ASSESSMENT OF EXPLOSION HAZARDS OF UNSTABLE SUBSTANCES

By V. J. CLANCEY, M.B.E., B.Sc., A.R.C.S., F.R.I.C.†

SYNOPSIS

Means are required to assess hazards by small-scale experiments. Those commonly used are based upon the science of conventional explosives with important modifications.

Several types of explosion may occur: a detonation, propagating supersonically; a deflagration, propagating subsonically; so-called homogeneous explosion in which reaction occurs almost simultaneously throughout the mass. The event may be initiated by mechanical shock or by thermal stressing. If a substance can explode it is important to know how readily it can be initiated. Because the various modes of behaviour are not necessarily correlated it is necessary to carry out a variety of tests.

Tests for detonability, deflagration, response to both ignition and external heating, and sensitivity are described.

The interpretation of test results presents certain difficulties because of complex and sometimes imperfectly understood scaling laws. Some fundamental principles of explosion theory are invoked to aid extrapolation to large-scale situations and assessment of potential damage.

Definitions

By an unstable substance is meant one which can undergo an exothermic change by itself under conditions which are likely to occur during manufacture, processing, storage, or transport.

The characteristics of such a substance may be such that the exothermic change, when initiated, leads to what is commonly known as an explosion. Initiation may be by ignition, by the application of heat from an external source, or by mechanical stressing. Response to the various kinds of initiation are not necessarily correlated. For example, it is well known that if T.N.T. is ignited it will burn quietly, yet when subjected to a strong mechanical shock it will detonate. Consequently it is necessary to study the responses of the substance to each kind of initiation.

Several kinds of explosion are involved: detonation, deflagration, and homogeneous thermal explosion. Explosions which occur solely by the bursting of the container under pressure are excluded from present consideration.

A detonation is characterized by its mode of propagation through the mass from its point of initiation. Propagation reaches a steady state wherein a shock-front moves forward with a velocity which is supersonic in respect of the unreacted zone into which it is moving. The pressure in the shock front rises abruptly to a very high value—in the case of a conventional solid high explosive of the order of \(1 \times 10^5 \text{ atm} \) with a velocity of about 6000-7000 m/s. Lower velocities, which are still supersonic and therefore true detonations, may occur: for example, in certain organic liquids in which sonic velocities are about 1000 m/s and detonations at 1200 m/s occur or in some granular solids for which the sonic velocity may be under 1000 m/s.

A deflagration is a surface reaction propagating itself by heat transfer. It is analogous to what is commonly described as burning except that in respect of the substances under consideration atmospheric oxygen is not involved. Examples of deflagrations are the "explosion" of solids such as gun-powder and cordite, of liquids such as the monopropellants, for example, isopropyl nitrate, and of gaseous mixtures of hydrocarbons and air.

Definitions

By an unstable substance is meant one which can undergo an exothermic change by itself under conditions which are likely to occur during manufacture, processing, storage, or transport.

The characteristics of such a substance may be such that the exothermic change, when initiated, leads to what is commonly known as an explosion. Initiation may be by ignition, by the application of heat from an external source, or by mechanical stressing. Response to the various kinds of initiation are not necessarily correlated. For example, it is well known that if T.N.T. is ignited it will burn quietly, yet when subjected to a strong mechanical shock it will detonate. Consequently it is necessary to study the responses of the substance to each kind of initiation.

Several kinds of explosion are involved: detonation, deflagration, and homogeneous thermal explosion. Explosions which occur solely by the bursting of the container under pressure are excluded from present consideration.

A detonation is characterized by its mode of propagation through the mass from its point of initiation. Propagation reaches a steady state wherein a shock-front moves forward with a velocity which is supersonic in respect of the unreacted zone into which it is moving. The pressure in the shock front rises abruptly to a very high value—in the case of a conventional solid high explosive of the order of \(1 \times 10^5 \text{ atm} \) with a velocity of about 6000-7000 m/s. Lower velocities, which are still supersonic and therefore true detonations, may occur: for example, in certain organic liquids in which sonic velocities are about 1000 m/s and detonations at 1200 m/s occur or in some granular solids for which the sonic velocity may be under 1000 m/s.

