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PLASTIC EXPLOSIVE COMPOSITIONS

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This invention relates to detonative explosive compositions and more particularly to plastic type explosive compositions of improved characteristics.

Plastic explosives and especially gelatinous and semigelatinous plastic explosives have been known to the explosives art for many years. Blasting gelatin, gelatin dynamites and semigelatin dynamites have been and are widely used in a wide variety of blasting operations, both commercial and military. The original gelatins, of course, were the result of attempts of early workers such as Nobel to immobilize and desensitize nitroglycerin in order that the explosive oil could be safely used as a blasting explosive. As would be expected, gelatin dynamites are characterized by an explosive strength proportional to the amount of liquid explosive nitric ester employed.

Aside from their explosive strength, it was soon found that gelatin type explosives had many desirable physical characteristics. Because of their plastic consistency, the gelatins held themselves in an integral plastic mass and did not flow when employed in overhead drill holes or in capping. It was soon found that substantially higher loading densities were obtainable with gelatins than with dry mixes. In addition, the gelatins exhibit substantially greater water resistance and are substantially less sensitive to shock than other conventional types of explosive. As a result, the art has attempted to maintain gelatinous consistency even when the amount of liquid nitric ester in the composition is greatly reduced. Thus, in semigelatin dynamite now employed in large volume, only about 20% of nitroglycerin is employed and is gelled by a small amount of nitrocellulose. The rest of the composition is made up of dope ingredients such as oxygen carrying salts, carbonaceous ingredients, fillers and stabilizers.

However, the gelatinous explosives now in use have several undesirable features. In the first place, the nitroglycerin-nitrocellulose gel is expensive. Furthermore, the presently used gelatin explosives tend to break down in hot storage and lose their desired plastic consistency. In addition, in low temperature conditions frequently encountered in the field, the gelatinous explosives become hard and incapable of molding or packing in irregular holes. It would, therefore, be highly desirable to replace the nitroglycerin-nitrocellulose gel, at least in part, with a less expensive gelling agent which is not subject to these undesirable characteristics.

Plastic explosives have more recently achieved considerable importance in the field of military explosives. These plastic explosives range from hard, horny plastic castings and shaped charges to gelatinous compositions. Some of the commercial gelatinous compositions, such as blasting gelatin, are currently employed as military explosives without change. However, there is a definite need for a thermally stable, gelatinous explosive containing a major proportion of highly potent, crystalline explosive such as cyclonite, the physical characteristics of which will not change appreciably during extended hot or cold storage.

The object of the present invention, therefore, is a new type of plastic explosive which may, by a simple

variation in the method of preparation, be prepared in gelatinous or hard form. A further object of the invention is a type of plastic explosive which has greatly increased storage stability. An additional object of the invention is a plastic type explosive which does not undergo an appreciable change in physical characteristics after extended storage at either high or low temperatures.

Generally described, the present invention is a plastic explosive composition comprising explosive material selected from the group consisting of liquid explosive nitric esters, nitrocellulose, nitrostarch, and crystalline explosives, and a silicone gel comprising a polysilicone. An additional embodiment of the invention, generally described, is a process for the manufacture of plastic explosive compositions which comprise the dispersion of high explosive material in a gelatinous matrix phase comprising polysilicone.

In accordance with one embodiment of the invention, plastic explosive compositions may be prepared by initially heating a catalyzed, polymerizable silicone to form a gell of the desired consistency. The explosive material is then admixed with a predetermined quantity of the polysilicone gel to form a gelatinous explosive composition. In accordance with a second embodiment of the invention, the explosive material is intimately admixed with a catalyzed, polymerizable silicone and the resulting mixture is heated at a temperature below the decomposition point of any of the explosive ingredients. When liquid explosive nitric esters are employed, it is preferred to initially form the nonexplosive silicone gel. Where more stable explosives are employed such as cyclonite, pentaeryithritol tetranitrate, and the like, it is preferred to polymerize the silicone in situ to form the plastic explosive composition.

