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TENNESSEE VALLEY AUTHORITY

CHEMICAL ENGINEERING DEPARTMENT

CHEMICAL RESEARCH AND ENGINEERING BRANCH

CHEMICAL RESEARCH DIVISION

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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period January 1 to March 31, 1947, Under Contract W-18-038-CWS-1318

Wilson Dam, Alabama

Tennessee Valley Authority
Chemical Engineering Department
Chemical Research and Engineering Branch
Chemical Research Division

PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period January 1 to March 31, 1947, Under Contract W-18-035-CWS-1318

By

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

Wilson Dam, Alabama

Tennessee Valley Authority
Chemical Engineering Department
Wilson Dam, Alabama
April 23, 1947

Commanding Officer
CWS Technical Command
Building 330
Edgewood Arsenal, Maryland

Attention: Chief, Munitions Division

Gentlemen:

Transmitted herewith are six copies of the third quarterly progress report on our studies of phosphorus fillings for munitions. The report covers work performed under contract W-18-035-CWS-1318 during the period January 1 to March 31, 1947.

Very truly yours,

TENNESSEE VALLEY AUTHORITY

K. L. Elmore

K. L. Elmore, Chief
Chemical Research Division

PHOSPHORUS FILLINGS FOR MUNITIONS

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SUMMARY

In a continuation of the study of phosphorus fillings for munitions, additional resin binders for granulated white phosphorus have been tested. Resins prepared in the laboratory lacked either strength or durability, and the search for methods of preparation of resins has been discontinued. Several commercial preparations have been found to harden readily at room temperature and to form stable mixtures with granulated phosphorus. Tests of commercial resins are being continued.

Firing tests have shown that the performance of rigidly solid phosphorus fillings is dependent upon the bursting charge. High-brisance bursters invariably fragment the filling excessively with resultant pillaring of the combustion products. Burster charges of a propellant powder produced relatively little fragmentation and little pillaring. Burster charges will be investigated more thoroughly.

The thermal stability tests used in evaluation of the PWP prepared at Edgewood Arsenal are not applicable to phosphorus fillings of the type prepared by TVA. It is assumed that the major adverse effect of thermal instability of a phosphorus filling in a projectile is the lateral shift of the center of gravity that would result from storage of the projectile on its side under tropical conditions. Attempts will be made to measure the shift in static balance of a filled projectile as a measure of the thermal stability of the projectile.

PHOSPHORUS FILLINGS FOR MUNITIONS

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In a continuation of the search for suitable resins for binding granulated white phosphorus in fillings for munitions, several additional preparations of resins from laboratory reagents were investigated, and several additional commercial casting resins were tested.

Firing tests showed that the MSA4D fuze supplied with the M15 grenades is too brisant for satisfactory performance of rigidly solid fillings of the type prepared by TVA. Attempts therefore were made to develop a burster more suitable for use with the experimental fillings.

Work was started on the development of a thermal stability test for evaluation of the behavior of the experimental fillings in projectiles stored under tropical conditions.

RESIN BINDERS FOR GRANULATED WHITE PHOSPHORUS

Laboratory Preparations

Resins were prepared in the laboratory by methods described by Carleton Ellis in his book, "The Chemistry of Synthetic Resins" (Reinhold Pub. Corp., New York, 1935). The parenthetical page numbers in this section refer to Ellis' book.

Condensed urea-formaldehyde resin (p. 594) proved unsatisfactory in mixtures with granulated phosphorus, because it shrank markedly on setting, cracked, and eventually disintegrated on standing in the air.

A resin prepared from urea and furfural (p. 669) was the best of the laboratory preparations. At room temperature the mixtures hardened at about the desired rate to yield a product having several desirable properties. The hardened resin disintegrated, however, upon exposure to a temperature of 65° C.

