INITIATION OF MILITARY EXPLOSIVES.*

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I. INTRODUCTION.

THE first use of an initiator—in other words, of a small amount of some sensitive substance through which explosive action of a less sensitive main charge might be brought about—came in the early part of the nineteenth century. The slow and cumbersome matchlock had given way to the flintlock during the previous century, but, even with this improvement, the time between the decision to fire and actual ejection of the bullet was still considerable, loading was slow and difficult, and the action was by no means certain. In 1805, the Rev. A. J. Forsythe, a Scottish clergyman, proposed to the British military authorities the use of a mixture of potassium chlorate, charcoal, and sulphur as a primer for small arms; a number of experiments were made, but the method was not adopted. Nine years later, several men, of whom J. Shaw of Philadelphia seems to have been the first, independently developed the percussion cap loaded with fulminate of mercury. With this cap, our modern methods of igniting propelling charges came into being; the only essential changes since then have been the introduction of electric firing for certain purposes, and the interposition of auxiliary ignition between the initiator and the main charge to ensure proper initiation of large charges.

The invention of the percussion cap brought about another development, and one which, perhaps, the inventors themselves did not foresee. As early as 1588, an Italian refugee in the employ of the Dutch, had used an explosive shell filled with black powder, employing as a fuse a tube or pipe filled with slow-burning powder which was ignited by the discharge of the gun. Such shells were only of use against material, for men usually had plenty of time to get out of the way before they exploded. Efforts were made to improve timing and to get

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greater certainty, but this type of fuse was never satisfactory even in the low velocity artillery of that period. The application of the percussion cap to this problem was soon seen; in 1846, Quartermaster Freeburn of the British Army brought out a time fuse in which a percussion member was operated by the shock of discharge of the gun, and four years later Commander Moorson, of the British Navy, invented a fuse firing on impact. In 1853, the Russian fleet made the first use of the percussion fuse, against the Turkish at Sinope; the effect was great.

This was only the first step in the development of the modern shell—two further discoveries were necessary to its development. The first of these came in 1864. In 1859, Alfred Nobel, a Swedish engineer, became convinced that nitroglycerine, which had been discovered eight years earlier, was destined to be of great importance to the engineering profession. It was admittedly the most powerful explosive known at the time—perhaps the most powerful that ever would be known. Unfortunately, it could not then be used, for the only practical way of setting off an explosive for use in blasting was by a spark or flame, and nitroglycerine, instead of exploding under such conditions, would usually only burn quietly. After five years of constant research, Nobel found that a small charge of fulminate of mercury, which can be exploded readily by heat or flame, would completely and surely detonate a large charge of nitroglycerine. “The step from the use of fulminate of mercury in caps for the ignition of powder in weapons to its use as a means of converting the igniting flame of safety fuse into the percussive effect necessary for the ignition of the new explosives may at the present time seem to be a small and simple one, but nevertheless, as has been rightfully acknowledged, it is the one which has made possible the commercial use of nitroglycerine and most modern explosives.” (Colver, p. 5.)

Nobel's invention was immediately applicable to mines and torpedoes for military use, and in 1868, E. O. Brown, a chemist attached to the British Ordnance Department, demonstrated that fulminate would detonate gun-cotton, which had been discovered in the same year as nitroglycerine, and which was being investigated by the ordnance departments of several nations. It was quite different with shells; here the filler must be sufficiently insensitive to shock to withstand discharge from the gun with-

out exploding. Experiments made with the powerful new explosives had failed on this account; some chemists of the day, indeed, feeling that sensitiveness and power were closely related in the organic explosives, held that an explosive sufficiently inert for use in shells would show no particular advantage over black powder. The possibilities of the trinitrated benzene derivatives had not yet been recognized, although several of them had been prepared, and one, trinitrophenol or picric acid, had been known for a hundred years and had been used extensively as a dye. It was not only that these substances are difficult to explode by any ordinary means; in addition to this, it was then considered that, for good effect, the oxygen content of an explosive system must be sufficient to burn all the carbon present to carbon dioxide, and that an excess of oxygen was desirable. By this reasoning, it appeared that compounds of the picric acid type, which do not contain enough oxygen to burn the carbon present even to the monoxide, would only be of value as a substitute for charcoal in the familiar black powder mixture.

The first hint of the possible use of any of these substances was given by Sprengel, a noted explosives chemist, in a lecture delivered before the chemical society in London in 1873. In the course of this he stated: "It is here noted that picric acid alone contains a sufficient quantity of available oxygen without the addition of any foreign oxygen carrier for it to be an extremely powerful explosive, provided that it is ignited by means of a detonator." The full significance of this statement was not realized, and no further developments were made until 1885, when Eugene Turpin, a Frenchman, announced that, provided the initial impulse was sufficiently violent, pure picric acid was one of the most powerful of explosives, and announced to the world its value as a filler for shell. The design of shell he proposed, in fact, is essentially the one used to-day. After more or less hesitation, for it seemed inconceivable to many authorities that an explosive of such power could be at once reliable in action and safe in the bore of the gun, picric acid was universally adopted as a shell filler (lyddite, melinite, schimose, pertite, etc., are all either pure picric acid or mixtures consisting mainly of this substance). The subsequent replacement of picric acid by other explosives, notably trinitrotoluene, detracts in no way from the importance of Turpin's work; the principal, and often the only

components of these explosives are nitrated benzene derivatives like picric acid, and therefore of a class generally neglected before Turpin's discovery.

It will be noted that a differentiation has been made between the initiation of propellants and of high explosives. The two actions are quite different. Propellants are explosives of the first order, which may be exploded by direct action of a flame; the high explosives used are of the second order, and full explosive effect is to be obtained only when they are subjected to an intense initial impulse, such as that given by the detonation of another explosive. Propagation of the explosive impulse through propellants is slow, being never much in excess of one metre a second; the velocity of propagation through a high explosive may exceed 8000 metres per second. For best results with propellants, the initiating effect should be constant—an increase as well as a decrease of the effect is undesirable; the value of high explosives is dependent upon their energy being released in a very brief time, and their effectiveness increases as the time required for the explosive reaction is decreased; it follows that an increase of initial impulse above the standard is never detrimental, and may be advantageous. The initiation of propellants, or ignition, and that of high explosives, or detonation, will therefore, be considered separately.

II. IGNITION AND THE IGNITION SYSTEM.

The requirements of the ignition system are as follows:

(a) Certainty of functioning; a single firing impulse must be sufficient to cause ignition;

(b) Rapidity of action; many weapons, such as small arms and naval guns fired by gun pointers, can be held on the target only for a brief interval of time;

(c) Regularity of ballistics; the charge must be ignited in such a manner as to give the desired muzzle velocity to the projectile, without causing pressures in the gun in excess of those set by the gun designer;

(d) Regularity of firing interval; this quality becomes of importance with naval guns fired by director, and aeroplane machine guns firing through the propeller.

Under the conditions actually obtaining, these requirements

will be satisfactorily fulfilled if the action of the ignition system is sufficiently uniform. Smokeless powders differ enough from lot to lot to make it necessary to determine the weight of charge for each lot experimentally; this procedure automatically takes up any constant ballistic error due to ignition. Assuming that the system is so designed as to give the required rapidity of action—and the experimental data indicates that this is generally true—the only requirement in practice is that the igniting effect always be the same.

There is little definite quantitative data available upon the effect of changes in ignition. As in all problems connected with interior ballistics, it is difficult to control experimental conditions to a satisfactory degree, to obtain accurate data, and to analyze correctly the results obtained. It is certain, however, that changes in ignition effect exert their influence by changing the rate of combustion of the charge. The rate of combustion of propellants is a direct function of the temperature and pressure, and the changed initial conditions resulting from a change in ignition tend to persist throughout the decomposition; one of the advantages claimed for powders of the cordite type, which contain nitroglycerine as well as nitrocellulose, is that their rate of combustion is less sensitive to changes of pressure than that of the "straight" nitrocellulose colloids, and that, therefore, ballistic results are more uniform.

