD 1352 DEXTRINATED LEAD AZIDE	2	0	0
RD 1303 LEAD STYPHNATE	2	0	0
RD 1337 LEAD 2,4 DNRESORCINATE	2	0	0
RD 1359 LEAD TNPHLOROGLUCINATE	2	0	0
RD 1355 LEAD MCNOBASIC AZOTETRAZOLE	2	0	0
RD 1357 TETRAZENE	2	0	0
MERCURY FULMINATE	1	5	Not done
	2	1/1	Not done

With 2 g of initiator plus 2g of water, lead azide RD 1333 and silver azide RD 1336, which did not ignite in the first series of tests, were ignited from a 7 mg detonator. Apparently indicating that the mass of material tested was a significant factor.

Once again dextrinated lead azide, lead stypnnate, lead 2:4 dinitroresorcinate and tetrazene did not ignite, even from a 15 mg detonator.

Similarly, two new compositions, of potential service application, lead trinitro-
phioroglucinate RD 1359, and monobasic lead azotetrazole RD 1355, also did not
ignite.

An interesting brisance effect occurred with RD 1333. When detonation occurred with service lead azide, lead azide RD 1343, or silver azide, the discs were punched out cleanly from the witness plates, but with RD 1333 the discs were not completely detached apparently indicating that this detonant is less efficient. In view of its high azide value this seems unlikely, and it was thought that the effect could be due to the water gelatinisation of the uniformly dispersed 1% lead carboxymethylcellulose present in this composition. To test this assumption, RD 1333 was thoroughly dried and fired immediately after adding the water - that is within 2 to 3 minutes - and it was found that the discs were punched out cleanly, but when RD 1333 was left under water in the container for one week prior to testing partial ignitions were obtained giving shallow indentations on the witness plates and substantiating the theory that the reduced efficiency would be due to gelatinisation.

These results posed two interesting questions:

1 Why did no ignitions occur with 1 g of RD 1333 and RD 1336, but 100% ignitions with 2 g?

2 Is this a mass explosion effect or is it due to some configuration factor of the test apparatus?

Dextrinated lead azide, RD 1352 appears to be quite insensitive even to the 15 mg shock impulse which lends confidence to the American practice of bulk transporting dextrinated lead azide under water. But for some years now the United States have been manufacturing large quantities of RD 1333, which, by analogy with dextrinated lead azide they have been also bulk-transporting under water, and this test shows RD 1333 to be more sensitive than dextrinated lead azide.

With regard to the newer compositions, RD 1359, RD 1355, and RD 1357, which did not ignite, it will be difficult to decide whether the results justify recommending their bulk-transport in the wet state.

The tests showed that mercury fulminate under water could be ignited as readily as lead azide.

Mercury fulminate was first prepared by Howard in 1800 and became a Government Authorised Explosive in 1876. Subsequently large quantities have been transported under water without explosion incident.

The result of the test casts some doubt on whether it is safe to transport mercury fulminate in bulk. On the other hand, one might argue; if it is safe to transport wet mercury fulminate, why not permit the bulk transport of wet lead azide?

However, when dealing with lead azide other important factors must be considered:

1 For no apparent reason explosions have occurred during the washing stage in the manufacture of service lead azide, when the crystals were stirred in water.

2 Lead azide hydrolyses in water giving hydrazoic acid which is a highly sensitive explosive and an extremely toxic compound.

3 Lead azide is slightly soluble in water, changes in temperature could lead to undesirable crystal growth.

To summarise: The test shows that a difference exists in the ease of ignition

of the various initiators under water, but does it provide sufficient valid information to decide which initiators may or may not be bulk-transported in the wet state.

HAZARDS ASSOCIATED WITH THE HANDLING OF WET LEAD STYPHNATE

Large quantities of lead styphnate RD 1303 are handled at ROF Chorley where 4½ kg batches are made and stored wet.

For VH2 mixture a process has been developed which eliminates the operative handling dry lead styphnate. The water content is reduced to about 20% by gentle suction, on a filter. Portions are weighed and formed into cakes which are dried and handled remotely. Using the test apparatus, experiments were carried out to determine the ease of ignition of water-wet lead styphnate.

Dry lead styphnate, RD 1303 was weighed into the test container and mixed with water to give a uniform slurry. In the slurry was immersed, either a lead styphnate igniter, or a lead azide detonator. The results obtained on firing are given in Table 3.

TABLE 3
FUSEHEAD IMMERSSED IN WET INITIATOR SLURRY

Initiator	Dry Weight g	Wet Weight g	Per cent Water	Temp	Fired by	
					15 mg Lead Styphnate Fusehead	15 mg Lead Azide Fusehead
Lead Styphnate RD 1303	1.0	1.11	10	Amb	1/1C	1/1C
		1.80	15	"	1/1C	0/5
		1.25	20	"	0/5	0/5
		1.43	30	"	0/5	Not done
	2.0	2.50	20	Amb	1/1C	0/5
		2.86	30	"	1/1C	Not done
	3.0	3.75	20	Amb	1/1C	1/1C
		4.30	30	"	1/1C	0/5
		5.0	40	"	1/1C	0/5
		6.0	50	"	3/3C	0/5
		4.30	30	-5°C	1/1p	Not done
		6.0	50	-5°C	1/1p	Not done
Service Lead Azide	1.0	2.0	50	Amb	0/5	5/5C
	3.0	6.0	50	"	0/5	Not done
RDX RD 1347	2.0	2.0	Nil	Amb	0/5	1/1C
	2.0	2.5	20	"	Not done	0/5

Examination of the results obtained using a 15 mg lead styphnate fusehead ignitor shows:

- 1 With 1 g of lead styphnate plus 20% water: No ignitions in five tests.
- 2 2 g with 20% or 30% water: Positive ignitions obtained. "C" indicates that all the lead styphnate was consumed.
- 3 3 g with 20%, 30%, 40%, or 50% water: Positive ignitions obtained.

At 20% water the consistency is that of a buttery paste and with 25% water the crystals are saturated with the appearance of a free liquid layer on top. Hence

the slurry can contain about 22½% water and adding more water merely increases the height of the free liquid above. Examination of the extent of indentation on the witness plate showed decreasing brisance with increasing percentage water content.

In these experiments it appears again that ignition is obtained more readily when the mass of initiator tested is increased.

Two experiments were carried out at -50°C. Here the fusehead was frozen in the slurry. With 30% water present a large partial ignition occurred and with 50% water present a small partial ignition was obtained, indicating that, in ice, propagation becomes more difficult.

The results obtained using a 15 mg lead azide fusehead detonator, show that no ignitions of lead styphnate with water content above 20% were obtained, although the lead styphnate was ejected from the container by the impulse of the detonator. These results suggest that wet lead styphnate is more readily ignited by flash than by shock. On the other hand, when the acceptor is service lead azide the results confirm that lead azide is more readily ignited by shock than by flash. It is of interest that when dry unconfined RDX was tested no ignitions were obtained with the lead styphnate igniter, and RDX with 20% water appears to be quite insensitive to shock.

Finally, further tests were carried out to determine whether the ignition of a small amount of dry lead styphnate on the surface of a water-damp cake could propagate explosion throughout the mass. In all previous tests the fusehead had been immersed in the wet initiator but in this series a 7 mg igniter was positioned just to touch the surface of the wet lead styphnate in the container. Even with a water content as high as 20% mass explosion is possible when a small amount of dry lead styphnate in close proximity to the wet material is ignited. The brisance effect on the witness plates is shown diagrammatically in Table 4.

The results show that when handling water-damp lead styphnate every precaution should be taken to avoid any drying of crystals on or near the surface of the exposed cake.

Since surface drying of crystals can take place if the ambient relative humidity is less than 100% it is evident that water-damp lead styphnate should be treated as having an explosion risk of the same order as dry lead styphnate, and full anti-static precautions should be taken.

TABLE 4

SINGLE-DIP 5-7 mg LEAD STYPHNATE FUSEHEAD TOUCHING SURFACE
LEAD STYPHNATE RD 1303

Dry Weight g	Weight g	Percent Water	Temp	Number of fires	Brisance effect
2.0	2.0	nil	Amb	1/1C	— — —
	2.22	10	"	1/1C	— — —
	2.35	15	"	1/1C	— — —
	2.50	20	"	1/5C	— — —
	2.67	25	"	0/5	— — —
3.0	3.75	20	Amb	1/5C	— — —
	4.30	30	"	0/5	— — —
	4.30	30	-5°C	0/1	— — —

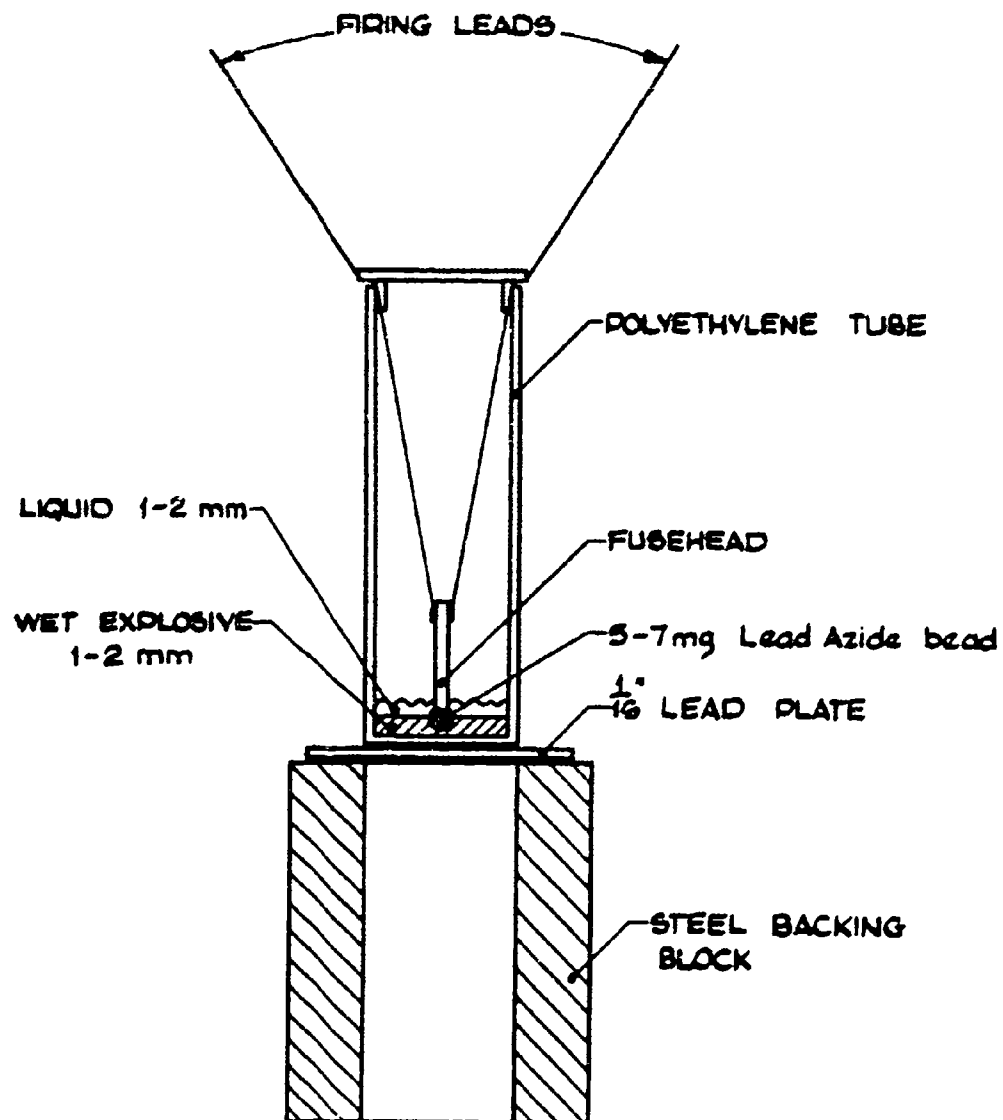


Fig 1

SUMMARY

A simple test has been devised to determine whether a wet explosive can be ignited by flash or shock. The test has indicated that initiators such as lead azide and lead styphnate can be ignited more readily from a given stimulus when the mass of material tested is increased, although the geometry of the test vessel may have a bearing on this effect.

