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EXPLOSIVE COMPOSITION CONTAINING ALUMINUM, POTASSIUM PERCHLORATE, AND SULFUR OR RED PHOSPHORUS

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The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to an explosive composition, the products of which are soluble in water.

In the area of underwater explosive research the characteristics of explosion are generally determined by limiting the boundary conditions for simplification of the mathematics involved. Two assumptions made are that generally the gaseous products of detonation do not dissolve in water to any appreciable extent, and the gaseous products at all times assume the form of a spherical bubble and behave as a permanent gas. It is postulated that on detonation of an underwater explosive a shock wave is first produced, then the gaseous products of the explosive expand to form a bubble. Inertial effects cause the bubble to overexpand to a low pressure, following which the hydrostatic pressure of the surrounding water recompresses the bubble. This process may repeat itself five or six times before the bubble breaks up or escapes from the water. A great amount of the energy of explosion is by this mechanism dissipated in the formation of the bubble and its oscillations. Experimental evidence reveals that approximately 50% of the original energy of the explosive is stored in the bubble. To avoid this loss research was carried on to find an explosive which produces condensable products. Systems based on the conventional C—H—O—N explosives are not satisfactory because of the insoluble gases produced after the detonation. In cases where the amount of gaseous products were a minor fraction of the mass, as in metal-perchlorate binary systems, the results gave a low yield on a calories/gram basis. The present invention produces greater energy per gram and the end products (gases or condensable solids) are extremely soluble in water.

An object of the present invention is to provide an explosive for use in underwater weapons systems which produce condensable products.

Another object of this invention is to provide an explosive which will produce a sharply-defined detonation underwater aimed at production of a single pressure-time pulse with increased explosive-energy yield and power, and minimum energy loss through bubble formation and osscillation.

Still another object is to provide an explosive for use in cratering operations.

A further object of the invention is the provision of an explosive with increased energy yield and power which is inexpensive, efficient, reliable, and stable to high temperatures.

Other objects, features and many of the attendant advantages of this invention will become readily appreciated as the same become better understood by reference to the following detailed description.

The underwater explosive composition of this invention consists essentially of a metallic element or alloy which produces an oxide exothermically, such as aluminum, vanadium, and uranium; a perchlorate which does not contain a gas forming element selected from the group consisting of potassium, sodium, barium, and lithium; and an inflammable non-metal selected from the group consisting of sulfur and phosphorus.

The following examples are illustrative of the invention but should not be considered as limiting it.

EXAMPLE I

Ingredients:	Percent by weight
Aluminum	18.3
Sulfur	14.6
Potassium perchlorate	67.1

The above ingredients were dry blended for about one-half hour. Every precaution must be taken to prevent the accumulation and discharge of charges of static electricity as the dust produced within the blender makes it hazardous. The thoroughly mixed composition is then transferred to air-tight containers for temporary storage.

The composition may be wet mixed using hexane or other suitable liquid compatible with the ingredients. The weighed ingredients are placed in a pan with sufficient liquid to form a thick paste. The material is mixed until the composition becomes sufficiently granular to be screened but is not dry. The time required for this is from 20 minutes to two hours. The mixture is then granulated by screening, dried at about 80° C. in an oven and transferred to an airtight container.

The potassium perchlorate used herein was sufficiently fine to pass through 325 mesh. The sulfur was sublimed flowers of sulfur with a screen mesh size varying from 100 to 325. Two grades of aluminum were used; namely, flake aluminum of 100 mesh size and atomized aluminum with a mesh size ranging from 100 to 325.

