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GELATIN DYNAMITE COMPOSITION CONTAINING SULFUR

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The present invention relates to an improvement in gelatin dynamite compositions, and, in particular, to a gelatin dynamite explosive composition especially advantageous for use in oil-well blasting and prospecting, which explosive will not be rendered insensitive by prolonged exposure to pressure and water. It has long been known that gelatin dynamite explosives, upon the application of continued pressure, become passified or insensitive and cannot be detonated in the intended manner by commercial detonators. Such passification is a serious detriment to the use of gelatin dynamite explosives in certain important applications, for instance in seismic prospecting.

In seismic prospecting, explosive charges are detonated at the bottoms of bore holes and from the rate and direction of propagation of the resulting shock waves, the geological structure of the given area can be constructed. Seismic prospecting is an important geological tool, particularly in the discovery of petroleum.

The bore holes within which the explosives are fired are usually of great depth and filled to a considerable extent with water or drilling mud. Commercial practice in seismic prospecting often demands that the explosive remain under this mud or water and subjected to the pressure thereof for days. In such cases, it has been a common experience for gelatin dynamite to become passified or insensitized and fail to fire with commercial detonators. While the exact reason for such passification has not been determined, it is theorized that the extended subjection of the gelatin dynamite to high water pressures renders the air particles, normally distributed throughout the composition, inoperative as propagation-sustaining media.

Normally gelatin dynamite explosives have had included in their composition cork, bagasse pulp, and the like in an attempt to offset this passifying effect. However, this has not in general been effective in retaining the sensitivity of the explosive under high water pressures for more than a few hours. It has been suggested in U. S. Patent No. 1,778,718 that this problem might be solved by the use of hollow pellets of alkali metal nitrates as ingredients of the explosive mix. Experience has indicated, however, that under the severe conditions encountered in seismic prospecting, pelleted alkali metal nitrates are, at times, not sufficiently resistant to compression and in particular that they are not mechanically stable when exposed to water. In addition, they often do not stand up satisfactorily in storage.

It is, therefore, an object of the present invention to provide an explosive composition having improved resistance to pressure and water.

A further object is the formulation of a gelatin dynamite which will retain, after long storage, its ability to detonate when subjected to high water pressures.

A further object of the invention is to provide a gelatin dynamite explosive having improved utility for seismic prospecting.

Other objects of the invention will be apparent from a consideration of the following specification and claims.

According to the invention, a gelatin dynamite explosive composition having improved resistance to high water pressures and increased stability in storage is provided by including in the gelatin dynamite composition comprising the usual ingredients thereof, a substantial portion of pelleted interiorly cavitated elemental sulphur. By including pelleted interiorly cavitated elemental sulphur in the gelatin dynamite, explosives may be obtained which exhibit markedly superior propagation-sustaining properties under high water pressure, in comparison with compositions hitherto employed. To illustrate this, the following general comparison may be made (for a more detailed comparison see the tables of specific examples):

Explosive	Head	Time	Results
Ordinary gelatin dynamite	200 ft.=87 p. s. i	2 hrs	No detonation in ⅔ of trials.
Gelatin cynamite containing pelleted $NaNO_3$.	300 ft.=130 p. s. i	24 hrs	Do.
Gelatin dynamite according to invention.	500 ft.=215 p. s. i	9 days	Detonation in all cases.

Gelatin dynamite is basically a mixture of nitroglycerine with nitrocotton and generally includes in addition such materials as an oxygen-supplying salt, such as sodium nitrate or ammonium nitrate; antacids such as chalk ($CaCO_3$); and fuels, particularly solid carbonaceous fuels such as corn flour, bagasse, wood pulp, apricot pit meal, and the like. In addition, it may include other ingredients such as other explosive nitro compounds such as dinitrotoluene. The gelatin dynamites which include ammonium nitrate are called ammonia gelatin dynamites. Gelatin dynamites contain from about 20 to about 80% nitroglycerine, depending upon the strength desired, and from about 0.3%

to about 7% nitrocotton, usually from about 0.4% to about 5%, the amount of nitrocotton being sufficient to provide a viscous liquid or a gel of the desired consistency with the nitroglycerine as is standard practice. The particular proportions of nitroglycerine to nitrocotton selected will depend, as is well known, upon the amount of solid ingredients included in the explosive. When substantial amounts of solid ingredients are present the proportion of nitrocotton to nitroglycerine may be such as to provide a more or less viscous liquid, the adsorption and absorption of the solid ingredients being relied upon to render the mixture plastic. As the proportion of nitrocotton to nitroglycerine is increased the mixture becomes more viscous until a gel is obtained, and this gel may be relied upon to render the composition plastic. At any rate the amounts and proportions of nitroglycerine and of nitrocotton, as well as any solid ingredients, will be selected in accordance with common practice to provide a plastic solid mass.

