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NEW POTENTIALS IN RED PHOSPHORUS COMPOSITIONS

NAVAL WEAPONS SUPPORT CENTER
APPLIED SCIENCES DEPARTMENT
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New phosphorus compositions have been demonstrated which meet the current burning rate and smoke volume requirements but do not contain pyrolusite and/or magnesium. Phosphorus composition which used chlorotrifluoroethylene as an oxidizer-binder combination and magnesium as a fuel had reciprocal burning rates of 42-73 s/in. Phosphorus compositions which used calcium sulfate as the oxidizer and boron as the fuel had reciprocal burning rates of 80-130 s/in. These compositions have the advantages of (1) containing no pyrolusite, a foreign-supplied material, and (3) containing no magnesium. The elimination of magnesium reduces the possibility of hydrogen generation in sealed units when subjected to high temperature storage. Recommendations for further work are given.

PREFACE

The authors would like to thank Mr. John Brown, Mr. Ed Colvin and Mr. William T. Biggs for their assistance in the production of the flare candles. The typing of Ms. Sondra Williams is also acknowledged.

A

INTRODUCTION

Red phosphorus compositions are currently in use in Navy pyrotechnic devices which are used as Marine Location Markers. With the increased interest in new screening capabilities, it seems likely that the red phosphorus compositions will find increased use in this area. A typical red phosphorus composition contains 51% phosphorus, 35% pyrolusite (MnO_2), 8% magnesium, 3% ZnO and 3% binder.[1] When this composition is ignited, the magnesium and MnO_2 react as a thermite to generate heat and vaporize the phosphorus. The phosphorus vapor then burns in the surrounding atmosphere to produce a dense white smoke and a yellow flame. The phosphorus composition is typically long burning with an average rate of 2.42×10^{-2} cm/sec.

The phosphorus compositions as they now exist in the Mk 25 and Mk 58 Marine Location Markers suffer from two basic problems. One problem is that one of the key ingredients, pyrolusite (MnO_2), is a foreign-supplied material. The material as it is now used is an ore and had many impurities, up to 20%. Pyrolusite is not mined in the United States at this time.

The second more severe problem is the production of hydrogen in the sealed Mk 25 and Mk 58 units often causing them not to pass the required standard temperature and humidity tests. This problem is probably a result of the reaction of magnesium with the water trapped in the signal during production. Magnesium is known to react with water according to the equation[2]

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2.$$

The reaction rate is increased at higher temperatures. This generation of hydrogen in a sealed pyrotechnic system leads to severe pressure build-ups which could result in explosion and accidental ignition of the units. While this has not happened in the current phosphorus units, it has

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[1] H. Ellern, *Military and Civilian Pyrotechnics* (Chemical Publishing Company, New York, 1968), p. 359.

[2] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Volume IV (John Wiley and Sons, Inc., New York, 1922), p. 266.

happened for identical reasons in sealed aircraft parachute flares.[3] Bulging of the case and end cap has been observed in the Mk 25 and Mk 58 phosphorus units.

The purpose of this work was to explore new phosphorus compositions which (1) contain no magnesium or pyrolusite, (2) contained no pyrolusite and used a radiation polymerization processing technique which "encapsulates" the magnesium, and (3) used a refined grade of manganese dioxide to improve efficiency and reliability. The compositions should have the same burning characteristics in terms of burning rates and smoke volume as standard phosphorus units. The compositions without pyrolusite and magnesium and with encapsulated magnesium were developed to eliminate the problems of foreign-supplied materials and degradation of units during high temperature storage. The composition with refined manganese dioxide was developed to show that this material could be used successfully in phosphorus composition leading to more reliable signals.

EXPERIMENTAL

Radiation Polymerized Candles

These compositions were developed to demonstrate a phosphorus composition which contained no pyrolusite and which "encapsulated" the magnesium in such a way as to reduce the possibility of the magnesium-water reaction occurring.

The compositions were produced by the radiation curing technique described by Parrish, Short and Biggs.[4] Red phosphorus, magnesium and zinc oxide were mixed and loaded into aerosol cans. These cans were then filled with chlorotrifluoroethylene (CTFE) gas to a pressure where CTFE became a liquid. The aerosol cans were placed in a 10000 curie Co-60 irradiation chamber. The total dose level was approximately 8 megarads. At this dose level, all the CTFE was converted to polymeric CTFE.

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[3] *Airborne Weapon Corrective Action Program, Pyrotechnic Devices*, NAVAIR Report No. 5400.2, Naval Missile Center, Point Mugu, California (November 1973).