Ignition less than the standard is far more common than excessive ignition. Its effect is to decrease the rate of combustion of the charge. As a result, the maximum pressure is lower and occurs later, the muzzle pressure is higher, and the muzzle velocity somewhat lower, since more of the energy of the propellant is lost through the muzzle after ejection. Dispersion will be increased somewhat, partly because under conditions of slow combustion the powder itself does not burn with the best regularity, partly because high muzzle pressures of themselves tend to cause erratic flight of shell. With still smaller ignition effect, and a still slower rate of combustion, the projectile will leave the muzzle before all the powder has been burned; a decided drop in muzzle velocity and a considerable increase in dispersion will result. At the same time, excessively high pressures may occur, due to "waves" of pressure (this phenomenon is not uncommon with powders too slow for the gun). Complete

failure to fire the main charge may be regarded as the limiting case of insufficient ignition. In addition to its effect upon ballistics, insufficient ignition will at the same time cause increase and irregularity of the firing interval, thus bringing about still further loss of accuracy under service conditions.

The tendency of excessive ignition is to increase maximum pressure, to cause slightly greater muzzle velocity, and to reduce the firing interval. Of these variations from standard, only the first can ever be great enough to be of importance; practically, it is almost impossible for the excess in ignition effect in service to be enough to cause dangerous pressures. Excessive pressures in service, if due to ignition, are apparently quite as likely to be caused by insufficient ignition effect.

Part of the trouble in the ignition system is due to the powder itself. Smokeless powders, and particularly the "straight" nitrocellulose powders, are rather hard to ignite, and burn very slowly at atmospheric pressure. In all except the smallest guns, it is necessary to employ an ignition train of more inflammable explosives, not only to ensure adequate ignition of the propellant, but to build up the pressure somewhat so that the initial rate of combustion may be higher. The action is simple—the initiator, in exploding, ignites the inflammable ignition charge, and this in turn sets off the main charge. Not uncommonly there is an additional step—the first ignition charge, instead of acting directly upon the main charge, sets off a second and larger ignition charge, and this fires the propellant itself; other ignition charges may be distributed through the main charge. The last stage in the ignition train usually consists of black powder; the intermediate stage, where used, may be of finely-divided black powder, or of an even more sensitive and quick-acting substance. The first ignition charge is assembled in the same unit as the initiator, thus forming the "primer"; the final charge in the train, where more than one is used, is usually assembled with the charge. The size and distribution of the ignition train, especially of the final stage, varies considerably with different designers.

The ignition train tends to make for regularity of ignition effect even when the action of the initiator—the member most likely to function badly—is not satisfactory. The substances

used in the intermediate stages have a sufficiently high rate of combustion to give about the same effect even when not ignited thoroughly. Poor functioning in other than the final stage, however, tends to lengthen the firing interval somewhat, and does cause a decrease of ignition effect; for instance, a change in the distance between two members of the train may cause a distinct change in ballistics. A defective final stage—such as may be produced by allowing the black powder to get wet—will of course always result in insufficient ignition. It has never been conclusively proved that variations in size of standard ignition charges (provided, of course, they are not made too small) or in distribution, make any considerable difference in regularity; the constant change in ballistics which results is, of course, taken up in fixing the charge at the proving ground.

In small arms, the initiator is required to ignite the propellant directly; with this system, ignition irregularities are far more common than in larger guns. It is commonly believed, in fact, that the primer (or initiator) has more effect upon the ballistics of small arms than any other factor. In the first place, the margin of operation is much smaller—an initiator which can set off the inflammable explosives used in the ignition train may entirely fail to ignite smokeless powder. Again, the substances used for initiators, as will be seen later, are from their very nature especially liable to deterioration in storage, with consequent change in ignition effect. Not infrequently the charge does not fill the cartridge case completely and the distribution of the charge around the primer differs from round to round, with a corresponding change in the ignition effect of the initiator; this is the foundation for the belief that a rifle or pistol shoots more accurately if pointed vertically first and then brought down on the target. Finally, the tendency toward regularity of action found in the ignition train is absent here; variations in action of the primer will inevitably result in corresponding variations in ignition effect. The space available is too small to permit use of a train; the problem, therefore, resolves itself into a question of obtaining an initiator which will have an adequate margin of effective operation, will be constant in its action, and will retain these qualities under the various conditions encountered in storage and in service.

III. DETONATION.

In order to obtain full explosive effect from explosives of the second order—the class which includes all military high explosives—it is necessary to use a small charge of an explosive of the first order. The high explosives in use, as has already been pointed out, can be employed in shell only because they are insensitive to shock or impact; when ignited, they usually burn, if at all, rather slowly and quietly, and detonation, if produced, is rarely complete. To insure rapid and complete release of the potential energy of these substances, a strong initial impulse such as that obtained from another explosive is required. There is, in fact, a close connection between initial impulse and effectiveness. “The character and intensity of the initial impulse influence the course of an explosive reaction to such a large extent that it has been said, and not without justification, that the effectiveness of an explosion depends more upon the initial impulse than upon the explosive itself.” (Brunswick, p. 31.)

The manner in which the explosion of one substance brings about the explosive decomposition of another has been the subject of experiment and discussion ever since Nobel announced his discovery that fulminate of mercury was an efficient detonating agent for nitroglycerine. The explosive impulse is not transmitted from one charge to the other by the direct transfer of heat, nor does it seem to depend upon the propulsion of particles of the primary explosive against the secondary charge; detonation still occurs when a film of water, glass, or metal is interposed between the two charges, although a distinct loss of explosive impulse results from such interpositions; it has been found, indeed, that the substitution of a film of water for an air-gap has resulted in an increase of initiating effect.

Abel brought forward, in 1869, the view that the action was due to synchronism of molecular vibrations; he had found that 6.5 grams of nitrogen iodide is insufficient to detonate nitroglycerine or gun-cotton, and that 3.25 grams of nitrogen chloride was required, while 0.3 grams of fulminate of mercury, which is less powerful and has a lower velocity of detonation, was always enough to produce satisfactory action. This hypothesis has never been accepted. According to it, each explosive should show such perfect synchronism with itself that it would furnish the best detonator for itself (Victor Meyer). Gun-cotton ex-

ploded over nitroglycerine will cause detonation of the latter, but the converse holds only when the charge of nitroglycerine is large; if wave synchronization is assumed, the action must be completely reciprocal (Berthelot). If the various explosives be arranged in the order of sensitiveness, as determined by the minimum quantity of a given detonator agent required to detonate completely a fixed weight, the order will be different with different detonating agents (Brunswick). Some authorities feel, however, that the wave-synchronism theory should not be totally disregarded; for instance, the detonation of a cast or pressed charge of the trinitrated benzene derivatives, such as picric acid, is accomplished best through a "booster" charge of material of the same class as the charge. (Colver, p. 595.) The efficiency of the nitro-aromatic explosives as boosters, as compared to nitroglycerine, for instance, has not yet been explained in a satisfactory manner.