A deflagration is a surface reaction propagating itself by heat transfer. It is analogous to what is commonly described as burning except that in respect of the substances under consideration atmospheric oxygen is not involved. Examples of deflagrations are the "explosion" of solids such as gun-powder and cordite, of liquids such as the monopropellants, for example, isopropyl nitrate, and of gaseous mixtures of hydrocarbons and air.

† Dr. J. H. Burgoyne and Partners, Drake House, 3-5 Dowgate Hill, London, E.C.4 R25L

Potentially Hazardous Substances

Given appropriate conditions any substance capable of exothermic decomposition can produce an explosion. The conditions are dependent upon the reaction energy, the activation energy, the speed of reaction, and the rate of dissipation of energy. In many instances the requisite conditions do not arise during the course of handling, transport, or storage. Hence some substances which could, under extreme conditions, present an explosion hazard are not regarded as being hazardous when the requisite conditions for an explosion could not conceivably arise in the ordinary course of events.

For example, ammonium nitrate can detonate. In fact the three largest accidental explosions ever known involved this substance—in 1923 at Oppau, Germany; in 1947 at Texas City, U.S.A.; and in 1947 at Brest, France. In each case some other substance was present acting as a fuel or sensitizer. Pure ammonium nitrate can be caused to detonate under special conditions but it has never been known to do so accidentally. Hence the pure salt is not regarded as presenting a hazard during transport and this fact is incorporated in the several international regulations.

CLANCY. ASSESSMENT OF EXPLOSION HAZARDS OF UNSTABLE SUBSTANCES

It is clearly necessary that laboratory tests must be related to the conditions which could occur in practical situations. Tests which give positive results under extreme conditions may well impose unnecessary restrictions upon industry. Therefore not only must the tests be designed accordingly but the interpretation of their results must also take account of the conditions to which it may be exposed.

An important consequence is that a substance may be judged to present an explosion hazard in certain circumstances but not in other circumstances. For example, it may be hazardous during processing but when packed in a specified manner for transport it may be free from hazard. Thus hazard-testing involves not only the properties of the substance itself but also the conditions to which it might be exposed.

Hazardous Species

Amongst organic compounds, certain groups, described by Lothrop and Handrick as "phosphanes", are known to contribute to a tendency to explode. The most powerful of these are those containing oxygen and nitrogen, for example, nitrate (–ONO₂), nitro (–NO₂), and nitramine (–N–NO₂ and –NH–NO₂) compounds. Less powerful, but generally more sensitive, are compounds with the following groups: nitroso (–NO), diazo (–N=N–), diazo sulphone (–N=N–SO₂–), halogen amines (=N–X) and azide (–N₃). Other potential phosphanic groups are acetylenic (–C≡C–) and peroxide (–O–O–). The presence of a metal, particularly a heavy metal, may markedly increase the danger.

Examples are given by the well-known copper and silver acetylides and the lead and mercury salts of nitro compounds. Less well known is the fact that some salts of other metals are more dangerous than their parent substances. Examples are the sodium salt of picramic acid and the zinc chloride double salts of some diazo compounds.

Another class of potentially explosive organic compounds are the salts in which the acid radical is an oxidising agent, for example, chlorates, perchlorates, bromates, iodates, chlorites, etc.

This list is not exhaustive. Many substances, both organic and inorganic, which can undergo an exothermic rearrangement can be explosive. Examples of compounds which have exploded accidentally are alloxan, hexammine cobalt and chromium nitrates, perchlorates, etc., ammonium bi- and trichromates, ammonium periodic acid, ammonium peroxybromate, anisyl chloride, potassium carbonyl, potassium peroxide, potassium peroxyferrate, silver oxalate, tin nitrate, and triaryl phosphate.

Many attempts have been made to associate explosibility with the quantity of available energy. Thus Yallop and Martin and Lothrop and Handrick have claimed that the oxygen balance in nitro and similar compounds is a good criterion but this has been disputed by Price. Van Dolah has pointed out that the heat of detonation of the notoriously sensitive lead azide is 220 cal/g whilst that of the less sensitive TNT is 1160 cal/g and has indicated that knowledge of the simple thermodynamic data is insufficient for the assessment of hazard.

