

1

3,303,074

AQUEOUS EXPLOSIVES SLURRIES CONTAINING SULFUR COMPOUNDS HAVING A LOW COEFFICIENT OF EXPANSION**William L. Schwoyer, Allentown, Pa., assignor to Trojan Powder Company, Allentown, Pa., a corporation of New York****No Drawing. Filed Dec. 6, 1965, Ser. No. 511,968
14 Claims. (Cl. 149—41)**

This application is a continuation-in-part of U.S. application Serial No. 226,728, filed September 27, 1962, now abandoned, and of Serial No. 350,550, filed March 9, 1964, now Patent No. 3,222,232, granted on December 7, 1965.

This invention relates to aqueous explosive slurries resistant to expansion upon exposure to elevated temperatures due to an unusually low coefficient of expansion with temperature.

Explosive slurries containing appreciable quantities of water or other fluids have recently become of considerable interest in the explosive art. These mixtures have a greater versatility than dry mixtures, because they can be used under conditions where water cannot be excluded. The fluid content of the slurries is more than that which is absorbed by the components of the mixture, and is sufficient to act at least in part as a suspending agent for the explosive ingredients. Such as fluid content in most cases ranges from about 0.5% to more than 30%, depending upon the materials present in the mixture, and upon the consistency desired.

A slurry having a reasonably stiff consistency, containing as little as 10% fluid, may be preferred for use in bulk in wet bore holes where the composition may be diluted with fluids such as water already present. Thickening or gelling agents are employed when thick slurries are required containing high proportions of fluids. A slurry that can be poured may be desired for use in bulk in dry bore holes, and such as slurry is easily obtained by using a rather large proportion of fluid, for example, 20 to 50%, without a thickening or gelatinizing agent.

Such slurries, however, present a packaging problem not encountered with dry mixtures, because, due to their liquid content, they have a high coefficient of expansion with temperature. This expansion creates special difficulties when explosive slurries are packaged in flexible plastic containers, since the explosive slurry must fill the entire plastic container so that air is excluded therefrom, leaving no air space for expansion. This means that the container must either expand and contract with the slurried contents, or rupture. Even if it expands, dimensions change, usually unevenly, with the result that the container may become oversized for a particular bore hole, and wedge at a bend in the bore hole, if it even fits the hole.

Expansion and contraction within the resiliency limits of the plastic cartridge can be tolerated, and by selecting an appropriate type, grade and thickness of plastic material, the relative expansion coefficients can even be matched. However, some explosive mixtures, particularly those employing an inorganic nitrate as an oxidizer and a metal such as aluminum as a fuel, have an unusually high expansion coefficient, and require either thick containers, to prevent rupture, or very thin containers which have a high coefficient of expansion. Neither alternative is very desirable. In addition, such explosive slurries have a tendency to expand irreversibly. That is, upon being subjected to relatively hot day temperatures, the slurries will expand, but when the temperature decreases, as at nightfall or during normal climatic changes, the explosive compositions do not return to

2

their original size, but to a size short of that. As a result, the explosive composition contained within the cartridge continuously exerts an undue pressure on the plastic container which is sufficient in time to cause rupture. Rupture is, of course, undesirable whenever it occurs.

While it is believed that the high expansion coefficient may be due, in some small part at least, to phase changes or changes in hydration of the inorganic nitrate, it appears that only when an active metal fuel, especially aluminum, is present does the volume change assume large and undesirable proportions.

U.S. application Serial No. 350,550, filed on March 9, 1964, now U.S. Patent No. 3,222,232, dated December 7, 1965, of which this case is a continuation-in-part, describes and claims explosive slurries based on inorganic nitrates, aluminum and water so formulated as to have a low coefficient of expansion with temperature, due to a small amount of a thiosulfate or organic sulfonate. Not only do such compositions display a markedly reduced tendency to expand on heating, but if they expand, they return to approximately their original normal dimensions when the temperature is again lowered. Thus, they display essentially no irreversible expansion characteristics. Such explosive slurries are therefore more readily stored under a wide range of temperature, and hence are safer to handle and use over such temperatures.