If sodium nitrate is employed, it will generally be present in an amount from about 3% to about 65%, while fuels will usually be between about 3% and about 25%. In accordance with conventional practice the proportions of fuel and of sodium nitrate, when used, may be varied to provide a desirable oxygen balance in the explosive. If ammonium nitrate is used, it may be present in an amount from about 2.0% to about 50%, depending upon the particular grade of ammonia gelatin dynamite desired.

The nitroglycerine used in the present compositions may be relatively pure nitroglycerine or it may be a nitrated mixture of glycerine, ethylene glycol and corn or sugar or other nitratable substances, as is usually employed in the art. The aforesaid nitrated mixture, as well as relatively pure nitroglycerine, is designated in the trade as nitroglycerine and that term is used herein to include both materials.

By pelleted sulphur is meant small interiorly cavitated (hollow) pellets or beads of elemental sulphur the interiors of which are air-filled. Such pellets can be obtained by spraying molten sulphur into air in fine droplets with subsequent solidification or freezing of the droplets in flight. While the size of the sulphur pellets employed in the composition of the invention may vary over a wide range, the pellets are usually smaller than a U. S. S. No. 6 screen aperture and larger than a U. S. S. No. 80 screen aperture. Preferably, they are smaller than a U. S. S. No. 14 screen aperture and larger than a U. S. S. No. 45 screen aperture. It has been found that pellets larger than those which will pass through a U. S. S. No. 6 screen tend to break upon handling or milling. To the extent that such breakage occurs, the advantages of the invention are not realized. This tendency to break is not found in the smaller particles, but, when the pellet size is less than that which will be retained on a U. S. S. No. 80 screen, the pellets tend to be ineffective to prevent pressure passification.

The quantity of pelleted sulphur present in the novel composition may vary widely depending upon the particular conditions of use to which the explosive is intended but generally the pelleted sulphur will be present in an amount from about 5% to about 50% by weight, preferably from about 10% to about 45% by weight.

It has been found that improved results are obtained when the composition contains a material which serves to prevent water from entering the hollow sulphur pellets. Preferably, this is accomplished by providing the sulphur pellets in the composition with an exterior coating of a water-resistant film-forming substance, for example, a coating of wax or of a resinous material of the type hereinafter described. Such a coating appears to seal off the pores of the sulphur and increase the resistance of the resulting composition to water pressure. Preferably, a microcrystalline hydrocarbon wax or a convertible urea reaction product, for example, a convertible urea-formaldehyde reaction product including dimethylolurea, a convertible urea-melamine reaction product or a convertible urea-melamine-formaldehyde reaction product is employed, to provide the water resistant coating although other film-forming materials may be used if desired. In the event a convertible material is employed, conventional curing catalysts, for example, an ammonium salt, such as ammonium chloride, may be employed to facilitate the conversion of the reaction product into the insoluble state, but even in the absence of a catalyst, the convertible urea reaction product will be converted as cured with the passage of time. The amount of coating material added may vary, but generally from about 0.5% to about 5.0% will be used, and the preferable range is from about 1.0% to about 3.0% by weight of the sulphur.

To prevent the pellets from sticking or agglomerating when treated with wax, a coating of clay may be applied following the treatment with the wax. If used, the amount of clay will depend on the amount of wax used and may comprise from about 1% to 3% by weight of the sulphur. In place of coating the sulphur pellets, prevention of water-penetration into the sulphur pellets may be accomplished by adding a convertible reaction product of the stated type to the dry dope used in preparing the composition, as hereinafter described.

To aid in preventing the deterioration of the compositions on storage, a stabilizer is preferably added. For this function, organic amines are preferred, in particular urea, carbazole and diphenylamine. While the amount of stabilizer added to the composition will vary with the particular composition and the length of time and conditions of storage (especially temperature), in general from about 0.5% to about 5.0% may be employed.

