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PHOSPHORUS FILLINGS FOR MUNITIONS

Summary Report on Work Performed in the Period July 1, 1946, to March 31, 1948, under Contract W-18-035-CWS-1318

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AUTH: E.O. 10501 dtd 5 Nov 53
By Chester C. Becker
Signature and Grade
Date 23 October 61

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Division of Chemical Engineering
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PHOSPHORUS FILLINGS FOR MUNITIONS

Summary Report on Work Performed in the Period July 1, 1946, to March 31, 1948, under Contract W-18-035-CWS-1318

By

J. C. Brosheer, F. A. Lenfesty, P. L. Imes, and G. W. Richardson

Wilson Dam, Alabama

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Tennessee Valley Authority
Division of Chemical Engineering
Wilson Dam, Alabama
April 30, 1948

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Commanding Officer
Chemical Corps Technical Command
Building 330
Army Chemical Center, Maryland

Attention: Chief, Munitions Division

Gentlemen:

~~Transmitted~~ herewith are six copies of a summary report on our studies of phosphorus fillings for munitions. The report covers all the experimental work performed under contract W-18-035-CWS-1318.

Very truly yours,

TENNESSEE VALLEY AUTHORITY

K. L. Elmore/gtw

K. L. Elmore, Chief
Chemical Research Division

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PHOSPHORUS FILLINGS FOR MUNITIONS

Summary Report on Work Performed in the Period July 1, 1946, to March 31, 1948, under Contract W-18-035-CWS-1318

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SUMMARY

White phosphorus fillings in munitions have considerable tactical use as a means of providing screening smokes at any point within the range of the weapons employed. White phosphorus alone is not a satisfactory filling, however, because it burns so rapidly that much of the smoke is wasted in forming a pillar when the munition is burst. Furthermore, the phosphorus may melt under conditions encountered in storage or even in service under desert conditions, with resultant ballistic instability of the munition. Work under the present contract was undertaken with the objective of developing phosphorus fillings for munitions that would produce screening smokes with little pillaring and that would remain ballistically stable on prolonged storage at temperatures above the melting point of white phosphorus.

During the period covered by this contract, the Chemical Corps Technical Command itself has studied fillings comprising granulated white phosphorus and gels of rubber in certain organic solvents. This type of filling was not investigated by TVA.

In experiments on modification of the physical properties of the ~~phosphorus~~ fillings, a procedure was developed for conversion of white ~~phosphorus~~ to red ~~phosphorus~~ in the munition itself. The resultant massive red ~~phosphorus~~ filling is very stable ballistically, but it ignites and burns somewhat less rapidly than is desirable.

Most of the work done ~~by TVA under this contract~~ concerned mixtures of granulated white ~~phosphorus~~ and fluid binders which set to solid masses at room temperature. Attempts to prepare suitable binders from laboratory reagents were unsuccessful, but several commercial products appeared to be satisfactory. A method of producing white ~~phosphorus~~ granules of suitable particle size was developed in the course of the work.

The experimental fillings were charged into M15 grenades for preliminary tests. The performance of the fillings was evaluated in firing tests under simulated service conditions. A thermal stability test was developed and used to measure the effect of storage at high temperatures on the ballistic stability of the fillings.

Several 4.2 CM shells were charged with each of the most promising experimental fillings and were sent to the Army Chemical Center for storage and firing tests.

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PHOSPHORUS FILLINGS FOR MUNITIONS

Summary Report on Work Performed in the Period July 1, 1946, to March 31, 1944, under Contract W-18-035-CWS-1318

The present report is a summary of the work performed by TVA under Contract W-18-035-CWS-1318 on the development of phosphorus fillings for munitions. The details of the work have been reported in seven quarterly progress reports.

The work by TVA on phosphorus fillings developed along two major lines. Attempts to alter the physical properties of white phosphorus resulted in further development of a known method for conversion of white phosphorus to massive red phosphorus in the munition itself. In the other line of approach, search for binders for granulated white phosphorus that would solidify to form solid masses, similar to cement mortar, with the phosphorus granules resulted in the use of several commercially available cementing materials to form apparently satisfactory fillings.

The M15 grenade served as a test munition for evaluation of the experimental fillings. Firing tests, with M6A1D fuzes as burstors, indicated the tendencies of the fillings to form pillars or to produce screening smoke. A thermal stability test was devised to measure the effect of storage under desert conditions. In this test the center of gravity of a munition charged with the experimental filling was determined before and after storage at 65° C.

Several 4.2 CM shells were charged with each of the experimental fillings that appeared to be promising and were sent to the Army Chemical Center for further test. The fillings were massive red phosphorus and mixtures of granulated white phosphorus with binders of (1) plaster of paris, (2) plaster of paris set with an emulsion of white phosphorus in aqueous polyvinyl alcohol, (3) Duralon casting resin, (4) Thiokol LP-2 cured with furfural and formic acid, and (5) binder 4 modified with mercaptoethanol.