It has now been found that these thiosulfate or organic sulfonate-stabilized slurries have a tendency to decompose when stored at elevated temperatures, especially when more than about 15% aluminum or other active metal is present, and require further stabilization. Although the reason for the deterioration of the expansion reducing material is not known, it has been found that by adding certain stabilizers to such explosive slurries, this deterioration is minimized and in most instances arrested.

It has now been found, in accordance with the invention, that explosive slurries based on inorganic nitrates, active metal fuel and water, formulated so as to have a low coefficient of expansion with temperature by incorporating therein a small amount of a thiosulfate or organic sulfonate, can be modified to reduce their tendency to decompose on storage by incorporation therein of an ionizable metal compound, such as a salt, oxide or hydroxide, of a metal selected from Groups I to VIII of the Periodic Table, other than alkali and alkaline earth metals, aluminum, iron and chromium.

The metal compound preferably is soluble in the explosive slurrying liquid, but relatively insoluble compounds having a solubility product, $K_{S.P.}$, of 10^{-20} or greater can be used. Apparently, the only property common to the operative metals necessary for stabilization is that the metal form a relatively insoluble sulfide salt having a $K_{S.P.}$ of less than 10^{-24} .

The metal compound should be unreactive to the components of the explosive composition in slurry form to form decomposition products that destroy the explosive, but reactive in the sense of stabilizing activity towards the thiosulfate or sulfonate. For example, it has been found that most salts of copper and mercury tend to produce a rather vigorous reaction when mixed into some explosive slurries. Accordingly, care must be taken when using salts of copper or mercury to ensure that they are inert to the particular slurry used.

Compounds of the following metals have been found to be particularly useful for stabilizing the explosive slurries: zinc, cadmium, cobalt, nickel, lead, silver, molybdenum, tin, manganese, antimony and bismuth. Generally, any inorganic anions forming salts with these metals which are sufficiently soluble and inert to the explosive material art useful, such as, nitrite, sulfate, sulfite, phosphate, phosphite, carbonate, borate, cyanide, the various

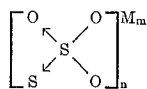
3

halides, especially the chlorides, fluorides and bromides, and the various organic anions, such as acetate, phthalate, benzoate, oxalate, tartrate and formate. In addition the oxides or hydroxides of the metals, where they are sufficiently soluble, can be used. The oxides and hydroxides may affect the pH of the explosive slurry, but this is normally unimportant. Zinc oxide is often added to explosive slurries containing an organic nitrate to increase the pH to stabilize the explosive materials. In this case, the amount of zinc oxide added must be sufficient to stabilize both the explosive materials as well as the thiosulfate or sulfonate compound present.

Examples of metal compounds useful for this invention are: zinc oxide, cadmium oxide, lead bromide, lead nitrate, lead chloride, lead acetate, tin chloride, tin sulfate, antimony chloride, antimony fluoride, zinc sulfate, zinc chloride, zinc nitrate, zinc fluoride, manganese sulfate, manganese nitrate, nickel chloride, nickel nitrate, cadmium hydroxide, cadmium chloride, cadmium nitrate, cadmium acetate, cobalt chloride, cobalt nitrate, bismuth hydroxide, bismuth nitrate, silver nitrate, silver acetate, silver fluoride, silver chlorate, molybdenum trioxide and molybdenum oxybromide.

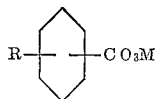
The amount of the metal compound required to stabilize the thiosulfate or sulfonate and to ensure a low coefficient of expansion in accordance with this invention is small. Generally, the amount of metal compound added should be between about 0.025 and about 500% by weight of the thiosulfate or sulfonate compounds in the slurry. Preferably, however, there will be at least about 0.5% by weight present.

The thiosulfates $M_nS_2O_3$ which can be employed can be represented by the following formula:



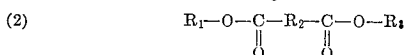
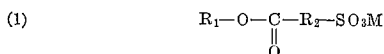
M is a cation and m and n are integers taken to satisfy the valences of M and the thiosulfate anion $S_2O_3^{2-}$. Exemplary are the sodium, potassium, lithium, ammonium, calcium, barium and magnesium thiosulfates, which may be either in the anhydrous form or in the form of the respective hydrates.