A furfural-acetaldehyde resin, hardened with hydrochloric acid (p. 521), set to a hard solid in about 3 days at room temperature. Mixtures of this resin with granulated phosphorus never set to a rigid solid, however, and it is assumed that evaporation of water was prevented by the container. Because of the marked acidity of the hardened preparations, the mixtures are considered to be undesirable for use in metallic projectiles.

Furfural-phenol resins (pp. 522-7) require much less hydrochloric acid than do the furfural-acetaldehyde resins. Experimental furfural-phenol resins set to hard solids in about 4 days at room temperature but cracked and disintegrated on standing.

Furfural alone is condensed to a hard solid by strong sulfuric acid (p. 521). The acid apparently acts only as a catalyst, for it can be leached with water from the hardened resin. The resin proved unsuitable, because it shrank on setting and cracked on standing.

Thiokol latex was prepared from sodium polysulfide, ethylene dichloride, and magnesium hydroxide (p. 1172). The latex, in mixtures with granulated phosphorus, was then coagulated with acetic acid, but the products were unsatisfactory.

Commercial Resins

Mixtures of granulated phosphorus with either Durez 7421A, produced by Durez Plastics and Chemicals, Incorporated, or Duralon 50, produced by the U. S. Stoneware Company, set to physically stable solids, provided the water was first washed from the phosphorus with alcohol.

A sample of Elobem 124 resin, prepared from dimethyl hydantoin, was obtained from the Electrochemicals Department of E. I. du Pont de Nemours and Company. Attempts to obtain room-temperature sets of mixtures of this resin with urea or with phenol, using either sulfuric acid or sodium hydroxide as the setting agent, were unsuccessful.

Baker casting resin No. 100,972, obtained from Baker Oil Tools, Incorporated, proved similar to the Durez casting resin and set to a physically stable solid in mixtures with granulated phosphorus.

Catabond 400, a product of the Catalin Corporation of America, is readily set at room temperature to a hard solid similar to hardened Durez. Mixtures of this resin with granulated phosphorus have been prepared but have not been subjected to firing tests.

Thiokol LP-2, a liquid polymer produced by the Thiokol Corporation, appears to be the most promising of the resins studied thus far. Room-temperature cures to rubbery solids were obtained readily by the addition of either 7.5 parts of lead peroxide or 20 parts of furfural and 2 parts of formic acid per 100 parts of the liquid polymer. The lead peroxide mixture is quite stiff when first prepared and is difficult to mix with granulated phosphorus. The mixture containing furfural and formic acid

is quite fluid and is easily mixed with granulated phosphorus. The lead peroxide mixture sets in about 24 hours, but at least a week is required for curing of the mixture containing furfural and formic acid. Mixtures of the liquid polymer with zinc oxide and hexamethylenetetramine set neither at room temperature nor at 70° C.

A study of phosphorus-water emulsions stabilized with polyvinyl alcohol has been started. Emulsions containing about 75 per cent phosphorus have been prepared, and a mixture of plaster of Paris with such an emulsion has been made. None of these preparations, however, has been subjected to firing tests.

Attempts are being made to obtain samples of the water-soluble resins that are said to increase the strength of plaster of Paris castings. Since plaster of Paris alone has several desirable properties as a medium for the preparation of phosphorus fillings, the use of suitable resins to increase the strength and decrease the porosity of plaster castings should result in improved mixtures with granulated phosphorus.

PREPARATION OF PHOSPHORUS FOR FILLINGS

Granulation of Phosphorus

Although phosphorus from the jet granulator consists of roughly spherical particles, irregularities in the shape of the particles result in an undesirably high proportion of interstitial space in a mass of the granulated phosphorus. The best mixtures of various sizes of the granulated phosphorus contain 33 per cent interstitial space, and careful mixing of the granules is necessary to maintain this minimum, for the different sizes tend to segregate on stirring of the mixture under water. With 33 per cent interstitial space, a mixture of granulated phosphorus and binder can contain a maximum of about 75 per cent by weight of phosphorus when the binder is a resin with a specific gravity in the usual range of 1.2 to 1.4 and a maximum of about 60 per cent by weight of phosphorus when the binder is plaster of Paris. Regardless of the type of binder, however, the amount of phosphorus present would be 67 per cent of the amount of massive phosphorus that could be put into the same space.