FILLINGS CONTAINING GRANULATED WHITE PHOSPHORUS

Granulated white phosphorus may be prepared by vigorous agitation and cooling of a mixture of molten phosphorus and warm water. The granules produced by this method are quite small, 50 to 80 mesh, and very irregular in shape. Furthermore, the prolonged intimate contact between molten phosphorus and warm water undoubtedly results in the formation of an appreciable amount of lower oxides of phosphorus which, in addition to the small size and

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irregular shape of the particles, makes the product difficult to dewater. Although the binders used in TVA experimental fillings are not affected adversely by the presence of small quantities of water, the relatively large amounts of water that would remain in superficially dewatered granulated phosphorus prepared by the agitation method probably would be undesirable. Moreover, this type of granulated phosphorus lacks the distribution of particle sizes that is required for production of a mass of phosphorus with a high apparent density; the voids in a mass of stirrer-granulated phosphorus occupy about 50 per cent of the total volume, whereas certain mixtures of larger granules contain about 37 per cent voids.

Granulated phosphorus more suitable for fillings of the type investigated by TVA was produced in a jet granulator that was described in detail in the progress report covering the period July 1 to September 30, 1947. Molten white phosphorus is run through an orifice into the top of a column of water that is heated above the melting point of phosphorus in the upper portion and cooled below that melting point in the lower portion. The stream of molten phosphorus issuing from the orifice breaks into drops that solidify during passage through the cold portion of the water column; seeding of this portion of the column with colloidal white phosphorus prevents supercooling of the drops of phosphorus.

The granules produced by this method are approximately spherical and vary in size from 4 mesh to about 20 mesh. The particle size of the granules may be controlled to some extent within these limits by variation of the size of the orifice and of the temperature in various parts of the system.

Orifices larger than 2.0 mm. permit flow too rapid for the formation of separate drops, and orifices smaller than 0.8 mm. reduce the flow, in a gravity system, below a practicable rate. The size of the granules is roughly proportional to the size of the orifice, and the screen analysis of the product may be varied, within limits, by the simultaneous use of several orifices of different sizes.

Increase in temperature of the phosphorus supplied to the orifice and increase in temperature of the water in the top of the column both tend to decrease somewhat the particle size of the phosphorus granules. The highest practicable temperature of the molten phosphorus is about 80° C. The temperature of the molten phosphorus or of the water in the top of the column must not be permitted to fall below about 50° C. or the phosphorus issuing from the orifice will solidify in strings.

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Granules larger than 4 mesh proved undesirable in the experimental fillings; satisfactory granules were separated into minus 4- plus 8-mesh and minus 8-mesh fractions. Mixtures of these two fractions, containing between 20 and 60 per cent of the finer fraction, had about 37 per cent voids, which is close to the minimum obtainable with granules prepared by the jet method, and any mixture of the two sizes between these limits will approach the maximum amount of phosphorus per unit of volume of a given filling. Mixtures containing larger proportions of the finer fraction usually give better performance in grenade firing tests than mixtures containing larger proportions of the coarser fraction.

Granulated phosphorus for preparation of the fillings described in the filling directives in this report should be dewatered, suitably by draining on a box filter in an inert atmosphere. A current of inert gas, passed downward through the mass of granules, will hasten the dewatering and will dry the phosphorus sufficiently for use with any of the binders considered. In these directives it is assumed that the granules will all be between 4 and 20 mesh and that the mass of granules will contain about 37 per cent voids.

Unsatisfactory Binders

Consideration of the properties desired in phosphorus fillings for munitions suggested that satisfactory fillings might be made by embedding granulated phosphorus in a solid binder. A suitable binder would be required to mix readily with the granulated phosphorus and to set to a solid at a temperature below 44° C., the melting point of white phosphorus. In addition, after curing, the binder must withstand temperatures up to 65° C. without cracking or disintegrating, and this property should be retained on aging. Many of the experimental binders failed to meet these requirements. Others gave poor performance in firing tests or failed to retain the phosphorus in thermal stability tests. The following binders were found to be unsatisfactory in some respect.

Portland Cement: A thin paste of portland cement mixed readily with granulated phosphorus, but the "free lime" in the cement reacted with the phosphorus to produce phosphine, which not only was a source of danger to the operator ~~but also~~ inhibited the set of the cement, with the result that the binder remained soft and mushy, rather than setting to a hard mass.

Laboratory Preparations of Plastics: Numerous combinations of urea, phenol, furfural, formaldehyde, and other aldehydes can be set in the cold by the addition of small percentages of acid or other reagents. Combinations of urea with formaldehyde or furfural and of furfural with formaldehyde, benzaldehyde, acetaldehyde, phenol, or sulfuric acid all gave solid products at room temperature, but were unsatisfactory because they cracked on aging or disintegrated when heated.

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Thiokol: Various thiokols, which are rubbery solids, can be prepared from sodium polysulfide and ethylene dichloride. Attempts to incorporate granulated phosphorus in a thiokol binder were unsuccessful. The method that appeared most promising entailed forming a latex which could be coagulated with acid. When attempts were made to coagulate the latex, in place, around the granules of phosphorus, however, the "rubber" did not enclose the granules.