The silicones operable in the invention have a repeating skeletal structure of alternate atoms of silicon and oxygen in which the remaining valences of the silicon atoms are satisfied by organic radicals, usually lower alkyl, aryl, alkaryl, and aralkyl such as methyl, ethyl, propyl, phenyl, benzyl, tolyl, xylyl and the like. Most commercially available silicones contain methyl, ethyl, or phenyl groups. The generally preferred process employed in commercial production of the silicones is reported to be the hydrolysis of organo halogeno-silanes followed by condensation to remove all or part of the hydroxyl groups. Discussion of the chemistry involved in the preparation and polymerization of silicones may be found in United States Patents 2,258,218 and 2,258,222 to Rochow and in United States Patent 2,469,888 to Patnode.

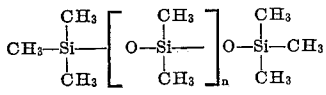
In the examples, presented for more specific illustration of various embodiments of the invention, the following silicone compounds and compositions, having the listed manufacturer's specification, were employed:

General Electric silicone fluid GE 9996 (redesignated SF–96)

Color	Clear, water-white.
Specific gravity at 68° F.	.964.
Flash point	600° F.
Heat of combustion	6130 cal./g.
Viscosity at 100° F.	1000 centistrokes.
Volatility	Weight loss less than 0.5% when 2 g. heated in 50 cc. beaker for 24 hrs. at 302° F.
Solubility characteristics	Soluble in carbon tetrachloride, chloroform, benzene, toluene, ether. Insoluble in acetone, butanol, ethanol, glycerol, methanol, water.

Chemically, GE 9996 is a chainstopped linear dimethylpolysiloxane in which the chainstopping group is a tri-

methylsiloxy unit having the following structural formula:

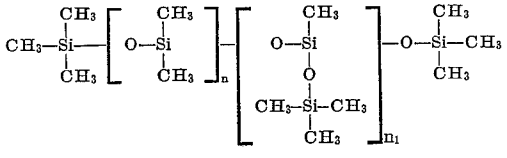


wherein the numerical value of n determines the viscosity of the fluid. The preparation of this and similar silicones is described in U.S. 2,469,888.

General Electric silicone fluid GE 9981 (redesignated SF–81)

Color	Clear, water-white.
Specific gravity at 68° F	.971.
Flash point	597° F.
Viscosity at 100° F	40 centistokes.
Volatility	Weight loss less than 1.0% when 2 g. heated in 50 cc. beaker for 24 hrs. at 302° F.
Solubility characteristics	(Same as for GE 9996.)

Chemically, GE 9981 is a chain stopped methylpolysiloxane similar to GE 9996 with the exception that it contains an amount, not exceeding 5 mol percent, of monomethylsiloxy units and has the following structural formula:



wherein the numerical value of n and n_1 determine the viscosity of the fluid and, as indicated, the value of n_1 is such that the mole percent of monomethylsiloxy units does not exceed 5. The preparation of this and similar silicones is also described in U.S. 2,469,888.

General Electric silicone fluid GE 81245

Stated by manufacturer to be "a blend of 9996 and 9981 type." Obtained uncured as a free-flowing water-white liquid and may be cured by heating with a polymerization catalyst such as benzoyl peroxide to a gel-like consistency. All three of these silicone oils are polymerizable in the presence of a polymerization catalyst and heat.

D.C. 122 Silastic paste

Uncured:	
Consistency	Paste.
Color	Gray.
Specific gravity at 25° C	1.5.
Williams plasticity	75 mils.
Cured: [1]	
Hardness, Shore A scale	90.
Tensile strength, p.s.i., minimum	630.
Elongation, percent, minimum	40.

[1] Cured 4 hours at 482° F.

Chemically, D.C. 122 is a polymerizable paste containing a dimethylsiloxane fluid catalyzed with benzoyl peroxide and diatomaceous earth as a filler.

D.C. 126 Silastic paste

Uncured:	
Consistency	Paste.
Color	White.
Specific gravity at 77° F	1.5–1.6.
Williams plasticity	15–35 mils.
Cured: [1]	
Hardness, Shore A scale	45–60.
Tensile strength, p.s.i., minimum	375.
Elongation, percent, minimum	150.

[1] Cured 4 hours at 482° F.

Chemically D.C. 126 is a polymerizable paste containing a dimethyl-siloxane fluid catalyzed with benzoyl peroxide and titanium dioxide as a filler.