[4] C. F. Parrish, J. E. Short and W. T. Biggs, *Radiation-Polymerization Binder for Mk 48 Decoy Flares*, RDTR No. 232, Naval Ammunition Depot, Crane, Indiana (February 1973). Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, AD No. 755476.

The magnesium used in this study was JAN-M-382 magnesium with an average particle size of 400 microns. The phosphorus was stabilized red phosphorus, JAN-P-670. The chlorotrifluoroethylene was a standard commercial grade obtained from Matheson Gas Corp. and was used without further purification.

After polymerization, the candles were removed from the cans and wrapped with masking tape prior to burning. Examination of the candle revealed that the composition was well mixed and there was no layering of the ingredients.

The exact composition of the candles are given in Table 1. The completed candles were 12.7 cm long, 4.45 cm in diameter, and weighed approximately 480 grams. A standard mix "6-6-8", composed of 30% PbO_2, 30% CuO and 40% Si, was used as the ignition composition.

Phosphorus-Boron-Calcium Sulfate Candles

These compositions were developed to demonstrate a phosphorus composition which contained no pyrolusite and no magnesium. The composition contained boron as the fuel and calcium sulfate as the oxidizer instead of magnesium and pyrolusite. Boron was chosen in these experiments since it does not react readily with water[5] thus eliminating the hydrogen generation problem. Calcium sulfate was used as the oxidizer since it has been previously reported as an oxidizer in phosphorus compositions.[6] The calcium sulfate was obtained from Matheson, Coleman and Bell Chemical, Norwood, Ohio. The anhydrous calcium sulfate was a purified grade and was used without further treatment. The boron used was MIL-B-51092.

This series of candles was produced using a more conventional technique. The process used has been called wet mixing, precipitation or coacervation.[7] In this process a mixture of

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[5] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume V* (John Wiley and Sons, New York, 1922), p. 14.

[6] M. G. Palmer and A. D. Ball, *Phosphorus-Containing Compositions*, U.S. Patent No. 3,884,734, Class 149-6 (20 May 1975).

[7] S. L. Howlett, *A Continuous Wet Mixing Method for Flare Compositions*, RDTP No. 138, Naval Ammunition Depot, Crane, Indiana (February 1969). Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, AD No. 684446.

Table 1. Radiation Polymerization Compositions

	1	2	3
Magnesium	25.3	17.8	12.0
Phosphorus	36.1	39.8	46.1
Zinc Oxide	1.9	1.8	1.8
Chlorotrifluoroethylene	36.7	40.6	40.1

Table 2. Conventional Compositions

	4	5	6	7
Boron	--	3	5	10
Magnesium	11	--	--	--
Calcium Sulfate	--	44	42	37
Electrolytic MnO_2	32	--	--	--
Phosphorus	51	50	50	50
Zinc Oxide	3	--	--	--
Viton A®	3	3	3	3

the ingredients is made in a binder/solvent solution. When the ingredients are thoroughly combined, a non-solvent is added. The addition of the non-solvent causes the polymer to precipitate and coat the solid ingredients in the solution with binder. The excess solvent and non-solvent are then evaporated leaving an intimate mixture of the ingredients coated with the polymer. This mixing technique was chosen for this study because it is somewhat safer than other processing techniques.

Viton A® was used as the binder in all formulas. The Viton® was dissolved in acetone and the phosphorus, boron and calcium sulfate were added to this mixture. Hexane was then added to the solvent mixture until the polymer-coated ingredients precipitated as described previously. The acetone and hexane were dried with calcium chloride prior to use. The mixture was then dried and pressed into fishpaper tubes.

The formulas for these compositions are given in Table 2. The candles were 12.7 cm long, 4.45 cm in diameter and contained 300 grams of composition. A standard ignition composition, 6-6-8, was pressed on the surface of each candle.

Electrolytic MnO_2 - Phosphorus Candles

This composition was developed to show that a phosphorus composition could be made using a refined grade of manganese dioxide. The composition had a formula similar to a standard unit with the exceptions that (1) electrolytic grade manganese dioxide was used instead of pyrolusite, and (2) Viton® was used as the binder instead of linseed oil.

The manganese dioxide was obtained from Kerr-McGee Chemical Corporation, Glen Ellyn, Illinois. The magnesium was JAN-M-382 magnesium with an average particle size of 150 microns. The candles were made using the same techniques and conditions described for the boron-calcium sulfate-phosphorus composition.