The explosive-wave theory of Berthelot, is the one generally accepted to-day. According to his idea, the transmission of the explosive impulse differs in no way from the propagation of the impulse through a charge; transmission and propagation both take place through the agency of an explosive wave, which also has the power of propagating itself, and therefore of bringing about explosion, through intervening mediums. The wave is considered as a recurring cycle of released and transformed energy, having four phases:

1. *Transformation of Mechanical Energy to Calorific Energy.*—A part of the mechanical energy set free in one layer of the explosive is converted instantly into heat energy in the adjacent layer by reason of the impact of molecules. Since the movement of the molecules is radial, the efficiency of this conversion is dependent upon the shape of the charge and the location of the detonator within it; for a long thin column of explosive detonated at one end, the efficiency will be less than 50 per cent., since the molecules are confined by the explosive only on one side; if, on the contrary, the action is taking place in the interior of a mass of explosive, the efficiency will be practically 100 per cent. The mechanical energy that is not converted into heat energy exerts pressure on the confining medium and thus becomes the vehicle through which work is accomplished. The thickness of the layer of the explosive which enters into this

phase is not only dependent upon the amount of energy available, but varies with the physical properties of the explosive material, principally with its elasticity. The less elastic the explosive material, the thinner the layer, and hence the more times the cycle will recur in a unit length of the explosive material. This phase, to put it briefly, subjects the layer to sudden heating under great pressure.

2. *Transformation of Calorific Energy to Chemical Energy.*—Some of the calorific energy of the layer is used to overcome the chemical stability of the explosive material, and thus to release the potential energy of the layer; the rest is used to accelerate and reinforce the chemical action.

3. *Transformation of Chemical Energy to Calorific Energy.*—Once the chemical stability of the material is overcome, its potential energy is converted into kinetic energy—largely calorific energy; all military explosives develop heat on detonation. This phase differs from the others in that it supplies kinetic energy to the cycle, while each of the others consists only of a transformation of the kinetic energy obtained from the preceding phase, and therefore can have no more kinetic energy than the preceding phase is capable of transferring.

4. *Transformation of Calorific Energy to Mechanical Energy.*—The large volume of gases formed from the layer of explosives is in an extremely active state of molecular vibration, and these molecules are therefore manifesting their energy as kinetic energy. (Bulletin 59, p. 9.)

The full action of a simple explosive system, according to this theory, is essentially as follows: sufficient heat energy to overcome the chemical stability of part of the detonator is supplied from outside the system, either by direct action of a flame or incandescent solid, or by the conversion of the kinetic energy of a blow into heat; the explosive wave is set up by the resulting decomposition of part of the detonator and passes rapidly from layer to layer until all the potential energy of the detonator has been set free, mostly in the form of mechanical energy; this mechanical energy the explosive wave transmits to the main charge, where it initiates the decomposition of the first layer and propagates itself through the explosive as already described.

This theory explains the intimate relationship between initial impulse and explosive effect. If a large amount of the second

order explosive is suddenly decomposed by the direct action of the detonator, the amount of explosive decomposed in the second cycle will be large, a large excess of energy will be available for accelerating decomposition in the second phase of the second cycle, and the time necessary for both cycles will be short, thus reducing the loss of energy by radiation and conduction to a negligible quantity. (The action is so rapid in case of detonation that the decomposition proceeds nearly adiabatically.) Since additional energy is furnished to the explosive wave in each of these cycles in excess of the amount lost as a mechanical energy, the velocity of propagation will increase to the value at which dynamic equilibrium obtains—in other words, to a maximum dependent upon a number of conditions such as the chemical and physical characteristics of the charge. Where only a small amount of explosive is decomposed by the detonator, or where the initial decomposition is slow, as by the action of a flame upon a second order substance, the radiation and conduction losses become significant, the first cycle furnishes little or no excess energy to accelerate decomposition in the second, and the decomposition proceeds as a simple combustion; in some explosives and under some conditions the reaction will die out entirely. It may not be going too far to say that explosives of the second order lack the ability to accelerate burning to the detonation stage, and the detonator supplies the required acceleration. (Tech. Paper No. 162, p. 22.)

The tendency of propagation to proceed at one of two definite velocities is well recognized. "Under conditions usually in force only one or the other limiting value of velocity of propagation obtains in explosive processes, and the corresponding phenomena are accordingly characterized either as deflagration, where the velocity of propagation is only a few metres, or as detonation, where the velocity reaches almost as many kilometres per second." Where escape of energy is prevented, as when the container is very strong, a deflagration can end with a detonation; similarly, where there are hindrances to the propagation of a detonation, such as large gaps in a column of explosive, a detonation may degenerate into a deflagration (Brunswig, p. 80). These phenomena are to be expected in light of Berthelot's theory.

The effectiveness of the explosion, it has already been stated, is largely dependent upon the rapidity with which the energy

is set free—in other words, upon the velocity of propagation. The total energy set free by a low order explosion¹ may be the same as that of a detonation, but the brisance, or shattering effect, is far greater in the latter case; the rate of increase of pressure and the maximum pressure produced are also greater, not only in contact with the charge, but at points removed from it—a matter of considerable importance in constructions in which the radius of effectiveness is of prime importance, such as depth charges. A secondary effect in low-velocity explosions is the driving out of a portion of the charge before the explosive impulse can reach it, with a consequent direct loss of energy. Under certain conditions, to be sure, the finely-divided powder which results will be of some value through its choking effect upon personnel; it is not, however, particularly toxic, and in confined spaces is not even as effective as the carbon monoxide produced by decomposition. (Colver, p. 591; after Lewin and Poggenburg.)

The course the reaction takes, as well as its velocity, may be dependent upon the initial impulse. For instance, of the various ways ammonium nitrate may be decomposed, three are explosive. If subjected to the impulse of a strong detonator, it yields nitrogen, water vapor, and oxygen; a weaker detonator causes decomposition into nitrogen, nitric oxide and water vapor; finally, gradual heating without material increase in pressure results in the formation of nitrous oxide and water vapor, no nitrogen being set free. (Brunswig, p. 32.) The table below (Brunswig, Table 6) gives the heat of explosion, the volume of gas, and the product of these two values—a quantity which Berthelot has proposed as a characteristic expressing the maximum work performed by the explosion.

TABLE I.
Decomposition of Ammonium Nitrate.

Impulse	Heat of Explosion Calories	Gas Volume Liters	Berthelot Characteristic
Strong detonator	421	976	411,000
Weak detonator	140	976	137,000
Gradual heating	151	836	126,000

Even if Berthelot's theory of the mechanism of transmission is accepted, the influence which the chemical and physical charac-

¹“Low order explosion” is frequently used instead of “deflagration”; similarly, “high order explosion” is synonymous with “detonation.”

teristics of the detonator exert upon the effectiveness of the initial impulse still remains to be explained. A small amount of fulminate of mercury, for instance, will effect the detonation of a large charge of an explosive of the second order, although many other explosives apparently more powerful in every way will accomplish the same result, if at all, only when used in large quantities. It would be expected that efficiency as a detonating agent would depend upon the rapidity of explosive decomposition primarily, and upon the energy content to a somewhat less degree, but there is apparently evidence that this does not hold. The velocity of propagation in nitroglycerine has been determined to be over 7000 metres per second, as against less than 4000 metres for fulminate of mercury, and its potential energy is four times that of fulminate, yet it has not the property of initiating detonation in other explosives unless used in large quantities; it has already been pointed out that nitroglycerine is not effective as a detonating agent for guncotton. Abel's demonstration of the detonating efficiency of fulminate of mercury as compared with the highly brisant nitrogen halides has also been referred to. The presence of a heavy metal was for a time thought to be necessary, because the high specific gravity of such compounds allowed high density of loading and correspondingly high maximum pressures, and possibly because the very heavy vapors of the metal had a special value in detonating the secondary charge; organic compounds are now known which are more effective, weight for weight, than any of the metal compounds. (Tech. Paper 162, p. 18.) The particular property or combination of properties which determine the efficiency of a substance as a detonating agent have not yet been successfully determined or measured.

