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WATER-DEGRADABLE CAP-SENSITIVE SELF-SUPPORTING EXPLOSIVE

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ABSTRACT OF THE DISCLOSURE

Cap-sensitive self-supporting explosive composition, which disintegrates in water within a predetermined period of time, comprising a mixture of a cap-sensitive high explosive and a binder comprising water-soluble polymer and water-miscible plasticizer.

BACKGROUND OF THE INVENTION

Flexible self-supporting explosive compositions comprising cap-sensitive high explosives admixed with binding agents have been prepared for many applications such as for use in the fields of metal-treating and working. These explosive compositions, which usually comprise cap-sensitive high explosive such as pentaerythritol tetranitrate and a binding agent consisting of an organic rubber and a thermoplastic terpene hydrocarbon or of high viscosity nitrocellulose and water-insoluble plasticizer, also have been used below the surface of the water for such uses as seismic prospecting, underwater signaling, detection echo-ranging and debris destructing.

These explosive compositions have many advantages with respect to their physical characteristics in that they are readily formulated and possess rheological properties which permit easy forming, e.g., by rolling or extrusion into shaped articles of various configurations. However, there is now needed a water-degradable cap-sensitive self-supporting explosive which can function normally under water for a certain period of time, but after a more prolonged exposure to water, will disintegrate, thereby disarming the explosive so that accidental initiation cannot occur should the composition misfire and wash ashore.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a cap-sensitive self-supporting explosive composition which will function normally up to about fifteen minutes in water but will then disintegrate and become desensitized so that accidental initiation cannot occur should the composition misfire and wash ashore.

More specifically, this invention provides an explosive composition which comprises a mixture of about from 50 to 80 percent of cap-sensitive high explosive and about from 20 to 50 percent of water-degradable binder comprised of about from 5 to 25 percent of water-soluble polymer and about from 5 to 25 percent of water-miscible plasticizer therefor. The use of the water-degradable binder in the instant invention enables the explosive composition to function normally in water up to a certain period of time, e.g., about fifteen minutes, and then to disintegrate into its constituent components after a more prolonged exposure to water, e.g., about twelve to twenty-four hours, thereby rendering the explosive composition inoperative.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Any cap-sensitive high explosive is suitable for use in this invention. As used in this invention, cap-sensitive high explosive is meant to include a single cap-sensitive high explosive, mixtures of two or more thereof and mixtures

of one or more thereof with one or more other high explosives, e.g., trinitrotoluene or ammonium nitrate, the mixture being cap-sensitive, i.e., sensitive to initiation by a No. 8 electric blasting cap.

Especially suitable for use in this invention are cap-sensitive high explosive organic nitrates, nitramines and aromatic nitro compounds.

Examples of cap-sensitive high explosive compounds that can be used in this invention include pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), ammonium picrate, 2,4,6-trinitrophenyl methylnitramine (Tetryl), bis(trinitroethyl)urea, mannitol hexanitrate, lead azide, and mixtures thereof. PETN is preferred in this invention. The high explosive component should be compatible with the other ingredients of the final composition under processing, handling and storage.

The particle size of the high explosive is not particularly critical in the compositions of this invention. However, for ease of incorporating the particulate high explosive in the binder, particles which pass an 80-mesh U.S. Standard sieve, which are smaller than 200 microns, are preferred. Especially preferred are particles whose average major dimension does not exceed 100 microns. These are described as superfine explosives. In addition, the explosive compositions are more sensitive to initiation if the high explosive particles are prepared by the process of mixing a solution of the explosive with a non-sovlent, which is miscible with the solvent, in a jet-impingement mixer, such as the process disclosed in Canadian Pat. 533,487.

The high explosive constitutes about from 50 to 80 percent, preferably about from 60 to 70 percent, of the final composition. If substantially greater amounts of the explosive component are utilized, the final compositions lack the desired degree of cohesiveness and have a tendency to crack, whereas the use of substantially lesser amounts of the high explosive results in products which have unreliable detonation characteristics. When the proper proportions of high explosive and binder components are used, the compositions of the present invention can be initiated in sheet form, or otherwise, by commercially available blasting caps and will detonate at velocities of about from 4000 to 7000 meters per second.