The formula for this composition is also given in Table 2. The completed candles were 12.7 cm long, 4.45 cm in diameter, and contained 300 grams of composition. The standard 6-6-8 ignition composition was pressed on the surface of each candle.

RESULTS

The seven compositions given in Tables 1 and 2 were burned and the burning times were measured. In all cases, a yellow flame and a dense white smoke were produced. Ignition of the candles was very easy with only the 6-6-8 starter mix. Figures 1, 2 and 3 show typical smoke and flame production during the course of the burn for compositions 1, 4 and 5, respectively. For the radiation polymerized candles, compositions 2 and 3, where the ratio of magnesium to CTFE was smaller, the smoke cloud tended to be gray. Table 3 gives the measured burning rates and reciprocal burning rates. Since all the compositions contained essentially the same amount of phosphorus, the volume of smoke was approximately proportional to the burning rate, i.e., the faster the burning rate the larger the smoke cloud produced, as one would expect.

CONCLUSIONS AND RECOMMENDATIONS

Radiation Polmerized Candles

Phosphorus compositions have been demonstrated which use chlorotrifluoroethylene as a binder/oxidizer combination. The compositions were prepared by a gamma-radiation polymerization technique. When burned, these compositions produced a yellow flame and dense white or gray smoke depending on the ratio of magnesium to chlorotrifluoroethylene. The burning rates vary from 1.5-2.5 times the burning rate of a standard phosphorus composition. The increased burning rate can be lowered by using a larger particle size magnesium, by substituting a less energetic fuel for the magnesium or by increasing the ratio of phosphorus to the fuel/oxidizer combination. These compositions have the advantage that they do not contain pyrolusite. Although it was not demonstrated in this study, compositions could be made with a fuel other than magnesium, e.g., boron, by this technique without difficulty. This would then eliminate the hydrogen generation problem. The compositions have the additional advantages that (1) they are safer and easier to process, and (2) the processing technique is a "castable" system which allows for the production of candles in virtually any shape or configuration.

For example, the phosphorus/fuel combination could be loaded into a spiral tube, filled with CTFE and polymerized. This would result in a shorter coiled candle which when placed in the bottom of a location marker would lower both the centers of buoyancy and gravity and thus improve the functioning of marine location markers.