D.C. 7 mold release compound

Consistency	Like petroleum jelly—penetrometer value 240–300 mils.
Color	Light gray—translucent.
Specific gravity at 25° C	1.0.
Solidification point	Lower than —40° C.
Bleed, percent, 24 hrs. at 200° C	10.
Evaporation, percent, 24 hrs. at 200° C	5.
Melting point	Nonmelting.
Solubility characteristics	Dispersible in benzene, gasoline, mineral spirits, carbon tetrachloride and methyl ethyl ketone.

Chemically, D.C. 7 is an uncatalyzed composition containing a dimethylsiloxane fluid and silicon dioxide as a filler.

All of the silicone compounds in these commercial products are polymerizable in the presence of a suitable polymerization catalyst and heat. D.C. 122 and D. C. 126 are furnished with catalyst in the composition while catalyst must be added to GE 9996, GE 9981, GE 81245 and D.C. 7.

EXAMPLE 1

A polymerizable silicone oil having a viscosity of 1000 centistokes at 100° F. (General Electric Product 81245) was catalyzed with 0.5% by weight of benzoyl peroxide. When heated for 10 minutes at 125° C., the oil polymerized to a rubbery, tacky gel. Fifteen parts by weight of the silicone gel was intimately admixed with 85 parts by weight of particulate cyclonite. The resulting gelatinous explosive composition exhibited whiskers when pulled apart, was sensitive to a No. 6 blasting cap and detonated completely. The composition exhibited good plasticity at both 170° F. and —65° F.

EXAMPLE 2

Ten parts by weight of the gel of Example 1 was intimately admixed with 90 parts by weight of particulate cyclonite. The resulting gelatinous composition had good cohesion and a rubbery doughlike consistency. Plasticity was good at both 170° F. and —65° F. The composition was sensitive to a No. 6 blasting cap and detonated completely.

EXAMPLE 3

Three parts by weight of the gel of Example 1 was intimately admixed with 97 parts by weight of particulate cyclonite. The resulting gelatinous composition had good cohesion but was not quite as rubbery as the composition of Example 2. Plasticity was good at both 170° F. and —65° F. The composition was sensitive to a No. 6 blasting cap and detonated completely.

EXAMPLE 4

Brisant plastic explosives of varying sensitivity to detonation are obtained when trinitrotoluene,, pentaerythritol tetranitrate, tetryl, nitroguanidine, picric acid, nitrolactose, mannitol octanitrate, and sucrose octanitrate are substituted for the cyclonite of Examples 1 to 3. These compositions show little change in physical characteristics when exposed to temperatures of from —65° F. to 170° F.

EXAMPLE 5

A polymerizable silicone oil having a viscosity at 100° F. of 40 centistokes (General Electric Product 9981) is catalyzed with 1% by weight of benzoyl peroxide and heated at 125° C. until a rubbery, tacky gel results. Fifty percent by weight of this gel is admixed with 50% by weight of particulate pentaerythritol tetranitrate to form a stiff gelatinous composition. This composition remains gelatinous at temperatures of 170° F. and —65° F. and detonates when primed with a booster cap containing a 10-gram pentaerythritol tetranitrate base charge.

EXAMPLE 6

Two parts of polymerizable silicone paste (Dow-Corning Silastic 126) were blended with 3½ parts of polymerizable silicone oil having a viscosity of 40 centistokes at 100° F. (General Electric Silicone Oil 9981) with a mechanical stirrer. The resulting heavy cream-like mix was raised to a temperature of 150° C. over a period of 15 minutes with vigorous stirring. Gelation appeared to begin when the temperature reached 125° C. and was completed when 150° C. was reached. A slight thickening was observed when the gel was cooled to room temperature. Fifteen parts of this gel was then intimately mixed with 85 parts by weight of particulate cyclonite. The resulting explosive was gelatinous, and had excellent cohesion, exhibiting definite whiskers when pulled apart. The composition was sensitive to a No. 6 blasting cap and detonated completely at a rate of 6990 m./sec. The plasticity of the composition was good at both 170° F. and —65° F. The density of the composition was 1.44.