Storm and Cope believe that the initial rate of detonation is the most important property of detonating agents. In view of the difficulty of determining accurately the rate of detonation of detonating compositions, they made a comparison of the relative rates of four such substances by observing the minimum weight of each which would be sure to shatter completely a small open glass test tube in which it was placed, when exploded by rapid heating. The results were as follows:

Mercury fulminate	0.07 gram
Fulminate, 90 per cent.; potassium chlorate, 10 per cent.	0.06 gram
Fulminate, 80 per cent.; potassium chlorate, 20 per cent.	0.05 gram
Lead azide	0.01 gram

Even 0.001 gram of lead azide in every trial blew the bottom out of the test tube. The quantities of the various compositions required correspond with the minimum quantities of these substances necessary to detonate a given weight of an explosive of the second order, indicating a relationship between shattering effect and efficiency as a detonating agent. Storm and Cope believe that, since the particular property of explosives upon which shattering effect depends is apparently the initial rate of detonation, this property must be one of the factors of greatest importance. They further consider it likely that the usual method of measuring rate of detonation, using a column of explosive of considerable length, gives a value of initial rate for these substances much smaller than the true one. (Tech. Paper 125, p. 39.) In other words, the rapidity with which fulminate of mercury decomposes at the beginning of the action is greater instead of less than that of nitroglycerine, for instance, and for this reason it is a better detonating agent than nitroglycerine. The greater efficiency to be obtained by increasing the rapidity of explosion of fulminate of mercury itself has been shown by Wöhler. He found that the finely-divided fulminate obtained by precipitating it with an acid from a potassium cyanide solution at 0° C. was about three times as effective as the coarser original fulminate, as a result of the faster decomposition of the finely-divided material. (Marshall, p. 513.) Taylor and Cope, following a suggestion of Wöhler, reported that the action of fulminate of mercury was considerably strengthened by superimposing a small charge of a quicker-acting explosive. Lead azide and silver acetylide, although the latter is not of itself a good detonator, reduced by one-half the amount of fulminate necessary to fire a given weight of trinitrotoluene.

Accepting the idea of Storm and Cope that the initial rate of detonation is much greater than the value determined by the methods in use, Wöhler's theory may be taken as a basis for further discussion of the matter. He believes that detonation of second-order explosives is initiated by a sudden and enormous local pressure. Any substance, mixture of substances, or combination of substances that, when placed in the detonator shell and ignited, detonates with such velocity that the walls of the shell do not yield until the entire gaseous product has accumulated so that it can escape all at once and deliver by its kinetic

energy a colossal blow, will be an efficient detonator. (Tech. Paper 162, p. 7.) The action is thus dependent primarily upon the rapidity of decomposition, and to a somewhat less degree upon the volume of gas produced (as determined by the composition itself and the density of loading) and to the heat of the explosion.

The views of Taylor and Cope are in general accord with those of Wöhler. In their opinion, the effectiveness of a detonator in practice depends upon explosive energy that may be separated into an intensity factor and a capacity factor. The intensity factor may be called "quickness" and depends upon acceleration of the explosive decomposition. The capacity factor is "strength," and is measured by the total energy of the primer. Of the two factors "quickness" is the more important. According to this idea, greater effectiveness should be obtained by keeping one factor constant and increasing the other, but, if a substance is deficient in one factor, increase of the other should not be particularly effective. This is actually the case. Storm and Cope found that the amount of sand pulverized by a given weight of fulminate of mercury, compared to that pulverized by the same weight of mixtures of fulminate with 10 per cent. and 20 per cent. of potassium chlorate, is a measure of the efficiency of the respective mixtures. (Tech. Paper 125.) Taylor and Cope established the fact that this sand test is a measure of "strength," and that the effect is, therefore, that of varying the "strength," keeping the "quickness" practically constant. The increased effectiveness of mercury fulminate, brought about by a small quantity of lead azide or silver acetylide, illustrates the case of increasing the "quickness" only. Finally, lead azide could not accelerate silver acetylide (which has the necessary "quickness," but not the "strength") sufficiently to improve its action. (Tech. Paper 162, p. 22.)

Tests of the comparative efficiency of detonating agents, such as those referred to above, are made by determining the minimum weight of the agent which will produce detonation of a given weight of some explosive of the second order, conditions such as density of loading, granulation, and the like being kept constant. The explosive effect obtained from the second order explosive, when detonation is secured, is always practically the same, regardless of the amount of the initial impulse or the agent used. Storm and Cope found, in fact, that the total strength shown by

four nitrocompounds (trinitrotoluene, tetranitromethylaniline or tetryl, tetranitroaniline, and picric acid) was nearly the same when equal weights of the same priming composition (0.4 gram) were used and the charges subjected to similar pressures. (Tech. Paper 125, p. 59.) The dividing line between complete and partial detonation is sharp; it is possible to determine within 0.01 gram (around 5 per cent.), the weight of a detonating agent necessary to detonate completely 0.4 gram of TNT (trinitrotoluene) or tetryl, although strong detonations sometimes occur with charges several hundredths of a gram less than the minimum charge certain to produce detonation. (Tech. Paper 162, p. 12.)

IV. THE DETONATING SYSTEM.

The detonating system in military explosive constructions is still not at all satisfactory in its action. One man in close touch with munitions manufacture during the World War has estimated that 50 per cent. of the shells made for the various belligerents were "duds," because of mechanical faults or defects of the detonating system proper; this includes the large number which were rejected on inspection and never reached the front, but does not include those which would function, but with less than maximum effectiveness. Where the detonating system was responsible, the fault frequently lay in the explosive substances, which deteriorated with time and thus became less sensitive or effective; in a great many cases the design was unsatisfactory, and failed to provide an adequate margin between operation on the one hand and partial or complete failure on the other.

An underlying cause of many of these failures is the paramount necessity for provisions against premature explosions; one premature explosion may be more serious in its results than a rather large percentage of failures. The mining squadron which laid the North Sea barrage carried over 1,500,000 pounds of trinitrotoluene on each excursion, the larger mine-layers carrying 250,000 pounds each—the accidental explosion of a single mine might have wiped out the entire force and defeated the project. As they went in and out of the base, indeed, they passed the wreck of a British mine-layer which had been blown up in just this way; among those killed were several of the British officers most experienced in mining, the loss of whose services was more serious than the loss of the ship.

Safety precautions of two kinds are usually taken; in the first place every effort, both in design and in handling, is taken to prevent accidental explosion of any member of the system; besides this, provisions are made in the design so that if premature explosion of the detonator, which is very sensitive and far more liable to be fired accidentally than the booster or the main charge, will not cause explosion of the main charge. The first kind of precaution rarely affects the design of the detonating system directly, except in so far as reduction in the size of the detonator tends to reduce the danger of an explosion. The second precaution consists essentially in the introduction of a gap or break in the detonating system between the detonator and the booster (or main charge, when no booster is used), the gap being eliminated automatically when the assembly is launched, shot from a gun, or dropped, as the case may be; the detonator must not be so large that it may transmit the explosion across the gap. In mines, torpedoes, and bombs the detonator is very often not inserted until immediately before use, and then is put in the firing position; in this case there is no limit to the size of the detonator, but there is increased danger of premature explosion of the charge after the detonator is inserted, and the necessity for quick and easy insertion may complicate the mechanical design.

The arrangement of different detonating systems differs greatly with the purpose of the construction in which they are used, the particular conditions of use for which the safety precautions must provide, the size and shape of the space available, and a number of other variables. The general action is, however, the same in all cases: the initiator, a first-order explosive, is exploded by the firing impulse; this explosion ignites the detonator charge, composed of a detonating agent, which converts the ignition into a detonation; this detonation may be used as the initial impulse for the main charge, but almost invariably acts through a booster, which, like the main charge, is an explosive of the second order.