Commercial Binders: The field of laboratory preparations of plastic binders was not explored thoroughly. The primary object of this phase of the work was to find a binder that could be formed in place around the granulated phosphorus. The results indicated that binders formed from laboratory reagents were not sufficiently durable. Since a great amount of work has been done commercially in the development of plastics, and since many resins are available on the market, it did not seem advisable to attempt further experimental development of a plastic binder.

The properties required in a binder for granulated phosphorus eliminated from consideration all thermoplastic resins and those thermosetting resins which require a temperature higher than 44° C. in setting. This left for consideration the so-called casting resins. In ordinary practice, many of these resins are set by moderate heat; others attain initial set at room temperature and subsequently are cured by baking. Some that ordinarily are set by heat may be set in the cold by incorporation of a larger proportion of accelerator, although the potential strength of the resin is not attained fully when the baking cycle is omitted. Several commerical resins were investigated, the choice being limited to those that were claimed to set at room temperature.

Palestic, apparently a condensation product of urea and formaldehyde, is marketed as an impregnant for plaster of paris. The resin set readily to a hard solid at room temperature but cracked on aging. Kriston and Marco casting resins, both apparently allyl esters, could not be set satisfactorily at room temperature. Furtone, a furane resin, set in the cold to a rubbery solid, but phosphorus inhibited the set so that the complete filling did not cure beyond the viscous liquid stage.

Most of the casting resins on the market are phenol-formaldehyde condensation products known commercially as phenolics. Samples of this type of resin, marketed under the trade names Duroz, Baker, Catabond, Marblette, Synvaren, and Syncast, all with quite similar properties, were tested as binders in the preparation of phosphorus fillings. The fillings had fair thermal stability, but they performed rather poorly in grenade firing tests. Phenolic resins are relatively inexpensive, however, and it is suggested that any further work on fillings of the type investigated by TVA include at least enough tests to evaluate the performance of phenolic resin-phosphorus fillings in munitions larger than the M15 grenade.

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Satisfactory Binders

Of the several binders investigated, five formed fillings that were sufficiently promising to warrant further tests in larger munitions. Fillings prepared with each of these binders were charged into 4.2 CM shells and sent to the Army Chemical Center for storage and firing tests.

Plastic Binders: Duralon 30, a furane-base casting resin, sets to a solid at room temperature when activated with accelerators supplied by the manufacturer. Fillings prepared with this binder had satisfactory thermal stability, and the performance in grenade firing tests was generally better than that of fillings in which phenolic casting resins were used as the binder.

Thiokol LP-2 is described by the manufacturer as "a low molecular polysulfide polymer having reactive mercaptan terminals and side groups capable of further polymerization and cross-linkage." This liquid polymer sets readily to a rubbery solid at room temperature on addition of furfural and formic acid. The addition of a "chain stopper," such as mercaptoethanol, decreases the extent of polymerization and yields a cured product which is a softer, more flexible rubber. Fillings prepared with these binders had satisfactory thermal stability and performed well in grenade firing tests.

Plaster of Paris Binders: Plaster of paris has the marked advantage of being both cheap and readily available in large quantity. Its property of setting to a hard mass when mixed with water is well known, and both plaster and water are substantially inert to white phosphorus under the conditions usually encountered in the preparation and storage of phosphorus fillings. Plaster-water mixtures formed a very satisfactory filling with granulated phosphorus. The filling was stable on storage under desert conditions, and the performance of the filling in grenade firing tests generally was good, although some erratic results were obtained.

Several organic compounds of high molecular weight retard the set of plaster of paris, polyvinyl alcohol being an example. Polyvinyl alcohol is a strong emulsifying agent as well, and aqueous solutions of the alcohol have been used in the preparation of emulsions of white phosphorus in water. Plaster of paris can be set with a 50 per cent emulsion of phosphorus in a 4 per cent solution of polyvinyl alcohol, and this plaster mixture has been used as a binder for granulated phosphorus. The performance of the fillings in grenade firing tests was consistently excellent, but the thermal stability of the fillings was not so good. The poor thermal stability appeared to be due to the occlusion of gas when the plaster, emulsion, and granulated phosphorus were mixed. Gas pockets apparently were formed when the plaster dehydrated the emulsion in the process of setting. The density of this filling probably could be increased, and the thermal stability improved, by mixing the ingredients under a greatly reduced pressure of an inert gas.

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PASSIVE RED PHOSPHORUS

White phosphorus ignites readily and burns rapidly in air, whereas red phosphorus is ignited with more difficulty and burns relatively slowly. The optimum characteristics for producing screening smoke lie between these two extremes and, presumably, would be obtained by use of mixtures of the two forms of phosphorus. Ballistic stability also would be obtained by the use of such mixtures, for mixtures containing more than 50 per cent red phosphorus behave as solids at all temperatures below 593° C., the melting point of red phosphorus.