Two main problems with which we have been concerned during this work and on which we would welcome observations are; does the test give realistic and pertinent information on:

- 1 The safety aspect of the bulk transport of initiators wetted with water, and
- 2 The hazard associated with the handling of wet lead styphnate.

On the handling of wet lead styphnate we consider that the test demonstrates clearly that maximum safety precautions should be taken, but regarding bulk, wet transport of initiators: Does the information obtained warrant the introduction of such a test as a criterion for authorising transport?

DISCUSSION

B H Newman

The azide samples which blew a hole through the witness plates are pretty good evidence of a detonation, but the speaker used the term ignition regularly throughout. I was somewhat confused as to whether for ignition you really meant detonation, and when you say you got no response for many of the initiator materials you mean literally no response at all. Didn't they even ignite?

Chairman

We use the term ignition if any event at all takes place. This is rather a defensive way of expressing it because when one starts to consider whether it is an explosion only or a detonation one has to bring forward other evidence.

H K Black

Dealing with the question of safe transportation over a long period of time as to whether in fact the tests done are the right tests to carry out or, alternatively, whether in the course of transport people have been jolly lucky. It is rather difficult to sustain the view that they have been very fortunate in transport, particularly when such transport has been carried out over a period of many years without incident. The question that arises is whether the tests as described are related to the practical problem of transportation. It would seem that they are not in fact, one could do many laboratory tests with many dangerous substances which indicate that these substances should not be transported, but the fact remains that they are safely transported and hence one has to devise a test or series of tests which are related to the particular problem you are looking at. The tests carried out in this paper are not related, in my view, to the particular problem that is involved in transportation.

However, it does indicate a number of things. I have only had a limited opportunity

of looking at the figures produced and it is quite clear that certain things should be done. Mainly that the materials of course should be wetted, but above all it is quite clear that the transportation of these materials must be such that there is no prospect of the material drying out during the course of transport, this is very important. As regards this particular test, in my view it is not necessarily related to the problem of transportation but I am not at this stage going to try to introduce tests which might be. This is always a very difficult problem relating what is done in a laboratory to what is done in transportation.

Chairman

I think our essential problem here is that we have the experience of many years with mercury fulminate and lead styphnate and we are reasonably happy on this, but now we have introduced new explosives such as lead trinitrophenylmercurate. Here we have no experience and there are no tests. What do we do about it, do we say that this cannot be transported? In ERDE we have to make a decision as to whether this material should be transported or not and I would like to know going back into history, on what evidence the original decisions were made that mercury fulminate and lead styphnate could be carried.

F E Ball

I think the point that has been overlooked here is the very careful wording of some of the classification in the groups of explosives and you will note that the distinction is often between those which contain or do not contain their own means of ignition. This I think is the underlying philosophy. The point of adding water is not to ensure absence of propagation in the wet explosive, much of which was recognised years ago and was tested to be so, it is in fact an intention to eliminate the means of ignition by keeping it wet, once a propagation occurs you might as well have it dry. The point is you are trying to avoid the possibility of ignition.

J Urquhart

I wonder if you can tell me Mr Chairman what your views are on wet storage of lead azide and the dextrinated form in particular.

Chairman

If we can deal with that generally, we are not very happy about storing wet lead azide. Lead azide has a definite solubility and we know that if it goes into solution we can get recrystallisation occurring and this could give rise to at least 3, probably 4, polymorphic modifications and therefore we are not very keen on storing wet lead azide, we much prefer to dry it after manufacture because we feel it is not at a steady state, in other words some solution and deposition of small crystals is occurring all the time. You mention specifically dextrinated lead azide. With dextrinated lead azide there is a relatively large excess of dextrine which goes into solution first of all so you haven't got a situation where you have got the lead azide dissolved in pure water and I do not think I should personally be concerned about it. On the other hand I do feel that certainly long storage and long storage under conditions where you can get fluctuating temperatures where deposition can occur is undesirable.

FACTORY SAFETY PRECAUTIONS AND SAFETY CERTIFICATES

R M H WYATT AND J V GRIFFITHS

R M H WYATT

We want to discuss the purpose of safety certificates from two points of view: Firstly, are we satisfied with what they tell us as regards known materials, those of which we have had a fairly lengthy experience, and secondly, are we satisfied with what they tell us about the relatively new ones, for which we have had much less experience?

Perhaps before we go too far we should consider whether we want a safety certificate at all. What I would like to do is to read the first few lines on the certificate. It says: "This certificate describes those properties of the materials specified which are important for the safety of its manufacture, handling, filling and disposal. Responsibility for the safety of all operations involving the material described in this certificate remains with the user. The results present a summary of the available information regarding hazards likely to arise." And, the poor chap who has to sign it, says he "certifies that this material has been subjected to tests as stated in this certificate and has given the results recorded".

Some people have asked whether we want a safety certificate at all. I think that we must have information on the explosive properties listed and it is just as convenient to have it on this particular document as any other. Some people would say that one certificate would do for all the initiatory explosives since by and large, we take much the same precautions with them all. This is not really true and I don't think it is desirable because (a) we are concerned with a number of different types of chemical compound, (b) their properties vary as regards compatibility in particular, and (c) they certainly need different methods of disposal. It is not possible to get all this information on one certificate. Going to the other extreme some people say we ought to have a certificate for every material. Again I don't think this desirable or necessary and the best solution is the one I think we have adopted and are adopting, and that is to group together in relatively small groups on one certificate all the materials which are either the same or very similar chemically. For instance we put several normal lead styphnates on one, lead dinitroresorcinates on another, basic lead styphnates on another and so on.

Earlier today we saw that the figures of insensitiveness of the majority of these explosives was 10 or 20, sometimes 30, and, rarely up to 50.

What does this mean in practice as far as actual precautions are concerned? As far as containers are concerned, the old type papier mache pot with a paper liner is gradually being replaced by the conducting polythene pots. The previously used conducting rubber pots, and these conducting polythene pots are as soft if not softer than papier mache ones but of course they have to be rigid to do the job they are meant to do. The conducting polythene pot does fill the role of a soft but rigid container and it is likely to replace the papier mache pot entirely. We cannot use the soft type of material for all the plant in a filling shop. We do have to use metals. Here I think it is essential that everything fits well, that is you have a minimum clearance wherever it is possible. It is necessary to avoid the ingress of grit and there is also I think a minimum temperature for operation in a filling shop to avoid frictional problems to do with the metals themselves irrespective of whether you happen to have explosives there.

Now we come to the electro-static sparkside, for which of course the conducting polythene pots are part of the safety system. As you know, during the war when electro-static problems really came to the fore, a sub-division of precaution was made at 0.02 joule on the basis that the highest potential that a person was likely to be charged to in this country, ie in February and March, was 10 kilovolts, and if an operator has a capacitance of 400 pico farads, which is fairly reasonable for a virtually insulated person that gives you that figure of 0.02 joule energy.

In practice, particularly with pyrotechnic compositions, there are quite a number of materials which have ignition energies in the order of .01 joule and or less which, if one obeyed the rules, ought to have second degree precautions for handling. You will remember that if the minimum energy for ignition is greater than 0.02 joule, then first degree precautions, ie lower degree precautions, are adequate. With less than 0.02 joule minimum energy then second degree (or higher degree) precautions are required. There are a number of materials which ignite at the 0.01 joule level, which according to the rules, ought to be handled under second degree precautions. We know this is not the case, never has been and probably never will be. We accept this and have written it out in one of the appreciations which is to go in the hazard manual SCC No 3. We realise there are three groups of precaution. If the material is not ignited with energies of less than the .45 joules then certainly first degree precautions are perfectly adequate, that is you merely earth all the large pieces of equipment you have, and you do not need to do anything else. If you have a primary explosive and its ignition energy is less than 10,000 ergs, that is 1000 micro joules, then you need full anti-static precautions. In other words you have to deal with a human being by earthing him throughout by means of the floor and his shoes, and keep the humidity well up, and try to keep capacitances as small as possible.

In between these two figures which on first sight looks a rather large area but on a log scale is brought into the correct perspective, you can have a gradation of precaution. For example with a material not ignited at 0.045 joule first degree precaution plus earthing of medium size containers etc, will suffice. At the other end of this middle group, if the ignition energy rises above 1,000 micro joules you can relax somewhat either on the humidity or the floors and shoes, but not both. Certainly if it is below 1,000 micro joules then I think you definitely need full precautions.

J V Griffiths

Eventually the responsibility for completing safety certificates, and particularly forsigning them, falls to me and I would like to run quickly through the remaining clauses, the remaining information that these certificates attempt to provide. Dr Wyatt has already dealt with the testing and we now have a number of points.

First of all Stability: Of course these things are in general satisfactory, they have to be otherwise they would not be in service, although there are occasions, as for instance stability of lead azide in water, where there is a necessity to make some reference to this.

Incompatibility: This is one of these areas where not only has the certificate evolved but a stereo-type approach to the answers has also evolved, so that in the first instance the certificate tells us in print without any need for additions that all explosives are regarded as incompatible with acids, alkalis, highly reactive materials and grit. There are, however, other incompatibilities and I think this is one of the areas where you could make a case for not having

one omnibus certificate for initiators. We have these particular things, for instance lead azotetrazole is incompatible with soluble salts of copper and silver, potassium 4,6, dinitroresorcinate is obviously going to be incompatible with lead compounds. In general, safety certificates carry very little of this information.

Having gone from incompatibilities, we come next to the clause which is Process Materials, (a) containers and, (b) tools. Again we have evolved this very stereotypical three-word clause which says "As for Initiators". I am rather sorry this discussion has come at this point because we have just recently produced a considerable number of new initiator safety certificates which have not yet been issued and it would have been very useful to have had some of these discussions before this work had to be done. Now this may very well be satisfactory for people in Ordnance Factories who are accustomed to handling initiators and who appreciate the problems involved. I would be very uneasy if a safety certificate had to go to someone new to the materials to provide him with sufficient information for their safe handling.

The next clause deals with health hazards; Safety Certificates make reference to Technical and Medical memoranda, some of which were published by the Ministry of Supply and which have since been continued by the Ministry of Aviation. The things that are covered here are lead azide, sodium azide and hydrazoic acid and I think as far as initiators are concerned these are the only ones. The general toxicity of lead salts is not covered, the general toxicity of nitro phenolic materials is not covered. So, failing a Technical and Medical Memorandum the certificate really contains some very brief comments such as for instance "lead salts are toxic".

The next thing is Special Recommendations relating to the method of preparation, mixing and filling: We are fortunate in this respect in the initiator field that practically all the work on initiators has been meticulously written up so I consider that it is reasonable at this stage that we refer the reader to the relevant ERDE Report. An advantage of this also is that - something Mr Taylor is very insistent on - all our initiator safety certificates are unclassified; by merely referring to the report we can produce an unclassified certificate which can have a much wider circulation than one which carried classified information.

Again, a recommended method of destruction: Now this is also always dealt with quite briefly, either mix it with oil and burn it or destroy by a suitable chemical means.

Finally, of course, the fire extinguisher: Well in this class of compound that really isn't a relevant point. Myself I am not entirely sure that this really is a good safety certificate in this form and I am hoping that the discussion now is going to tell us first of all to what extent people rely on safety certificates as a basis for their safety precautions and, secondly their views on our safety certificates and in particular on what additional information could well be incorporated in these in order to make them much more useful. We may have come to a point where a change in format of the safety certificate would be useful. At the present we have a quarter of the area printed out with detailed information which is now being supplied in the new safety testing manual and we could very well get rid of a lot of this and make quite a bit more space available because at the present we are strictly limited by the amount of space - for instance to get Dr Wyatt's spark data on requires quite a measure of compression - I think that is all I like to say.

DISCUSSION

Chairman

We issue these documents and of course we are not the only people who issue safety certificates; RARDE have the same sort of problem. For some time we have been rather concerned. We get many enquiries of the factual data, especially for numerical information such as F of I figures for particular materials. However, we are sometimes worried that there has been such concern for getting the data exact that the overall usefulness and purpose of the certificate may have been overlooked, so I would particularly ask the safety people to comment.

C K Bowe

We place great reliance upon the safety certificate in the Ordnance Factories. In the Ordnance Factories we have many new people coming in with little or no background of explosives; for this reason we have always laid down that we will do no work on a new explosive for the factory unless we have a safety certificate. This does at least give them some guidance as to what the properties are.