The water-degradable binder constitutes about from 20 to 50 percent, preferably about from 30 to 40 percent, of the final composition and comprises about from 5 to 25 percent, preferably about from 10 to 20 percent, of water-soluble polymer and about from 5 to 25 percent, preferably about from 10 to 25 percent, of water-miscible plasticizer therefor.

Any polymer which is chemically inert with the other ingredients of the composition and which is soluble in water at less than about 20° C. (68° F.) is suitable for use in this invention. The solubility should be at least about 1 gram per 100 milliliters of water and, preferably, greater than 10 grams per 100 milliliters of water.

Examples of water-soluble polymers that can be used in this invention include water-soluble vinyl, acrylic and alkylene oxide polymers such as polyvinyl alcohol, polyethylene oxide, hydrolyzed polyvinyl acetate, polyacrylamide and mixtures thereof. Especially preferred is the polyethylene oxide water-soluble resin available from the Union Carbide Chemicals Company as "Polyox" WRS-205.

Any plasticizer for the water-soluble polymer which is chemically inert with the other ingredients of the composition and which is miscible with the water-soluble polymer and soluble in water at less than about 20° C. (68° F.) is suitable for use in this invention. Such plasticizers include the water-soluble aliphatic polyols and esters thereof such as the polyethylene glycols and their diacetate

derivatives. Representative examples of suitable plasticizers are glycerin, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, glycol diacetate, diethylene glycol diacetate and mixtures thereof. Especially preferred in this invention are glycerin and ethylene glycol.

Optionally, various additives may be incorporated into the explosive composition. For instance, about from 0 to 5 percent of nitrocellulose (NC) can be added to modify the rheological properties of the composition so as to aid in the extrusion and rolling of it. The requirements of the NC are based on its activity as a binding agent rather than as an explosive. Preferred is NC of a standard "dynamite grade" material of the soluble type having a nitrogen content of about from 12.15 to 12.35 percent and a degree of polymerization of about 3000. When NC is present in the explosive composition the plasticizer softens and partially solubilizes it, normally up to about 35 percent by weight of the NC. The NC can be wet with alcohol, with water or with combinations of the two.

Water-soluble salts such as ammonium nitrate, sodium nitrate, sodium chlorate and potassium hclorate can be added to the explosive composition in order to modify the dissolution rate of the explosive. The amount of water-soluble salt is preferably that which yields final products having an "oxygen balance" of ±10 percent. "Oxygen balance" as used herein refers to the percent excess of deficiency of oxygen required for complete combustion and is calculated as the molecular weight of oxygen required or given up in complete combustion divided by the molecular weight of the material in question.

Finally, aluminum flakes, e.g., pigment grade flake aluminum powder, can also be added to the explosive composition to improve the physical and explosive properties of it, e.g., aiding in the lubrication of sheets. The use of aluminum flakes is particularly desirable when the nitrate content of the explosive composition is increased, in order to maintain the sensitivity of the composition. In addition to aluminum flakes, other metals can be used, such as for example powders, flakes or chopped foil of magnesium, titanium, aluminum alloy, silicon, zirconium, ferrosilicon, ferrophosphorus and combinations thereof.

The explosive compositions of this invention can be prepared by uniformly blending the ingredients. The high explosive is used, preferably, in a water-wet state to decrease safety hazards. Mixing can be accomplished at room temperature, but it is preferred that the mixing temperature be in the range of about from 130–135° F. (54–57° C.). If NC is to be used, it is then added and mixed in until good incorporation is achieved, the mixture preferably being maintained at the elevated temperature. Preferably, the NC should be wet with water or alcohol. Water, which has been incompatible in previous explosive compositions, can be present (up to about 16 percent) in the instant explosive compositions and produces no detrimental effect on the sensitivity of the compositions.