White phosphorus is converted to red phosphorus when heated at 280° C., the boiling point of white phosphorus, at atmospheric pressure under a reflux condenser in an inert atmosphere. Under these conditions a mixture of substantially equal parts, by weight, of the two forms is produced in 4 to 6 hours. The mixture is a thick slurry of solid red phosphorus in liquid white phosphorus, fluid at temperatures above the melting point of white phosphorus. Mixtures sufficiently fluid to be charged into munitions also would be fluid at temperatures encountered in storage under desert conditions, however, and munitions filled with such mixtures would not be stable ballistically. Mixtures that contained enough red phosphorus to be stable ballistically would be a solid mass at all temperatures below 593° C., and could be transferred from one container to another only with difficulty.

One way around this dilemma is to prepare the mixture of red and white phosphorus directly in the munition, an operation that could be performed with relative simplicity by charging the munition, burster well in place, with a fluid mixture of red and white phosphorus through an aperture, preferably in the base of the munition, to which a reflux condenser could be attached. Heating of the charge to the boiling point of white phosphorus under an inert gas at, or slightly above, atmospheric pressure would produce a mixture of red and white phosphorus that would be ballistically stable after storage under any conditions that would be encountered in the field. The operation would require a considerable time of treatment for each munition, however, and the modification of the munition to permit use of the reflux condenser probably would add materially to the expense of fabrication.

The rate of conversion of white to red phosphorus increases rapidly with increase in temperature. In the method of conversion described above, the temperature obtainable is limited to the boiling point of white phosphorus under the imposed pressure. Attempts to carry out the conversion in sealed containers were successful, but the large amount of heat generated

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in the exothermic conversion carried the conversion substantially to completion. The conversion was initiated at temperatures as low as 240° C., but quenching the container failed to stop the reaction short of virtual completion; maximum temperatures as high as 560° C. and pressures of about 600 pounds per square inch were developed by the reaction.

The product was massive red phosphorus containing about 1 per cent white phosphorus. It was unaffected by exposure to temperatures higher than those specified in thermal stability tests and may be assumed to be ballistically stable. In grenade firing tests, massive red phosphorus appeared to ignite completely on explosion of the bursting charge. The fragments of the filling burned rather slowly, but were not extinguished when thrown into about 2 inches of melting snow overlying a cinder fill.

Sulfur has been used successfully as a catalyst for the conversion, both when the operation was carried out at atmospheric pressure and when it was carried out in sealed munitions. The sulfur is most conveniently added to the initial charge in the form of the 80-20 phosphorus-sulfur liquid eutectic; 1 per cent of sulfur in the final mixture gives very satisfactory results.

Conversion in sealed containers was effected in both M15 grenades and M2A 4.2 CM shells. It was necessary to hold the burster well in the shell in place with a plug that screwed into the adapter and bore upon the top of the burster well. Both munitions were assembled with silver solder (Class 4, m. p. 627° C.). The solder was softened sufficiently by the heat generated in the conversion to result in failure of the munition under the imposed internal pressure unless the munition was quenched in water soon after initiation of the rapid conversion reaction. The quenching apparently cooled the soldered joints without significant effect on the conversion reaction.

White phosphorus has a much higher thermal coefficient of expansion than steel. Closed steel containers charged with more than about 1.55 grams of white phosphorus per cubic centimeter will be burst by expansion of the liquid white phosphorus before initiation of the conversion reaction.

EVALUATION OF FILLINGS

For satisfactory performance in the field, a phosphorus filling must produce a persistent screening smoke with minimum loss of smoke in the formation of a pillar, and must remain ballistically stable on storage

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of the munition in any position under any conditions that may be encountered, even in desert areas. The 4.2 CM shell is the standard test munition for phosphorus fillings, and tests of the performance of phosphorus fillings in this munition are designed for simultaneous evaluation of both requisites.

Work on phosphorus fillings at TVA was on a relatively small scale, and the M15 grenade was selected as the preliminary test munition, both to conserve material and to permit firing tests in the limited space available for such tests at Wilson Dam. Since the M15 grenade is not fired from a rifled weapon, it was impractical to determine the ballistic stabilities of phosphorus fillings directly in this munition; instead it was necessary to devise a static test that would yield data from which the ballistic stability might be estimated.

Firing Tests

Firing tests of experimental fillings in M15 grenades, burst with M6A4D fuzes, were made to select those fillings that might be expected to perform well in 4.2 CM shells. Extrapolation of performance in grenades to performance in shells was not possible, for it was observed that PWP, which performs well in shells, performed very poorly in grenades. The tendency of the smoke to pillar when the munition is burst, and the ability of the scattered filling to produce smoke at a rate sufficiently high to maintain a screen appeared to be adequate basis for evaluation of performance of a filling. These criteria were used in the selection of experimental fillings for further tests in larger munitions.