I would like to add a personal view, that over the years the safety certificate does seem to have been undergoing some changes and also, more important, the method of doing the test for F of I does seem to be varying and I realise that to bring all the certificates up to date would probably be an enormous task but I do feel that there is an urgent demand particularly by the younger people to the explosive field to have some sort of table of standard explosives, RDX, TNT, and all these related to one another on the up to date method of doing the test.

Some pyrotechnic compositions are quoted on certificates with different figures of insensitiveness and I think we should get the more common materials tabulated to give a degree of comparison.

I do feel that, if at all possible, the certificate should be related to the particular use to which the explosive is going to be put. A typical case, for instance, when we had lead trinitrophloroglucinate come along the other day we wanted to know what the filling mould should be made of, whether it should be a brass mould and steel punch, or whether both steel. This is something which I think could be helpful in the certificate.

Chairman

We do appreciate your comments but it is alarming to hear you refer to your own people coming fresh into the factory and you give them this document which we realise has deficiencies for this type of use. We now approximate our F of I figures to the nearest 10 but in factories there have been occasions when certain materials with an F of I of say 18 and another of 22 has been referred to as "the more and the less" sensitive. This over-emphasis on numerical data, especially if it is printed and certificated is something that worries us; we are trying to get away from it. I think you have really put your finger on our dilemma.

H K Black

I wonder whether you would permit me to make some general remarks about this because I think it is perhaps one of the most important things that has been dealt with today, certainly from my point of view. First as to whether a safety certificate is required at all - in my view yes. As to whether it should be complicated is another matter. It has always seemed to be a much too complex a document and

could be simplified with profit; but that depends to whom the document is addressed. I am rather horrified at the suggestion that someone quite new to the field, or relatively new without the requisite background, can attempt to use such a certificate and interpret it and devise the necessary safety precautions. I think to simplify the document might be much more helpful from this point of view, but the safety certificate will give a general guidance and to those who are competent to read it, would give expert guidance in a number of directions as to what should be done in the Ordnance Factories or in factories where this certificate might be required to be used. Much depends upon the experience of the people in the factory, how they are going to use it, it involves not only the questions of plant, quantities that may be required, compatibilities, but is also directed to the people who have actually to do the operations. My own experience in the Naval Factories and in private industry in the last few years, is this: The Safety Certificate in the end has to be translated into proper safety precautions within operating shops. It is no good devising safety rules for people to obey if they do not understand what these rules mean.

We had a number of accidents where it is quite clear that things have happened because people have not understood what the safety rules mean and where this does occur they have disregarded them because in some cases they think the rules are daft, because they do not understand what lies behind them, so I would commend to all Safety Officers this; that this is a matter of education in explaining to people - that is the operatives in the shops - why the rules are made, what purpose there is in the rules so they understand what they are doing instead of blindly following the system of rules in which in some respects they have no confidence because they do not understand the rules and some of them to the uninitiated look silly, whereas if they understood the reasons they would obey the rules.

C K Bowe

In the case of safety certificates they are always vetted by the Safety Officer and the Assistant Manager in charge of the particular job before the job goes up to the development section. We do make full use of the ERDE reports and other background work so we normally always use the certificate for a new material in conjunction with any report which has been written. The other point is, when we do come to the shop floor in the filling factories, and the Royal Ordnance Factories, we do have what we call the Director's Safety Orders which are vetted right the way up through the Safety Officer to the Director himself and these Director's Safety Orders are posted in every shop where the work is carried out. Moreover in addition to the Director's Safety Orders, to follow Dr Black's point, we have what we call process instructions and these not only state the operation but, the reason for doing it, the particular safety aspect of doing it. This is one of the ways in which we do endeavour to educate the actual chap who does the job on the shop floor.

Chairman

Do you think that there is a feeling that these instructions are rather routine? I have been in a shop where half the wall is full up with instructions, it is almost physically impossible to go through and read them all. Once you have got more than half a page no operative is really prepared to stop and read them. You get the feeling that the operative often regards this as merely a safeguard for the management in case anything goes wrong.

C K Bowe

We are making a drive to really cut down the extent of the actual Director's Safety Orders and concentrate on the vital points and the rest of it can be given in the more detailed Process Instructions which usually only apply to a specific person or perhaps a limited number of people.

J Wilby

One really wonders whether it is best not to put the answers on the certificates at all. Perhaps what the factory really wants is advice on how to handle the composition, they may not really want all results. After all the most important thing probably with any composition is the experience that people have had with it during the development stage and this is not really written down on the certificate at all except simply to say handle it under such and such precautions. Should we put the Rotter test and the spark test at all? By all means do the test so that those writing the certificates can build up evidence on how to write them but should they really be on the certificate itself?

C K Bowe

Mr Chairman, as far as I am concerned I would like to see as much information on the Certificates as possible. It is alright but we do particularly want information on the methods and procedures of handling the material but on the other hand it is most useful to have the degree as well, if for instance we say that this material is relatively safe to handle under certain conditions, we would like to know how safe. I would always like to see the actual figures that are produced even though we might have to take some with a pinch of salt.

J Wilby

I wonder when you say take them with a pinch of salt whether there could be the danger of going the wrong way that one might take a test out of context and perhaps get the wrong impression.

F E Ball

Isn't this leading us in the direction we thought of before in which we do have a very much simplified safety certificate. I am in favour of outlining in detail all the requirements for the factories and then in addition you have a data sheet on which you place all the information obtained during the development of the explosive and all this sort of information we have been discussing. That would be held by D/Safety and issued to those in authority who required to have it. I think this would facilitate the issue of a safety certificate which would be purely and simply a guide to the use of the composition and this is what you want.

A RECENT INCIDENT WITH LEAD STYPHNATE

R M FERGUSON

What I want to try and do is to attempt to tie in the subjects that have been discussed today with a very severe accident which we had, I think it has elements in it which show a relationship to some of the things which have been discussed and may indicate deficiencies in the controls of processes or of safety that need to be looked at. They may indicate too that perhaps there is further testing required to categorise these materials.

I would like to start by saying that the Canadian Arsenals are very much the same type of organisation as the Ordnance Factories here. Our main responsibility is the filling of ammunition and among the jobs we do is to make lead styphnate. We make this in fairly large quantities, 15 lb and up to 150 lbs a day. In an independent programme which we set up 3 or 4 years ago we decided that, although we are essentially a production facility, the work being done over here on these RD compositions needed to be looked at in Canada. We set up an independent programme to look into these things, to make sample materials, and in order to do this we felt we needed as much test equipment as possible. We tried to set up equipment which is as close a copy as possible to the equipment that Dr Wyatt uses outside of the Rotter machine which we don't have, but the friction pendulum, the ball and disc machine, the temperature of ignition, - we also use differential thermal analysis these days - and particularly the electro-static testing. We do this because we feel that starting with new materials we want to be able to fingerprint them as well as possible and we do not think that chemical testing alone is good enough. I mention that because that brings us up to the date of this particular accident which was the 28th December 1968.

We had completed about 800 lbs of a particular order, although none of the material had been shipped. In mid-afternoon a batch had been completed and had been washed out of the precipitating pan - the pan incidentally is an exact copy of the lead azide plant which is so familiar in this country - the mother liquor had been disposed of and the lead styphnate had been washed by hose into a collecting cambric cloth which was contained in a non-conducting polythene pan. The 15 lbs at that particular time was awash with water but it was part of the process to dispose of the surplus water and for the operator to form a kind of Christmas pudding with the cambric cloth and the 15 lbs of lead styphnate and gently squeeze some of the excess water out. We know from experience that this leaves between 20 and 15% water with the lead styphnate. The material should then have been quickly sampled twice. It should have been sampled first of all for a microscope slide to ensure that complete conversion from the intermediate stage had taken place and it should also have been sampled for the lab analysis. We know that the microscope sample was taken but there seems to be a very good possibility that the material in the wet cambric but now exposed to the air in this non-conducting polythene pan was left for between 20 and 40 minutes and, left in an atmosphere which we now know was not very humid. Our Process Instructions require that people have wet and dry bulb thermometers and that they record relative humidities and so on. Many people seem to think that there is no need for instrumentation and the mere fact that a floor is flooded with water is apparently sufficient assurance for certain people that there is a high relative humidity. We have since proved that in our climate flooding a floor with water means, under certain conditions, that the relative humidity may be less than 40%. The polythene pan was a commercial dish pan type and had about 2" of water in the bottom. The squeezed bag of styphnate, squeezed tight at the neck sat in the pan with all of the top surface capable of being exposed to the air. From that point on we had no clear story of what did happen. We know that one sample was taken for a microscope slide examination, that should have been done immediately, there is a good

chance that the man responsible for doing it did not do it immediately and this was the reason the material was left for so long. After he had finished he told the second operator that the material was satisfactory for sampling for lab analysis and it was while approaching the cloth and probably in pulling the cloth away from the styphnate that the material blew up in the man's face.

The result of this explosion was obviously not a high order detonation because the man in fact did survive, but a great deal of explosive energy was released. We found no unburned material though we searched the entire area. We felt certain at first that in an explosion of this kind large quantities of wet styphnate had probably been hurled into remote corners but, despite our considerable efforts, we found none whatever. It had apparently all exploded or deflagrated. At any rate it released sufficient energy for it to blow out walls 15 feet away, lift the roof, and wreck the particular working area. The man lost an arm and for a few days it looked as if he would lose his life.

Fortunately for us as a result of the work we had set up 3 or 4 years ago, we did have direct contact with Mr Taylor and his group and with their help we then proceeded to go into an investigation of what might have happened. Their help was very considerable. We immediately froze the 900 lbs, we would not ship any of it. We sampled it on the electro-static teste, with the metal to metal test to find out if there was any evidence whatever that this material was abnormally sensitive. We did about 50 batches and we found no abnormality, in fact the material was very similar to materials tested in this country. The lowest ignition occurred at about 100 ergs with a capacitance of 500 picofarads. There was one ignition, at this moment we do not know whether it was a valid test or not, but it has to be recorded that apparently there was an ignition as low as 53 ergs, but this may have been a bad test. I have not been able to duplicate that test with the same material even though I have made over 1,000 individual tests. Out of 12,000 individual tests we had none below 100 ergs except this one, it is still possible that one may have been around our 0% point that we were talking about this morning.

We also had verification of this by independent tests done by Dr Wyatt. By one of those rather fortunate coincidences they happened to have available the same kind of material made at Woolwich as we were making in Canada, this is not RD 1303 but a material which uses higher concentrations, and were capable of testing it immediately. We had this verification on our own test results as far as metal-to-metal was concerned. Also they managed to supply us with some conducting rubber so that we were able to begin doing the rubber-to-metal testing and here a difference did occur. This material is more sensitive under this test than RD 1303, minimum energies of 25 to 30 ergs were experienced. However, this is not considered a dangerous level because for certain other types of lead styphnate which are made and used in the hundreds of pounds every day throughout the world, sensitiveness of 10 or 15 ergs are experienced. We set aside the possibility that this was due to bad material in terms of being too sensitive. An investigation was, of course, going on all this time during which testimony was being taken and various other testing was done, people attempted to get this material to go off by hammering away with a wooden mallet on cambric that had been impregnated and allowed to dry but despite noble efforts with a hammer they never did manage to get it to go off. This was with damp material by the way. We set up a test in which we tried wetting the styphnate to make it into a slurry. We soaked a cambric and then put the wet slurry on the cambric and began testing at 2,500 ergs, 500 picofarads and 1,000 volts. We began testing the same sample over and over again. This is not a particularly good test and we will do it again properly, later but, we wanted some quick information. We simply allowed the material to come into

contact with air at 45% relative humidity, and re-tested on a time lapse basis. After 3 minutes we began to get partial ignitions. By partial ignition I do not mean the material propagated to any extent whatever, but there was a distinct sound of ignition; there was a pop and under the needle there would be a black area showing burned material. This began at three minutes and by about 12 to 15 minutes this became almost 100%, you could do it on practically every test. We continued this test and at 29 minutes there was quite a loud explosion with a large flame and the material burned completely off the cambric. This was not a detonation and in fact we later took the cambric and washed it and there was no damage and not even any evidence of singeing on the cambric. Nonetheless there was a lot of energy released in the way of flame and heat. That occurred after 29 minutes and these figures have to be taken in context too, because we could only do one of the two tests at a time so that the chances of this happening are almost 100% by the time you reach 29 minutes. Certainly there was enough flame and enough energy released to set off other lead styphnate or other initiators in the area. We have not carried this test on to its logical conclusion of using this as a means of setting off wet lead styphnate but this is something we would certainly like to look into. It does seem to relate very closely to the work which has been done at Woolwich described earlier today.