The generally granular explosive products obtained by blending the components in the aforedescribed manner are readily converted into compact, self-supporting yet flexible articles such as sheets, tubes, tapes, cords, blocks and other rectilinear and curvilinear shaped articles, including those of relatively complex configuration, e.g., having V-grooves or cavities therein as well as those, such as sheets or blocks, of relatively plain configuration. The shaping can be accomplished by pressure molding, rolling extrusion and similar forming operations and can be conducted at ambient or elevated temperatures, depending on the particular composition and type of forming involved. The shaped articles can thus be obtained in a variety of shapes and thicknesses or diameters. Of the aforementioned shaped explosive products, sheets, preferably about from 0.05 to 0.50 inch in thickness with a weight of about from 1.3 to 14.0 grams per square inch of surface area, and cords, preferably about from 0.12 to 0.75 inch in diameter with a weight of about from 0.3 to 1.2 grams per inch of length, are especially suitable, in that such sheets and cords make optimum use of the desirable properties of the compositions of this invention.

The density of the compositions of the present invention is generally high, e.g., about from 1.40 to 1.55, preferably about 1.50, grams per cubic centimeter. The modified drop test impact sensitiveness index is generally greater than 56 inches. The drop test, a standard method of measuring the sensitiveness to initiation of detonation by impact, is conducted with a modification of the apparatus described in U.S. Bureau of Mines Bulletin 346 (1931). In the test, the maximum height from which the impacting weight (5 kg.) falls on the test specimen is 56 inches, and the test samples are placed in a small metal cup rather than directly on an anvil. Impact sensitivity is reported as the minimum distance of weight drop in inches that causes detonation in 50 percent of the samples (20 trials in each case). Samples that consistently fail to detonate when the weight is dropped from the maximum height of 56 inches are reported to have a sensitivity of 56+ inches.

The following examples provide further specific illustrations of the cap-sensitive self-supporting explosive compositions of this invention and their explosive and physical characteristics. In the examples, parts and percentages reported are by weight.

Example 1

A 50 percent water (deionized) solution of 10 parts of glycerin and 10 parts of "Polyox" WSR–205 [1] is added to 80 parts of regular refined PETN and mixed thoroughly. After mixing, the resultant mix is spread out manually on a "Teflon"® TFE resin sheet and placed into a hood overnight to air-dry partially. Sheets rolled from the mix are strong, flexible and felt-like in feel and appearance and have a density of about 1.48 grams per cubic centimeter. The modified drop test impact sensitiveness index is 56 inches.

In the above example ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, glycol diacetate, diethylene diacetate, mixtures thereof or mixtures of one or more of the above with glycerine can be substituted for glycerine on an equal weight basis.

Examples 2 to 4

Additional mixes as shown in Table 1 are prepared by adding a 50 percent "Polyox" WSR–205-water solution to (dry or water-wet) superfine PETN and glycerin. The resultant solution is mixed for approximately 20 to 25 minutes in a heated bowl (about 135° F. jacket temperature). If NC is to be used, half of the amount to be used is then added to the bowl. After further mixing for several minutes the remaining amount of NC is added, and the mixing is continued for approximately twenty minutes. The last five minutes of the mixing cycle is carried out under reduced pressure.

TABLE 1

Example	2	3	4
Parts PETN	65	60	60
Parts "Polyox" WSR–205	10	20	17
Parts glycerin	20	20	23
Parts NC (dynamite grade)	5	----	----

The mix of Example 2 extrudes extremely well into ¼-inch-diameter cords, which closely resemble a highly plastic, elastic "bread-dough" before extrusion. The cords are left exposed to warm (80° F.) air overnight and tested six days later for rate of velocity. This is accomplished by initiating the cords with a blasting cap, having

[1] "Polyox" WSR–205 is a polyethylene oxide water-soluble resin available from the Union Carbide Corporation with an approximate molecular weight of 600,000 and a viscosity of 4100 to 8000 centipoises in a 5 percent aqueous solution at 25° C.

a base charge of 2 grains of PETN. The cords detonate with a velocity of about from 6529 to 6580 meters per second.