The organic hydrocarbon sulfonates which can be employed have the general formula RSO_3M , where M is a cation, such as an alkali metal, such as sodium and potassium; ammonium; an alkaline earth metal, such as calcium or magnesium; or an organic amine such as triethanolamine, and R is an organic hydrocarbon group, such as an alkyl, aryl, arylalkyl, alkylaryl or cycloalkyl group containing from about three to about fifty carbon atoms. Such hydrocarbon groups can also be substituted with carbonyl groups, ester groups, ether groups, sulfide groups, sulfonyl groups and additional sulfonate groups. Typical are the sodium petroleum hydrocarbon sulfonates, and the sodium benzene sulfonates, such as sodium benzene sulfonate, sodium dodecyl benzene sulfonate and sodium keryl benzene sulfonate. The benzene sulfonates have the structural formula:



where M is a cation and R is hydrogen or an alkyl group of from one to thirty carbon atoms.

A preferred class of hydrocarbon sulfonates are the ester-substituted sulfonates. Such compounds have the structural formulae:



wherein M is a cation as above and R_1 , R_2 and R_3 are

4

hydrocarbon groups containing from about one to about fifty carbon atoms. R_1 and R_3 can for example each be alkyl, aryl, alkylaryl, arylalkyl or cycloalkyl, and R_2 can be a bivalent alkylene, arylene, alkylarylene, arylalkylene or cycloalkylene group. Preferably, R_2 is a bivalent alkylene group and contains from about two to ten carbon atoms, and R_1 and R_3 are alkyl groups containing from about five to about twenty carbon atoms.

The choice of thiosulfate or sulfonate will be made with regard to the fluid or fluid mixture used as a vehicle for the slurry. It should be soluble or easily dispersible in the vehicle. If only certain compounds are available, their solubility characteristics may determine the nature of the vehicle. Thus, water or aqueous vehicles are usually required for the thiosulfates. The organic sulfonates, on the other hand, can be used with water, oil, or mixtures thereof.

The oxidizing agent employed in the explosive slurry of this invention should be an inorganic nitrate. Ammonium nitrate and nitrates of the alkali and alkaline earth metals, such as sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate, strontium nitrate and barium nitrate, are exemplary inorganic nitrates. Mixtures of several nitrates such as, for example, mixtures of sodium and ammonium nitrates, also yield excellent results. The inorganic nitrates may be fine, coarse, or a blend of fine and coarse materials. Mill and prill inorganic nitrates are quite satisfactory. For best results, the inorganic nitrates are usually fine grained.

In addition to the nitrate oxidizers, there is generally employed one or more fuels, including metal fuels and carbonaceous fuels, and an amount of water or water and oil sufficient to give the mixture the consistency desired, be it the consistency of a semi-solid material or the consistency of a free-flowing slurry. A sensitizing explosive can also be included, as an optional component.

The preferred sensitizing explosive is nitrostarch, but any sensitizing explosive known to the art can be used, alone or in admixture. Known sensitizing explosives which are useful include, for example, trinitrotoluene, dinitrotoluene, pentaerythritol tetranitrate, nitrostarch, trimethylolethane trinitrate, Pentolite (a mixture of equal parts of weight of pentaerythritol tetranitrate and trinitrotoluene), Cyclonite (RDX, cyclotrimethylene trinitramine), nitrocellulose, Composition B (a mixture of up to 60% RDX, up to 40% TNT and 1 to 4% wax), Cyclotol (Composition B without the wax), tetryl, and smokeless powder such as carbine ball powder.

The amount of thiosulfate or sulfonate required for a low coefficient of expansion in accordance with this invention is small. Generally, from 1 to 3% is employed for optimum results, although amounts as low as 0.3% give a reduction in the coefficient of expansion. More than about 3% would not usually be employed, as such large amounts are unnecessary to achieve the desired result, and therefore wasteful.

The relative proportions of nitrate oxidizer, and of sensitizing explosive, if used, will depend upon the sensitivity and explosive shock wave desired and these, again, are dependent upon the particular nitrate and sensitizing explosive. The proportions are not critical in any way. For optimum effect, the nitrate oxidizer is used in an amount within the range from about 10 to about 95%, and the sensitizing explosive can be used in an amount within the range from 0 to about 40% by weight of the explosive composition. From about 25 to about 30% sensitizing explosive and from about 50 to about 70% nitrate oxidizer give the best results.