Other testing that was done included microscopic examination of all those batches plus the drop test which has been associated with the testing of lead styphnate in this country for many years. We had one or two batches in which there was an abnormally large number of large crystals and the reports from the labs stated that with those batches the sensitivity was much more marked and very close to going off at the high level established. Those large crystals incidentally showed no increase in electro-static sensitivity, they gave exactly the same results as the mixtures did.

We have gone back into production and have looked at the possible causes. There seems to be no question that the mechanism involved an electro-static discharge. The material should not have been left exposed to the air so that dry material could form on the surface and then the operator separate the cloth from the styphnate. Dr Wyatt has since told me that you can probably develop about 300 volts by simply peeling the cloth back from the styphnate in a case of this kind. It certainly should not have been sitting in a non-conducting pan. People no longer rely on flooding floors for relative humidity we now have what we have had in many other areas of the plant for years, the water projecting heads which control humidity to 65/70% and sampling is entirely done under water. The sampling now is done with the material before it is brought up into a bundle of that kind and the technique is to do a "Scuba dive" under the surface and come up with the material that has been completely flooded with water.

We have also installed for evaluation a personnel tester of the type that Mr Sumner was talking about this morning. This is a personnel tester which I modified from one which I saw at Chorley a few years ago but it is reasonably portable and tests through the operator's hands, feet and his conducting shoes and through the floor. We can move it to various parts of the room at least at the start of operations and, we try to pick those areas where most of the traffic is likely to be. Having checked this we then establish the thing at the doorway to the operating cubicle and insist that everyone who decides he is going to work in there must climb on it. This was rather embarrassing because despite conducting shoes I couldn't pass the test.

We had felt it only necessary to take an occasional sample and do a rubber-to-metal electro-static test on it. I am not entirely sure that this is in fact good enough and I left a design behind me to make a modification of the electro-

static equipment which would be applicable just to production testing. For a while I want to get data on batch to batch testing. The reason for this is that from the data I have acquired there appears to be the possibility of considerable batch to batch variation with the styphnate. Whether this is due to bad testing on my part or whether it is actually due to variable characteristics from batch to batch at this moment I am not absolutely certain. I do know that we have had individual batches which presumably have been made with the same raw materials and made by the same process which have given variations in minimum energy, for instance from 30 ergs to 140 ergs and I think this is a little bit too wide to ignore at this time so we want to acquire test information on the basis of production material. The regular tester is too slow and too complicated for production testers so we will try to have a one or two energy level tester only and try to acquire some information on this basis. We will also continue doing the impact testing or a modification of it using the ball and disc machine.

Chairman

Do you regard your wet stage processing as free from static hazards under the conditions in which you work? You see before the accident this was the situation in the Canadian Arsenal's plant. We are trying to benefit from their experience.

R M Ferguson

There are three other accidents that we have become aware of with wet lead styphnate. One of these occurred ten years ago in a plant in the US. As a result of it I do know that about a million dollars worth of mechanised equipment was installed to ensure that nobody handles wet styphnate.

The accident which occurred did happen with 20% wet styphnate and it occurred when they were shovelling portions of this onto a scale pan for weighing.

There was a second accident and in this case I have very few details. The operator had wet styphnate which he wanted to get dry in a hurry so he put it on a Buchner funnel. He had about a couple of pounds on a funnel of this type when it blew up.

Finally, I know of another accident with 20% wet styphnate and in this case it was lead styphnate of a common commercial type. A Cap composition was being prepared by weighing the ingredients and about 700 grams of lead styphnate was on a scale and another couple of hundred grams on a table, all in a wet state, or what had been a wet state. An aluminium shovel was used to pick up the explosive and it was allowed to slide on the scale. According to the accident report, at the point when the last element slid along the shovel on to the scale there was a splatter heard and the 700 grams blew up. In that particular case the people who reviewed the accident felt that it could not possibly be due to electro-static discharge but I am not at all convinced that this is so. In their particular case they were almost as badly off as we were. Although they had their aluminium shovel and a grounded operator, they had a plastic pan sitting on a non-grounded scale and this is an excellent way - assuming there is a mechanism for charging the styphnate - of making the whole mass into a large capacitor. If you happen to touch a large charged capacitor with an aluminium shovel and you are conducting, then you can get a pretty good discharge. I know it is very difficult to charge material of this kind, just sitting in a pan. We have measured the equivalent of 15 lbs of styphnate sitting in a pan of this kind and it gives a capacity of about 5,000 picofarads. It also has a relatively large leakage resistance, about 14 kilo megohms.

E G Whitbread

As I see it there are two possible mechanisms. One is that by some means unspecified, the "inner" electrode of this condenser has acquired a charge and then the operator who is merely a moving earth, discharges it. The other mechanism is that the charge was generated by the physical separation of the cambric from the explosive, in which case there are two discharge routes. The charge could either go down through the bowl if the bowl is conducting, or it could go through the operator if the bowl is insulated.

R M H Wyatt

I think the second situation should be safer than the first. When the cambric is peeled away from the styphnate some charge will be obtained by the cambric and the styphnate. This charge could dissipate via the cambric to the conducting bowl which is presumably on some other conducting surface so that it can leak away. Alternatively the charge on the cambric may go via the person touching it.

E G Whitbread

Presumably what you do is to generate two charges and you are saying that the operator is always earthed because he is in an anti-static condition. Therefore the charge on the cambric leaks away via this route but with an insulated pot there can only be a discharge across the gap of the charge on the explosive to the operator.

J F Sumner

We have in fact here a picture of a conductor, insulated by the polythene. Let us assume for the moment that the cambric bag is sitting close to the polythene. In lifting it up a charge is generated by virtue of the separation of surfaces. Simultaneously with lifting it up the man would grip the bag a little bit tighter, thereby coming closer to the conducting mass of styphnate - conducting because it is wet. A discharge would be most likely from his fingertips through the bag to the mass of styphnate.

E G Whitbread

Supposing you replace that pot by a conducting pot, what influence would this have on the situation?

J F Sumner

With a conducting pot some leakage back would occur as the cambric is separated from it, during the few seconds of this operation, ie a smaller charge should result. I would not like to say what sort of reduction in potential might be found, but the charge would certainly be less than in the case of insulating polythene which has an effective leakage resistance of 10^4 to 10^6 ohms. I think we must remember that polythene itself would be a very highly insulating material even in the presence of this wet lead styphnate because polythene is a hydrophobic material.

R M Ferguson

There is this other difference too, that with a non-conducting pan you in fact have two capacitors. You have a capacitor formed by the bottom plate which is the conducting table, the dielectric is the pan and the cambric, and the lead

styphnate is in effect the other electrode. When the man approaches he represents 4-500 picofarads so in either condition if there is a charge on the styphnate or a charge on him, then there is the possibility of sharing of charge. However, if the pan is conducting then you do not have a second capacitor or you have a very much smaller one made from the cambric as dielectric.

R E Goodman

We have been aware for many years that wet styphnate could be set off with an explosion of a small amount of dry styphnate. This information came strangely enough from CIL in Canada. They had an accident of this nature about 10 years ago and I would like to ask: Is it not time that some organisation was able to act as a clearing house for reports of these accidents?

Chairman

This is something we try to do in ERDE because our responsibility is in these special types of initiator preparations and although the ERDE range contains many well established initiators we accept responsibility in which the product is related to the controlled and authorised method of preparation. When you start talking about the characteristics of lead styphnate or lead azide, first of all you have got to know what it is. If you just say they make lead styphnate in South America, well they may make it from nuts for all we know. We do know that the question of impurities can have a very profound effect on the electro-static sensitiveness. What we are trying to do in ERDE is to connect the method of preparation with certain definite data on sensitiveness related to experience in as many areas as possible. The answer to your question is that we would like to do our part in ERDE; as you see we have maintained close collaboration with our friends in CAL as you have with CIL and I think that the more we can exchange information on these experiences the better it is for everyone. We want to have the discussion before the accident not after it on the basis that prevention is better than cure.

I think this is extremely important and something you will have to think about in the factories and clearly IMI are also directly concerned. It is not just a question of styphnate but also of wet compositions based on styphnate. We are not going to solve any problems today but at least we can point out certain features so that we can go back and have another look at the operations being performed with a view to getting our ideas sorted out. It has been accepted generally in the past that with wet lead styphnate you have nothing to worry about. Now there is occasion to question this; we have the present case of the Canadian accident which has prompted a whole series of tests from which we hope to make some progress in understanding what is happening.

THE EXPLOSIVE REACTIVITY OF THE METAL AZIDES

P G FOX

The problem of devising sensitiveness tests for explosive materials revolves around an understanding of the basic mechanisms by which the chemical reaction is initiated and how it subsequently develops to explosive proportions, for without this information, tests can only simulate in a rather unsatisfactory manner the complex situations in which the material may find itself in practice. Values for sensitiveness are then unsatisfactorily based on statistics. The results I am going to describe arose out of an attempt to look more closely at the fundamentals of the explosive reaction in the azides in order to define the factors which are of importance in initiation. Almost all of the studies have been carried out on single crystals but we hope to show that the results are relevant to what happens in practice with polycrystalline aggregates.

THE PROBLEM

In defining the problem our approach has been much influenced by the necessity of accommodating three experimental observations common to the explosive azides; (i) that some of the materials are sensitive to shocks of very low intensity (~ 1 kbar), (ii) that materials like lead azide show an unpredictable 'waywardness' which makes their behaviour very difficult to predict and thus their sensitivity almost impossible to define and (iii) that the slow thermal decomposition is a surface controlled phenomenon in which lead azide is appreciably less reactive than, for example, sodium azide in the temperature range above ca 200°C and moreover the rate of evolution of heat in decomposing lead azide becomes less than that for sodium azide above about 390°C. The relative decomposition rates for the three azides sodium, thallium and lead are shown in figure 1, (the results for sodium and thallium azides are derived from R F Walker, 1965 Ph D thesis, Cambridge University).

These observations taken together make it apparent that bulk 'hot spot' is no longer adequate for explaining explosive reactions in the azides and the problem becomes that of explaining why lead azide which is relatively unreactive should be so extremely sensitive.

SOLUTION I

To rationalise these observations, we have proposed a fracture mechanism for the initiation process in azide crystals in which the elastic strain energy which is released when a fast moving crack runs through the crystal, is used in chemical decomposition at the crack tip. The idea that fracture plays a role in initiation is consistent with the observation that reaction takes place on the surface of the crystal, predicts the correct value for the explosion velocity in single crystals of lead azide and is also in keeping with the observation that 1 kbar shocks are sufficient to bring about explosion since this is also equal to the fracture strength of 'as grown' crystals.

The test of the feasibility of this mechanism for initiation involves a study of the mechanical properties of the azide crystals since the energy available for chemical decomposition will depend upon how much is dissipated by other mechanisms when the crack runs through the crystal. The major dissipative process is that of plastic flow in which fast moving dislocations near the fracture plane 'siphon' off some of the elastic energy released, thus reducing the amount available for chemical decomposition. Thus the most brittle materials will best sustain a

fracture mechanism of initiation, since in these, dislocation movements are least energetically favourable. An idea of the relative elastic/plastic properties of the material may be obtained from measurements of the indentation hardness which is a test of the materials resistance to plastic deformation under the action of an applied load. Values for the three azides studied show that lead azide is the most brittle of the three, the order being $Pb > Tl > Na$ which is in the same order as the explosive sensitiveness. Hardness measurements however, correspond to strain rates in the material which are very small compared with those experienced by materials subject to impact loading such as that normally used in exploding the azides.