Phosphorus Sulfide Sludge

The semisolid sludge previously obtained as a byproduct in the preparation of the low-melting phosphorus-sulfur eutectic was reproduced when the eutectic was prepared with flowers of sulfur, but none of the sludge was obtained when the eutectic was prepared with lump sulfur. The sludge, a slightly rubbery semisolid with the consistency of soft putty, apparently is a mechanical mixture of liquid phosphorus-sulfur solution and undissolved solid sulfur. The sludge was separated from the liquid phosphorus-sulfur eutectic by filtration through paper on a Buchner funnel under water. Charges of the sludge in beakers performed fairly well when exploded with firecrackers, but this material appears to be more a laboratory curiosity than a practical phosphorus filling for munitions.

THERMAL STABILITY TESTS

The thermal stability tests used in evaluation of the puttylike PWP prepared at Edgewood Arsenal are not suitable for evaluation of rigid phosphorus fillings of the type prepared by TVA. An investigation was made of possible methods of evaluating the ability of a given solid binder to retain, at 65° C., the granulated phosphorus with which it was mixed. It was assumed that a thermally stable rigid filling should retain substantially all its phosphorus, even when the filling was not closely confined.

Several fillings were cast in plaster or glass molds. When the fillings had hardened, they were removed from the molds and suspended in either water or carbon dioxide at 65° C.

Fillings bound with urea-furfural laboratory resins disintegrated rapidly in water at 65° C. and lost 63 per cent of their phosphorus in 5 hours in an atmosphere of carbon dioxide at 65° C. Fillings prepared with Durez casting resin lost 5 per cent of their phosphorus when suspended in water for 5 hours at 65° C. and 13 per cent when suspended in carbon dioxide. It was apparent, however, that this test was much more drastic than would be encountered by a filling in a projectile under tropical storage conditions, and it appeared that the loss of phosphorus probably was due more to faulty mixing of the phosphorus with the resin than to undesirable properties of the hardened plastic. On the small scale on which these fillings are being prepared, however, mechanical mixing, which obviously would improve contact between the resin and the individual granules of phosphorus, does not appear feasible.

In the belief that thermal instability of an otherwise satisfactory filling would be serious only if it resulted in sufficient shift of material to displace the center of gravity of the munition, tests were made to evaluate this shift of material. Various fillings were cast in 45-mm. glass tubes, the ends of which were closed by rubber stoppers. When the fillings had hardened, one rubber stopper was removed from each tube, and the tubes were suspended, open end down, in a stoppered bottle full of carbon dioxide. The bottle was placed in a water bath at 65° C. for 24 hours, and the phosphorus lost from the filling was collected in the bottom of the bottle and weighed. The results of such tests of various fillings are listed in Table I. Each sample contained approximately 45 grams of granulated phosphorus and occupied about a 30-mm. length (40 cc.) of 45-mm. tubing.

TABLE I

Thermal Stability Tests

(Samples contained in 45-mm. glass tubes and suspended in CO_2 for 24 hours at 65° C.)

Binder	Age of sample, days	Loss of phosphorus, %
Urea-furfural	9	78
	28	64
Furfural-phenol	9	16
	28	15
Furfural-H_2SO_4	9	66
	28	40
Plaster of Paris	9	7
	28	12
Duralon resin	10	7
	26	14
Durez resin	10	30
	30	8
Baker resin	6	27
	26	10
Thiokol LP-2 with furfural-HCOOH	10	52
	30	30

A few samples were cast in tall-form beakers made from 57-mm. glass tubing. The fillings were of substantially the same size as those used in charges in 150-cc. beakers for firing tests. The binders were Durez, Duralon, Bakor, Catabond, and Thiokol LP-2 set with furfural and formic acid. Glass burster wells for firecrackers were inserted in the charges. The charges were covered with an atmosphere of carbon dioxide, and the beakers were closed with rubber stoppers.