EXAMPLE 7

Twenty parts of the gel of Example 6 was intimately admixed with 80 parts of particulate cyclonite. The resulting gelatinous composition was very cohesive. The composition was sensitive to a No. 6 blasting cap and detonated completely at a rate of 6820 m./sec. Its plasticity was good at both 170° F. and —65° F. The density of the composition was 1.37.

EXAMPLE 8

Ten parts by weight of the gel of Example 6 was intimately admixed with 90 parts by weight of particulate cyclonite. The resulting gelatinous composition had good cohesion and was sticky but lacked the rubbery consistency of the compositions of Examples 6 and 7. The composition was sensitive to a No. 6 blasting cap and detonated completely. The composition exhibited good plasticity at both 170° F. and —65° F.

EXAMPLE 9

Five parts by weight of the gel of Example 6 was intimately admixed with 95 parts by weight of particulate cyclonite. The resulting composition was still of a gelatinous nature, was sticky and had fairly good consistency. The composition was sensitive to a No. 6 blasting cap and detonated completely. The composition exhibited fairly good plasticity at both 170° F. and —65° F.

EXAMPLE 10

Eighty-five parts by weight of particulate cyclonite was thoroughly admixed with 15 parts by weight of polymerizable silicone oil (General Electric Product 81245). The silicone oil contained 2% of benzoyl peroxide. The resulting mixture was oily and had a greasy feel but exhibited no plastic properties. The mixture was placed in an oven and maintained at 100° C. for two hours. When removed from the oven, the mixture was gelatinous, exhibited an excellent, rubbery consistency, and was readily moldable in any desired form. The composition was sensitive to a No. 6 blasting cap and detonated completely. The composition had good plasticity at both 170° F. and —65° F.

EXAMPLE 11

Eighty-five parts by weight of particulate cyclonite was blended at room temperature with 15 parts by weight of polymerizable silicone paste (Dow-Corning Silastic 126). The resulting mixture had the appearance and feel of greasy sand. One portion of the mixture was heated without addition of catalyst for 2 hours at 150° C. The remaining portion was heated without addition of catalyst at 150° C. for 72 hours. Both portions became plastic when the mixture reached 150° C. The resulting explosive compositions were identical in physical appearance. Both were hard, firm and resilient. Both bounced when dropped. Both detonated completely when primed with a No. 6 cap. It is apparent, therefore, that extended exposure to high temperatures was not deleterious to the properties of the explosive composition.

EXAMPLE 12

Nonexplosive silicone gels were prepared which were polymerization products formed by curing the indicated mixtures of silicone products. These compositions exhibited excellent consistency and plasticity and had the following formulations:

	Parts
A. Silastic paste (Dow-Corning Silastic 126)	2
Silicone grease (Dow-Corning 7)	7
Silicone oil (General Electric Product 9996)	1
B. Silastic paste (Dow-Corning Silastic 126)	1
Silicone oil (General Electric Product 9996)	2
C. Silastic paste (Dow-Corning Silastic 122)	1
Silicone grease (Dow-Corning 7)	4

EXAMPLE 13

Polymerizable silicone oil (General Electric Product 81245) was catalyzed with 0.5% benzoyl peroxide, heated at 125° C. for a period of 15 minutes and allowed to cool to room temperature. The product obtained was a tacky, resilient, viscous gel. Two percent of this nonexplosive gel was uniformly incorporated in a mixer in a semigelatin dynamite having the following formula:

	Percent
Nitroglycol-nitroglycerin 70/30	14.00
Ammonium nitrate	72.35
Nitrocellulose (dynamite grade)	0.35
Sodium nitrate	8.3
Chalk	0.5
Wood pulp	1.0
Oat hulls	0.5
Corn starch	1.0
Silicone gel	2.0

The semigelatin dynamite thus formed was soft, easily packaged and readily moldable. The composition showed substantially improved low temperature plasticity when compared with semigelatin dynamites not containing the silicone gel. The above semigelatin dynamite detonated completely when primed with a No. 6 blasting cap. In the standard halved-cartridge gap sensitivity test, this composition shot at 16 inches. Eight by one and one-fourth inch cartridges of the composition weighed 200 g. and had a cartridge count of 113.

EXAMPLE 14

Excellent cap-sensitive gelatinous dynamites are obtained when the composition of Example 13 is varied to contain from 10 to 30% liquid explosive nitric ester, from 65 to 85% oxygen carrying salt and from 2 to 10% of silicone gel.