When the amount of sensitizing explosive is in the lower part of the range, or zero, a large booster is needed. At amounts beyond 40%, the sensitizing effect falls off, and is no longer proportional to the amount of sensitizing explosive added, and therefore amounts beyond 40% are not usually used.

Sensitizing explosives of any particle size can be used.

5

They can, for example, be fine, coarse, or a blend of fine and coarse material. Some materials, such as nitro-starch, are commercially available as very finely-divided powders, and so also is trinitrotoluene. Such available materials are employed to advantage, because in most cases they tend to produce compositions having a greater explosive effect and sensitivity.

In addition to these materials, as has been indicated, the explosive compositions of the invention include an active metal fuel, usually, aluminum and preferably in particulate form, for example aluminum powder, atomized aluminum, granular aluminum, or flake aluminum, which also serves as a lubricity-improving agent. Aluminum can be used in the form of alloys such as aluminum-magnesium alloys. Other metal fuels can also be used alone or in conjunction with the aluminum, such as, for example, magnesium, ferrosilicon, beryllium, and lithium, and nonmetal element fuels, such as boron.

The metal fuel will usually comprise from about 0.5% to about 50% and preferably from 0.5 to 40% of the composition, of which fuel preferably at least 50% is aluminum. The size of the metal particles is not relevant to the stabilization of the slurry.

In addition to the metal or nonmetal fuel, a carbonaceous fuel can be included, such as powdered coal, petroleum oil, coke dust, charcoal, bagasse, dextrine, starch, wood meal, flour bran, pecan meal, and similar nut shell meals. A carbonaceous fuel when present will comprise from about 0.5 to about 30% of the mixture. Mixtures of metal and carbonaceous fuels can be used, if desired.

An anticid, or other stabilizing material, such as zinc oxide, calcium carbonate, aluminum oxide and sodium carbonate, can also be added. Such ingredients will comprise from about 0.3 to about 2% of the mixture.

The amount of water and other fluid employed in the composition will vary with the consistency desired of the final mixture. Generally, when a semi-solid mixture is desired, especially for use in preparing cartridges, as little as 0.5% of water or mixture of water and other fluid such as oil can be used, and generally not more than 10% is needed. Where free-flowing slurries are desired, larger amounts of water of aqueous mixtures are generally employed, in most cases within the range of from about 10 to about 40%, although in some cases as much as 50% of fluid can be used.

In the case of oil, of course, the viscosity of the oil is a factor to be taken into consideration in determining the amount of fluid added. When mixtures of oil and water are used, there would generally be employed from 2 to 10% water and from 10 to 30% oil, to give a slurry having a satisfactory fluidity.

The consistency of this slurry, particularly of a free-flowing slurry, can be decreased to meet any need by incorporating a thickening or gelatinizing agent. In this way, it is possible to prepare a thick slurry containing a large proportion of fluid for use in bulk in dry bore holes. The thickening agent should be soluble or dispersible in the dispersing fluid and inert to the other ingredients present. The thickened slurry can be used to form explosive cartridges in the same manner as the slurries normally having a semi-solid consistency.

An oil slurry can be thickened by any of the non-carbonaceous inorganic oil thickeners useful in making thickened oils and greases, such as finely-divided silica, available under the trade names Cab-O-Sil and Ludox, and silica aerogels, for example, Santocel ARD and Santocel C, and like inorganic gelling agents, such as alumina, attapulgite and bentonite, can be used. Other oil-gelling agents are disclosed in U.S. Patents Nos. 2,655,476 and 2,711,393. These are well known materials, and any of these known to the art can be used. The amount of such thickening agent will depend on the consistency desired, and usually will be within the range from 0 up to about 5%. Enough thickener can be added to gel the

6

oil, and waterproofing agents such as are disclosed in U.S. Patents Nos. 2,554,222, 2,655,476 and 2,711,393 also can be incorporated as well to impart water resistance to the gelled oil slurry.