In order to determine the chemical stability, the above formulation was heated to a temperature of 300° C. and the only reaction recorded was an endothermic reaction between 100 and 115° C. This was probably due to the change of state of the sulfur which has a crystalline transition from rhombic to monoclinic at 96° C. and melts at 114.5° C. The furnace was then adjusted to permit studies at higher temperature and a second analysis was performed. Again, an endothermic reaction occurred just above 100° C., while a second endothermic reaction with a magnitude nearly eight times the first, started at 300° C. and continued on up to 315° C. This excursion possibly resulted from a change of phase in potassium perchlorate. At approximately 350° C. the reaction slowly started going exothermic, the first indication of a chemical reaction in these tests. At 380° C. this exothermic reaction suddenly accelerated and peaked at 385° C., though at a relatively low amplitude. Another exothermic reaction reached an amplitude about twice that of the former and peaked at 495° C. A thin stream of white smoke evolved from the sample from 350° C. to 500° C. at which temperature the runs were terminated. The sample residue was examined after cooling and appeared changed very little from its initial state. A match was applied to the residue which ignited readily and burned violently, very similar to the burning of smokeless powder. It appears that very little reaction occurred up to 500° C. Therefore, it may be concluded that this composition is safe up to 500° C. (in the absence of flame).

The average heat of explosion of this formulation, by calorimeter, was 1450 calories/gram, compared to a computed value of 1690.

A standard Bureau of Explosives drop test apparatus (8 lb. drop weight, 3/16" pellet diameter) was used to test the impact sensitivity of the formulations. Five out of seven samples tested had consistently 50% fire level at 2½ inches. This shows the sensitivity similar to PETN. All the tests were made with samples having approximate densities of one gram per cubic centimeter.

EXAMPLE II

Ingredients:	Percent by weight
Aluminum	12.09
Phosphorus (red)	17.11
Potassium perchlorate	70.80

The above formulation was dry blended by the same method described in Example I. Red phosphorus is used because it is safer to handle and it is much less active in its chemical behavior. The aluminum contributes much heat to the reaction and the other two products produce the gas necessary to provide explosive power.

The heat of explosion of the above formulation, by calorimeter, was 1844.7 calories per gram. The calculated value was 1878.

The reactions which occur when either of the above formulations are detonated may be represented as follows:

Al—S—$KClO_4$ formulation:

$$2Al+S+\frac{5}{4}KClO_4 \rightarrow Al_2O_3+SO_2\uparrow+KCl\uparrow$$

Al—P—$KClO_4$ formulation:

$$Al+P+KClO_4 \rightarrow \frac{1}{2}Al_2O_3+\frac{1}{2}P_2O_5\uparrow+KCl\uparrow$$

Perhaps a more meaningful reaction would be the following using the Al—S—$KClO_4$ formulation:

$$aAl+bS+cKClO_4 \rightarrow \frac{a}{2}Al_2O_3+bSO_2+cKCl$$

Inspection will show that this reaction can be balanced in a number of ways, so long as the oxygen balance is maintained. This requires that

$$c=\frac{1}{4}\left(\frac{3}{2}a+2b\right)$$

or, in other words, the amounts of aluminum and sulfur can be varied independently and stoichiometry still be obtained by controlling the perchlorate. This system suggests that with the reaction supplying 400 Kcal./mole of aluminum trioxide, as much Al_2O_3 should be formed as possible, and the number of moles of SO_2 formed should be as high as possible to boost the explosive power. To achieve the optimum energy from this system, it is necessary to maximize the heat output due to product formation and to maximize the gas produced as well. (The perchlorate and chloride quantities can be neglected because the heats of formation of these compositions are almost identical and do not contribute significantly to the overall reaction.) Further considerations indicate that the initial volume of gas produced is not limited to SO_2 or P_2O_5 as the case may be, but includes KCl, also, since enough heat is liberated to form gaseous KCl. The total heat of reaction is then given by:

$$\Delta H_r=-\left[400\times\frac{a}{2}+72\times b\right]$$

where the negative sign implies an exothermic reaction, and the other terms are heats of formation in Kcal. and moles.