From the foregoing examples it will be seen that plastic explosives may be prepared which range in physical characteristics from a pliable and moldable semigelatin dynamite to a hard, unmoldable mass. The gelatinous explosives are characterized by all the desirable characteristics of gelatin explosives containing nitrocellulose-nitroglycerin gels. The gelatinous explosives of the invention are water resistant, readily moldable and give high loading densities. In addition, however, these gelatinous explosives do not change appreciably in consistency in hot or cold storage and many are readily moldable at temperatures much lower than those met even in arctic conditions.

The hard plastic explosives, in accordance with the invention and as illustrated by Example 11, which comprise a substantially fully polymerized silicone and a crystalline high explosive such as cyclonite, exhibit a greatly reduced tendency to undergo physical change during high and low temperature storage as compared with similar plastic explosives in which the matrix phase is resinous or formed, from natural or synthetic rubber,

The hard plastic explosives of the invention retain their resiliency even at extremely low temperatures while currently employed explosive bodies of this type tend to become brittle at low temperatures.

As has been illustrated in the examples, the silicone gels employed in the compositions of the invention may be initially formed and subsequently admixed with the remaining ingredients or else the silicone gels may be formed by in situ polymerization.

Polymerizable silicone oils and pastes are broadly operable in the invention. The thickness of the gel obtained will naturally depend on the viscosity of the starting oil or paste and the degree to which these materials are polymerized. Stiffer gels will be obtained with polymerizable silicone compositions of higher molecular weight. Stiffer gels are also obtained by employing greater amounts of polymerization catalyst and keeping the curing temperature below the point at which the catalyst may decompose. In general, temperatures between 100° and 150° C. have been found desirable and are preferred.

When forming gelatinous compositions it is preferred to employ polymerizable silicone oils or combinations of polymerizable silicone oils and pastes. The oils alone or oil-paste combinations are preferred in all cases when the silicone gel is not formed by in situ polymerization. Polymerizable silicone pastes by themselves are operable in forming gelatinous explosives but are not preferred because of the relatively greater difficulty encountered in uniform incorporation of the cured gel in the other ingredients of the explosive composition. When the explosive composition is formed by in situ polymerization, the polymerizable pastes are often desirable and are preferred when preparing hard plastic type compositions such as that of Example 11. The polymerizable silicone pastes commercially available are normally already catalyzed and contain as much as 50% or even more of an inert extender-filler such as titanium dioxide, silica, diatomaceous earth, and the like.

The amount of silicone gel employed in accordance with the invention will vary widely in accordance with the silicone composition used, the type of explosive, the degree of gelatinization or plasticity desired, the degree of sensitivity desired for the particular application, and the strength of the primer employed. Excellent results were obtained, as shown in the examples, with gelatin dynamites containing only 2% of silicone gel. The examples further illustrate that excellent gelatin type explosives containing essentially silicone gel and crystalline explosive may be prepared using from 3% to 20% of silicone gel. It will be noted that all of these compositions detonated readily and completely when primed with a standard No. 6 blasting cap. It is apparent, therefore, that if a more potent primer and/or a more sensitive explosive is employed, the amount of gel which may be used will be greatly increased. For example, a plastic explosive containing only 50% cyclonite will detonate readily and completely if primed with a booster cap containing a 10-gram pentaerythritol tetranitrate base charge. Such relatively insensitive explosives are actually preferred for many military uses.

In commercial explosives where it is desirable to obtain maximum effect per unit volume primed with a standard blasting initiator, it is normally preferred to employ not more than 10% of silicone gel. From the standpoint of physical properties, it is preferred to use at least 2% of the gel although noticeable benefits are obtained when 1% and even less of the silicone gel is employed. For most military purposes, it is preferred to employ not more than 50% of silicone gel with crystalline high explosive. As previously indicated, however, more than 50% may be used if found desirable. Where the explosive composition consists essentially of crystalline high explosive and silicone gel, it is especially preferred to employ from 5% to 25% gel and 95% to 75% crystalline high explosive. In the preparation of gelatinous dynamites, it is preferred to employ from about 20% to about 10% of silicone gel in admixture with from about 10% to about 20% liquid explosive nitric ester and from about 65% to about 85% of oxygen carrying salt such as ammonium nitrate, sodium nitrate, potassium chlorate and the like. In all cases it is necessary to use less gel to obtain the required plasticity and consistency if the gel is formed completely from a polymerizable silicone oil. In order to obtain given plasticity and consistency, relatively increased amounts of gel must be used when silicone oil-silicone paste gels are employed or when nonpolymerizable silicones such as the nonpolymerizable oils, greases, and mold release compositions are incorporated.