Thermal Stability Tests

In evaluation of the thermal stability of the experimental fillings, the location of the center of gravity of a filled grenade, both along the longitudinal axis and laterally from that axis, was determined before and after heating the filled grenade for 8 hours at 65° C. while lying on its side, with subsequent cooling in the same position. The shift in center of gravity of the entire grenade, or of the filling alone, is a measure of the thermal instability of the filling and can be used to estimate the ballistic stability of any munition containing the same filling. The shift in the center of gravity can be used also to evaluate the ability of the binder to retain molten phosphorus and to estimate the tendency of the phosphorus remaining in the binder sponge to settle under the influence of gravity.

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Plaster of paris fillings in M15 grenades consistently retained at least 98 per cent of the phosphorus in the body of the filling, but the phosphorus remaining in the filling tended to settle to the lower portion of the body of the filling. The change in the position of the center of gravity of the munition was small, however, and plaster of paris fillings probably will remain ballistically stable under desert storage conditions.

Fillings in which the binder was plaster of paris set with an emulsion of white phosphorus in aqueous polyvinyl alcohol contained large gas pockets. These pockets not only decreased the effective strength of the binder, but also permitted relatively large movements of phosphorus through and out of the body of the filling in thermal stability tests. Unless some method is devised for eliminating the gas pockets from this filling, the ballistic stability of the filling after storage under desert conditions probably will be unsatisfactory.

Fillings in which Duralon or Thiokol LP-2 were used as binder lost an average of about 5 per cent of the total phosphorus in 8-hour thermal stability tests. This is the amount of phosphorus that is calculated to be displaced because of the difference in the coefficients of expansion of white phosphorus and the binders. Resultant shifts of the center of gravity of munitions containing these fillings were slight, however, and these fillings probably will prove to be stable ballistically.

Firing tests of fillings that had been subjected to thermal stability tests showed no difference in performance from fillings that had not been heated.

FILLING DIRECTIVES

The experimental phosphorus fillings developed by TVA fall into three classes: mixtures of granulated white phosphorus with thermosetting resins that set at room temperature to form solid masses, mixtures of granulated white phosphorus with plaster of paris and water that also set to form solid masses, and massive red phosphorus prepared by thermal conversion of white phosphorus in the munition. The several fillings in each of the first two classes behave very much alike, and a method devised for the preparation and charging of one filling into a munition is suitable for any other filling in the same class.

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Work at TVA was confined to laboratory-scale operation, and the filling for each munition was compounded in a separate batch. All mixing, with the exception of the preparation of the emulsion of white phosphorus in aqueous polyvinyl alcohol, was done by hand, and all fillings were charged into the munitions by rodding through a funnel. The operations are all simple, however, and could be carried out on a larger scale in standard mixing equipment and in fairly simple devices designed to charge the freshly mixed filling into the munition.

The fillings comprising granulated phosphorus and the various binders probably will set as rapidly in a mixer as in any other container. Hence, it will be necessary to clean the equipment used to prepare and handle these fillings at intervals no longer than the period for which the binder remains workable. The maximum time that should be permitted to elapse between successive cleanings of the equipment is suggested for each binder.

White phosphorus is a hazardous material, and its well-known property of spontaneous ignition on exposure to air necessitates certain precautions. Dry solid phosphorus may be handled safely in an inert atmosphere, preferably carbon dioxide, and accidental fires are extinguished readily by flooding with cold water. Provision for handling dewatered phosphorus and its mixtures in an inert atmosphere, and for flooding affected equipment with cold water in the event of a fire, are sufficient to ensure safe operation in the preparation and handling of TVA experimental fillings.

The phosphorus probably will be granulated under water, and most of the various binders may be compounded in the air. Other operations, such as dewatering of the granulated phosphorus, preparation of phosphorus-water-polyvinyl alcohol emulsions, mixing of the granulated phosphorus with the binder, and charging of the filling into the munition, should be carried out in an inert atmosphere, exceptions being that Duralon and Thiokol fillings probably can be charged in air.

It is recommended that operations in an inert atmosphere (carbon dioxide) be carried out in a chamber sufficiently large to contain the equipment for all the operations. The chamber should be gastight around the bottom and sides and should be fitted with necessary observation windows and a loose-fitting sectional cover. A continuous slow stream of carbon dioxide should be introduced near the bottom of the chamber. Operations could be observed and controlled from outside the chamber, preferably from the top. Minor maintenance, repair, or inspection work could be performed by an operator supplied with air for breathing from appropriate equipment; the usual safety precautions when workers enter inert atmospheres should be observed.

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Fillings Containing Plastic Binders

The quantities of filling specified in these directives are based on the assumption that each batch of filling will be large enough to fill ten 4.2 CM shells. The specifications are given by weight; the binder for each 10-shell batch will have a volume of about 7.5 liters (2 gallons) and the filling will have a volume of about 20 liters (5 gallons). The compositions of the plastic binders are as follows:

Duralon (resin manufactured by U. S. Stoneware Co.)

Activator F	0.63 kg.	1.39 lb.
Activator G	0.26 kg.	0.57 lb.
Duralon 30	8.77 kg.	19.30 lb.

Thiokol LP-2 (liquid polymer manufactured by Thiokol Corp.)

