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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period October 1 to December 31, 1947, under Contract No. W-18-035-CWS-1318

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By

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Wilson Dam, Alabama

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Tennessee Valley Authority
Chemical Engineering Department
Wilson Dam, Alabama
January 19, 1948

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

Attention: Chief, Munitions Division

Gentlemen:

Transmitted herewith are six copies of the sixth 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 October 1 to December 31, 1947.

Very truly yours,

TENNESSEE VALLEY AUTHORITY

K. L. Elmore

K. L. Elmore, Chief
Chemical Research Division

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# PHOSPHORUS FILLINGS FOR MUNITIONS

## Progress Report on Work Performed in the Period October 1 to December 31, 1947, under Contract No. W-18-035-CWS-1318

## SUMMARY

Fillings in which granules of ~~phosphorus~~ P are cemented with Duralon, Thiokol LP-2, Thiokol LP-2 modified by the addition of ~~mercaptoethanol,~~ $HSCH_2CH_2OH$, plaster of paris, or polyvinyl alcohol-phosphorus emulsions and plaster of paris appear to be sufficiently stable in thermal stability tests at 65° C.

A pendulum-type balance for determining the location of the center of gravity along the axis of a munition has been constructed and used in evaluating the thermal stability of various ~~phosphorus~~ P fillings. ~~Shifts in the center of~~ gravity of the fillings are due entirely to movement of molten phosphorus through and out of the body of the solid sponge formed when the binder sets around the phosphorus granules. None of the binders appeared to undergo appreciable change during the thermal stability tests.

Conversions of white to red ~~phosphorus~~ P in sealed M15 grenades have been carried out with initial charges that contained about 35 ~~per cent~~ % red and 65 ~~per cent~~ % white ~~phosphorus~~ P. The reduction in maximum temperatures, and concomitant pressures, effected by the substitution of red ~~phosphorus~~ for a part of the white ~~phosphorus~~ P charge was much less than was expected, and the work entailed in partial conversion of white to red ~~phosphorus~~ P before charging into the munition does not appear to be justifiable by the small lowering in temperature that is obtained in the final conversion.

## PHOSPHORUS FILLINGS FOR MUNITIONS

### Progress Report on Work Performed in the Period October 1 to December 31, 1947, under Contract No. W-18-035-CWS-1318

In the 3-month period covered by this progress report, work was confined largely to a study of the physical properties and thermal stabilities of fillings comprising granulated white phosphorus bound with Duralon, Thiokol LP-2, ordinary plaster of paris, and plaster of paris set with an emulsion of phosphorus in polyvinyl alcohol. The immediate objective was a determination of the optimum compositions of fillings to be charged into 4.2-inch CM shells for tests at the Army Chemical Center.

Since fillings consisting largely of massive red phosphorus, prepared by the thermal conversion of white phosphorus in the sealed munition, had shown promise, study was directed toward a reduction in the peak temperature and attendant pressure during the exothermic conversion through the use of a mixture of red and white phosphorus as the initial charge.

## PHYSICAL PROPERTIES OF FILLINGS

### Specific Gravity

The specific gravities of cast specimens of the various binders used in the preparation of phosphorus fillings were determined by the water-displacement method. The results, together with estimates of the specific gravities and phosphorus contents of fillings prepared with the binders, are listed in Table I. Each of the fillings in the table contained the same amount of granulated white phosphorus, 63 per cent of the amount of massive white phosphorus that would occupy the same space as the fillings.

Emulsions of phosphorus in aqueous polyvinyl alcohol solutions were found to contain relatively large quantities of gas that apparently had been incorporated in the mixtures in their preparation. The amount of occluded gas and the rate of its escape from the emulsions are indicated by the apparent specific gravities listed in Table II. The specific gravities were determined by measuring the apparent weight of a steel bob suspended in the emulsions; the reproducibility of the measurements was of the order of ±3 per cent.

TABLE I

Specific Gravities of Binders and Phosphorus Fillings Prepared with Them

| Binder | Sp. gr. of binder | Phosphorus filling[a] Sp. gr. | Phosphorus filling[a] Phosphorus content, wt. % |
|---|---|---|---|
| Durez casting resin | 1.225 | 1.59 | 71 |
| Baker casting resin | 1.184 | 1.58 | 71 |
| Durelon 30 | 1.286 | 1.62 | 70 |
| Thiokol LP-2[b] | 1.278 | 1.61 | 70 |
| Plaster of paris[c] | 1.509 | 1.70 | 66 |

[a] Estimated on the assumptions that the granulated WP contains 37% voids and that the amount of binder is 105% of that required to fill the void spaces.