Because of these uncertainties, when one is faced with a novel substance which might be able to decompose exothermically, it is necessary to carry out tests.

Test Methods

The test methods generally adopted have been derived from those developed in explosives technology. Difficulties arise for several reasons. Rather surprisingly, even after many years the explosives technologists have not finalized their own tests, some of which are still the subject of controversy. The tests are designed to assess properties which are of specific interest in relation to conventional explosives and are not necessarily related to hazardous substances and the interpretation of the results and the criteria applied are different; a conventional explosive is always treated as an explosive with multitudinous precautions whereas when assessing a potentially hazardous substance the purpose is to find out whether it requires to be treated as an explosive.

Logically, the first tests to be done should be those to determine whether the substance can explode. Then, if it can, to ascertain the ease with which it can be caused to explode and whether dangerous conditions could arise in practice. In the interest of safety in the laboratory it is usual, however, to carry out first tests to ascertain the sensitivity of the substance.

Sensitivity Tests

Three types of tests are in common use: impact or falling weight, friction, and card-gap tests.

Impact testing

A wide variety of equipment is in use for impact testing. The general principle in all of these is the same. A weight is caused to fall from a measured height onto a small sample. It has been found that direct impact on the sample gives irregular results. Hence the sample is spread on a hard steel anvil under a hard steel striker onto which the weight impacts. Whether or not the sample is fired is normally judged by ear. In most cases firing gives a sharp crack. In doubtful cases discolouration or marks on the anvil are indicative of a positive result.

Originally the apparatus was used to determine the maximum height at which no ignition occurred in a specified number of tests, generally five or ten. Nowadays most laboratories use the Bruceton "up and down" method, in which the statistics of which have been described by Dixon and Massey. By this method a fairly reliable estimate is obtained of the "50% height" from a limited number of tests. The "50% height" is the height at which it is expected that ignitions would occur with a probability of 0.5.

One weakness of this method is apparent when it is desired to estimate what would be the safe height, that is, the height at which an ignition would not occur, or occur very infrequently —this being, of course, the important factor when assessing hazards. The Bruceton method provides no information regarding the shape of the distribution curve. It is assumed that the shape is the same for all substances, and this is not valid. However, to obtain a true "safe height" would require an immense number of tests.

Another weakness arises from the fact that the result is a function not only of the substance tested but also of the apparatus used. Boyers and Levine have published a critical review of the subject. The results from one laboratory cannot be compared exactly with those from another. Whilst the ranking is generally the same there are occasional marked discrepancies.

It is the practice of some laboratories, especially those on the Continent of Europe to express the result in terms of kilogramme-centimetres. This would imply that ignition is a function of energy. It is in fact dependent upon time as well. Hence it is necessary to specify the height and the...
Friction tests

When determining sensitivity it is important to assess the response of the substance to the kind of blow to which it might be exposed. The impacts of the falling weight tests do not meet this requirement. Real blows are often of a glancing kind involving an element of friction. It is known that the response of some explosive substances to frictional forces is different from and not necessarily correlated with their response to impact. For these reasons the so-called friction tests have been in use for many years.

In the U.S.A. the Bureau of Mines uses a ° Pendulum Friction apparatus °. A shoe, covered with steel or hard fibre, is swung on a pendulum about six and a half feet long, to give a glancing blow on the sample spread on a steel anvil. The length of swing and weight of shoe are adjustable and is referred to in R.I.D. and A.D.R. It is probably unique in that the apparatus for it is made and sold commercially.

In the U.K. a simple apparatus is used in connection with the official Home Office classification of explosives and hazardous substances. I have described this apparatus, designed and used in the Royal Armament Research and Development Establishment, elsewhere.