Thiokol LP-2	7.72 kg.	17.05 lb.
Furfural	1.54 kg.	3.40 lb.
Formic acid	0.31 kg.	0.68 lb.

Thiokol LP-2 modified with mercaptoethanol

Thiokol LP-2	7.66 kg.	16.90 lb.
Furfural	1.52 kg.	3.35 lb.
Formic acid	0.31 kg.	0.68 lb.
Beta-mercaptoethanol	0.08 kg.	0.18 lb.

Prepare the binders immediately before use. Mix the components of each binder in the order in which they are listed above, and after each addition blend the mixture thoroughly to form a homogeneous liquid. Both Duralon and Thiokol LP-2 are thick, viscous liquids with about the consistency of heavy molasses. The other components of the binders are thin liquids and may be proportioned by volume as readily as by weight.

The working life of activated Duralon and of the Thiokol LP-2 binders is about 24 hours, but all three binders become quite thick and sticky in about 3 hours. It is suggested that the equipment used to handle these binders and fillings containing them be cleaned every 2 or 3 hours. Equipment coated with Duralon can be cleaned with alcohol, and that coated with Thiokol LP-2 binders can be cleaned with furfural.

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Mixing of Filling: For each 10-shell batch, thoroughly mix 22.05 kg. (48.6 lb.) of dewatered granulated phosphorus with 9.66 kg. (21.3 lb.) of Duralon binder or with 9.57 kg. (21.1 lb.) of either of the Thiokol LP-2 binders. Any mixer that is suitable for handling a mixture similar in consistency to one of uncooked rice and enough heavy molasses to fill all the interstitial spaces between the rice grains will be satisfactory. It is essential, however, that the design of the mixer permit frequent, thorough cleaning of all parts that come in contact with the filling.

Charging Filling into Munitions: Freshly prepared fillings comprising granulated white phosphorus and Duralon or Thiokol LP-2 binder flow slowly under the influence of gravity, but with some segregation of the binder from the phosphorus, especially when the mixture is forced to flow through the relatively small orifice required in charging the filling into a munition through the burster-well seat. At least the upper part of the filling probably should be stirred continuously during the charging operation, and if provision is made for such partial agitation, these fillings probably could be extruded into the munition.

A suggested design for a charging device is a cylinder, with a capacity large enough to hold a 10-shell batch, that discharges through a conical section terminating in a short cylinder that may be inserted through the burster-well seat to extend just below the bottom of the seat. Either mechanical or gas pressure could be applied to the filling in the large cylindrical portion of the charging device. If gas pressure is used, a blade stirrer should be provided to prevent caking of the filling with resultant channeling of the fluid binder, and subsequently the gas, through the mass of granulated phosphorus. Although a stirrer may not be essential if the pressure is applied mechanically, a stirrer that extends through the piston probably would improve the operating characteristics of the device. The charging device should be thoroughly cleaned every 2 or 3 hours to prevent sticking as the binder begins to set. Shells should be filled on a scale to specified weight, 3.17 kg. for Duralon or 3.16 kg. for Thiokol.

In the most convenient arrangement of equipment, the charging device probably would be filled from within the inert-atmosphere chamber in which the filling is mixed, but would eject the charge into the munition in the open air. Since the filling is quite viscous, care must be taken that portions of it are not left in the adapter of the munition when the munition is withdrawn from the charging device. With these fillings the burster well may be inserted by hand and easily pushed down until contact with the seat is made.

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The standard charge (1923 ml.) of these fillings in a 4.2 CM shell is 3.17 kg. (6.99 lb.) of Duralon filling, or 3.16 kg. (6.97 lb.) of either of the Thiokol-LP-2 fillings. Munitions charged with any of these fillings should be allowed to stand upright for at least 5, and preferably 15 days, after charging to permit complete set of the binder. The extent of set is followed conveniently by observation of a sample of the filling in a small screw-top glass sample bottle.

Fillings Bound with Ordinary Plaster of Paris

Because of the rapid set of ordinary plaster of paris, fillings bound with it should be mixed in batches no larger than can be charged into munitions within about 15 minutes after the plaster has been wetted. The plaster binder is quite fluid and the filling has a marked tendency to segregate. Hence, it is advisable that the charging device be designed to handle single-shell batches. The amounts specified in this directive are based on the assumption that each batch of filling will fill one 4.2 CM shell. The specifications are given by weight; the binder for each batch will have a volume of about 0.75 liters (0.2 gallon) and the filling will have a volume of about 2 liters (0.5 gallon). The composition of the binder is as follows:

Plaster of paris	0.565 kg.	1.346 lb.
Water	0.565 kg.	1.346 lb.

Prepare the binder immediately before use. Mix the plaster and water thoroughly in any suitable mixer, probably in the same mixer that is to be used to mix the entire filling. Wash the mixer with water after discharge of each batch. The amount of water specified in the composition of the binder may be decreased somewhat to allow for water retained in the granulated phosphorus that is to be added.