[b] Cured with 20% furfural and 4% formic acid. Incorporation of 1% mercaptoethanol has little effect on the tabulated values.

[c] Prepared with equal weights of plaster and water.

TABLE II

Apparent Specific Gravities of 50 Per Cent Emulsions of

White Phosphorus in Aqueous Polyvinyl Alcohol

| Viscosity rating of alcohol → | High | High | High | Medium |
|---|---|---|---|---|
| Concn. of alcohol in soln., wt. % → | 8 | 8 | 4 | 8 |
| Time after prepn., hr. | Apparent specific gravity | | | |
| 0.25 | - | - | 0.37 | 0.67 |
| 0.50 | 0.74 | 0.93 | 0.48 | 0.78 |
| 1 | - | - | 1.26 | 0.93 |
| 2 | 1.04 | 1.15 | 1.30 | 1.30 |
| 3 | - | - | 1.30 | 1.37 |
| 4 | - | - | 1.30 | 1.41 |
| 5 | - | - | 1.30 | 1.30 |
| 24 | - | - | 1.30 | 1.30 |
| 48 | 1.33 | 1.35 | - | - |

Although Table II indicates that substantially all the occluded gas escaped from the emulsion in 4 hours, fillings prepared with granulated phosphorus, polyvinyl alcohol-water-phosphorus emulsions, and plaster of paris more than filled M15 grenades when the weights of the materials taken were calculated to occupy a volume of only 225 cc. A sample of the filling was allowed to set in a glass sample bottle. The filling then was observed to contain numerous gas pockets, and rough measurements indicated that the apparent specific gravity of the filling was 1.42 instead of approximately 1.75 as estimated from the known specific gravities of the components. Hence, the gas pockets must have occupied about 19 per cent of the total volume of the filling. The occluded gas evidently was incorporated into the mixture when the granulated phosphorus, emulsion, and plaster of paris were mixed in a beaker with a spatula. Rodding the freshly charged filling in the grenade and tapping the grenade on a solid base before the burster well was inserted were of no avail in settling the filling so as to expel the occluded gas. In spite of this undesirable property of occluding gas, however, this type of filling has performed excellently in all firing tests, and grenades filled with this material contain more phosphorus than grenades filled with any other filling prepared from granulated white phosphorus. Moreover, the plaster-emulsion fillings appear to be thermally stable and quite promising.

Thermal Stability

In evaluating the thermal stability of phosphorus fillings, a filled munition is heated for 8 hours at 65° C. while lying on its side and then is allowed to cool in the same position. The static unbalance of the munition is determined by measuring the weight, suspended from a string wrapped around the munition, required to maintain the munition at equilibrium on a horizontal plane when it has been rotated 90° from its natural rest point. The unbalance is reported as the shift of the center of gravity of the munition from the geometric longitudinal axis.

A method was devised for determining the position of the center of gravity of the filled munition along its longitudinal axis as well as the lateral shift from the axis. The apparatus is a rectangular cradle in which an M15 grenade can be supported so that the longitudinal axes of the cradle and the grenade approach parallelism in a vertical plane. The cradle is suspended from a pair of knife edges, a line through the bearing edges being substantially perpendicular to the vertical plane that passes through the longitudinal axis of the cradle. A mirror, attached to the beam connecting the knife edges, reflects the ray of light from a galvanometer lamp to a vertical scale.

To locate the center of gravity of a grenade along its longitudinal axis, the munition is placed in the cradle and weights are suspended from the appropriate end of the cradle at a known distance from the center of gravity of the cradle to bring the ray of light reflected from the mirror on the knife-edge beam back to the original zero point on the vertical scale. The weight of the munition being known, the distance of the center of gravity of the munition from the center of gravity of the cradle is calculated readily. The munition is placed with its base at a known position, so that the distance of the center of gravity of the munition from its base, which is taken as the most convenient reference point, is determined.

Previous results of thermal stability tests have been reported as the actual shift, in millimeters, of the center of gravity of the munition from the longitudinal axis. Work covered by the present report included samples in both M15 grenades and glass sample bottles. Since neither the ratio of the weight of the filling to that of the container nor the dimensions of the containers are the same, the present results are reported in percentages. All values are calculated on the basis of the filling alone.