When the fillings had hardened, the stoppered beakers were suspended upright in a 65° C. water bath for 24 hours. In each test the filling shrank slightly and pulled away from the walls of the beaker, although none of the fillings completely loosened from the container. Some phosphorus separated from each filling and collected between the filling and the walls of the container, like a liquid film between the walls of a cylinder and a loosely fitting piston.

Although the vapor pressure of white phosphorus at 65° C. is only about 0.7 mm. of mercury, small amounts of phosphorus apparently were distilled out of each filling and collected on the walls of the containers above the fillings. The total movement of material in these tests appeared to be insufficient, however, for significant displacement of the centers of gravity of the fillings.

Additional thermal stability tests will be made on samples prepared in the same manner, but the samples will be suspended horizontally during the tests. In addition to measuring the amounts of phosphorus which run out from the fillings, attempts will be made to determine shifts in centers of gravity of the fillings for the purpose of evaluating the ballistic stability of the fillings after storage under tropical conditions in a horizontal position.

FIRING TESTS

To conserve time and material, exploratory firing tests of fillings prepared from granulated phosphorus and various binders were carried out in beakers with firecrackers as bursters. Tests of various types of bursters were made with M15 grenades.

Many bursts and pillars were photographed, and the photographs were of material assistance in the evaluation of the several fillings. Pictures of the screening smokes were, on the whole, of little value because of the variations in wind velocity, even between successive shots in the same series of tests.

Tests of Various Fillings

In the exploratory firing tests with charges in 150-cc. beakers, each charge was about 60 per cent of the amount that would be charged in an M15 grenade. The beaker generally was laid on its side on the ground and burst with a firecracker.

The explosion usually threw fragments in the directions of the radii of the beaker, very little material being thrown in either direction along the axis of the beaker. Many of the fragments thus were thrown considerable distances through the air, and the smoke emitted by the flying fragments tended to increase the apparent amount of pillaring. Because of the excessive scattering of the fragments, as well as the marked variations in the wind velocity during the tests, observations of the amounts of pillaring and the persistence of a screening smoke are considered to be much less reliable as bases of evaluation than the total burning time, which was the time elapsed between the explosion and persistence of a flame from the largest fragment of the shattered filling. The maximum throw of fragments by the explosion is a rough measure of the resistance of the filling to fragmentation; it appears probable that larger particles of a burning filling will be thrown farther than smaller particles, assuming the same initial velocity.

With the exception of fillings prepared with coagulated thiokol latex and Thiokol LP-2, all the fillings in the series were rigid bodies. The results of firing tests of the various fillings are listed in Table II. Since each filling was tested with two or more shots, minimum and maximum values are recorded for each observation. From Table II it is apparent that, of the laboratory preparations, only the urea-formaldehyde and urea-furfural resins are of sufficient promise to warrant further investigation. All the commercial resins performed better than any of the laboratory resins.

A beaker charge of the semisolid phosphorus sulfide sludge pillared slightly on explosion, but the total burning time was 300 seconds. Addition of a small amount of liquid phosphorus-sulfur eutectic to the sludge increased the pillar markedly and decreased the burning time to only 15 seconds.

In a few shots, the beakers were set upright on the ground and exploded with firecrackers. Since the fragments were rolled along the ground by the burst, rather than thrown through the air, pillaring was reduced and burning time was increased. From these shots it was concluded that the optimum burster would be one that would scatter fragments of the filling only far enough to give satisfactory distribution of the fragments, since more vigorous scattering would result in increased pillaring.