Mixing of Filling: To the 1.130 kg. (2.69 lb.) of plaster-water mixture, add 2.205 kg. (4.86 lb.) of dewatered granulated phosphorus. Any mixer that could be used to mix cement mortar containing aggregate no larger than 4-mesh is suitable. Wash the mixer with water after each batch of filling has been discharged, and return the granulated phosphorus from the washing operation to the process.

Charging Filling into Munition: In contrast to the fillings bound with plastics, the slurry of plaster and water does not wet the particles of granulated phosphorus very well, and the freshly mixed filling has physical properties similar to those of very wet sand. The mixture cannot be poured easily through a funnel, nor does it lend itself

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readily to extrusion. The most satisfactory charging device probably would be a steep-sided funnel equipped with a paddle stirrer to scrape the sides of the funnel and with a reciprocating rod, extending through the axis of the stirrer, to force the filling into the munition. The stem of the funnel should be as large as the burster-well seat will permit, and should extend just below the burster-well seat in the munition. With this filling the burster well often cannot be inserted by hand farther than about half way into the munition. Any filling remaining in the adapter after the burster well is seated may be removed by flushing with a forceful stream of water.

The standard charge of this filling in a 4.2 CM shell (1923 ml.) is 3.34 kg. or 7.57 lb. Munitions charged with the plaster filling should be allowed to stand upright for at least 4 hours, preferably 24 hours, to permit complete set of the binder.

Fillings Bound with Modified Plaster of Paris

Fillings bound with plaster of paris set with an emulsion of phosphorus in polyvinyl alcohol have a somewhat longer period of workability than fillings in which the binder is straight plaster of paris and water. Also, the crumbly body that results from setting of the emulsion-plaster mixture is more easily cleaned off equipment than is the harder plaster. With respect to the partially set mixtures, however, ordinary plaster can be flushed off most surfaces with a gentle stream of water, whereas the emulsion of phosphorus in polyvinyl alcohol is tenacious, and equipment coated with it must be scrubbed or brushed while it is washed to ensure thorough cleansing.

In the preparation of emulsion-plaster fillings, the aqueous polyvinyl alcohol solution must be prepared several days in advance, the phosphorus emulsion must be prepared between 12 and 18 hours before use, and the actual binder, which includes plaster of paris, must be made up immediately before use. The binder may be workable for as long as 1 hour, but the operating procedure should be so designed that the filling is charged into munitions within 30 minutes after the plaster has been wetted.

Preparation of Emulsion: Prepare a 4 per cent solution of polyvinyl alcohol ("Elvanol" polyvinyl alcohol, type A, medium viscosity, grade 52-22, a product of E. I. du Pont de Nemours and Co.) in water, by stirring the alcohol slowly into cold water until it is wetted thoroughly and all lumps are broken up. High-speed stirring causes foaming and should be avoided. Prepare the solution about a week before it is to be used, and stir it intermittently to ensure complete solution of the alcohol.

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All subsequent operations involving this material must be performed in an inert atmosphere.

Place equal weights of molten phosphorus and 4 per cent polyvinyl alcohol solution in a jacketed vessel equipped with a high-speed, emulsifying stirrer. The temperature of the phosphorus should be 50° C., and that of the solution should be 60° C. The solution must not be heated above 65° C., but must be warmer than the phosphorus, else the phosphorus will form the continuous phase of the emulsion and become worthless for the present application. The mixture foams badly when stirred and attains an apparent specific gravity as low as 0.3. Emulsification is rapid; as soon as the mixture is uniform, circulate cold water through the jacket and continue stirring until the emulsion is cooled to about 25° C. Then run the emulsion into a storage tank to facilitate elimination of occluded gas. The emulsion attains a specific gravity of about 1.35 in 12 to 18 hours; it should be used as soon as practicable after it has attained a specific gravity of about 1.3. On prolonged standing, the emulsion, originally a creamy white liquid, settles into a compact mass of phosphorus under a layer of clear supernatant liquid. Although freshly settled emulsions may be remixed by slow stirring, the settled mass consolidates in a few days to a solid body that cannot be stirred back into suspension. Heating of the once-cooled emulsion to temperatures above the melting point of white phosphorus results in immediate break of the emulsion.

Preparation of Filling: The emulsion-plaster mixture readily occludes gas, even on gentle stirring. It is recommended that the binder and the filling be mixed under reduced pressure to decrease the occlusion of gas.

~~For a~~ 10-shell batch, the binder is composed of:

Emulsion	7.0 kg.	15.44 lb.
Plaster of paris	2.5 kg.	5.52 lb.

Thoroughly mix these ingredients and add 20.50 kg. (45.22 lb.) of dewatered granulated phosphorus. Mix the phosphorus with the binder, preferably in an inert gas at low pressure.

Wash the mixer with water at intervals no longer than 1 hour.

Charging Filling into Munition: Because of the marked tendency of the emulsion-plaster filling to occlude gas, a denser filling might be obtained if the munition is charged under reduced pressure. A filling device similar to that suggested for use with plaster of paris fillings probably would be satisfactory.