Card-gap test

The card-gap test is of a different type. The substance under test is subjected to a shock-wave produced by an explosive. By inserting cards in the gap between the donor explosive and the sample, the shock wave is attenuated. Repeated trials are carried out varying the number of cards to determine the weakest shock capable of initiating an explosion of the sample. Favoured materials for the cards are aluminium, plexiglass, or cellulose acetate. Jaffe, Beauvegard, and Amster have calibrated the attenuation by cards so that the shock may be expressed in terms of peak pressure or, as more frequently used, in terms of the thickness of material. Details of the test are given in various publications by the U.S. Bureau of Mines, U.S. Army authorities, Price, Liddiard, Pepe and Whitbread and Cacchia and Whitbread who were responsible for its original development.

In relation to the assessment of unstable substances the test has several serious defects. As ordinarily used detonation of the sample is recognised by the fracturing of a steel witness plate. However, fracturing occurs only if the detonation velocity is greater than the velocity of sound in steel, that is about 5000 m/s. The detonation velocity of most unstable substances is considerably less than this so that there is no clear indication. This difficulty can be overcome by using a sensing device such as that described by Amster and others to indicate the establishment of a steady state.

Another defect stems from the small diameter of the cylindrical sample. Many substances have a critical diameter below which they cannot detonate. For instance certain forms of ammonium nitrate have a critical diameter of 12 inches or more. This may be overcome by confining the sample in a thick-walled steel tube but further difficulties are introduced. The thickness of the wall becomes an arbitrary parameter. Many liquids have a detonation velocity less than the velocity of sound in steel, that is about 5000 m/s. The detonation velocity of most unstable substances is considerably less than this so that there is no clear indication. This difficulty can be overcome by using a sensing device such as that described by Amster and others to indicate the establishment of a steady state.

A third defect arises from the fact that it is by no means certain that response to a shock of one characteristic form is correlated with response to shocks of other kinds. Martin has found, for example, that certain organic peroxides, whilst they are not initiated by the high-velocity shock from a high explosive, may be initiated by a shock of lower intensity but longer duration.

At present the card-gap test must be regarded as a research tool rather than a standardised method for assessing unstable substances. Despite its defects it is most promising and work is currently being done by Lindeijer in Holland and Owen in the U.K.
Detonability Tests

No sharp dividing line can be drawn between detonability tests and sensitivity tests. Some perform both functions, for example, the card-gap test. Such a test devised in Holland has recently been described by Aris. In this test the sample is subjected to a graduated series of shocks produced by pellets of a high explosive diluted with an inert substance. In Belgium, Deffet carried out a series of tests using a number of detonators bunched together, the sensitivity being judged by the number of detonators needed to give a positive result. Medard described the method adopted in France for a similar purpose. Turner and Clancy have used detonators of graduated strengths in association with a ballistic mortar. Tests which are more specifically designed to assess detonability fall into two groups: those in which the evolution of energy is measured, and those in which detonation is assessed qualitatively under an arbitrary set of conditions.

The lead block test

Of the former the best known are the Trauzl “Lead Block” test and the ballistic mortar.

The Trauzl test was standardised in 1903 by an international convention. Since then it has been modified by various workers so that data quoted as “Trauzl values” may have in fact been obtained in variants which yield significantly different results. The form in which it is now most extensively used is described by Koenen, Ide, and Swart. It is necessary to adhere precisely to the specified conditions.

A weighed standard volume of the substance is initiated by a detonator in a recess in a cylindrical lead block. Confinement is effected by sand stemming. The energy evolved is assessed by comparing the volume of the cavity swollen by the explosion with the effect produced by a standard explosive, picric acid.

Ballistic mortars

Many designs of ballistic mortars have been used for assessing explosives. Most of them are somewhat cumbersome for use with unstable substances. As far as is known the only designs which have been used for this purpose are the two developed by R.A.R.D.E. and used successfully by me for many years. Both are used as standard tests in connection with Home Office classifications.

The two mortars, more correctly ballistic pendulums, are suspended so that they swing by recoil when the charge is fired. The angle of swing produced is compared with that given by a standard explosive, picric acid. One of the mortars, known as the Mark III, was designed to simulate the conditions in the Trauzl test. The sample is confined by the heavy body and by sand stemming. Initiation is by a No. 8 detonator. Its main advantage over the Trauzl test is that time and work are saved. As many as 50 to 60 shots can be fired in one day and the difficulties of casting good lead blocks, each weighing a hundredweight, are avoided.