The use of an initiator to ignite the detonator charge has no bearing on the effectiveness of the explosion, but is, nevertheless, of distinct practical advantage. It need not necessarily be a detonating agent; it is possible, therefore, to use substances which are less likely to deteriorate, or are more sensitive to the firing im-

pulse, or which have some other advantage over the detonating agent employed in the charge. In percussion firing, the initiator must be small, for increase above a given size for a fixed value of impact causes a notable proportion of misfires. In delayed action and time fuses, where a slow-burning powder train is used to cause a certain time to elapse between the firing impulse and detonation, an initiator separate from the detonator charge is obviously necessary. In very small charges, however, the initiator may be eliminated, and the detonator receive the firing impulse directly; in such cases the booster is also omitted. The initiator and the detonator charge are always assembled in the same unit—in shell they are contained in the fuse, and in torpedoes, mines, and bombs they are placed in a single container to form the “detonator.”

The principal reason for use of a booster is to reduce the amount of detonating agent required, and thus to decrease the danger of a premature explosion. High densities of loading, with a consequent decrease in sensitiveness, are habitually used in main charges in order to obtain the maximum explosive effect. Instead of increasing the power of the detonator sufficiently to overcome this decrease in sensitiveness, the detonator is made to act through a booster of somewhat greater sensitiveness than the main charge. The manner in which the booster acts can best be understood by taking a case where the same nitro-aromatic explosive is used in both booster and main charge. Assuming that the detonator gives an impulse slightly less than that required to detonate the main charge, no advantage will result from using a booster of the same density of loading; as the density of loading is decreased, the thickness of the layer decomposed increases, rapidly at first, but more slowly as the distance of the farther side of the layer approaches the rather small maximum distance at which the impulse is able to effect any decomposition; the amount of explosive in unit thickness of layer decreases directly with the density of loading; there is, then, a given density at which the amount of explosive decomposed by the impulse is a maximum. The velocity of propagation through the booster charge, and therefore its effectiveness, also decreases with decreased density; the most effective density for the booster, therefore, is somewhat above that at which the initial impulse causes directly decomposition of the largest amount of the booster. This value for new

substances is at present determined by "cut-and-try" methods; it appears to be dependent upon the state of division of the explosive, and perhaps other factors, as well as upon the booster material itself.

The nitro-aromatic explosives are the only substances now used for boosters; in former years, when guncotton was the only high explosive used for military purposes, it was customary to add a large proportion of water to the main charge to decrease its sensitiveness, and to use a booster (or "primer," as it was then called) of dry guncotton to ensure detonation; now nitro-aromatic explosives are used even here. Tetryl and TNT are the ones most often used, tetryl being generally preferred. It is easier to detonate than TNT, although far from being dangerously sensitive, and is more powerful; a distinct advantage is that moisture in a fulminate of mercury detonator, a small amount of which will prevent its detonating TNT, has considerably less effect upon its effectiveness with tetryl. Tetryl, on the other hand, is considerably more expensive than TNT, and is less stable, especially when not carefully purified. Several other explosives of this class, picric acid in particular, also find an extensive use in boosters. Whatever the substance employed, it is used in a finely-divided state, thereby still further increasing its sensitiveness to the explosive impulse without making it more sensitive to shock. The booster material is always of a high degree of purity in order to obtain the best possible power, stability, and uniformity.

No increase in explosive effect seems to result from the use of a booster, except perhaps for the slight improvement obtained by better distribution of the explosive impulse through the main charge. The results will be practically the same if the detonator is increased to a suitable size and made to act directly upon the main charge; in blasting work, in fact, where the size of the detonator is not limited by considerations of safety, boosters are rarely used. The booster in shell is often assembled in one with the fuse; in mines, torpedoes, and bombs the booster is a separate unit.

No general rules for the size of detonator or of booster necessary to accomplish detonation can be given. The weight of the primary charge (the one which furnishes the impulse) for best results is dependent not only upon the chemical and physical

characteristics of both explosives, but also upon many other factors, including the shape of both charges, their location with reference to each other, the design of containers, and especially the distance between the two charges and the medium filling the gap. It is a question whether increase in size of the primary charge above that just sufficient to produce detonation has any influence upon the effectiveness of the explosion. Waddell believes that increase of impulse above the minimum does result in a certain degree of increased effectiveness, even when the secondary charge is of a more powerful explosive than the primary—in other words, that it requires an impulse somewhat larger than that just able to produce detonation to bring out the full power of a second order explosive (private communication); the difference is far smaller, of course, than that between a high order and a low order explosion. Everything considered, the chief point to be considered in determining the size of the detonator and the booster, as far as explosion of the main charge is concerned, is to make them both powerful enough to provide the excess of energy necessary to make the action certain. It may not be amiss to point out, in this regard, that while great power on the part of the detonator will tend to make up for a weak booster, no booster, however large or powerful, can function when the detonator is too weak.

The detonator, in particular, since its power is limited, must be so located that the largest possible proportion of its explosive energy will act upon the material of the booster. The explosive wave, if unhindered, proceeds radially from the exploding substance, and only that portion of it which impinges upon the secondary charge is useful in transmitting the explosive impulse. This point is of importance with boosters only as far as questions of space, assembly, and cost limit the size. Confinement of the explosive wave so that, to escape, it must all traverse some part of the secondary explosive increases the efficiency with which the energy of the primary charge is used; in the long cylindrical detonators which are in common use, the confinement exercised by the shell results in a large proportion of the impulse radiating out from a point at or near the end opposite the initiator; by burying this end of the detonator in the booster material most of the energy of the detonator will be forced to act on the booster.

The location of the detonator and booster, it may be said

in passing, exerts some influence upon the effectiveness of the explosion. The speed of decomposition will obviously be best when the impulse upon the main charge acts as if it were proceeding from the centre of gravity of the charge. The distribution of the explosive effect of the charge in different directions is also dependent upon the part decomposed by the initial impulse as well as on the shape of the charge itself, on the design of the container, and probably on other factors; other things being equal, the tendency seems to be for the effect to be at a maximum on the side farthest from the impulse, but no complete study of the matter has as yet been made. The distribution of the primary charge also may be of importance; for example, in a long, slender charge of an explosive of which the rate of detonation is less than that of the booster material, the speed of explosion may be built up practically to that of the booster by having the latter extend the full length of the charge; at the same time, if this explosive be so insensitive that the detonation tends to drop to a deflagration within a short distance, the long booster will improve certainty of action.

A distinct loss of effectiveness of the explosive impulse results from air-gaps between the different charges of the explosive system—the loss is so great that a small air-gap (of an inch or less) between the detonator and the booster is an excellent means of preventing transmission of an accidental explosion of the detonator to the booster. Where a gap exists when the system is in the “armed” or firing position, a considerable increase in the size of the primary charge is necessary, for the radius of effectiveness varies only as the square root of the primary charge, if not even more slowly. As a result of limitations in design, or of poor functioning of the arming mechanism, air-gaps are sometimes found between the detonator and the booster. Air-gaps between the booster and the main charge may result from shrinkage of a cast charge leaving cavities around the booster, or, in shell where the booster does not extend down into the charge, from the charge moving bodily away from the booster on firing, when a nose fuse is used, or on impact in the case of a base fuse. The cavitation difficulty may be eliminated by care in casting; shifting of the charge is to be prevented by use of a sufficiently high density of loading. The detonator and booster cases also reduce the effectiveness of the impulse, but

to a much less degree, for denser substances are better mediums for transmission of the effect; the specific ability of a medium to transmit the impulse is probably a function of the velocity of sound through it.

Two or more complete detonating systems are sometimes installed, both being fired simultaneously. This method results not only in greater certainty of action, but, particularly in long charges when a system is placed at either end, in more rapid decomposition, and greater explosive effect. Extra detonators are occasionally distributed through long charges, with the idea of increasing explosive effect and of ensuring complete detonation; these detonators take their firing impulse from the main charge. The advantages obtained are probably not great. (For tests in blasting explosives, see Bulletin 59, p. 68.) Two boosters in series are sometimes used, but usually only for convenience in assembly, to avoid the use of a single booster of a shape awkward to handle or for which the case would be expensive, or for some similar reason. As might be expected, no advantage in explosive effect results from dividing the booster charge into two parts.