The reported values can be converted to values applicable to M15 grenades by dividing by 2, since the weight of the container is approximately equal to that of the usual filling, or to values applicable to 4.2 CM shells by dividing by 3, since the weight of the container is approximately twice that of the usual filling. The lateral shift of the center of gravity from the longitudinal axis is expressed as a percentage of the internal diameter of the cylindrical section of the munition, and the shift of the center of gravity in the direction parallel to the longitudinal axis of the munition is expressed as a percentage of the original distance of the center of gravity of the filling from the outside bottom of the munition. In a normally filled M15 grenade the original center of gravity lies between 40 and 45 per cent of the total length of the grenade case, while the center of gravity of the empty case with burster well in place is between 64 and 66 per cent of the length of the case above the base.

It is assumed that the maximum shift in center of gravity would be obtained with a material such as massive white phosphorus, which is a solid at room temperature but which behaves as a fluid at the temperature of the test. The values in Table III show the shifts in center of gravity of the filling that are obtained when M15 grenades containing various amounts of massive white phosphorus are subjected to thermal stability tests.

TABLE III

Shift of Center of Gravity of Massive White Phosphorus

Fillings in M15 Grenades in Thermal Stability Test

| Wt. of phosphorus filling, g. | Lateral shift from long. axis | | Distance from base of grenade | | |
|---|---|---|---|---|---|
| | Cm. | % of dia. | Orig., cm. | Heated, cm. | Change, % |
| 372 | 0.54 | 9.3 | 4.36 | 5.34 | 22.5 |
| 383 | 0.49 | 8.4 | 4.50 | 5.35 | 18.9 |
| 392 | 0.41 | 7.2 | 4.59 | 5.35 | 16.6 |
| 404 | 0.35 | 6.1 | 4.71 | 5.28 | 12.1 |
| 411 | 0.34 | 5.9 | 4.80 | 5.37 | 11.9 |
| 415 | 0.29 | 5.0 | 4.85 | 5.34 | 10.1 |

Three series of fillings prepared from granulated phosphorus with Duralon and Thiokol LP-2 binders were placed in 4-oz. glass sample bottles. When the preparations had cured, the center of gravity was located, and the samples then were subjected to an 8-hour thermal stability test. The results of the tests are shown in Table IV. The bottles were about 4.5 cm. in diameter and 10 cm. tall, inside dimensions. Included in Table IV are estimated values that could be anticipated in similar tests with massive white phosphorus fillings occupying the same volumes as the experimental fillings.

An inspection of the samples showed that molten phosphorus had run out of the filling and settled between the top of the filling and the top of the bottle. The amount of phosphorus that ran out of each filling is shown in column 3 of Table IV. The lateral unbalance resultant from this displacement of phosphorus amounted to between 50 and 90 per cent of the total lateral unbalance of the entire sample, so that there apparently had been some settling of phosphorus through the solid sponge of cured binder. When the treated samples were reheated for 8 hours at 65° C., standing upright, the lateral unbalance decreased substantially to zero, but the centers of gravity of the fillings remained slightly above the original centers of gravity. Much of the phosphorus remained on top of the body of the filling rather than returning to its original position.

TABLE IV

Thermal Stability Tests of Duralon and Thiokol LP-2

Fillings in Glass Sample Bottles

| Sample no. | Binder, %[a] | Loss of WP, %[b] | Shift of center of gravity: Lateral, % of dia. | Shift of center of gravity: Long., % of orig. | Estd. shift of c.g. for massive WP with same volume: Lateral, % of dia. | Estd. shift of c.g. for massive WP with same volume: Long., % of orig. |
|---|---|---|---|---|---|---|
| Duralon | | | | | | |
| E56 | 56 | 34 | 12.6 | 50.9 | 17.9 | 61.8 |
| E80 | 80 | 36 | 7.7 | 27.7 | 17.2 | 58.0 |
| E100 | 100 | 7 | 2.6 | 4.0 | 14.8 | 45.3 |
| E120 | 120 | 3 | 1.8 | 3.5 | 12.2 | 34.6 |
| Thiokol LP-2[c] | | | | | | |
| J80 | 80 | 16 | 4.8 | 10.3 | 17.4 | 58.8 |
| J100 | 100 | 4 | 1.9 | 6.4 | 14.0 | 42.1 |
| J120 | 120 | 2 | 1.8 | 3.3 | 12.6 | 36.3 |
| Thiokol LP-2 with mercaptoethanol[d] | | | | | | |
| M80 | 80 | 18 | 5.8 | 15.0 | 17.0 | 56.5 |
| M100 | 100 | 11 | 1.9 | 4.8 | 14.8 | 45.3 |
| M120 | 120 | 5 | 2.5 | 2.7 | 14.8 | 45.3 |