While cyclonite and pentaerythritol tetranitrate are preferred crystalline high explosives, other crystalline explosives such as trinitrotoluene, tetryl, nitroguanidine, picric acid, ammonium nitrate, nitrolactose, mannitol octanitrate, sucrose octanitrate and the like may be employed. As indicated, both organic and inorganic crystalline explosives may be employed.

As polymerization catalysts it is preferred to employ a catalyst of the peroxide type, particularly benzoyl peroxide. Other known silicone polymerization catalysts are operable such as tert-butyl perbenzoate and di-tert-butyl diperphthalate. Benzoyl peroxide is preferred because of its short cure time.

It is, therefore, apparent that greatly improved plastic explosive compositions can be prepared in accordance with the invention. Without sacrificing any of the desirable characteristics of presently known plastic explosives, the compositions containing silicone gels in accordance with the invention exhibit better consistency and plasticity over a wide temperature range and do not lose their desirable characteristics after extended storage.

This application is a continuation-in-part of my copending application Serial No. 432,899, filed May 27, 1954, now abandoned.

What I claim and desisre to protect by Letters Patent is:

1. A plastic explosive composition comprising from 75% to 95% by weight of the composition of crystalline high explosive of the group consisting of cyclonite, trinitrotoluene, pentaerythritol tetranitrate, tetryl, nitroguanidine, picric acid, nitrolactose, mannitol octanitrate, and sucrose octanitrate and from 5% to 25% by weight of the composition of a silicone gel comprising a polysilicone.

2. A plastic explosive composition comprising from 75% to 95% by weight of the composition of particulate cyclonite disposed in from 5% to 25% by weight of the composition of a silicone gel comprising a polysilicone.

3. A plastic explosive composition comprising from 75% to 95% by weight of the composition of particulate cyclonite dispersed in from 5% to 25% by weight of the composition of a polymerized silicone paste.

4. A plastic explosive composition comprising from 75% to 95% by weight of the composition of particulate cyclonite dispersed in from 5% to 25% by weight of the compositon of a polymerized silicone oil.

5. A plastic explosive composition comprising from 75% to 95% by weight of the composition of particulate cyclonite dispersed in from 5% to 25% by weight of the composition of the polymerization product of a mixture of polymerizable silicone paste and polymerizable silicone oil.

6. A plastic explosive composition comprisng from 75% to 95% by weight of the composition of particulate cyclonite dispersed in from 5% to 25% by weight of the composition of a matrix consisting essentially of the polymerization product of nonpolymerizable silicones and a substantial portion of polymerizable silcones.

7. A process for the manufacture of plastic explosive compositions which comprises admixing from 75% to 95% by weight of the explosive composition of crystalline high explosive material of the group consisting of cy-

clonite, trinitrotoluene, pentaerythritol tetranitrate, tetryl, nitroguanidine, picric acid, nitrolactose, mannitol octanitrate, and sucrose octanitrate with from 5% to 25% by weight of the explosive composition of silicone composition consisting essentially of catalyzed polymerizable silicone and heating the resulting mixture at a temperature below the decomposition point of the explosive material until a plastic composition is obtained.

8. A process in accordance with claim 7 in which the silicone composition essentially comprises a catalyzed, polymerizable silicone oil.

9. A process in accordance with claim 7 in which the silicone composition essentially comprises a catalyzed silicone paste.

10. A process in accordance with claim 7 in which the silicone composition essentially comprises a catalyzed mixture of a polymerizable silicone oil and polymerizable silicone paste.

11. A process in accordance with claim 7 in which the silicone composition essentially comprises a catalyzed mixture of a nonpolymerizable silicone and polymerizable silicone.

No references cited.