5 An aqueous slurry can be thickened by any water-soluble or water-dispersible thickener, such as, for example, carboxymethyl cellulose, methyl cellulose, guar gum, psyllium seed mucilage, and pregelatinized starches such as Hydroseal 3B. The amount of such thickening agent will depend on the consistency desired, and usually will be within the range from 0 to about 5%.

The explosive of the invention can, if desired, be fired with the aid of a booster charge. Any conventional cap-sensitive booster charge available in the art can be employed. Pentaerythritol tetranitrate, Composition B and pentolite are exemplary. The booster charge preferably is non-shock or impact sensitive. The amount of booster charge required depends, of course, upon the amount and sensitivity of the explosive mixture.

20 The explosive mixture is readily prepared by simple mixing of the ingredients. The solid materials, including the thiosulfate or sulfonate, the stabilizing compound, the inorganic nitrates and sensitizing explosives, if any, fuels, and antacids, if any, would usually be mixed at first, to form a homogeneous blend, and the slurring liquid and slurry liquid thickener, if required, would be added with stirring to bring the mixture to the desired consistency. Where cartridges are to be formed, the consistency is usually comparable to that of a gelled oil or thick, barely pourable mixture, and the mixture is filled or extruded into open-ended containers, using conventional filling or extrusion equipment, to produce the explosive package.

The containers can be formed of any container material not dissolved or attacked by the slurry liquid or liquids. Heavy plastic is inexpensive, and available in sufficient thickness of wall, and is therefore preferred. Typical plastic and cellulosic materials which can be used include polyethylene, ethyl cellulose, cellulose acetate, polypropylene, polytetrafluoroethylene, nylon, polyvinyl chloride, polystyrene and polyvinylidene chloride, and non-ferrous metals, such as tin, copper and aluminum. Fibrous materials such as wood, paper, and cardboard can be used, if waterproofed or otherwise made resistant to the slurring liquid.

The following examples in the opinion of the inventor represent the preferred embodiments of his invention:

Examples 1 and 2

A slurry explosive mixture, Table A below, was prepared using ammonium nitrate prills, fine grained sodium nitrate, flake aluminum, anhydrous sodium thiosulfate, water, guar gum and the stabilizing metal compound noted in Table I, below. The sodium thiosulfate and metal compound were dissolved in the water and then thoroughly mixed with the flake aluminum, mixed nitrates and guar gum. The proportions of the final explosive compositions were as follows:

TABLE A

Ingredients:	Percent
Aluminum (flake) ¹ -----	20.00
Ammonium nitrate (prills) -----	47.50
Sodium nitrate (grained) -----	20.00
Water -----	12.00
Guar gum -----	0.50
Sodium thiosulfate (as noted in Table I).	
Stabilizing compound (as noted in Table I).	

¹ Screen analysis on:	Percent
18 -----	T
30 -----	T
35 -----	T
60 -----	T
80 -----	0.8
120 -----	1.6
230 -----	9.2
325 -----	72.0
Thru 325 -----	16.4
	100.0

The compositions were semi-fluid and were easily extruded through conventional extrusion nozzles into cartridges 8 inches long by 1¼ inches in diameter made of polyethylene, 3 mils in thickness. Some of the cartridges of each type were detonated and found to be satisfactory explosives.

Four formulations were prepared. The first formulation, Control A, did not contain any stabilizer against expansion. Control B contained 3% sodium thiosulfate, and was accordingly, a composition in accordance with U.S. Patent No. 3,222,232. The two remaining formulations, Examples 1 and 2, contained 1.5% lead nitrate and 1.5% lead acetate, in addition to the sodium thiosulfate.

Control B is a formulation of excellent stability against expansion during normal storage conditions. Explosive cartridges of this type are normally stored in magazines in the dark, at normal or cool atmospheric temperatures, ranging below 70° F. However, when subjected to extreme conditions, such as rather elevated temperatures in direct sunlight, this composition is of less durable stability against expansion.

Two cartridges of each formulation were then subjected to expansion tests comprising placing the cartridges in a wooden box of the type usually used for storing such cartridges and placing them in the open exposed to severe abnormal storage conditions, in direct sunlight with an average daily temperature of 85° F. during the day. The cartridges were each inspected and measured daily and the first day when any change occurred in their condition was noted. The results are recorded below in Table I.