In the other mortar, the Mark I, the sample is virtually unconfined. It is suspended in a cavity of which the diameter is several times greater than that of the sample. Initiation is by a weaker, No. 6, detonator. Interpretation of the results from the two mortars requires some understanding of the processes.

In both the Trauzl test and the Mark III Mortar, the sample is exposed under very strong confinement to a powerful impulse. The conditions are so severe that substances which could not be expected to detonate under practical conditions will yield a positive result.

When a new substance gives a low value in the test there may be some doubt as to the validity of the result. The low value may be due to detonation with a low specific energy or to overdriving of part only of the sample adjacent to the detonator. This may be resolved by carrying out a separate test to measure the velocity of detonation and determine if a steady-state propagation occurs. Alternatively the energy available may be determined in a bomb calorimeter and this can be compared with the ballistic mortar result. Although this result is usually expressed as a percentage of that given by a standard explosive the actual energy produced can be calculated from the weights of the sample and of the mortar and the length of the pendulum.

When a positive result is obtained in the Mark III mortar a test is carried out in the unconfined condition in the Mark I mortar. This is very much less severe.

Qualitative tests

Many arbitrary qualitative tests have been used. Typical are the inch, inch, and inch steel tube tests described by Koenen et al. The sample is confined in a steel tube. It is important to specify the internal diameter and wall thickness. Initiation is by a detonator with a high explosive booster. Detonation is indicated by a witness plate across the end or by the nature of the fragmentation of the tube. As stated before this is not a good indication for substances with a low velocity of detonation. Observation of a steady velocity would be preferable. Lindeijer has stated that the tube should be at least one metre long.

Each of these tests merely shows whether the substance can be brought to a steady-state detonation under the conditions of the test. Selection of the test conditions has to be made to provide a result which is applicable. This is generally done in an arbitrary manner based upon practical experience with a few hazardous substances such as ammonium nitrate. It is argued that pure ammonium nitrate has been proved by experience to be safe whereas in the presence of 0.5 to 1.0% oil it can detonate in a fire as occurred at Texas City. If the test can distinguish between these two it is regarded as useful. I do not think this is a good basis for assessment.

Thermal Explosion Tests

The hazard to which substances are most likely to be exposed during storage, transport, etc. is that of fire. They may be ignited or they may be exposed to external sources of heat. As a result they may deflagrate, detonate, or undergo homogeneous explosion. The response to these stimuli is not always correlated with response to mechanical shock. Although this is of primary importance in assessing hazard comparatively little attention has been devoted to it.

Tests for sensitivity to thermal initiation which are used by the German railways and some other authorities have been described by Koenen et al. In the main the tests are simple and crude. The sample is exposed to sparks from a cigarette-lighter, to a gas flame, to the flash from a burning fuse; a red-hot iron rod is dipped into the sample; or some of the sample is dropped into a red-hot iron dish. In the sheet-iron box test originally developed at Spandau for the German Railways the sample is heated in a crude thin-walled box.

A more sophisticated test, known as the Koenen steel tube test, was described by Koenen and Ide. A very similar test is the pressure vessel test of Lindeijer. Details of both tests are given in R.I.D. The sample is heated in a bomb which is fitted with a vent. Vents of different sizes are selected for successive tests, thus applying degrees of confinement. When an explosion occurs the German steel tube, which is expendable, is split or fragmented; with the Dutch pressure vessel a bursting disc is ruptured and this preserves the bomb itself from damage. The tendency to produce a thermal explosion is judged by the
diameter of the smallest vent necessary to prevent an explosion. In the case of the German test the criterion is a vent of two millimetres diameter. If an explosion is not produced at smaller diameters the substance is considered to be non-explosive. In the Dutch test the criterion is eight millimetres. Although the German test is more widely used it is considered that the Dutch test has certain advantages.