The fact that a very slight decrease in the effectiveness of a detonating system just capable of always producing a detonation will result in a system which is never able to bring about anything more than a deflagration, is a point of considerable practical importance in view of our present inability to measure the properties upon which effectiveness of the explosive impulse depends. A newly-designed detonating system may operate in an entirely satisfactory manner in tests, and yet the margin of positive operation may be so small that a large percentage of partial or even complete failures will occur in service. In one case during the World War, a new design which had given detonation on every firing test preliminary to adoption, and which gave every promise of good results in service, failed badly; it was only by making the action of the detonating system more positive that it could be used at all. In another, the inventor of a new construction, finding that the detonator used was wholly incapable of detonating trinitrotoluene across the air-gap which separated them in his design, substituted tetryl for trinitrotoluene and obtained detonation; this he considered satisfactory, although it is obvious that the surplus of power available for taking care of the varia-

tions sure to come up in service was not large, and may have been very small.

One of the best ways at present available for determining the operating margin is by lowering the efficiency of the detonating system until the minimum impulse which will produce detonation is found, or until the margin has been proved to be sufficient. This is done better by changes in the explosive materials used than by decreasing the weight of the detonating charge and the booster, for the latter inevitably involves alterations of distribution, of size of air-gaps, of densities of loading, and other important conditions. For instance, suppose the system as designed has a detonator charge of an 80/20 mercury fulminate-potassium chlorate mixture, and a tetryl booster. The effectiveness of the detonator can be reduced by substituting the same weight of "straight" fulminate of mercury for the fulminate-chlorate mixture; similarly, the sensitiveness and the power of the booster can be lowered by the use of TNT instead of tetryl. The detonating system described should, in the opinion of the author, operate satisfactorily under these conditions if it has a satisfactory excess of effectiveness over that barely necessary. If it is desirable to carry the test still further, there can be mixed with the fulminate other substances—oxides of the heavy metals which reduce only to lower oxides and not to the metals themselves, for example—which reduce but do not prevent effectiveness. (See Tech. Paper 162, pp. 13 and 14, for the effect of certain substances upon the efficiency of fulminate of mercury.) At the same time, the sensitiveness and effectiveness of the booster can be lowered still further by mixing with the TNT some such explosive as dinitrotoluene or dinitrobenzene. Whether this or any other test is used, the effectiveness of the detonator in its action upon the booster as well as the effectiveness of the entire system should be determined, as malfunctioning between the detonator and the booster is perhaps the commonest fault in the system.

Direct tests of detonators can be made by the sand test described by Storm and Cope. (Tech. Paper 125; description also appears in Colver, p. 554. For comments, see Tech. Paper 162, pp. 19-21 and p. 23.) It appears possible to develop this method to take care of the entire detonating system, although it is a measure of strength rather than of detonating ability, and

therefore not adapted to give direct comparisons of substances differing widely from each other. The sand test will also be of some value in connection with the method described in the previous paragraph, for obtaining comparisons between the materials specified and those used in the tests.

V. INITIATING COMPOSITIONS.

The value of a primary ignition agent, it is seen from the foregoing, depends upon its ability to develop the heat necessary to ignite another explosive; similarly, the value of a primary detonating agent is dependent upon its exploding in the particular manner which will result in the detonation of a secondary charge; in either case, the agent must be sensitive enough to be exploded by a rather weak initial impulse, given by the direct application of heat or by a blow, but must not be so sensitive as to be liable to accidental explosion in necessary handling or in use. From the practical standpoint, the ability to retain these qualities unchanged is equally essential; what we are interested in is the sensitiveness and effectiveness when the composition is used, not what they were when it was first prepared.

It is obvious from the use of these substances that they are particularly liable to deterioration. They are valuable for the purpose of initiation because they are unstable; in other words, the atoms composing the system will rearrange themselves to form other compounds upon slight provocation. In an explosion, this rearrangement takes place with great rapidity and with the evolution of heat and of gases in large quantities; under conditions often prevailing in storage and in service, however, it may take place slowly and give out much less heat, and the products of the reaction may all be solids or liquids. A rearrangement of the latter kind may involve only a single substance, its molecules passing over into a new compound having the same percentage composition as the old, but a different configuration and therefore different properties, or it may result from the interaction of the different substances of the composition with each other or with the container or its coating if it has been painted or varnished; whatever takes place, the new substances formed may react on those still unaltered. Temperature has a decided influence upon the rate with which the action progresses; most reactions are doubled in velocity by a rise of about 10° C. in tem-

perature; compositions which are satisfactory for use in a cold climate may, therefore, prove useless in the tropics. Deterioration, it must be understood, is not a fault peculiar to the initiating agents—the explosives of the second order, which are very stable in comparison with these sensitive substances, very often show changed sensitiveness and effectiveness after being stored for some years. The usual course of deterioration is toward decreased sensitiveness and effectiveness, although products more sensitive than the original composition sometimes result; in any case, heat is evolved, and, unless it is carried away, may increase the temperature above the ignition point of the system.

A condition contributing directly to deterioration, and at the same time directly causing decreased sensitiveness and effectiveness, is the presence of moisture in the initiator composition. If the system could be made and kept absolutely dry, it would for the most part retain its properties indefinitely. Efforts are made to exclude moisture, but a certain amount (often quite sufficient to start deterioration) is always taken up from the air between removal from the driers and final sealing; it is impossible, too, to make the sealing air-tight in every case, and, where leaks occur, moisture is drawn from the air until equilibrium is established. The effect of moisture on the explosive qualities, and the chemical behavior of the constituents in the presence of small amounts of moisture must be given great weight in the choice of initiating compositions.

The size of the particles which compose the initiating agent has considerable bearing upon sensitiveness and rapidity of explosion. In the case of compounds which are in themselves detonating agents, such as fulminate of mercury, it has been repeatedly demonstrated that sensitiveness to impact increases with size of crystals, although the ignition point remains the same. The opposite is true where the system is a mixture of substances which alone are fairly stable; in this case the more intimate mixture resulting from finer division tends toward increased sensitiveness. The time required for the explosive reaction is always less with the finer material, because of the increased surface; the increased effect obtained from very finely divided fulminate of mercury by Wöhler can only be ascribed to more rapid action; it has also been found that the time taken by small-arms initiators to act was much more regular when the sizes of the components

were more closely controlled than is ordinarily thought necessary.

The greater exposed surface resulting from decreased size of particles permits deterioration to proceed more rapidly, and increases the amount of moisture which a given weight of composition can absorb. The volume occupied by a given weight of initiation charge under a given pressure is greater with small particles,² thus making necessary an alteration of either weight, loading density, or volume, sometimes at the expense of efficiency. The explosion of a very finely-divided composition may be altogether too rapid and violent for good results, and it is impossible to maintain any control of the exposed surface when the ingredients pass the 200-mesh sieve, the finest which can be practically used. (The total surface of a given weight of a substance consisting wholly of particles of the same size and shape increases in inverse ratio to any given linear dimensions, as length of the particles. See "Air-Elutriation of Fine Powders," by A. S. Cushman and Prevost Hubbard, *Journal of the American Chemical Society*, April, 1907, p. 594.) Finally, it is unsafe to grind many of the compounds used, and it is a matter of considerable difficulty and increased expense to make them separate out of solution in a state of very fine division. Everything considered, the size usually taken is the smallest practically obtainable under good manufacturing conditions without the use of expensive additional operations.