TABLE I

	Expansion Reducing Additives (Percent)			Condition	
	Sodium Thiosulfate	Lead Nitrate	Lead Acetate	5 Days	42 Days
Control A	-----	-----	-----	Expanded and split.	
Control B	3	-----	-----	do.	
1	3	1.5	-----	No expansion.	Expanded.
2	3	-----	1.5	do.	Do.

The results of Table I above show that the two control compositions (A and B) expanded and split the cartridge open after 5 days of storage. However, Examples 1 and 2 containing 1.5% of the lead salts showed no expansion after five days and showed a slight expansion after 42 days, but the cartridges had still not split open.

Thus it can be seen that the presence of a small quantity of the stabilizing compound of this invention increases the stability against expansion of the explosive composition of No. 3,222,232.

Examples 3 through 7

The slurry explosive mixture of Examples 1 and 2 was used and mixed with the stabilizing compounds set forth in Table II, below. The slurry was extruded into cartridges 1¼ inches by 6 inches and stored in a wood box outdoors at an average daily temperature of 85° F., but not in direct sunlight. The cartridges were examined daily and the date which the first expansion was measured in was noted. Control C contained no sodium thiosulfate, Control D and Examples 3 through 7 contained 3% sodium thiosulfate and Examples 3 through 7 also contained 1.5% of the stabilizing compound.

TABLE II

	Sodium Thiosulfate	Stabilizing Compound	Days Stored Before Expansion
Control C	None	-----	7
Control D	3	-----	12
3	3	Zinc Nitrate	104
4	3	Nickel Acetate	27
5	3	Silver Acetate	27
6	3	Cobalt Nitrate	104
7	3	Cadmium Chloride	104

Under the abnormal storage test conditions, the cartridges containing the composition of Patent No. 3,222,232 (Control D) were stable against expansion for 12 days, 5 days longer than the cartridges of Control C. The cartridges of Examples 3 through 7, containing the stabilized composition according to this invention, however, lasted 27 and 104 days. The stabilizing influence of the metal salts in decreasing the expansion of explosive slurries containing a high proportion of an active metal and stored at a high temperature is well illustrated.

Examples 8 through 10

In order to test the effect of prolonged heating on the explosive composition of this invention, additional material having the compositions of Examples 3, 6 and 7, respectively, were prepared and subjected to a more rigorous test. After preparation, the slurry was stored at 110° F. in cartridges of 140 cc. or 135 cc. and the volume measured after 3 and after 152 days. The results are set out in Table III.

TABLE III

	Volume, cc.		
	Start	After 3 days	After 152 days
Control C	140	165	-----
Control D	140	165	-----
8	135	135	145
9	135	135	130
10	135	135	130

The results show that the explosive compositions of this invention are capable of withstanding severe storage conditions without danger of excessive expansion and resultant splitting of the cartridge container.

Examples 11 through 13

A series of experiments testing stability at the very high storage temperature of 90° C. in an accelerated heat storage test was run to determine the effect of various stabilizing compounds on expansion of additional explosive slurry compositions. The base explosive slurry composition contained a very high 40% aluminum content, composed of flake aluminum, 85% passing through 325 mesh, ammonium nitrate and water. This is a considerably higher proportion of aluminum than in most slurries and the particle size is smaller than usual.

In preparing the compositions, the soluble materials were completely dissolved in the water, and then the slurry with aluminum was formed by mixing. The formulations and volume change on heating at 90° C. for 90 minutes and 210 minutes are given in Table IV below.

Control E contained no expansion stabilizer and Control F contained sodium thiosulfate as the expansion stabilizer.

TABLE IV

Ingredients	Control E	Control F	11	12	13
Ammonium Nitrate, gms.-----	10	10	10	10	10
Water, gms.-----	50	50	50	50	50
Aluminum (flake), gms.-----	40	40	40	40	40
Sodium thiosulfate, gms.-----		2	2	2	2
Cobalt Nitrate, gms.-----			2		
Zinc Nitrate, gms.-----				2	
Zinc Oxide.-----					2
	100	102	104	104	104

RESULTS

After 90 minutes.-----	Considerable expansion.	Moderate expansion.	Slight expansion.	Slight expansion.	Slight expansion.
After 210 minutes.-----	do-----	do-----	do-----	do-----	Do.