A more direct indication of the amount of chemical decomposition produced by fracture under conditions of high strain rate (impact loading) is by direct measurement of the evolution of gas when a fast fracture runs through the material. Dr J Soria and I have performed such a series of experiments on a number of thermally unstable materials of varying degrees of brittleness. These include the endothermic carbonates of calcium and magnesium and the exothermic azides of sodium and lead. The results of such a study are shown in the Table together with the hardness values and the amount of energy released by the two azides on fracture decomposition. In addition a figure is given for the crack tip temperature in each material, and this is derived from a knowledge of the rate of decomposition (knowing the time taken for the crack to traverse the specimen) and the activation energy and pre-exponential factor of the rate equation measured independently for each material. It can be seen that the difference in energy released between sodium and lead azides is considerable and it is to be expected that because of the large exothermicity of lead azide, the reaction, once started, would become explosively self sustaining.

Direct experimental evidence that fracture mechanism plays a significant role in the explosive decomposition of lead azide is difficult to obtain since the gas cloud around an exploding crystal obscures direct observation of the crystal in which fracture may be occurring. However, inherent in the fracture hypothesis are some predictions which can be tested experimentally, for instance, the explosive velocity cannot exceed the velocity of sound in the crystal and this seems to be born out by recent high speed camera observations of Mr M M Chaudhri in this laboratory. Moreover, for unconfined crystals, the explosion velocity would be of the order of the Rayleigh wave velocity (the velocity of surface waves) in the crystal and here again good correlation is obtained experimentally. These measurements have been made on lead and silver azide crystals initiated by 1 kbar shocks and as yet no information is available on the behaviour of such crystals under very high shock intensities.

TABLE

Material	Amount decomp. by fracture monolayers	Energy released ergs/cm ²	Crack tip temperature °C	Vickers Hardness kgm/mm ²
CaCO ₃	0.09		580	160
MgCO ₃	0.37		860	460
NaN ₃	0.02	3.5	300	10
Pb(N ₃) ₂	10	2.4 x 10 ⁴	570	130

SOLUTION II

A second possible solution to the problem and one which probably bears more relationship to the initiation of polycrystalline compacts is that the reaction may be started by adiabatic heating of the gas in the interstices of the crystals when a shock wave passes through the aggregate. A simplified model of this situation has been studied by Mr Chaudhri in which a single crystal and single gas pocket in contact with each other, are subjected to a shock of such intensity as to heat the gas adiabatically to about 1500°K but not sufficiently intense to heat the crystal adiabatically by more than about 20°. The experimental arrangement is shown in Figure 2. The tungsten rod is 1 mm in diameter. The camera sequences for lead and silver azides are shown in Figures 3 and 4 in which the bubble is allowed to collapse onto the crystal with subsequent initiation. Two other possible mechanisms for initiation could operate in this situation and both are shown in Figure 5. These are (i) that secondary shocks set up by the re-expanding bubble may initiate the reaction and (ii) that micro-jets produced by involution of the bubble may, by impact on the crystal, cause initiation. In Figure 5 the direction of the primary shock wave was such that the bubble was not pressed into good thermal contact with the crystal and therefore does not itself bring about explosion by its own collapse. In no case studied do these last two effects seem to be important in initiation.

It seems highly likely therefore that adiabatic heating of the gas pockets between the crystals of a compact can be a very important mechanism of initiation in lead and silver azides and is perhaps the most important single factor in real situations.

ON SENSITIVENESS TESTING

The difficulty of devising sensitiveness tests which are specific for a given type of stimulus stems from our poor understanding of the factors which are important in initiation and our ability to separate these factors in any test. The following thoughts relate to some of the problems associated with each type of test in common use.

a Impact tests on aggregates involve a complex combination of the two types of consideration described under solutions I and II. Thus not only are low energy shocks involved, which may produce adiabatic heating between the crystals but the mechanical properties of the crystals will undoubtedly play an important part with the possibility that the fracture mechanism may operate. It would seem to be impossible to separate the two effects for this type of test.

b Friction tests are normally considered to involve the heating of material by rubbing. This seems to me very improbable when two brittle materials are rubbed together (as in the case of a friction test on initiator materials) since frictional heating is produced by plastic deformation of the materials rubbed and this will be small for brittle materials and moreover will decrease rapidly with rubbing speed. Friction tests on brittle materials are more likely to produce fracture with the resultant high crack tip temperatures as already described. There is some evidence for instance that a fracture mechanism operates in the polishing of the most brittle material known, namely diamond.

c Electrostatic spark sensitiveness tests again combine the possible effects of heating and mechanical deformation and it is presumably the very high and localised energy density which is important in this type of test (assuming that it is not simply the hot plasma cloud in the vicinity of the crystal which is responsible for initiation).

We take as a close analogy, the example of laser impact on a surface. Figures 6 and 7 show respectively the effect of impacting the surfaces of a ductile and a brittle material with a giant laser pulse. It can be seen in Figure 6 that copper behaves in much the same way as it would if an electrostatic spark discharge impinged on the surface. Surface melting occurs and craters are produced at the points of impact. However, titanium carbide (fig 7) fractures in a brittle manner producing crystallographic strips which peel off the surface due to differential expansion on either side of the strips (rather like a bimetallic strip). The same problem exists here as in the case of the electrostatic spark discharge, of knowing how much of the energy is divided between thermal and mechanical effects and how much of the energy is degraded as heat.

SUMMARY AND CONCLUSIONS

By concentrating more on a study of the mechanical properties than the thermal properties of the azides, we have shown that fast fracture may be responsible for initiating the explosive reaction in these materials. This approach serves to focus attention on the importance of mechanical effects in the sensitiveness of initiator materials and this is appropriate to many of the tests for sensitiveness. However, it should be emphasised that this type of study only provides an alternative method for degrading the available energy to heat since the final step must always be the thermal decomposition of the molecule.

The alternative thermal mechanism which may be appropriate to the sensitiveness of polycrystalline materials is that of adiabatic heating of the gas pockets between the crystals and it is shown that this is an extremely effective way of initiating the explosive reaction. The production of secondary shocks and micro jets seems to be unimportant.

These two approaches provide a rationalisation of such observations that some of the azides are extremely sensitive to low intensity shocks, that lead azide is more sensitive than sodium azide although the thermal reactivity is in the reverse order and can also provide an explanation of why lead azide is so unpredictable in its explosive behaviour, eg why crystals can partially explode leaving fragments of totally unreacted material.

FIGURE CAPTIONS

- Figure 1 The relative thermal reactivities of sodium thallium and lead azides. These results illustrate two important aspects of azide decomposition namely that the rate of decomposition is proportional to the surface area of the reacting crystal over a wide range of temperature and also that lead azide is appreciably less reactive than sodium azide over much of the temperature range studied.
- Figure 2 Schematic arrangements for studying the effect adiabatically heated gas pockets on the initiation of lead and silver azides. C is the crystal mounted on a rod R. B is the gas bubble which is compressed by the shock wave S set up by a small electrical detonator D.
- Figure 3 Initiation of β -lead azide crystal by collapse of shock heated air bubble. Framing interval 1 μ sec. Crystal dimensions: length 6 mm, thickness 40 μ m, width 250 μ m.
- Figure 4 Initiation of silver azide crystal by adiabatically heated air bubble. Framing interval 1 μ sec. Crystal dimensions: length 7 mm, diameter 123 μ m.

- Figure 5 Illustrating the production of secondary shocks and micro-jets. Collapse of the air bubble occurs within 200 μm of the crystal surface but this does not initiate the reaction. Frames 11-20 show the development of a micro-jet travelling at about 100 m/sec. Framing interval 1 μsec crystal dimensions: length 7 mm, diameter 140 μm .
- Figure 6 Microcratering on copper produced by the impact of a giant laser pulse. Energy density, 100 MW/cm².
(This photograph was kindly provided by Dr T J Bastow)
- Figure 7 Fracturing of brittle titanium carbide by the action of a giant laser pulse. Energy density 100 MW/cm².
(This photograph was kindly provided by Dr T J Bastow)