[a] Per cent of amount of binder required to fill all void spaces in the granulated phosphorus. Granulated phosphorus consisted of 60% minus 4- plus 8-mesh and 40% minus 8-mesh granules.
[b] Per cent of total phosphorus charged that ran out of body of the filling.
[c] Cured with 20% furfural and 4% formic acid.
[d] Contained 1% mercaptoethanol; cured with 20% furfural and 4% formic acid.

The data in Table IV indicate, however, that the fillings were fairly stable thermally when sufficient binder was present to ensure substantially complete covering of the phosphorus granules. It is concluded that most of the shift of the center of gravity of these fillings is attributable to the movement of phosphorus into the void space in the container. The glass sample bottles were filled to only about 65 per cent of their capacity, whereas 85 per cent of the total space customarily is occupied by the filling in both M15 grenades and 4.2 CM shells. More complete filling obviously would permit less movement of molten phosphorus, so that a higher apparent thermal stability could be expected in actual munitions than was obtained in tests in the glass sample bottles.

Phosphorus fillings in which phosphorus granules were cemented with ordinary plaster of paris and with plaster of paris set with phosphorus-polyvinyl alcohol emulsion were placed in M15 grenades and subjected to thermal stability tests. The results are shown in Table V. Each filling occupied approximately the volume that would hold 420 grams of massive white phosphorus, the calculated shift of center of gravity of which may be estimated from the data in Table III. The thermal stability of the fillings bound with ordinary plaster of paris was uniformly high; the somewhat lower stability of the emulsion fillings apparently was caused by movement of phosphorus downward through the body of the fillings without a concomitant movement of phosphorus into the void space of the munition. The lateral shift of the center of gravity in the emulsion-bound fillings was about twice that in the ordinary plaster fillings, but the change in the distance of the center of gravity from the base of both types of filling was about the same.

TABLE V

Thermal Stability Tests of Plaster of Paris and

Polyvinyl Alcohol Emulsion Fillings in M15 Grenades

| Sample no. | Size of granulated phosphorus[a] | Lateral shift from long. axis | | Dist. from base of grenade | | |
|---|---|---|---|---|---|---|
| | | Cm. | % of dia. | Orig. cm. | Heated cm. | % change |
| Plaster of paris | | | | | | |
| C12A | 60-40 | 0.093 | 1.61 | 5.01 | 5.11 | 1.8 |
| C12B | 60-40 | 0.039 | 0.68 | 5.00 | 5.03 | 0.7 |
| C12C | 40-60 | 0.040 | 0.70 | 5.02 | 5.04 | 0.4 |
| C12D[b] | 40-60 | 0.041 | 0.71 | 4.97 | 4.90 | -1.4 |
| C12E[b] | 20-80 | 0.022 | 0.38 | 4.90 | 4.99 | 1.8 |
| C12F[b] | 20-80 | 0.043 | 0.74 | 4.86 | 5.25 | 7.9 |
| Polyvinyl alcohol emulsion-plaster of paris | | | | | | |
| L4A | 60-40 | 0.108 | 1.88 | 4.81 | 5.00 | 4.0 |
| L4B | 60-40 | 0.126 | 2.18 | 5.37 | 5.43 | 1.1 |
| L4C | 40-60 | 0.061 | 1.06 | 5.43 | 5.41 | -0.4 |
| L4D | 40-60 | 0.123 | 2.14 | 5.36 | 5.42 | 1.1 |
| L4E[b] | 20-80 | 0.130 | 2.26 | 5.39 | 5.51 | 2.1 |
| L4F[b] | 20-80 | 0.138 | 2.40 | 5.41 | 5.44 | 0.6 |

[a] The first figure is the percentage of minus 4- plus 8-mesh, and the second the percentage of minus 8-mesh granulated phosphorus.
[b] Leaked phosphorus through threads of burster well.

Thermal stability tests in M15 grenades have been complicated by leakage of phosphorus past the burster-well threads in about a third of the grenades. The threads generally have been doped with Aquadag. In the tests reported in Table V, however, attempts were made to seal the threads of the burster wells with solder. Since these attempts obviously were unsuccessful, burster-well threads now are being doped experimentally with activated Duralon and Thiokol LP-2 in the hope of obtaining a phosphorus-tight screwed fitting.