Controls E and F show that addition of sodium thiosulfate reduced the expansion considerably but that Examples 11, 12 and 13 containing the stabilizing compounds of this invention were more effective in reducing the expansion.

Example 14

An explosive mixture of semi-solid consistency (14 in the table below) was prepared using nitrostarch, fine grained mill ammonium nitrate, fine grained mill sodium nitrate, flake aluminum, anhydrous sodium thiosulfate, water and the additional ingredients noted in the table below. The nitrostarch, oil and mixed nitrates were thoroughly blended and were then added to the zinc oxide, flake aluminum, guar gum and sodium carboxymethyl cellulose. The sodium thiosulfate was dissolved in the water and then added to the mixture. The proportions of the final explosive compositions were as follows:

Ingredients	14 Invention	G Control	H Control
Nitrostarch.-----	25.8	26.2	26.2
Mill Ammonium Nitrate.-----	45.1	47.0	46.7
Mill Sodium Nitrate.-----	15.5	14.2	14.2
Flake Aluminum.-----	1.9	2.0	1.9
Zinc Oxide.-----	0.8		
Sodium Carboxymethyl Cellulose.-----	1.0	1.0	1.0
Guar Gum.-----	0.7	0.8	0.8
Oil No. 5.-----	0.3		0.3
Sodium Thiosulfate (anhydrous).-----	1.2		1.2
Water.-----	7.7	7.8	7.7

The compositions were quite stiff, and were easily extruded through conventional extrusion nozzles into cartridges 36 inches long by 1 1/4 inches in diameter made of polyethylene, 2 to 3 mils in thickness. A 4 gram cast pentolite booster containing a No. 6 blasting cap was inserted into the cartridge. The cartridge was then inserted in a bore hole 2 1/4 inches in diameter. The cartridge was fired, and gave a detonation rate greater than 5000 meters per second, indicating that the composition was a satisfactory explosive.

The test included a series of control cartridge prepared in the same manner except that the control explosive composition (G) did not contain sodium thiosulfate nor zinc oxide and the control explosive composition (H) did not contain zinc oxide.

Expansion tests were run as in Example 1. When control H was stored under normal conditions it showed suitable storage stability with substantially no expansion. However, when stored under the extreme conditions met with in summer in the southwest, at an average daily temperature of 100° F., the controls showed a substantial expansion after a month.

Example 15

Semi-solid aqueous slurries were made up, as in U.S.

Patent No. 3,087,127. The slurry compositions were as follows:

Ingredients	Percent by Weight	
	Control	Example 15
Pentaerythritol tetranitrate.-----	10.48	10.48
Trimethylolethane trinitrate.-----	2.62	2.62
Ammonium nitrate, crushed E-2 prills (1/4" screen).-----	58.2	58.2
Sodium nitrate, mill.-----	12.00	12.00
Zinc oxide.-----		0.20
Aluminum flake (mill).-----	3.25	3.25
Petroleum oil (No. 5).-----	0.25	0.25
Nut meal.-----	3.00	3.00
Guar gum.-----	0.30	0.30
Sodium thiosulfate.-----	0.30	0.30
Water.-----	9.60	9.40
	100.00	100.00

These materials were loaded into 1" x 4" cartridges extrusion nozzles into polyethylene tubing 1 1/2 inches in diameter by 12 inches long. The tubing was secured at both ends, and expansion tests were then run, as in Example 1.

When the control was stored under normal conditions it showed suitable storage stability with substantially no expansion. However, when stored under the extreme conditions met with in summer in the southwest, at an average daily temperature of 100° F., the control showed a substantial expansion after a month. Example 15, however, did not show any appreciable expansion even when stored under the extreme conditions for a month.