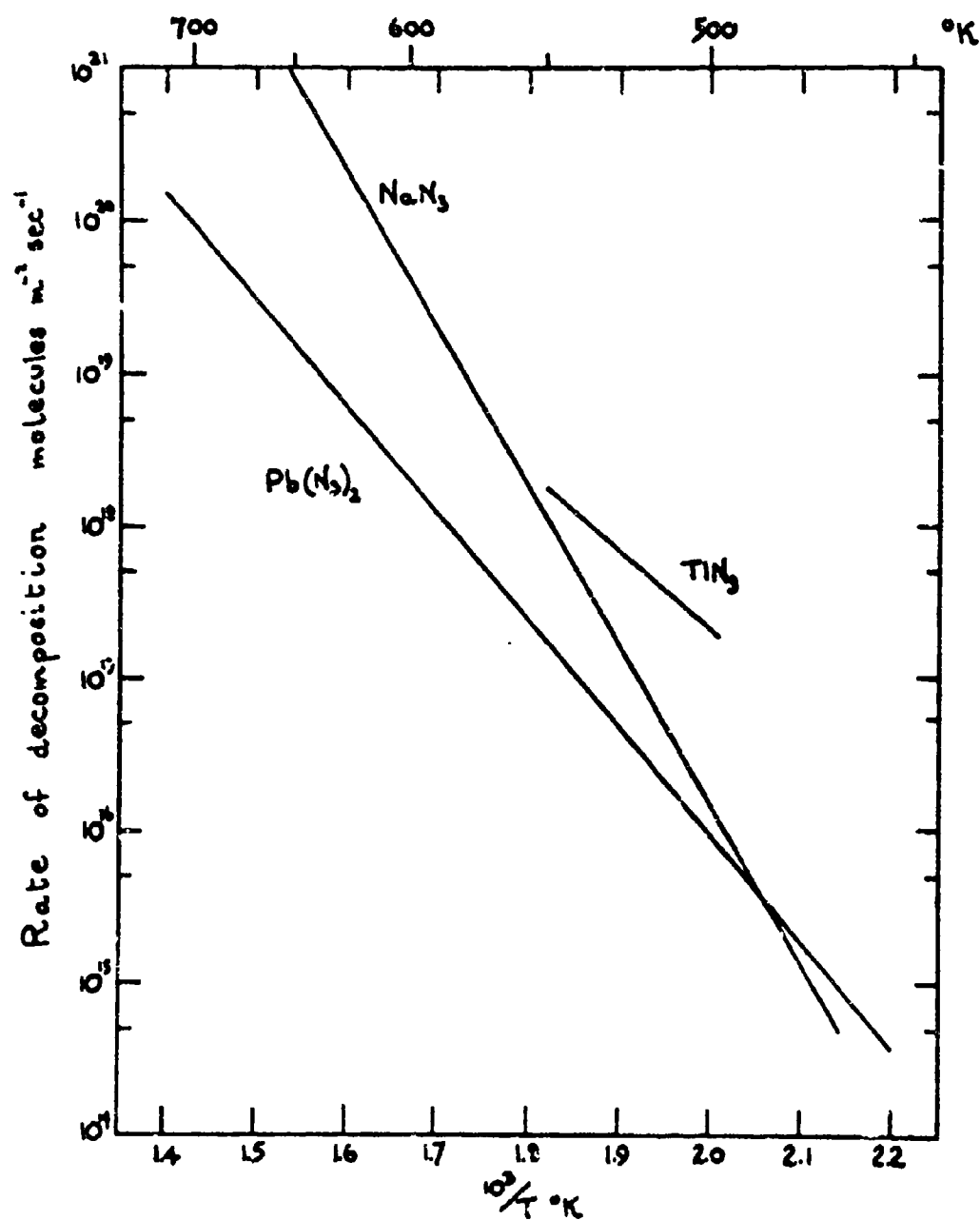


Fig 1

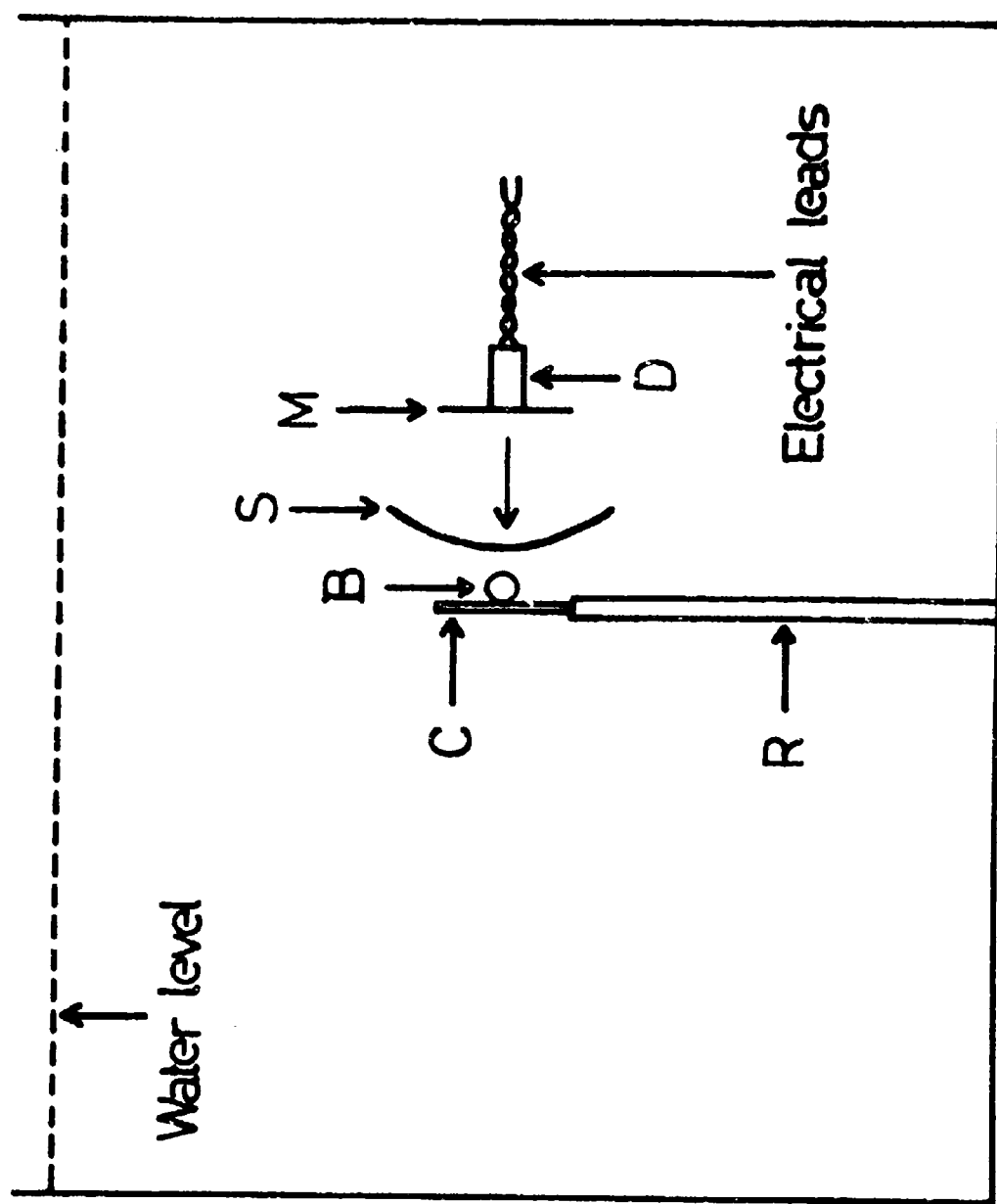


Fig 2

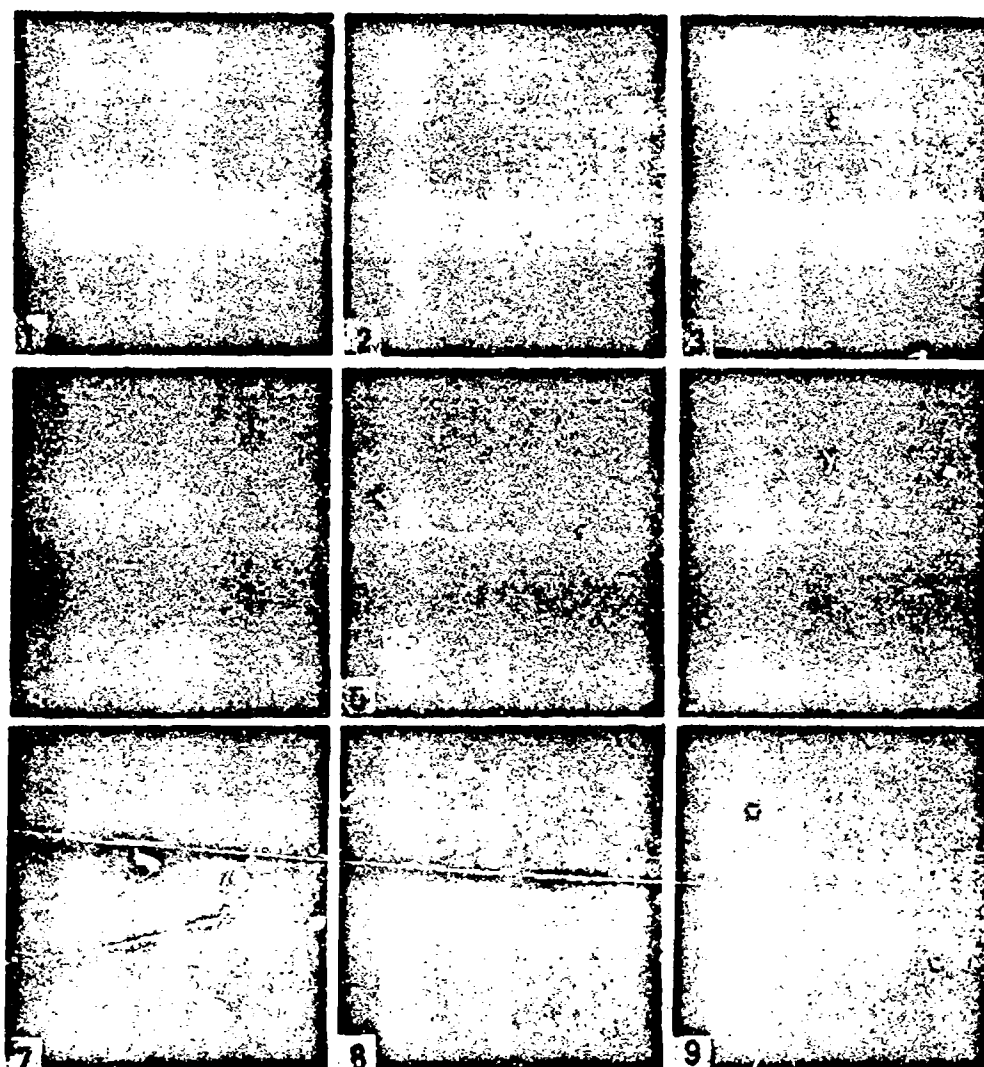


Fig 3

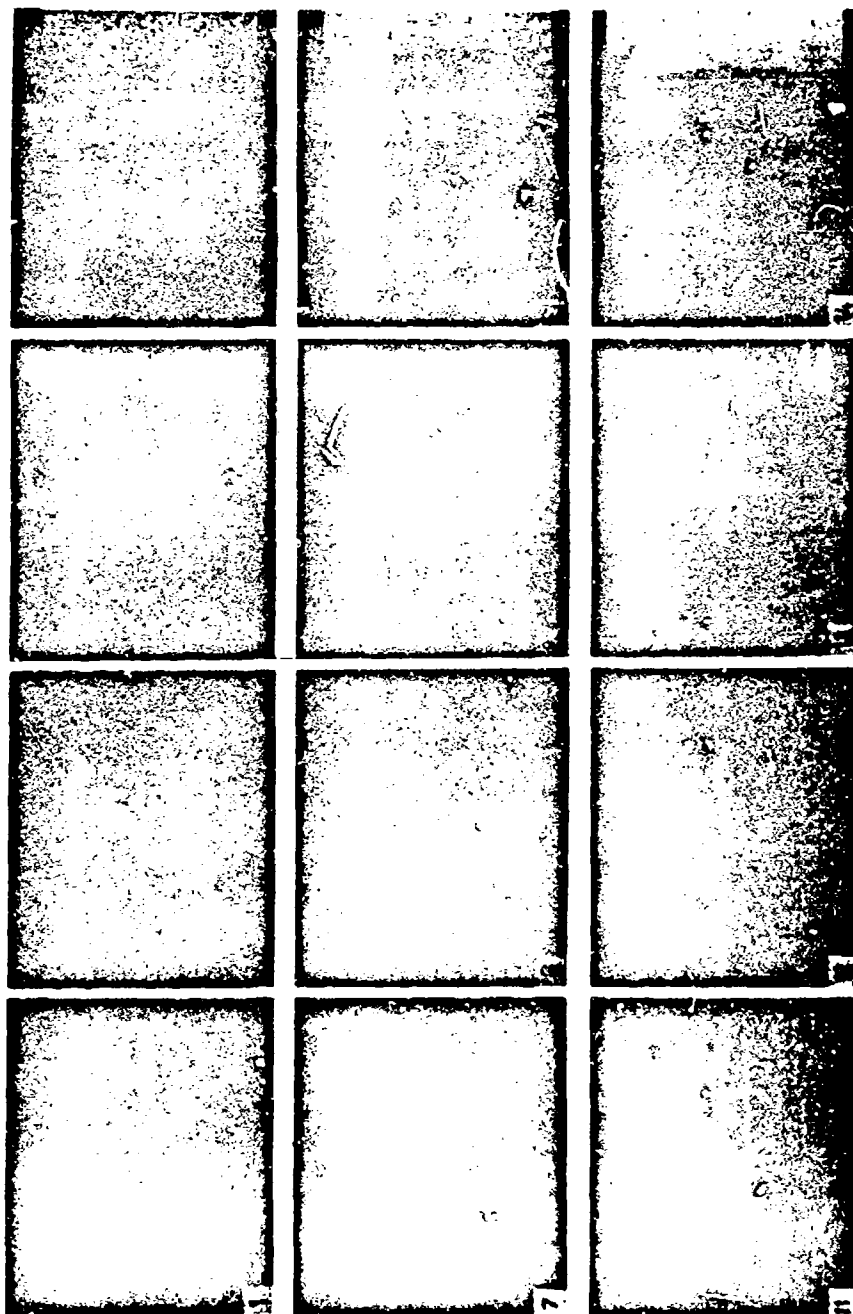
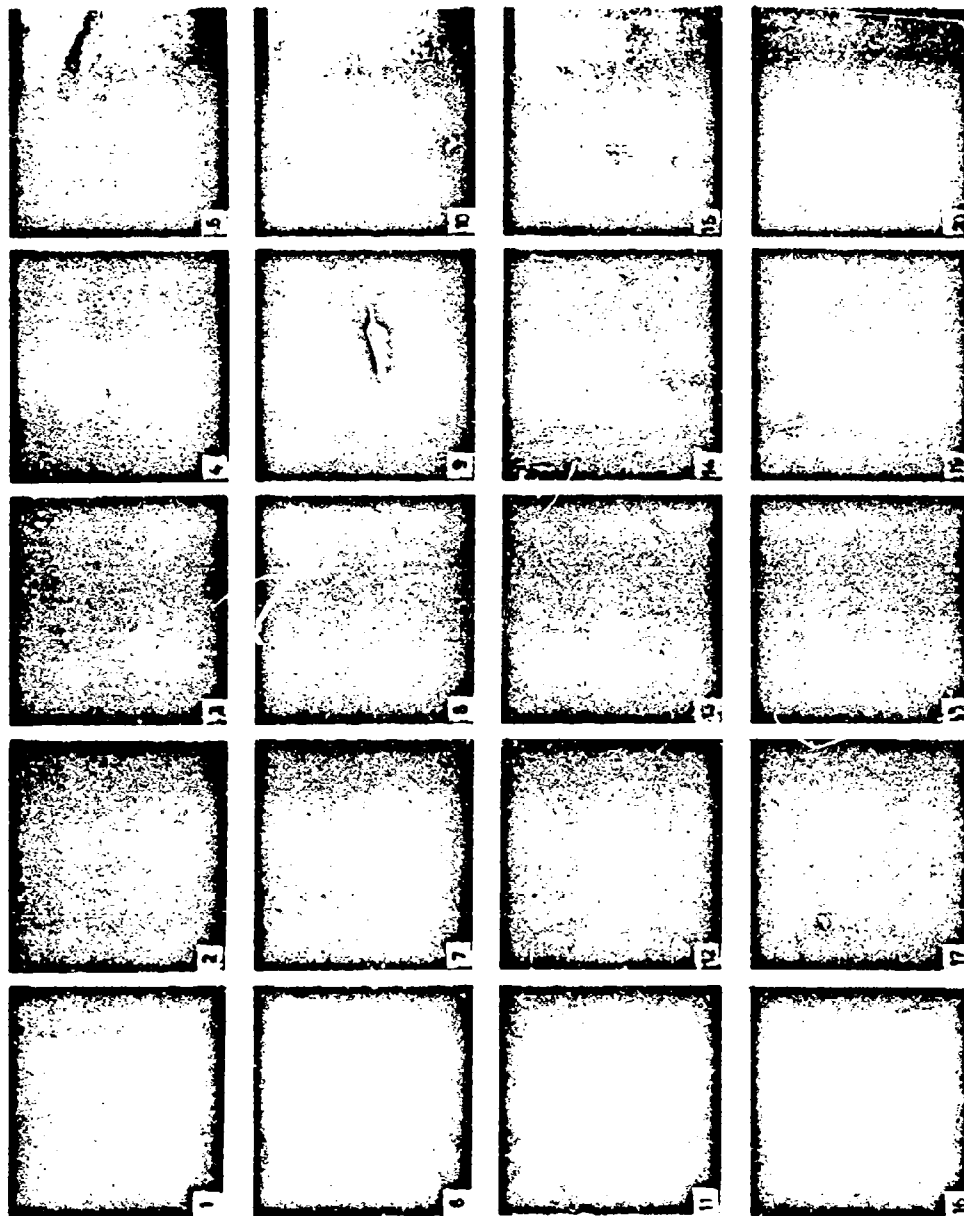