The pelleted sulphur used in the present invention may, as stated above, be prepared by blowing molten sulphur upwardly through a nozzle into the atmosphere. For best results, it is desirable that the temperature of the sulphur as it leaves the nozzle be as near to the crystallizing temperature as possible. After the pellets have formed, they are gathered and classified according to size.

If desired, pelleted sulphur of the desired size may then be provided with the water-resistant coating, for example, the wax or wax and clay, or the resin. This may be accomplished, for example, by adding the molten wax to a quantity of pellets in a heated paddle type mixer and mixing until a uniform coating is obtained. If a clay coat is also desired, the clay may then be added and mixing continued until the clay coat is evenly distributed.

If the pelleted sulphur is to be provided with a coating of resinous material, the material providing the resin, in finely divided form in suspension or slightly moistened or rendered slightly sticky by heating or in solution, may be mixed with the pelleted sulphur in a suitable mixing device. A particularly advantageous way of applying a resin coating to the sulphur pellets is as a suspension or partial solution in water. The pellets thus treated can be dried to provide the water resistant coating. In the event a thermosetting resin is employed the pellets may be heated to convert the resin coating to the insoluble state. A convenient method of applying a coating on the pellets is to suspend or partially dissolve the convertible reaction product in cool water containing a conversion catalyst such as about 10% of ammonium chloride based on the dry weight of the reaction product, and to apply the resulting liquid to the pellets which have been heated to an elevated temperature, for example to about 150° F. The heat contained in the pellets is sufficient to dry the coating and to convert the reaction product into an insoluble resin coating. Alternatively, the material providing the resin, in dry finely divided condition, may be mixed with the other dry ingredients to form a dry dope and it will be found that the resin will be distributed through the mixture and will serve to prevent water-penetration into the interior of the sulphur pellets.

The pelleted sulphur, coated or uncoated, as desired, is then added to the secondary ingredients, as, for example, sodium nitrate or ammonium nitrate, wood pulp, pit meal, corn flour, stabilizer, etc., to form a dry dope which in turn is worked into the nitric ester base (which is prepared according to standard practice) until the desired consistency is obtained. It may then be packed into cardboard cartridges which may be sealed by crimping in the usual manner.

To test the explosive effect of the novel mixtures, the following conventional procedure may be followed:

A charge, preferably two cartridges 2" in diameter and 14¼" long, together with an electric cap are loaded end to end into a steel bomb 3" in diameter and about 40" long, the cap leads being arranged for detonating the bomb. When two or more cartridges are employed they are preferably joined together with a cardboard sleeve to assure proper alignment and end to end contact. The bomb is then filled with water under the desired pressure and kept at that pressure, by the addition of water to compensate for that absorbed by the explosive composition, for the desired time. It is then sealed off and, while still at the desired pressure, taken to a bombproof structure for firing.

To determine whether the explosive composition propagates completely through the full length of the column, use is made of three lead crusher cylinders about 2" in diameter by 4" in length. The cylinders are each placed on a steel base plate under the bombs in an upright position and on a straight line on 12" centers and the explosive composition lies directly above them. To prevent their deformation when the bomb shatters, a steel cap plate about 1" thick and 3" square is interposed between each of the cylinders and the bomb. In this manner, the transmitted compression effect is recorded on each lead block. Complete or partial failures are shown by uncompressed or very slightly compressed lead cylinders. The bomb is detonated and the linear compression of the lead cylinders measured and then converted into percent compression.

The following specific examples given in tabular form further illustrate the present invention, and show clearly that gelatin dynamite compositions containing pelleted sulphur have remarkably improved resistance to water pressure. In the tables, the percentages are by weight. In Table I, compositions 1 and 3 are prior art compositions containing ground and pelleted sodium nitrate, respectively. Composition 2 contains non-pelleted sulphur. In Table III, compositions 1, 3 and 5 are prior art compositions while compositions 2, 4 and 6 are compositions of the invention. All tests were made with a No. 6 Seismograph Electric Blasting Cap.