Other tests for the effect of extreme heating, including my own thermal bombs have not been adopted widely and are tending to go out of use. Examples are those described by Burns, Scott, and Jones, Hainer, and Rapean, Pearson, and Sello.

For determining response to ignition Van Dolah has devised a test in which the sample is exposed in a vented bomb to the flash and pressure from a charge of cordite. Pressure is applied since deflagration is dependent upon pressure. By varying the vent size it is possible to determine the minimum pressure at which deflagration will become self-supporting. The only deflagration test which has received official recognition is the Home Office Time/Pressure test which I have used for many years and has proved to be of great value although for certain liquids its results are open to some doubt when it is used since they tend to quench the ignition system.

Thermal Stability Tests

Thermal stability tests may be regarded as sensitivity tests in that their purpose is to assess the ease with which a substance may start a run-away reaction which could lead to explosion. Most of the tests used consist of heating the substance or holding it at an elevated temperature under conditions approaching adiabatic. Conventional D.T.A. methods serve the same purpose. None of the tests has, as yet, received official sanction. Each laboratory adopts its own methods and interpretation.

Closely allied are tests to determine the temperature of self-ignition. The temperature of the sample may be raised at a specified rate (generally 5 degC or 10 degC per minute) until it ignites. Alternatively the sample may be introduced into a preheated cavity in a hot plate, successive trials being carried out.

Tests on Packages

The tests already described provide data on the properties of the substances themselves. For transport it is of particular interest to know the hazard status of the substance as packed. In the explosives field it has been recognised for many years that the hazard may be materially reduced by suitable packaging. In the chemical industry this may be of the greatest importance if by suitable packaging dangerous substances can be transported safely.

Hitherto this aspect has been somewhat neglected. Little has been done in the way of devising suitable tests and standards. But work is currently going on in the official laboratories in U.K., Germany, Holland, U.S.A., and elsewhere.

The tests which are likely to emerge will be performance tests on the packaged materials: dropping or other rough usage tests to assess response to mechanical stressing; bonfire tests for response to heating and some form of communication test. The last would be intended to determine whether an accidental explosion of the contents of one package would communicate to and cause explosions of neighbouring similar packages. The consequences of a single small explosion or even of a series of consecutive small explosions might well prove to be an acceptable risk.

Conclusions

Many tests have been described. Whichever is chosen, the problem arises of how to interpret the results obtained. It depends upon the purpose for which they are wanted. The hazards, which are largely dependent upon the stimuli to which the substance may be subjected are different during manufacturing processes, storage, and transport. All the tests give results which can only be used comparatively in association with experience of other hazardous substances in the main this is experience in handling conventional explosives. Thus if a substance is fired in an impact test with a 50% height about the same as that for lead azide, it indicates that it must be treated in the same way as is the practice with this extremely sensitive initiatory explosive—that is to say all operations are to be carried out behind barriers, by remote control, avoiding all possibilities of impacts or friction, and that it is too sensitive to be transported except in small quantities under very special packing conditions. The 50% height alone is of little value unless it can be compared with data obtained on the same apparatus for other substances of which there is also practical experience. Similar principles apply to the results of the other tests.

Further, it is necessary to take into account the results of all of the several types of test. To be considered safe they must show that it gives satisfactory results in all of them.

In the present state of the art it is not possible to specify a set of criteria. Consideration must be given to the chemistry of the substance and the circumstances which might arise, including the possibility of it becoming contaminated or coming into contact with a sensitizer, and so on.

In so far as transport problems are concerned, much useful information can be gained by studying the classifications and tests specified in codes such as R.I.D. and A.D.R., the “Blue Book” and the I.M.C.O. Code. An indication of how assessments can be made is given by Clancey, Owen and Taylor in a report in which the test results on a great many organic peroxides are set out together with the argument whereby they have been classified into several hazard categories.

In order to use the test results properly it is necessary to understand the phenomenology of explosions. Without this serious errors can be made.

References


Peters, J., Berlin NW21, Stromstrasse 39, West Germany.


The manuscript of this paper was received on 5 January, 1971.