Additional cords from Example 2 are placed in a beaker of water and remain intact for about from 5 to 15 minutes. However, after about four hours in water, the cords completely disintegrate.

Examples 3 and 4 are pressed into flat sheets about ⅜ inch thick and dried overnight at room temperature. They are also detonated with a blasting cap having a base charge of 2 grains of PETN.

EXAMPLE 5

In a Baker-Perkins mixer, 67 parts of superfine dry PETN and 20 parts of "Polyox" WRS–205, which has been screened through a wire mesh screen or cheesecloth, are blended for about 5 minutes at room temperature. 13 parts of ethylene glycol in a 40 percent ethylene glycol-aqueous solution is added with agitation to the mixer. The composition is mixed for about 45 minutes at about 130–140° F. (54–60° C.) and then discharged from the mixer. The mix is rolled into one 4 grams per square inch sheet and one 2 grams per square inch sheet. The sheets are very flexible when made but stiffen at room temperature. After eight days the 2 grams per square inch sheet is tested for detonation velocity by initiating the sheet with a No. 8 EB cap, having a base charge of 6.9 grams of PETN, laid on the top of the sheet. The sheet detonates at a velocity of 6860 meters per second. Thin sections of the 2 grams per square inch sheet are tested for propagation by cutting the sheet into one-inch width strips with various thicknesses and placing them on lead strips. The sections are initiated with a No. 8 EB cap overlaying the tops of the sections. Table 2 illustrates the results of the test.

TABLE 2

Thickness of the strip	Width of the strip, in.	Result
50 mil	1	Detonation.
35 mil	1	Do.
15–30 mil	1	Do.

EXAMPLE 6

39.8 parts of superfine PETN, 24.1 parts of ammonium nitrate, 3.6 parts of aluminum flakes and 19.3 parts of "Polyox" WSR–205 are blended dry in a beaker. 13.2 parts of ethylene glycol in a 40 percent ethylene glycol-aqueous solution are added and mixed into the above mentioned mixture for about five minutes. The mix, which is very stiff and hard to mix, is rolled into sheets manually, yielding a good flexible sheet. The sheets are stored at room temperature for five days, after which they are not dried out or stiffened and still retain their flexibility. Initiation tests are made on various thicknesses of sheets one inch in width and length. The sheets are initiated with a No. 8 EB cap and yield the results in Table 3.

TABLE 3

Weight, grams:	Results
8	Detonated.
6	Do.
4	Do.
3	Do.
2	Failed.

In the above examples polyvinyl alcohol, hydrolyzed polyvinyl acetate, polyacrylamide, mixtures thereof or mixtures of one or more of the above with "Polyox" WSR–205 can be substituted for "Polyox" WSR–205 on an equal weight basis.

What is claimed is:

1. A water-degradable self-supporting explosive composition comprising a mixture of about 50 to 80 percent of cap-sensitive high explosive and about from 20 to 50 percent of binder comprising about from 5 to 25 percent of water-soluble polymer and about from 5 to 25 percent of water-miscible plasticizer therefor.

2. An explosive composition of claim 1 wherein said water-soluble polymer is selected from the group consisting of polyvinyl alcohol, polyethylene oxide, hydrolyzed polyvinyl acetate, polyacrylamide and mixtures thereof.

3. An explosive composition of claim 2 wherein said water-miscible plasticizer is selected from the group consisting of glycerin, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, glycol diacetate, diethylene diacetate and mixtures thereof.

4. An explosive composition of claim 3 wherein said cap-sensitive high explosive is pentaerythritol tetranitrate.

5. An explosive composition of claim 4 wherein said water-soluble polymer is polyethylene oxide and said water-miscible plasticizer is glycerin.

6. An explosive composition of claim 5 comprised of about from 60 to 70 percent of said cap-sensitive high explosive, about from 10 to 20 percent of said water-soluble polymer and about from 10 to 25 percent of said water-miscible plasticizer.

7. A sheet explosive of the composition of any one of claims 1 to 6.

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