Example 16

Explosive mixtures of semi-solid consistency (table below) were prepared using nitrostarch, grained mill ammonium nitrate, mill sodium nitrate, flake aluminum, water and the additional ingredients noted in the table below. The nitrostarch, oil and mixed nitrates were thoroughly blended and were then added to the zinc oxide, flake aluminum, guar gum and sodium carboxymethyl cellulose. The sodium benzene sulfonate was dissolved in the water and then added to the mixture. The proportions of the final explosive compositions were as follows:

Ingredients	16 Invention	J Control	K Control
Nitrostarch.-----	22.75	22.75	22.75
Mill Ammonium Nitrate.-----	48.65	49.65	49.65
Mill Sodium Nitrate.-----	14.25	14.25	14.25
Flake Aluminum.-----	2.00	2.00	2.00
Zinc Oxide.-----	1.00		
Sodium Carboxymethyl Cellulose.-----	0.60	0.60	0.60
Guar Gum.-----	0.50	0.50	0.50
Sodium Benzene Sulfonate.-----	1.00		1.00
Water.-----	9.25	10.25	9.25

These formulations were packed in 1¼" x 8" cartridges and subjected to severe storage tests cycling between temperatures of 86° to 106° F. for a period of 7 days. Control J expanded considerably during the test while the expansion of Control K was only moderate. The cartridges containing the mixture of Example 16 showed no expansion at all during the test.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. An aqueous slurried explosive composition characterized by a relatively stable low coefficient of expansion with temperature comprising, in combination, an inorganic nitrate oxidizer in an amount within the range from about 10 to about 95%, a particulate active metal fuel in an amount within the range from about 0.5 to about 50%, an aqueous liquid in an amount to form a slurry, a sulfur compound selected from the group consisting of inorganic thiosulfates and organic sulfonates in an amount sufficient to inhibit the thermal expansion of the slurry, and a stabilizing metal compound unreactive with the explosive slurry components and selected from the group consisting of metals of Groups I to VIII of the Periodic Table, other than the alkali metals, alkaline earth metals, aluminum, iron and chromium, in an amount sufficient to lessen any decomposition of the sulfur compound and to inhibit thermal expansion.

2. An aqueous slurried explosive in accordance with claim 1 in which the sulfur compound is an inorganic thiosulfate.

3. An aqueous slurried explosive in accordance with claim 1 wherein the sulfur compound is an organic sulfonate.

4. An aqueous slurried explosive in accordance with claim 1 in which the stabilizing compound is a metal salt.

5. An aqueous slurried explosive in accordance with claim 4 in which the metal compound is a compound of a metal selected from the group consisting of lead, cobalt, zinc, cadmium, nickel and silver.

6. An aqueous slurried explosive in accordance with claim 4 in which the metal compound has a solubility product of at least 10^{-20} .

7. An aqueous slurried explosive in accordance with claim 4 in which the metal compound is an oxide.

8. An aqueous slurried explosive in accordance with claim 1 containing sufficient water to impart to the composition a semi-solid consistency.

9. An aqueous slurried explosive in accordance with claim 1 comprising a thickening agent in an amount to increase the consistency of the composition.

10. An aqueous slurried explosive in accordance with claim 1 comprising an explosive sensitizer.

11. An aqueous slurried explosive in accordance with claim 1 in which the slurried liquid is water.

12. An aqueous slurried explosive in accordance with claim 1 in which the slurrying liquid is water and oil.

13. An aqueous slurried explosive in accordance with claim 1 in which the metal fuel is aluminum.

14. A method of stabilizing aqueous slurried explosive compositions having a reduced coefficient of thermal expansion and comprising, in combination, an inorganic nitrate oxidizer in an amount within the range from about 10 to about 95%, a particulate active metal fuel in an amount within the range from about 0.5 to about 50%, an aqueous liquid in an amount to form a slurry, and a sulfur compound selected from the group consisting of inorganic thiosulfates and organic sulfonates in an amount sufficient to inhibit the thermal expansion of the slurry, which comprises incorporating therein a stabilizing metal compound unreactive with the explosive slurry components and selected from the group consisting of metals of Groups I to VIII of the Periodic Table, other than the alkali metals, alkaline earth metals, aluminum, chromium and iron, in an amount sufficient to lessen any decomposition of the sulfur compound and to inhibit thermal expansion.

References Cited by the Examiner

UNITED STATES PATENTS

3,094,069	6/1963	Hradel et al.	149—43
3,147,163	9/1964	Griffith et al.	149—39

CARL D. QUARFORTH, *Primary Examiner*.

B. R. PADGETT, *Assistant Examiner*.