Sensitiveness and rapidity of explosion are also dependent upon density of loading. The sensitiveness of practically all compositions, whether single compounds or mixtures, decreases continually with increased density, until in some cases the sub-

² This phenomenon is not generally recognized. The writer, following Cushman, has found the volume occupied by 10 grams of sand, sieved out of the same lot, and settled by tapping on the table, to be as follows (volumes accurate to 0.3 c.c. only):

Mesh	Volume
60-80	6.2
80-100	7.5
100-200	8.0
Past 200	8.5

Cushman has found it impossible to reduce the volume of the finely divided material to that of the coarser even with high pressures. For discussion, see A. S. Cushman, "On the Cause of the Cementing Value of Rock Powders," *Journal of the American Chemical Society*, May, 1903, p. 459.

stance is "dead-pressed" and will not explode at all; the sensitiveness of lead azide, to flame at least, seems to be practically independent of the density. The effect of density upon the velocity at which the explosion proceeds depends upon the composition itself; if it consists wholly or in large measure of a compound explosive in itself, the velocity usually increases with increased density; in the case of mixtures of substances not in themselves sensitive explosives, it increases to a maximum and then drops off. Reliable quantitative data upon this effect is not available because of the difficulty of measuring the velocity of propagation through these substances, but this is in accordance both with observations of the effectiveness of various compositions at different densities, and with the behavior of the less sensitive explosives.

Fulminate of mercury is by far the most important of the substances used in initiating compositions. It is the chief component of every detonating composition in common use, and, either alone or mixed with other substances, is found in a large number of the initiators proper, particularly those for percussion firing. Its relative importance is gradually becoming less, to be sure; non-fulminate compositions are coming to be used more and more for initiation in primers and, since 1907, when Wöhler and Matter announced the existence of more effective detonating agents, it has no longer been true that without it the valuable organic explosives could not be used.

Fulminate of mercury results from the action of alcohol upon a solution of mercury in an excess of nitric acid. It is a white crystalline substance; commercial fulminate, however, frequently has a grayish or brownish cast due to traces of resinous substances formed during the reaction, or possibly to enclosed particles of finely-divided mercury. It is very slightly soluble in water, somewhat more so in alcohol, and very soluble in pyridine and in aqueous potassium cyanide; the latter two solvents may be used for purification if desired, but it is usual to use the compound as originally formed, after thorough washing with cold water to remove all traces of acid, and drying.

The specific gravity of fulminate is 4.4; when merely tapped down, however, its apparent density is only about 1.7, the density at which it is usually used is around 2.2, corresponding to a loading pressure of 250 kilograms per square centimetre, or 3500 pounds per square inch. (Marshall, p. 512.) If subjected to

great pressure, it cannot be exploded by flame, but will apparently detonate with excellent effect if subjected to the impulse obtained from another detonation. When heated, even unconfined, it detonates at from 150° C. to 200° C., depending on the rapidity of heating; the violence of its action is greatly increased by slight confinement. The sensitiveness to impact is dependent on the size of crystals and upon experimental conditions; Will found the blow given by a 2-kilogram weight falling 2 centimetres to be sufficient. (Brunswig, p. 26.) It is, therefore, too sensitive as well as too expensive for use as a main charge—its only employment is in the initiating system.

Fulminate of mercury, as well as the compositions of which it is a constituent, has several undesirable qualities. It deteriorates rather easily, especially in the presence of moisture; in Austria there is an official regulation that detonators are to be stored over fused calcium chloride. Temperatures such as those often encountered in the tropics are of themselves sufficient to produce rather loss of effectiveness, apparently even in the absence of moisture. A moisture content of one per cent. is usually enough to make it ineffective, the explosive qualities being regenerated again upon drying; Storm and Cope found, however, that 0.75 per cent. moisture in 80/20 mercury fulminate-potassium chlorate detonator charges weighing 1.44 grams, caused a negligible reduction in strength as shown by the sand test; in the case of detonator charges consisting of the same fulminate-chlorate mixture superposed on an equal weight of TNT, exposure to an atmosphere saturated with moisture at laboratory temperature resulted in incomplete detonation of the combined charge. (Tech. Paper 125, p. 61.) Mercury fulminate attacks both copper and brass in the presence of moisture, cuprous fulminate, together with zinc fulminate in the case of brass, is formed, and metallic mercury is set free;³ the action is sometimes sufficient to eat through thin containers, and, if the brass has not been properly annealed, cracking will result. The new fulminates formed are in themselves brisant explosives, nearly equal in effectiveness to mercury fulminate itself, but they are less stable, and are considered by some to be dangerously sensitive. Finally, mercury fulminate is very dangerous to handle and is expensive.

³ If mercury fulminate and either zinc or copper are treated with boiling water, metallic mercury is set free, and zinc or copper fulminate, as the case may be, is formed.

Lots of fulminate of mercury obtained from different manufacturers, and even different lots obtained from the same plant, differ materially in their liability to deteriorate; this matter does not seem to have been studied thoroughly. (Marshall, p. 511.) The differences are such as not to be detected in the methods of inspection now in use. Some explosive chemists of to-day believe, in fact, that Howard, who discovered this compound in 1799 and was the first to describe a method for its production, consistently made better fulminate than any one has been able to manufacture since.

Initiators in electric primers, and to a large extent those in electric detonators, consist of finely-divided dry guncotton, of a mixture of dry guncotton and meal powder, or of some other highly-inflammable composition. This material, being soft, is practically insensitive to shock under the conditions of use and the danger of deterioration is considerably less. Largely as a matter of manufacturing convenience, the fulminate composition used in the detonator charge may also be used in the initiator.

Mercury fulminate when used alone is too quick-acting for good results in percussion primers, whether they are for the direct ignition of the propellant or of an ignition charge. From the very first the custom has been to mix with the fulminate other substances which at once decrease the violence of the explosion and add to its heat; the percentage of fulminate used has steadily decreased as time passed, and the content in most modern mixtures does not exceed 20 per cent. (Marshall, p. 504.) Saltpeter, sulphur, and meal powder were formerly mixed with the fulminate in various proportions, and powdered glass was frequently added to increase sensitiveness, which was very likely to diminish quickly because of the hygroscopic properties of the saltpeter. At the present time, potassium chlorate and antimony sulphide (obtained by powdering the sulphide occurring naturally as "stybnite," after purification by liquation if necessary) are used almost exclusively; in these mixtures, antimony sulphide acts as a fuel, the chlorate furnishes the oxygen necessary for its combustion, and the fulminate by its explosion raises the temperature high enough to start the combustion in the first place. The antimony sulphide, which comes in hard, sharp-edged particles, also contributes to the sensitiveness of the composition in the same manner as powdered glass did in earlier mixtures; the

decomposition products of antimony sulphide are soft, however, and do not erode the bore like powdered glass.

Work upon the development of primer compositions which contain no fulminate of mercury or other substance in itself explosive has been going on for a number of years. The earliest of these contain potassium chlorate and antimony sulphide, together with some other fuel which will react readily with the chlorate upon impact, and thus produce the heat necessary for combustion of the less reactive sulphide. From 10 to 35 per cent. of powdered sulphur was usually used as this second fuel. These mixtures showed a tendency to decompose gradually and the results obtained were very erratic; the output of a plant would be excellent for a time, and then, for some unaccountable reason, a markedly inferior composition would be produced. It now seems that the erratic results were due to improper methods of inspection, or even no inspection, of the ingredients, with the result that impurities fatal to stability were unknowingly introduced; Cushman has pointed out, for example, that under the methods commonly used for testing stybrite, an antimony sulphide content reported as above 98 per cent. might actually be below 80,¹ and sometimes there was no analysis of the raw materials. Since commercial potassium chlorate may contain traces of chlorate, hypochlorite, or bromate—all much less stable than the chlorate—or of the hygroscopic sodium chlorate, it is easily seen that differences in the raw materials themselves from lot to lot would readily cause variations. Even with an ideal inspection system, however, the sulphur was sure to be a source of deterioration; it is well established that finely-divided sulphur, in the presence of air and moisture, tends to oxidize with the final formation of sulphuric acid, which, of course, will attack the other constituents of the mixture and the container.