Table I

	1	2	3	4	5	6
Nitroglycerine	51.0	51.1	51.3	51.1	51.1	51.1
Nitrocotton	1.7	1.3	1.1	1.3	1.3	1.3
Sulphur	------	[1] 36.6	-------	[3] 36.6	[4] 36.6	[3] 18.3
Burnt cork (through 10-mesh, retained on 35-mesh)	1.0	-------	-------	-------	-------	-------
Ground sodium nitrate	------	4.3	-------	-------	-------	4.0
Coarse sodium nitrate	35.7	-------	[2] 36.6	-------	-------	18.3
Bagasse	4.1	-------	-------	-------	-------	-------
Wood pulp	------	5.7	6.0	6.0	6.0	6.0
Dry yellow corn flour	5.5	-------	4.0	4.0	4.0	-------
Chalk	1.0	1.0	1.0	1.0	1.0	1.0
Hydrostatic Pressure tests:						
Pressure in ft., H_2O	200	300	300	300	150	300
Time (hrs)	2	24	24	24	72	24
Percent Compression:						
Lead No. 1	38	22	5	22	19	31
Lead No. 2	0	0	0	17	20	12
Lead No. 3	0	0	0	14	20	28

[1] Non-pelleted sulphur passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen.
[2] Pelleted sodium nitrate coated with 2% wax and passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen.
[3] Pelleted sulphur interiorly cavitated passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen.
[4] Pelleted sulphur interiorly cavitated passing through a U. S. S. No. 8 and retained on a U. S. S. No. 20 screen.

Table II

	1	2	3	4	5	6
Nitroglycerine	51.1	51.1	51.1	51.1	51.1	51.1
Nitrocotton	1.3	1.3	1.3	1.3	1.3	1.3
Pelleted sulphur interiorly cavitated	[1] 36.6	[2] 36.6	[3] 36.6	[4] 36.6	[5] 36.6	[4] 21.3
Ground sodium nitrate	4.0	4.0	4.0	4.0	3.0	-------
Coarse sodium nitrate	-------	-------	-------	-------	-------	18.3
Wood pulp	6.0	6.0	6.0	6.0	6.0	6.0
Chalk	1.0	1.0	1.0	1.0	1.0	1.0
Urea	-------	-------	-------	-------	1.0	1.0
Hydrostatic pressure tests:						
Pressure in ft., H_2O	500	300	300	300	500	500
Time (hrs.)	72	24	24	144	9 days	6 days
Percent compression:						
Lead No. 1	28	26	29	23	27	28
Lead No. 2	28	20	14	18	25	20
Lead No. 3	26	23	14	14	27	30

[1] Passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen and coated with 2% of a microcrystalline hydrocarbon wax.
[2] Passing through a U. S. S. No. 8 screen and retained on a U. S. S. No. 14 screen.
[3] Passing through a U. S. S. No. 20 screen and retained on a U. S. S. No. 70 screen.
[4] Passing through a U. S. S. No. 14 and retained on a No. 35 screen and coated with 2% of a microcrystalline hydrocarbon wax and with an exterior coating of finely divided clay.
[5] Passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen and coated with 2% of a partially polymerized reaction product of urea and formaldehyde ("Cascamite"—a water-soluble urea-formaldehyde resin adhesive in dry powder form).

Table III

	1	2	3	4	5	6
Nitroglycerine	21.0	21.0	31.5	31.5	71.0	71.0
Nitrocotton	0.4	0.4	0.9	0.9	3.0	3.0
Ground sodium nitrate	40.0	46.1	27.0	34.8	------	------
Coarse sodium nitrate	20.0	------	20.0	10.0	18.5	------
Wood pulp	------	------	1.8	1.9	3.0	3.0
Coarse Apricot Pit Meal	4.6	------	------	------	------	------
Fine Apricot Pit Meal	------	------	7.8	------	------	------
Corn Flour	5.0	5.5	10.0	3.9	3.5	2.5
Urea	------	1.0	------	1.0	------	1.0
Pulverized Sulphur	8.0	------	------	------	------	------
Pelleted sulphur interiorly cavitated	------	[1] 25.0	------	[2] 15.0	------	[2] 18.5
Chalk	1.0	1.0	1.0	1.0	1.0	1.0
Hydrostatic Pressure Tests:						
Pressure in ft., H_2O	100	100	100	200	300	500
Time (hrs.)	2	2	24	24	24	24
Percent Compression:						
Lead No. 1	30	31	25	28	20	28
Lead No. 2	0	22	11	19	2	27
Lead No. 3	0	24	0	28	0	27

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[1] Passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen and coated with 2% of a microcrystalline hydrocarbon wax and with an exterior coating of finely divided clay.