TABLE II

Firing Tests of Various Phosphorus Fillings

(Charges contained in 150-cc. beakers and burst with 2-inch firecrackers)

Binder	Fragmentation		Persistence, sec.		Filler
	Max. throw, yd.	Max. size, cm.	Screening smoke	Total burning	
None (massive P)	25-40	-	30-60	80-150	Slight to marked
Laboratory resins					
Urea-formaldehyde	15	3.8	15	210	Marked
Urea-formaldehyde (condensed)	15-40	2.0-3.8	10-60	70-240	Generally slight
Urea-furfural	30-40	3.8	20-60	90-240	Slight
Urea-furfural-formaldehyde	40	-	-	120	-
Furfural-formaldehyde	30-35	-	25-60	70-120	Marked
Furfural-acetaldehyde	30	Large	10-40	60-210	Slight
Furfural-phenol	12-20	Small	-	40-80	Marked
Furfural-H_2SO_4	20-35	1.3	-	110-180	Slight
Coagulated thiokol latex	3-10	Soft	-	120	-
Commercial preparations					
Plaster of Paris	10-50	Generally large	15-75	120-240	Slight
Duralon	30-40	2.5	-	180-360	Little
Durez	20-75	2.0-2.5	-	150-300	Little
Thiokol IP-2	6-15	Soft	-	300-330	Little

Several beaker charges were burst with 3-inch firecrackers. These were more powerful than the 2-inch firecrackers and produced a marked increase in pillaring, a decrease in the size of the fragments, and a pronounced decrease in total burning time.

It was apparent that the small size of the charges in 150-cc. beakers made extrapolation of results of firing tests to estimated performance of actual munitions quite difficult. Charges of massive phosphorus and of urea-furfural and plaster of Paris mixtures with granulated phosphorus were cast in 600-cc. beakers. Each charge was cast to the same depth that is used in the 150-cc. beakers. The volume of filling used was then about 2.4 times that in the 150-cc. beakers and about 1.4 times that of the M15 grenade. Bursting of the massive phosphorus charge with a 2-inch firecracker resulted in marked pillar, fragments were thrown 13 yards, and the burning time was 210 seconds. With the urea-furfural and plaster of Paris mixtures the pillaring was slight, fragments as large as 2.5 cm. were thrown 20 and 10 yards, respectively, and they burned for 360 and 330 seconds, respectively.

Tests of Bursters

Pictures of bursts and of the marked pillars produced by explosion of charges in M15 grenades with M6A4D fuzes were indistinguishable when the fillings were liquid phosphorus-sulfur eutectic, massive phosphorus, or mixtures of granulated phosphorus with plaster of Paris, urea-furfural resin, or a commercial casting resin. Similar results, including the marked pillars and relatively short burning times, were obtained when the same fillings were charged in 150-cc. beakers and exploded with unattenuated No. 6 blasting caps. It was concluded that, in view of the consistent differences in performance of these fillings when burst with firecrackers, a highly brisant burster would not give optimum performance of rigid phosphorus fillings. A search was then started for more suitable bursters.

In one shot in which a beaker charge of a mixture of granulated phosphorus and plaster of Paris was exploded with a firecracker in a well located just inside the beaker wall, improved performance over that obtained with centrally located bursters in the same mixture was observed. To test the effect of relocation of highly brisant bursters, M15 grenade cases were fitted with burster wells of 8-mm. glass tubing set just inside the walls of the cases. Cases were fitted with one well, two wells 180 degrees apart, and three wells 120 degrees apart. Explosion of a single Primacord burster in these cases produced marked pillaring with each of the three fillings used; the massive phosphorus burned for 120 seconds, the urea-furfural filling for 240 seconds, and the plaster of Paris filling for

300 seconds. The grenade cases were split down one side only, and much of the filling remained in the case. Neither the case nor the filling was thrown very far. Explosion of two or three Primacord bursters in a grenade case produced excessive pillaring, and burning times of 30 to 120 seconds were obtained with all the fillings.

Although somewhat increased burning times resulted from a shift of the brisant burster from its normal central location to a position just inside the container wall, the filling was not well scattered by the explosion. It appeared that better performance would be obtained with a less brisant bursting charge in a central burster well.