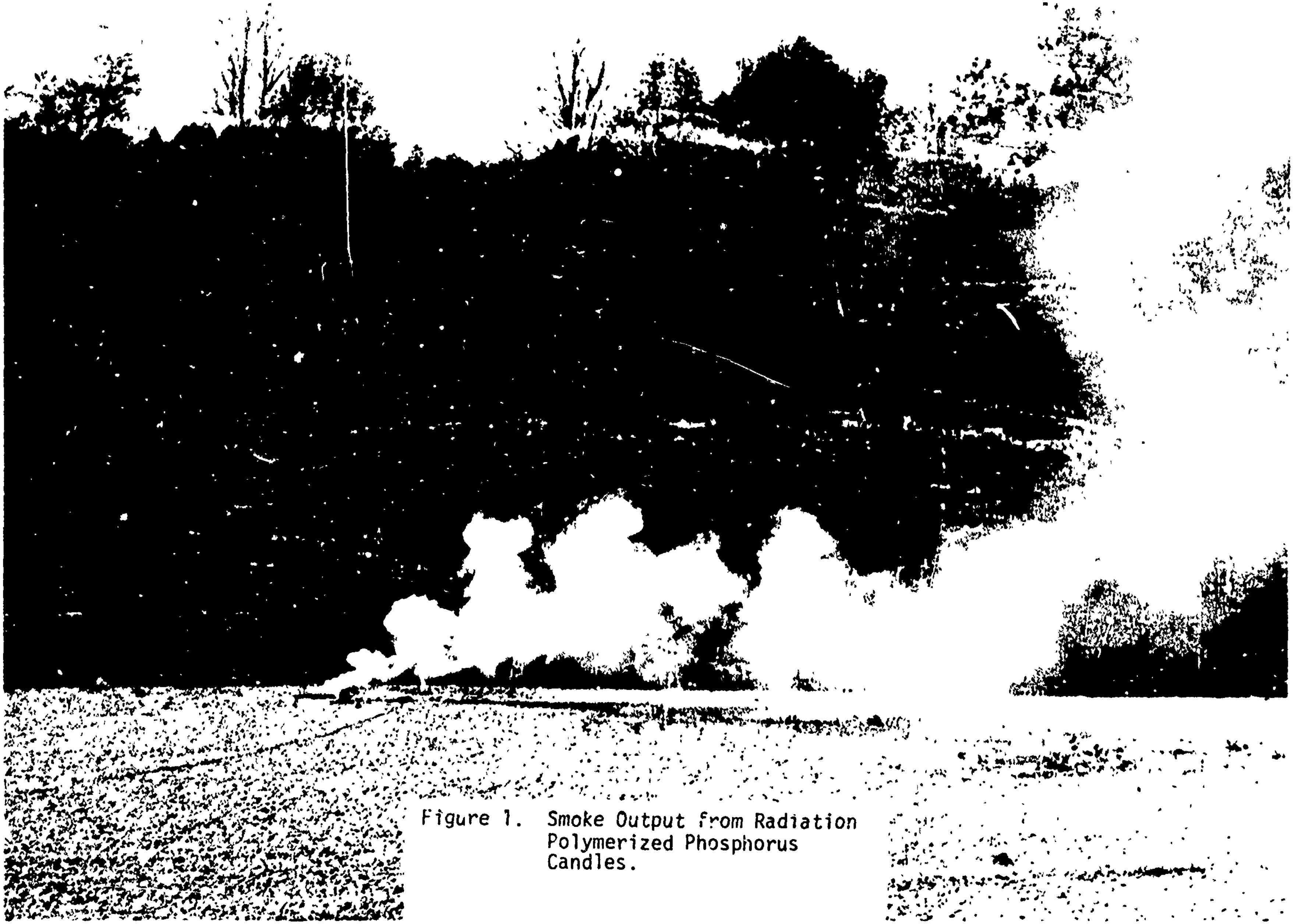

Figure 1. Smoke Output from Radiation Polymerized Phosphorus Candles.