The great problem then was to find a fuel which would react readily with the chlorate as result of the heat generated by a blow, but which would be stable under the conditions to be expected in service. Of a large number of substances tried, lead sulphocyanate (or thiocyanide—the lead salt of HSCN) has proved to be the most valuable, and compositions made up

¹“Antimony Sulphide as a Constituent in Military and Sporting Arms Primers,” by A. S. Cushman, *Journal of Industrial and Engineering Chemistry*, May, 1918, p. 376.

with it have given excellent results. It decomposes, to be sure, in the presence of considerable moisture—a mixture containing it will quickly “go sour” on a hot day—but after loading and drying the sulphocyanate compositions seem to promise a long effective life. An excellent mixture of this sort is that patented and used by one of the large American companies; this has the following composition:

Potassium chlorate	53 per cent.
Antimony sulphide	17 per cent.
Lead sulphocyanate	25 per cent.
TNT	5 per cent.

A. S. Cushman has developed and patented an interesting method of controlling the ignition effect of the primer composition. (This patent has been assigned to the Government.) It is clear that, even with the closest practicable inspection of raw materials, the ignition effect of one lot of primers may vary from that of another, and that this may have a serious effect upon ballistics in the case of small-arms. By substituting for the 5 per cent. of TNT in the above composition the same weight of a mixture of litharge (lead oxide) and tetryl, the effectiveness can be adjusted within limits by changing the proportions of the two. The litharge also acts as a “sweetener,” and by absorbing any acids formed by slight deterioration prevents them from attacking the constituents still unchanged. Lead sulphocyanate, for example, gives a very slight acid reaction when moistened; litmus shows its mixture with litharge to be neutral.

The initiator for percussion detonators may either be of the same composition as the detonator charge, or may be along the lines of the priming compositions just described. If there is an air-gap between the initiator and the detonator, the latter type is probably to be preferred, since more heat is generated and the initiating action continues longer, thus making for more certain action; in this case, the fulminate content usually runs higher than in the true primer compositions, in order to obtain somewhat increased sensitiveness. The non-fulminate compositions are at present not in favor for this purpose, largely because those tried in the past were not reliable after storage, and since the amount of fulminate is small as compared with the total amount in the system; it is possible that the new improved types may show sufficiently good results to overcome this prejudice.

In detonating charges, fulminate of mercury is often used alone, but manufacturers of commercial detonators have been accustomed to introduce a small percentage of potassium chlorate to reduce the quantity of the more expensive fulminate used and to get a composition running more freely in the loading machines. There was a decided difference of opinion between the various authorities as to the influence of the chlorate upon effectiveness, until, in 1916, Storm and Cope demonstrated that the addition of chlorate up to 20 per cent. steadily improved the action. (Tech. Paper 125, p. 46.) Taylor and Cope then showed that there are a number of oxidizing agents which increase the detonating ability of fulminate, principally the salts of oxyhalogen acids, and oxides and nitrates of heavy metals whose decomposition results in free metals; alkali and alkali earth nitrates, and heavy metal oxides which reduce to lower oxides are ineffective. (Tech. Paper 162, pp. 12-14.) It seems improbable, however, that potassium chlorate will be replaced in this use. The same two investigators, following Wöhler's work, also showed that small accelerating charges of lead azide and silver acetylide caused a considerable increase in the efficiency of the fulminate. (Tech. Paper 162, p. 16.)

A variation of the mercury fulminate detonator in common use in commercial work is the "reinforced" detonator, in which about half of the fulminate composition is replaced by a nitro-aromatic explosive, usually tetryl or TNT; the part of the charge nearest the fuse (which fills the same function as the initiator) still consists of fulminate or a fulminate-chlorate mixture. The explosives are in contact, and are given greater confinement by means of a copper shell fitting neatly within the detonator shell and pressed on the charge; this results in increased efficiency of the fulminate, because it attains its maximum velocity of detonation more quickly, and more of its energy is compelled to act upon the second order explosive. (Tech. Paper 125, p. 47.) This type of detonator is somewhat more powerful, size for size, than the ordinary kind. There may be more danger of deterioration because of the contact between the two explosives; the usual deterioration of the fulminate may also result in the detonator becoming ineffective more quickly, because of the small amount of fulminate used. (Marshall, p. 506.)

Lead azide⁵ appears likely to replace fulminate of mercury as a detonating agent. When finely divided, it is considerably less sensitive to shock than fulminate, it is far more effective as a detonating agent, its sensitiveness and effectiveness are apparently not affected seriously by moisture, at any rate not in the quantities likely to occur, and, instead of becoming "dead pressed," its effectiveness increases with density of loading up to the highest value attainable in practice, its sensitiveness to ignition remaining practically unchanged. No report upon its stability under all conditions has been published, but from the data available it seems to be much better in this respect than fulminate of mercury. Large crystals are likely to be formed, unfortunately, which can detonate on the slightest shock even under water; several accidents of this sort have already occurred. If adopted, it is probable that the reinforced detonator described above will be used, substituting lead azide for the fulminate composition. (Marshall, p. 511.) The Germans made some use of lead azide detonators during the late war, apparently with excellent results.

Little can be said about the future of the organic detonating agents; those proposed so far appear to be too sensitive to shock and too liable to deterioration of one sort or another to be of any practical value for military use. The mere fact that there are organic substances which are more effective detonating agents, weight for weight, than any of the metal compounds is nevertheless important, in that it shows that there is a possibility of finding somewhere among the organic compounds, with their wide range of properties, a detonating agent more useful than any we now know.

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⁵ The lead salt of hydronitric acid, HN_3 . These salts are also known as nitrides, hydronitrides, and as trinitrides.

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Physical Constants of Aniline.—Certain physical constants of pure aniline have been determined by C. L. KNOWLES (*Jour. Ind. and Eng. Chem.*, 1920, xii, 881-883). The freezing point is 6.24° below zero C.; the boiling point 184.32° to 184.39° C. at a pressure of 760 mm. of mercury; the specific gravity 1.0268 (both the aniline and the water being at a temperature of 15° C.); the index of refraction 1.5850 at 20° C. The purity (in per cent.) of a sample of aniline may be calculated by multiplication of its freezing point ($^{\circ}$ C.) by the factor 1.41, and addition of the product to 108.79.

J. S. H.

Asbestos in the United States. (*U. S. Geological Survey Press Bulletin No. 461*, December, 1920.)—The United States now obtains most of its high-grade, long-fibre asbestos from Canada, but geologists of the Geological Survey hope that large deposits which will yield material of good quality may yet be found in the Western States, especially in Arizona, where asbestos of unusually long fibre and silky texture has been discovered.

In the Apache and San Carlos Indian reservations, in Arizona, asbestos is found associated with rocks known by geologists as the Apache group, which is made up of several formations. The principal deposits are in the Salt River region, where the Apache group is represented chiefly by beds of quartzite and limestone, which are at many places invaded by diabase, an igneous rock. Throughout this area much diabase has been injected into beds of limestone, and the asbestos is found near the contact of the limestone with the diabase. Places where the limestone has been much broken by the diabase have been particularly favorable for the formation of asbestos. The asbestos is invariably associated with serpentine, a greenish mineral that is in some deposits in other regions mottled like a serpent's skin, and although serpentine occurs at many places without asbestos, serpentine "float" fragments of it that lie loose on the surface, having been washed out from its outcrop, are a valuable aid to the prospector for asbestos. In this region asbestos itself is also generally found as float for a considerable distance below its outcrop.