The bullets were extracted from U. S. Army .30-'06 service cartridges, and the powder was reserved for use as the bursting explosive. By attachment of short lengths of copper tubing, the cartridge cases were made to fit into the M15 burster well with the primer just below the bottom of the female threads in the well. Reclaimed heads of M6A4D fuzes or short, threaded collars were used to seal the cartridge case in the burster well. Eightpenny common nails were used as firing pins. The firing pins were struck by a falling pendulum that was released by remote control.

Various amounts of .30-'06 powder were placed in the cartridge cases and held in place by plugs of cotton. The results of firing several grenades containing various phosphorus fillings and various amounts of powder are listed in Table III.

The charges of .30-'06 powder usually tore about a 120-degree strip out of one side of the case and left the body of the case relatively undamaged otherwise. The long burning times probably are due largely to the fact that much of the fillings remained in the cases. In spite of the limited scattering of fragments of the fillings, however, smoke was produced steadily in what appeared to be very satisfactory volume throughout almost the entire burning time.

One grenade, filled with plaster of Paris and granulated phosphorus, was exploded with 2.5 grams of powder from regular-velocity .22-caliber cartridges. A marked pillar was produced, and the burning time was only 120 seconds. The burster shredded the grenade case much in the manner of M6A4D fuzes.

TABLE III

Firing Tests of Phosphorus Fillings Burst with Powder from .30-'06 Cartridges

Binder	Powder, grams	Throw, yd. Case	Throw, yd. Fragments	Pillar	Burning time, sec.	Filling left in case
None (massive P)	2	9	7	Marked	180	-
	3	0	7	Marked	480	Much
Urea-furfural	2	0	8	Some	1000	Half
	3	2	-	Slight	-	Half
	3	0	15	Slight	400	-
	3	11	-	Slight	300	Quarter
	4	-	8	Some	510	Much
	5.5	-	-	Some	800	Third
Plaster of Paris	1	Failed to burst well				
	2	-	4	Slight	570	Half
	3	2	-	-	360	Most
	3	3	5	Slight	210	-
	4.6	3	5	Slight	390	Quarter
Duralon	3	3	-	Slight	540	Half
Baker	3	1	-	Slight	300	Most

REVIEW OF RESULTS AND PLANS FOR FURTHER WORK

Of the various resins prepared in the laboratory, only the urea-furfural resin shows sufficient promise to warrant further work. Even this resin may be eliminated because of its instability under conditions of tropical storage. In view of the excellent performance and present relatively low cost of the several commercial casting resins available, the search for resins that may be prepared in the laboratory has been tentatively discontinued.

Fillings consisting of plaster of Paris and granulated phosphorus have shown up well in firing tests. Tests of such fillings will be extended to include compositions containing some of the commercial toughenors for plaster castings.

The commercial casting resins, Duralon, Durez, and Baker, have properties that appear to be very desirable. The value of these resins as components of phosphorus fillings in munitions will depend, however, upon the procurement or development of a bursting charge that will give satisfactory field performance with these fillings in actual munitions.

The Durez and Baker casting resins are of the phenol-formaldehyde type. ~~Another~~ resin of this type, Marblette, will be tested. Duralon is a furfural derivative and apparently is the only resin of its type on the market. Tests are planned with two other resins that apparently are of the vinyl type.

The liquid polymer, Thiokol LP-2, which may be cured at room temperature to form a rubbery solid, forms phosphorus fillings with physical properties that appear to be similar to those of PWP prepared with rubber-xylene gels. The Thiokol LP-2 fillings probably can be prepared more easily than PWP, however, and probably will prove to be more stable ballistically. Thiokol LP-2 will be tested further.

Firing tests with various bursters have indicated that rigidly solid phosphorus fillings give best performance when exploded with bursters of relatively low brisance. The search for suitable bursters is being continued.

Attempts to devise methods of determining the effect of storage under tropical conditions on phosphorus fillings also are being continued.