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When this filling is mixed and charged into munitions under 1 atmosphere of an inert gas, occlusion of the gas lowers the apparent specific gravity of the filling to about 1.5, and the charge of this filling in a 4.2 CM shell is 3.0 kg. (6.6 lb.). With no occluded gas the filling should have a specific gravity of about 1.7, and, if this density could be attained, about 3.3 kg. (7.2 lb.) of the filling could be charged into each shell.

Munitions charged with this filling should be allowed to stand upright for 24 hours after charging to permit complete set of the binder.

Preparation of Massive Red Phosphorus Fillings

The preparation of massive red phosphorus fillings by conversion, in the munition, of a charge of white phosphorus entails severe operating conditions. The exothermic conversion reaction (16.0 kg.-cal. per mole of P_4) heats the charge and the munition to a maximum temperature of about 560° C. (1040° F.), and the vapor pressure of the phosphorus reaches about 600 pounds per square inch. It is essential that the munition remain gas-tight under these conditions, which will persist from 5 to 30 minutes.

Two alternative methods are proposed for the preparation of massive red phosphorus fillings. If a munition is available that can withstand an internal pressure of 600 pounds per square inch at 560° C. without leaking, the munition may be passed through a furnace maintained at about 325° C. and removed at any time after the conversion is complete. If, however, the munition is silver soldered, like the M2A 4.2 CM shell, it will be necessary to quench the munition soon after the conversion reaction is under way.

The quenching operation can be performed automatically. The munition, suspended in a furnace at 325° C., can be heated to initiate conversion and then dropped into a quenching tank when the temperature in the burster well of the munition exceeds some predetermined temperature that is at least 25° C. higher than the temperature of the furnace. The quenching cools the silver-soldered joints in the munition, but the cooling effect is not sufficient to stop the conversion reaction.

Composition of Charge: The addition of sulfur as a catalyst lowers the temperature at which rapid conversion of the white phosphorus is initiated. Although larger amounts may be used, 1 per cent of sulfur gives very satisfactory operation. It is advisable to add the sulfur in the form of the 80-20 phosphorus-sulfur eutectic, which is easily prepared by dissolving sulfur, preferably in lump form, in molten phosphorus under water at about 60° C.

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Filling the Munition: Because of the high coefficient of expansion of phosphorus, the charge of white phosphorus must not exceed 1.55 grams per cubic centimeter of space in the munition. The standard charge of white phosphorus in a 4.2 CM shell (total volume 2310 cc.) is 3.50 kg. (7.72 lb.); any shells that contain more than 3.58 kg. (7.89 lb.) will be burst by the expansion of liquid phosphorus. The phosphorus may be stored under water immediately prior to loading into munitions, but free water must not be admitted to the munition.

The weakest part of the filled and sealed munition is the burster-well seat. The burster well should be held in place during the conversion by a threaded plug, screwed into the nose of the munition and bearing upon the top of the burster well. If the munition is to be quenched, the plug should be drilled and tapped to receive a length of pipe, suitably 1/4-inch standard pipe, that serves both to suspend the munition in the furnace and to exclude water from the burster well when the munition is dropped into the quenching tank. While admittance of water to the burster well probably would not affect the conversion, the cooling effect of the water would complicate considerably the operation of any device placed in the burster well to indicate whether conversion had been obtained in the munition.

Conversion Without Quenching: Munitions which will withstand an internal pressure of 600 pounds per square inch at 560° C. (1040° F.) can be placed upright on a conveyor that moves through a furnace at 350° to 400° C. (660° to 750° F.). The speed of the conveyor should be so adjusted that the munition is heated to a temperature not lower than 300° C. (570° F.). A suitable pyrometric cone or a piece of an alloy that melts at about 500° C. (930° F.) should be placed in the burster well before the munition is placed in the furnace.

On removal from the furnace the munition should be allowed to cool to room temperature, the plug removed from the nose, and the burster well inspected to determine whether a temperature of at least 500° C. (930° F.) has been reached. Attainment of this temperature, which is higher than that of the furnace, is good evidence that the conversion has gone to completion.

Conversion with Quenching: Silver-soldered munitions, such as the M2A 4.2 CM shell, must be quenched during the conversion and should be suspended from a pipe attached to a threaded plug which will screw into the nose of the munition. The munition should be conveyed through a furnace at a temperature between 325° and 375° C. (620° to 710° F.) with a quenching tank underneath. The method of suspension should be such that the munition will be released and dropped into the quenching tank by release of tension on a wire soldered to the inside of the burster well and passed through the threaded plug and the suspending pipe.

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The alloy with which the wire is soldered to the inside of the burster well should have a melting point of about 400° C. (750° F.). The munition should be heated until the conversion reaction is initiated, whereupon the temperature in the burster well will rise, the solder will melt and release the wire, thus actuating the release device at the point of suspension and dropping the munition into the quenching tank. The munition can be removed from the quenching tank when it has cooled sufficiently to permit handling. Complete melting of the solder in the burster well should be ample evidence that the conversion has gone to completion.

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