A function Q is now defined which can be optimized to give a maximum to both the heat of reaction and the number of gas moles produced. Assuming the above elementary reactions to occur during the detonation

$$Q=[200a+72b][b+c]$$

This relation can be optimized by means of the relations between *a*, *b*, and *c*. Differentiating the final expression and solving for a maximum shows a peak in the Q versus *a*/*b* curve when the aluminum/sulfur molar ratio is 2.053.

These formulations have impact sensitivity results which place them among the more sensitive secondary explosives on the basis of drop tests. Tests were made with samples

having approximate densities of one gram per cubic centimeter.

The following table shows the comparison with PETN as the control:

TABLE I

Sample	Formulation	Time lapse from mixing to testing (hours)	50% explosion on drop height (in.)
1	Al-S-$KClO_4$	3	2½
2	Al-S-$KClO_4$	2	2½
3	Al-S-$KClO_4$	0	3½
4	S-$KClO_4$	0	3
5	PETN		3⅛

It is apparent from the above that these formulations have a sensitivity comparable to PETN. The presence of aluminum in the composition decreases its sensitivity, although aluminum certainly adds to the strength after detonation gets under way.

The formulations were checked for ignition sensitivity by applying the flame from a wooden match to a small quantity of the mix. The most sensitive of the tested samples ignited from the flame of a burning wood match after being raised to 500° C. and cooled. The violence of burning of this particular sample appeared greater than the other samples tested.

Adding water to the formulations in proportions up to 25% of the mix weight increased the difficulty of ignition in proportion to the percentage of water. However, once ignition got underway, the mixes continued burning until consumed, though at a lower rate than the dry samples.

These tests indicated that sufficiently large batches of the composition could be safely mixed, handled, and fired to determine critical diameter and other characteristics of these explosives by exercising normal precautions against heat, sparking, and impact hazards.

Tests were made to determine the critical diameters of these formulations. In these tests the smallest charge diameter, in which detonation was sustained in charge lengths of at least six charge diameters. The following tabulation shows these results as determined to the nearest ½" charge diameter.

Sample No.	Formulation, Al/S/$KClO_4$/H_2O	Density, gm./cm.³	Critical diameter, inches
1	18.3/14.6/67.1/0	1.03	1½
2	17.6/14.04/64.51/3.85	1.08	1½
3	16.95/13.52/62.12/7.41	1.25	2
4	18.3/14.6/67.1/0	1.60	4

The formulations are listed in order of ascending densities and as might be predicted from the behavior of multi-component type explosives (in contrast to monomolecular explosives, e.g., TNT), the sensitivity decreases with increasing density thereby requiring increasing charge diameter to sustain detonation. Attempts to increase the density, by either using a denser grade of aluminum or addition of water, always resulted in increasing the critical diameter.

In summary these formulations for underwater explosives have an impact sensitivity that places it among the more-sensitive secondary explosives on the basis of drop tests. Its thermal stability is extremely high when compared to other chlorate and perchlorate formulations. In fact it has greater thermal stability than even the slurry formulations containing ammonium nitrate, water and secondary military approved explosive sensitizers. The ignition sensitivity is very high and sensitivity as indicated by critical diameter and minimum booster criteria, is similar to other multiple-component formulations and is very dependent upon density. The heat of explosion and available energy is high, but the rate of detonation is very low which results in low brisance.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. An underwater explosive composition consisting essentially of the following ingredients.

Ingredients:	Percent by weight
Aluminum	18.3
Sulfur	14.6
Potassium perchlorate	67.1

2. An underwater explosive composition consisting essentially of the following ingredients:

Ingredients:	Percent by weight
Aluminum	12.09
Red phosphorus	17.11
Potassium perchlorate	70.80

3. An underwater explosive consisting essentially of
18.3% by weight aluminum composed of flake and atomized grades ranging in mesh size from 100 to 325;
14.6% by weight sulfur ranging in mesh size from 100 to 325; and

67.1% by weight potassium perchlorate having a mesh size of 325;
said explosive having a density of 1.03 to 1.6 gm./cm.^{3}.

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