## PREPARATION OF RED PHOSPHORUS

### Analysis of Product

Two grenades in which red phosphorus had been prepared by conversion of a charge of white phosphorus were cut open, and portions of the products were analyzed for white phosphorus by extraction with benzene. A product of the conversion of white phosphorus with 1 per cent sulfur as catalyst contained 0.73 per cent white phosphorus, and a product prepared by the uncatalyzed conversion of white phosphorus contained 0.86 per cent white phosphorus.

The phosphorus was manipulated under water, and samples for analysis were dried at room temperature in a current of dry carbon dioxide. The product of the catalyzed conversion contained small drops of a liquid that appeared to be the 80-20 phosphorus-sulfur eutectic.

### Partially Converted White Phosphorus

The reaction by which white phosphorus is converted to red phosphorus is markedly exothermic, and when the conversion is carried out in a closed container the heat is generated so rapidly that external cooling of the container does not remove the heat fast enough to provide any effective control of the temperature and concomitant pressure in the reaction mass. Since maximum conditions of 590° C. and 630 pounds per square inch may be developed in the conversion, it seemed desirable to devise means by which the severity of these conditions might be reduced. It was assumed that an initial charge that contained some red phosphorus would develop lower temperatures and pressures during the conversion than would a charge consisting entirely of white phosphorus.

There was available a quantity of partially converted white phosphorus that had been left over from the operation of a pilot plant for the production of red phosphorus. This material melted and flowed like crude white phosphorus; the red phosphorus could be filtered from the molten mixture, and when the molten mixture was allowed to stand, the red phosphorus settled to the bottom of the container. The original mixture contained about 17 per cent red phosphorus, and a mixture containing about 35 per cent red phosphorus was obtained by a settling-and-decanting procedure.

Six M15 grenades were filled with the 65-35 white-red phosphorus mixture, and to three of these grenades there was added sulfur equivalent to about 1 per cent of the white phosphorus present. The grenades then were heated to convert the charge largely to red phosphorus. In the uncatalyzed samples, the rapid reaction started at temperatures between 265° and 295° C., and the maximum temperatures reached in the quenched grenades were between 500° and 526° C. In the catalyzed samples the rapid reaction started at 265° to 270° C., and the maximum temperatures in the quenched grenades were between 523° and 531° C. In comparison, the rapid conversion of initial charges of substantially pure white phosphorus started at 320° to 330° C. in uncatalyzed charges and at 280° to 290° C. in charges catalyzed with 1 per cent sulfur, and the maximum temperatures in quenched grenades were 563° C. in uncatalyzed charges and 544° C. in catalyzed charges. Partial conversion of white to red phosphorus before charging into the munition in which the conversion is to be completed does not seem to be worth the trouble it entails.

## REVIEW OF RESULTS AND PLANS FOR FURTHER WORK

The data in Tables IV and V on the thermal stabilities, as determined by movements of the centers of gravity of phosphorus fillings bound with Duralon, Thiokol LP-2, ordinary plaster of paris, and plaster of paris set with an emulsion of polyvinyl alcohol and phosphorus indicate that storage at 65° C. has slight effect on the fillings. The measurements were made by static methods, however, and the results cannot be projected to an evaluation of the ballistic stability of a rapidly rotating projectile containing such charges. Since these measurements are the only means available at present for estimating the thermal stability of experimental fillings, they will continue to be used to select, among such variables as particle size of the granulated phosphorus and proportion of binder in the filling, the optimum compositions of the fillings to be placed in the 4.2-inch CM shells that are to be subjected to storage and firing tests at the Army Chemical Center.

Although the substitution of red phosphorus for 35 per cent of an initial charge of white resulted in only a small decrease in the maximum temperature obtained in the conversion of white to red phosphorus in sealed grenades, several of the twelve 4.2-inch CM shells that are to be filled with massive red phosphorus will be charged with the red and white phosphorus mixture. Equipment for the conversion of white to red phosphorus in sealed shells is being procured and assembled.

Further work on fillings comprising granulated white phosphorus and binders will be limited to study of methods of preparation and to determination of thermal stabilities of the various fillings, so that the 4.2-inch CM shells may be charged with fillings that reasonably may be expected to give the best performance possible for each type of filling.

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