Fig 4

Fig 5



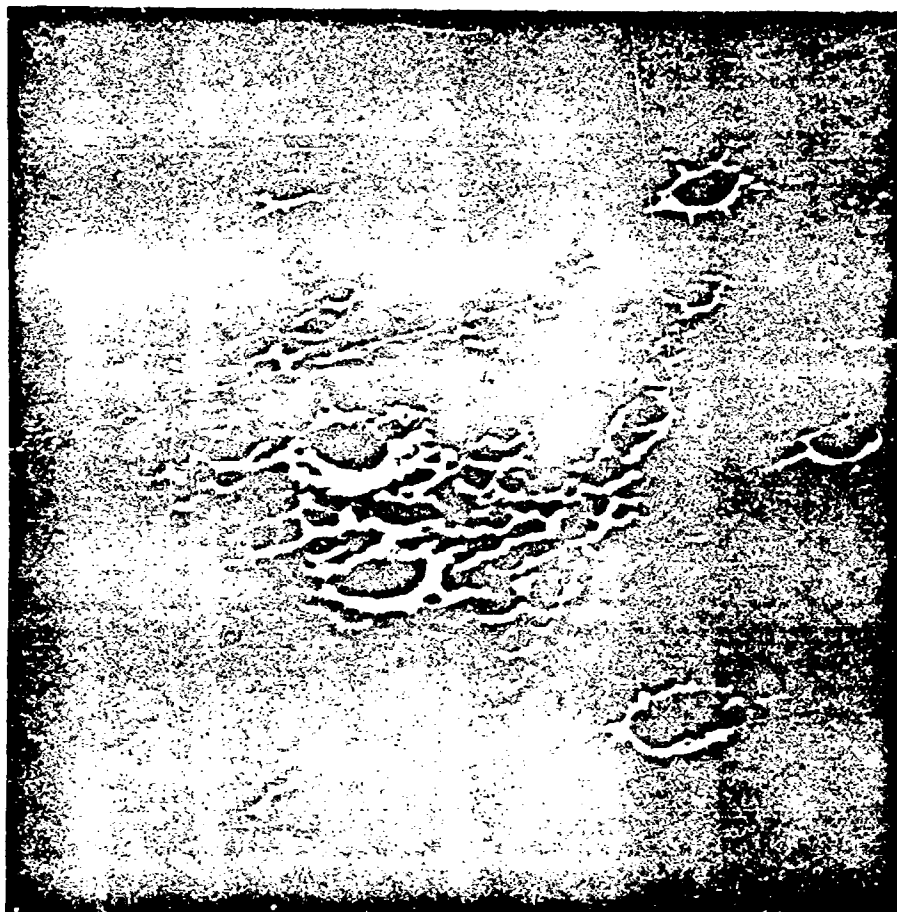


Fig 6

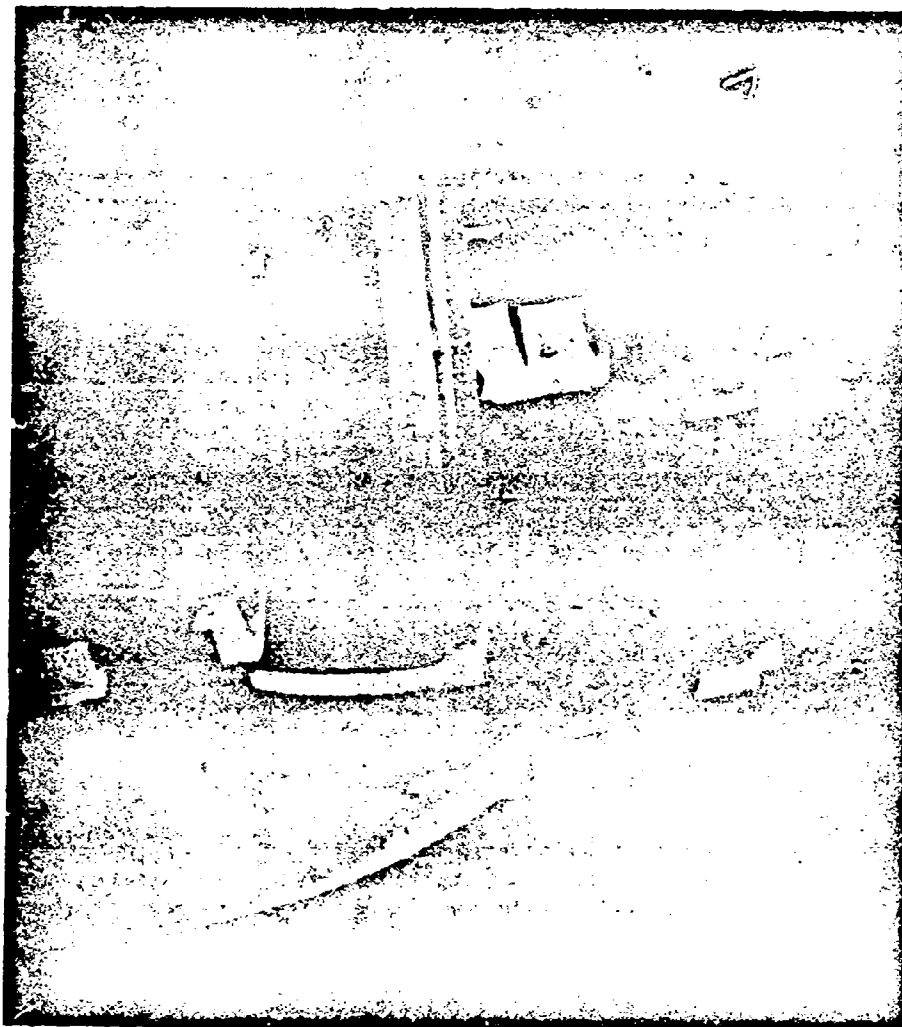


Fig 7

DISCUSSION

G W C TAYLOR

From your single crystal work it would appear that for many but not all cases the pure single crystal is an exception and that for most applications we tend to get either a degraded crystal or some crystals where the mechanical properties have been drastically changed. For example dextrinated lead azide. It is not only micro-crystalline but the material is in fact rubbery, I mean it is plastic and it is elastic so there is this tremendous range of physical properties. If we are looking for a material with the maximum sensitiveness we tend to discover that by precipitating lead azide not in a discrete single crystal form but in a colloidal form we can get the maximum sensitiveness. Similarly, from the American work which you are aware of, by micro pulverising the material you can get an even greater order of sensitiveness.

P G Fox

I think what you are saying admirably illustrates the differences in practical behaviour between these two mechanisms. You say that dextrinated lead azide is more plastic and is also less sensitive. According to my theory that is the way round we would expect. My only other thought is that pure lead azide is, as far as one can tell rather exceptionally pure in that if you look at the decomposition products of it you find almost no occluded impurities at all. Unlike sodium azide which contains a considerable quantity of occluded inert gases from the atmosphere. We believe this has relevance to the reactivity of the material; generally speaking inclusions in the material tend to make it less brittle, vice versa the smaller the number of inclusions the more brittle the behaviour of the material and therefore the more effective the fracturing mechanism will be. I think by and large when one deals with polycrystalline aggregates as in the case of this very sensitive American lead azide one is always dealing with this problem of adiabatic heating. Grinding it up to a very small size provides a very large surface to volume ratio, the surface is effective in the decomposition mechanism, the more surface the more effective the decomposition mechanism will be. It is a question of rate of reaction. If the reaction really is surface controlled then the more surface you provide the faster the rate per unit weight of material.

G W C Taylor

If we produce very small crystals by precipitation we can get a material which is significantly more sensitive than taking a relatively pure material and grinding it up to the same size. The precipitated material is more sensitive to electrostatic spark than the ground material.

P G Fox

There are these peculiar effects of grinding whereby one is supposed to accumulate stored energy in the material which one thinks would make it more sensitive rather than less sensitive. I should point out that the smaller one makes the crystal the more rapidly one runs out of plausibility of the fracture mechanism. The theory depends on the ability of a crack to propagate at maximum speed but it turns out that when you start to propagate a crack in the material it takes a little while to get it up to maximum speed. With your very fine powders it is wholly a question of adiabatic heating.

J M Jenkins

What would be the effect if it were practicably possible to fill detonators under vacuum or under gases in which gamma is high?

P G Fox

I would like to know myself because it would really sort out the effectiveness of this adiabatic heating - no gas, no heating so it should be much less sensitive. Chaudrhi is trying to do experiments along these lines. Butane has a very favourable low gamma, it should be much less effective at initiating a material. The experiments he has managed to do have been pretty conclusive in this respect. There has been some discussion in the literature on the variation of gamma with pressure, one never knows how gamma is varying and the sort of pressure developed in a real experiment.

R H Lynch

We are involved with Chaudrhi on this question and part of our programme involves trying to fill stab sensitive materials under vacuum. If you have aggregates of materials of different sensitivity with the same particle size and compress them to the same load then the adiabatic pressure in the interstices should be similar. Therefore the response to a given stimulus should be related to some physical or chemical property of the material such as hardness, ignition, temperature, vapour pressure.

P G Fox

It should be related to the pattern of the material. If one has an ideal situation where all the crystals are spherical and are all close packed then all the interstices would be of the same size and same shape. This would give a very good control of the response of the device.

G W C Taylor

We have a very definite policy and this is to get random orientation of any powder or any crystals. If crystals or powders are anisotropic in their rate of burning it follows that any variations in their packing will give a different rate of burning. We aim to overcome any anisotropic effect either by having crystal with habits which are compact and equant or are micro-crystalline aggregates which are randomly oriented.

A T Thomas

Having carried out your Vickers hardness test you have made a big crack, do you find the crystals are more sensitive and why doesn't the crack proceed and give a detonation?

P G Fox

In the hardness measurements the material is loaded very slowly and it is unlikely that any significant cracks develop. In all the experiments in which we actually fractured the lead azide and measured the amount of decomposition produced we never produced an explosion. The main drawback against getting a very energetic crack in a single crystal of lead azide is the fact that we are hamstrung by what we can do experimentally. In fact in this case the crystal was cracked by a 3 point bending technique. It was lain across two supports and a knife edge was hit as hard as we could producing the single fracture through the crystal. This is an unsatisfactory method of making a fracture in a crystal like this. We would have liked to have stood the crystal on end and run a crack all the way down the length of it. When these crystals are 100 microns across it is rather difficult. It would be very interesting to know whether or not explosion occurred if the fracture got to its maximum velocity, presumably it would. We know that if you hit lead azide hard enough it goes off.

NEW DATA ON THE ELECTROSTATIC SENSITIVENESS OF COPPER AND SILVER AZIDE

S LAMNEVIK

The spark test is frequently used as a method for electrical sensitiveness testing. It does give reproducible results for gaseous mixtures but it should be used with care on solid test samples such as explosives. In the normal test apparatus the test substance is on a metal plate which is usually grounded and there is a movable needle electrode above the sample. As the upper electrode is lowered there will be a spark discharge.