[2] Passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen and coated with 2% of a partially polymerized reaction product of urea and formaldehyde ("Cascamite").

Table IV

	1	2
Nitroglycerine	31.5	31.5
Nitrocotton	0.9	0.9
Ammonium Nitrate	26.3	26.3
Ground Sodium Nitrate	9.0	9.0
Coarse Sodium Nitrate	25.0	------
Wood Pulp	2.2	2.2
Corn Flour	4.1	3.1
Pelleted Sulfur interiorly cavitated	------	[1] 25.0
Urea	------	1.0
Chalk	1.0	1.0
Hydrostatic Pressure Tests:		
Pressure in Ft., H_2O	100	200
Time (Hrs.)	24	24
Percent Compression:		
Lead No. 1	34	28
Lead No. 2	20	25
Lead No. 3	0	22

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[1] Passing through a U. S. S. No. 14 and retained on a U. S. S. No. 35 screen and coated with 2% of a partially polymerized reaction product of urea and formaldehyde ("Cascamite").

As will be apparent to those skilled in the art, compositions according to the invention are susceptible of considerable variations in ingredients and percentages without departing from the features of the invention.

I claim:

1. A gelatine dynamite explosive composition comprising nitroglycerine in an amount between about 20% and about 80%, and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a U. S. S. No. 6 screen aperture and larger than a U. S. S. No. 80 screen aperture.

2. A gelatin dynamite explosive composition comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a U. S. S. No. 6 screen aperture and larger than a U. S. S. No. 80 screen aperture and having a wax coating comprising from 0.5% to 5% by weight of the sulphur.

3. A gelatin dynamite explosive as claimed in claim 2 wherein the wax-coated sulphur pellets are also coated with clay.

4. A gelatin dynamite explosive composition comprising nitroglycerine in an amount between about 20% and 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a No. 6 U. S. S. screen aperture and larger than a U. S. S. No. 80 screen aperture and containing a reaction product of formaldehyde and at least one compound selected from the group consisting of urea and melamine.

5. A gelatin dynamite explosive as claimed in claim 4 wherein said reaction product is provided as a coating for the sulphur pellets and is a urea-formaldehyde resin.

6. A gelatin dynamite explosive comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% of hollow sulphur pellets and from about 0.5% to about 5.0% of a stabilizing organic amine, said sulphur pellets being smaller in size than a U. S. S. No. 6 screen aperture and larger than a U. S. S. No. 80 screen aperture.

7. A gelatin dynamite explosive comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a U. S. S. No. 6 screen aperture and larger than a U. S. S. No. 80 screen aperture and having a wax coating comprising from about 0.5% to about 5.0% by weight of the sulphur; and from about 0.5% to 5.0% of a stabilizing organic amine.

8. A gelatin dynamite explosive composition comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 5% to about 50% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a No. 6 U. S. S. screen aperture and larger than a U. S. S. No. 80 screen aperture and containing a reaction product of formaldehyde and at least one compound selected from the group consisting of urea and melamine present in an amount from about 0.5% to about 5.0% by weight of the sulphur, and containing from about 0.5% to about 5% of a stabilizing organic amine.

9. A gelatin dynamite explosive composition comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7%, and containing from about 10% to about 45% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a U. S. S. No. 14 screen aperture and larger than a U. S. S. No. 45 screen aperture and having a wax coating comprising from about 1.0% to about 3.0% by weight of the sulphur; and from about 0.5% to about 5% of a stabilizing organic amine.

10. A gelatin dynamite explosive comprising nitroglycerine in an amount between about 20% and about 80% and nitrocotton in an amount between about 0.3% and about 7% and containing from about 10% to about 45% by weight of hollow sulphur pellets, said hollow sulphur pellets being smaller in size than a U. S. S. No. 14 screen aperture and larger than a U. S. S. No. 45 screen aperture and having a coating comprising a reaction product of urea and formaldehyde present

in an amount from about 1.0% to about 3.0% by weight of the sulphur, and containing from about 0.5% to about 5.0% of a stabilizing organic amine.

11. The explosive of claim 6 wherein said stabilizing organic amine is carbazole.

12. The explosive of claim 6 wherein said stabilizing organic amine is urea.

13. The explosive of claim 7 wherein said stabilizing organic amine is carbazole.

14. The explosive of claim 7 wherein said stabilizing organic amine is urea.

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