Figure 2. Smoke Output from Phosphorus Candles Using MnO_2

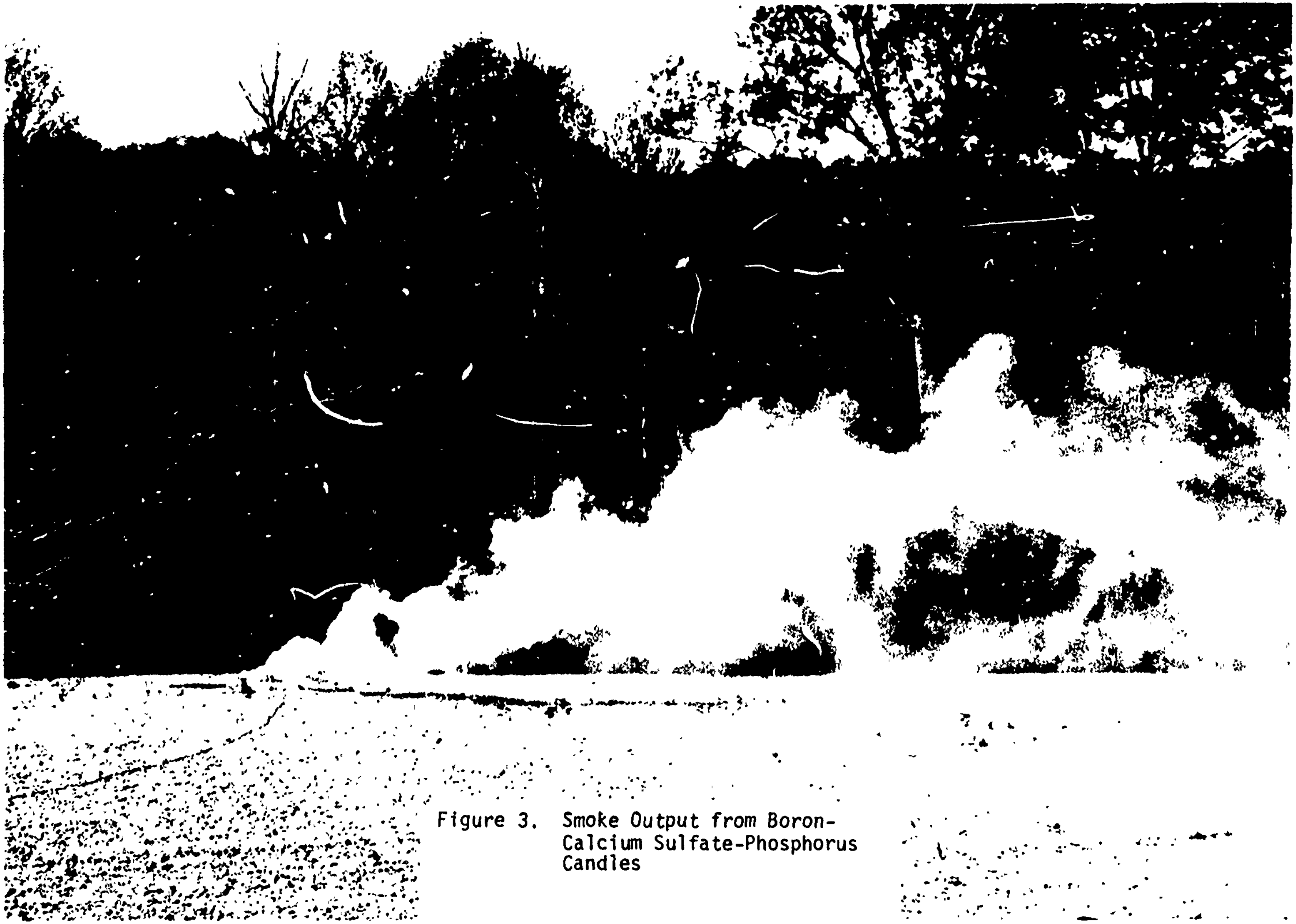

Figure 3. Smoke Output from Boron-Calcium Sulfate-Phosphorus Candles

Table 3. Experimental Results

Formula No.	Burn Rate (cm/sec)	Reciprocal Burn Rate s/cm	s/in
1 (Rad Poly)	6×10^{-2}	16.5	42.0
2 (Rad Poly)	5.3×10^{-2}	18.9	48.0
3 (Rad Poly)	3.5×10^{-2}	28.9	73.4
4 (MnO_2)	5.8×10^{-2}	17.2	43.8
5 ($B/CaSO_4$)	2×10^{-2}	49.7	126.0
6 ($B/CaSO_4$)	2.7×10^{-2}	37.8	96.0
7 ($B/CaSO_4$)	3.2×10^{-2}	31.5	80.0
Standard	2.4×10^{-2}	41.3	105.0

Phosphorus-Boron-Calcium Sulfate Candles

Phosphorus compositions which use boron as a fuel and calcium sulfate as an oxidizer have been demonstrated. These compositions were prepared using a Viton® binder and a precipitation technique for processing. When burned, the compositions produced a dense white smoke and yellow flame. The burning rates were comparable to a standard formulation. These compositions have the advantages of (1) no pyrolusite, and (2) no magnesium, the contributing factor in the production of gaseous species in a sealed unit. Although no attempt was made to determine the stability of the compositions when subjected to high temperature storage tests, there are no known water-related reactions of boron which could lead to the production of gases.

Electrolytic MnO_2 - Phosphorus Candles

A phosphorus composition has been made which used electrolytic grade MnO_2 instead of pyrolusite. The composition burns vigorously and produces a dense white smoke and a yellow flame. The composition tested burns 2.4 times faster than a standard composition. The burning rate can be lowered by reducing the amount of magnesium, substituting a less energetic fuel for magnesium or increasing the binder level.

This composition has the advantages of improving the reliability and effectiveness of phosphorus signals due to the use of a purer material. This purer material might also improve the storage life of phosphorus compositions.

The following recommendations can be made.

1. The phosphorus-boron-calcium sulfate system should be examined for gas production under high temperature storage requirements. Since the reaction of boron and water is very slow even at high temperatures, there is little possibility for the production of gaseous species from this composition. If this is in fact the case, the phosphorus-boron-calcium sulfate system can be recommended for direct substitution into the standard Mk 25 and Mk 58 Marine Location Markers thus providing the Navy with phosphorus signals which contain no foreign-supplied material and which will conform to standard temperature and humidity evaluations.

2. The radiation polymerized phosphorus composition should be tested for high temperature storage requirements. There is the possibility that the processing technique used will sufficiently "encapsulate" the magnesium to reduce the

magnesium-water reaction to an acceptable level. This composition should also be reformulated with different fuels and different particle sizes so that it will meet the slower burning rate requirements. There are no anticipated problems with carrying out this reformulation.

3. The radiation polymerization composition should be cast in various configurations to show the feasibility of this concept. A spiral phosphorus candle, i.e., the same amount of composition in a shorter candle, would reduce existing flotation problems and provide a more reliable phosphorus signal.

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