The substance itself, it may be an insulator, a semi-conductor, or a conductor. If it is an insulator it will be of a very high impedance and it is almost impossible to pass any current through it, but if it is a semi-conductor the impedance is rather moderate and a small current may pass through it, if it is a conductor a high current can pass through the substance.

If the tests are with an insulator the spark is probably going not through the substance, but across it and if there is initiation it will be by radiation or heat or light perhaps from the shock wave, from the spark, or even cracking. A rather high energy will probably be needed to fire it except when there is a substance that is very porous, so porous that electrically it can be regarded as air. In this case the spark will go through the substance and there will probably be a higher chance of initiation because there is much better heat transfer from the spark to the substance. The probability of initiation with an insulator should be proportional to the peak current and duration of the spark. This is determined by the output impedance of the voltage generator, because the impedance of the spark path itself is very low: in the order of 10 ohm. If there is a polycrystalline or a conducting sample there will be many potential hot spots and these are the contact surfaces between the crystals. The initiation is influenced by many factors, the dominating ones being the electrical and thermal properties of the total system. It must be remembered for instance that maximum power transfer occurs when the impedance of the voltage generator and the test samples are equal. For instance the increase of test sample conductance by small amounts of moisture may increase the probability of initiation of non-conducting explosive by making the impedance matching better.

There are very many parameters of electrical sensitiveness. In the voltage generator there are impedance, voltage, and frequency, and for the test substances there are the electrical, physical, chemical and thermal properties and they combine to form a complex system.

In Stockholm we have studied the electrical properties of thin polycrystalline layers of alpha cuprous azide and alpha silver azide. We have not used the spark tests but have used a rather different test circuit as shown in Fig. 1.

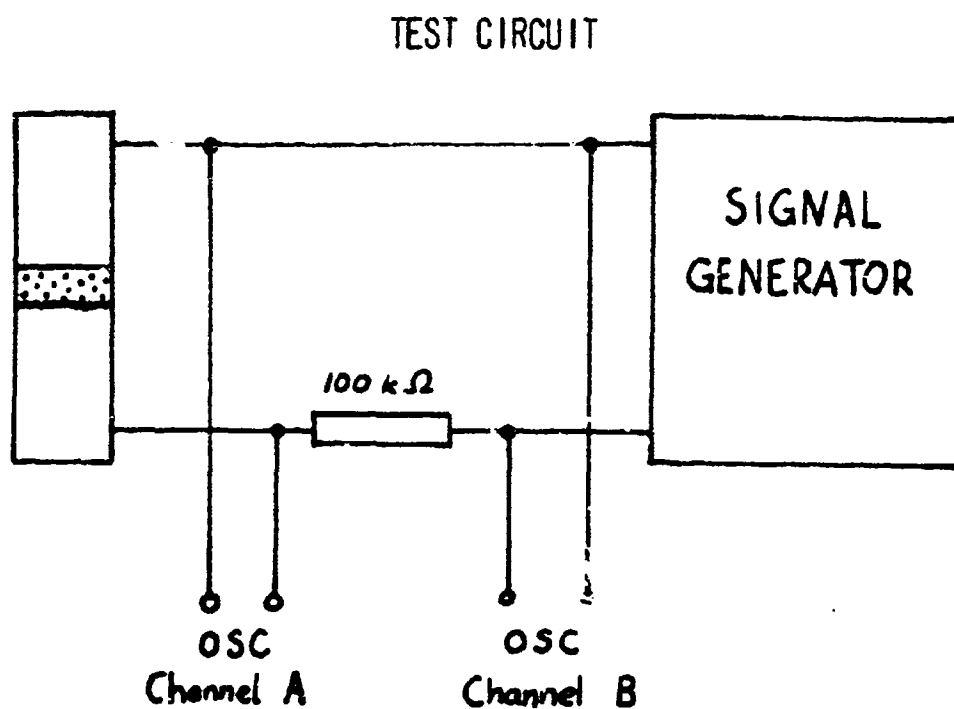


Fig 1

On to one electrode, which is made of copper or brass or silver, has been grown a thin layer, about 5 to 30 microns thick, of azide by electrolysis. Another electrode is pressed onto the azide layer. A current from the signal operator is passed through the sample and the total voltage amplitude is measured at B, the voltage across the test circuit is measured at A.

A typical electrode system is shown in Figure 2 and is made up as a printed circuit. The copper foil (1) is masked and a small area is exposed to give an azide deposit at (2). A gold foil (3) is used as the anode and the system is connected to the test circuit by the leads (4).

Metal strip

Azide

Gold leaf

Leads

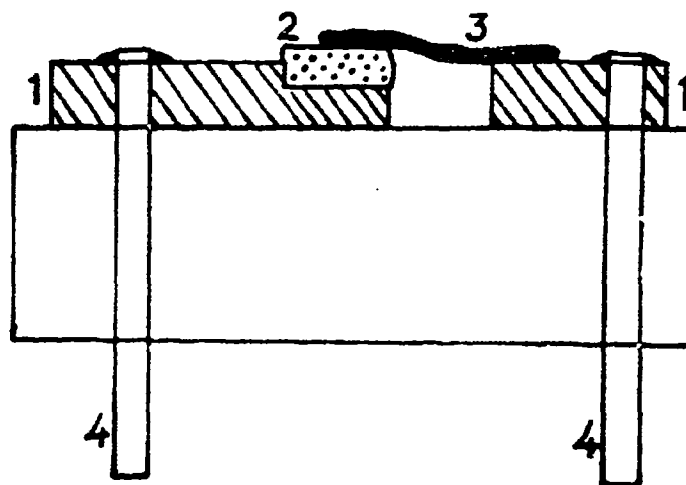


Fig 2

Application of Direct Current

With direct current up to 1½ volts there was no current flowing. Thereafter the current increased sharply to about 2 milliamps when ignition occurred. The lifetime of the circuit could be varied by using a rather large contact so it behaves exactly like a normal rectifier. If the voltage was increased in the other direction we could not record any current at all, but at a voltage depending on the thickness of the layer the sample ignited again. This behaviour is similar to that of a normal rectifier. (See Fig. 3)

Alternating Current

At frequencies above 10 cycles per second the rectifying action ceased, but below this value the behaviour was similar to that of direct current. When the voltage across the azide reached 2 volts it started to conduct on one half cycle only. The current was again related to the contact surfaces.

It was only a rectifier for low amplitudes and when we increased the total voltage to about 20 volts, it started to conduct in both directions and if the output voltage of the generator was varied and this voltage stayed very constant so it behaved like a voltage regulator. Explosion again occurred at a maximum current value and similar behaviour was observed with silver azide, not as a rectifier, but as a voltage regulator, at least when we used very thin layers.

This means of course that both cuprous and silver azide are semi-conductors and it is most probable that the main cause of initiation of these copper or silver azide layers is resistance heating of the crystals to temperatures high enough for decomposition. As I said, current density and thermal conductance of the electrode system determined the probability of initiation.

The investigations will be continued to include other explosives and we hope that in the future we will be able to predict and even calculate actual risks of handling electrically sensitive explosives by using a computer and a reference library on material data, but I think that will take time.

R M H Wyatt

I am very interested in the numerical values we have got for the potential difference applied and the curves you have got, they seem to fit in with the experience we have had that relatively small capacitors charged with quite a small voltage is sufficient to do the trick with these cuprous azide layers on copper base.

S Lamnevik

I should like to point out one thing for cuprous azide, when you have got it on the surface, which is grounded, it may initiate very easily and this has been observed many times at our laboratory. You need not touch it; you may be half a metre from it and it will go off.

J F Sumner

I would like to ask Mr Lamnevik if he has done any assessment of the time of ignition with these rather slow rates of administration of energy to copper azides. The voltage is small, the current is fairly small. Have you investigated the time factor.

CHARACTERISTICS OF CuN_3 ELEMENT
FROM DC MEASUREMENTS

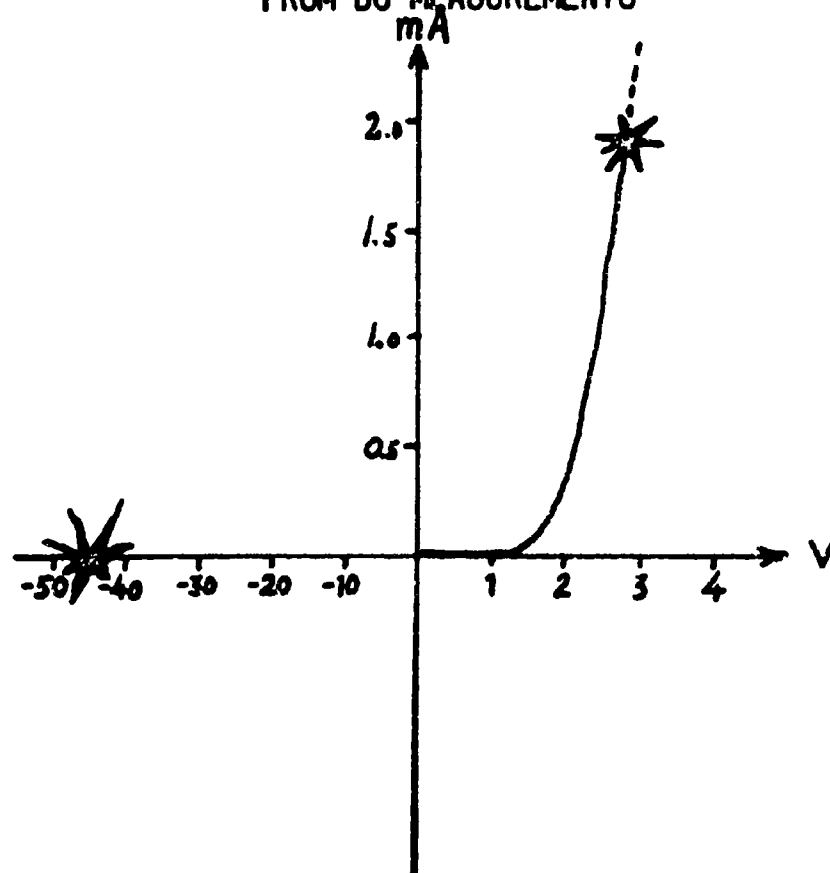


Fig 3

S Lamnevic

Yes. I have just started this work. When you pass a very small current through the test circuit it can take about up to one minute before it explodes, if you increase the current the time goes down which suggests that it is strictly related to heat dissipation.

SUMMARY (G W C TAYLOR)

The contribution on sensitiveness testing has brought up to date not only the listing of tests appropriate to primary explosives but also the limitations of the tests and the difficulties in the interpretation of results which were confirmed by the discussion. There is a tendency for numerical results to gain in status when they leave the testing laboratory, the interchange of views between interested parties has been especially useful.

The importance of selection and assessment of anti-static materials needs no emphasis and with the availability of new materials considerable progress has been made towards guiding the user. Thus although anti-static polythene can satisfy the electrical and compatibility requirements it may introduce mechanical difficulties such as cracking on ageing. The discussion on flooring brought out practical aspects which tend to be overlooked.

The study of the hazards associated with storage and transport of primary explosives has thrown new light on at least part of the problem and led to a lively discussion on the relevance of initiation and propagation stages. The presentation on safety precautions for the filling factory and the purpose of safety certificates reinforced the previous comments on the interpretation of sensitiveness results. This has been an excellent opportunity for the research and factory points of view to be expressed and coordinated and was regarded as one of the most important sessions of the Symposium.

The description of the events leading to a serious accident and the subsequent investigation and remedial actions was very pertinent to all the papers which had gone before. This contribution and discussion should be of direct practical help toward eliminating unsuspected hazards when handling wet primary explosives in bulk.

The mechanism relating mechanical properties of metallic azides and their effect on sensitiveness was discussed in relation to the alternative thermal theory. This emphasised the need for both theoretical and practical study of an explosive such as lead azide where severe crystalline fracture occurs without ignition yet ignition can occur with very low energy stimuli.

The final paper afforded a novel experimental approach for obtaining new data and understanding of electrostatic sensitiveness of very sensitive explosives.

It is believed that the proceedings of the Symposium have made a useful contribution to the knowledge and the practice of preparing, investigating and applying sensitive explosives.