

1

3,249,474

EXPLOSIVE COMPOSITION CONTAINING IN- ORGANIC SALTS AND COATED METAL

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The present invention relates to an improved explosive composition. More particularly, it relates to an explosive composition of high inorganic nitrate content plus a liquid, which also contains a metallic fuel. An especially preferred composition is one of the aqueous slurry type which contains enough water to establish a reasonably continuous liquid phase, i.e., enough to make it plastic or fluid and which also contains substantial quantities of inorganic nitrate, fortified and sensitized by a reducing metal, preferably aluminum, which is of such character as to resist wetting. By compositions of "high inorganic nitrate" content it is intended to mean compositions containing at least 40% by weight, and usually more, of such materials as ammonium nitrate, sodium nitrate or potassium nitrate and mixtures of any two or more of these.

As pointed out in the U.S. patent to Cook and Farnam, 2,930,685, it was long considered to be impractical to include water in explosives, although there were a few exceptions. It was discovered, however, that with appropriate sensitizing ingredients, etc., practical explosives can be made which include substantial proportions of water, e.g. 5 to 20%, or even more in some cases.

Other liquids such as hydrocarbon oils have been used in high inorganic nitrate explosives. In most cases the oils have been used as fuels to balance or partly balance the excess oxygen of the nitrates. The present invention also contemplates, in lieu of or in addition to water, the use of oils and other liquids having fuel value, along with ammonium nitrate and/or alkali metal nitrates, with finely divided metals of special character as the primary sensitizers. In general, the composition will contain at least 40% by weight of ammonium nitrate as a basic ingredient. In many cases it will also contain enough liquid preferably or mainly water, to establish a substantially continuous phase. However, under some conditions, e.g. at lower temperatures, the solids will predominate and the slurry will be a relatively dry one, though still pourable, e.g. something like a stiff concrete mix. A pumper slurry may be quite liquid when pumped into a borehole and still become relatively solid after it sets and cools. It will also include particulate aluminum or other metal equivalent for the purpose (boron or magnesium) which has the particular qualities of bulk density, particle size and character, and surface active properties set forth in detail hereinafter.

Along with the substantial proportions of ammonium nitrate, with or without other nitrates, the invention contemplates addition of other oxidizers, such as perchlorates, if desired, but these ordinarily will be used in only minor proportions. Establishment of a continuous or nearly continuous aqueous or other liquid phase, with its pressure transmission characteristics, is generally desired, being an important advantage of such compositions.

A suitable aqueous composition, for example, may be prepared by dissolving one of the common water-soluble inorganic nitrates, e.g. ammonium nitrate, or ammonium nitrate plus sodium nitrate in water to form a concentrated or preferably a saturated solution. This solution is then usually and preferably combined with

2

further inorganic nitrate ingredients to make a slurry containing solid particulate nitrate. The final composition may include additional oxidizers either in solution or in undissolved particulate or crystalline form such as inorganic perchlorates, along with or in lieu of further quantities of either an ammonium or sodium nitrate. It may also include other fuels, e.g. non-explosive fuels such as sulfur, solid or viscous liquid hydrocarbons, which do not wet the particulate metal surface, as well as liquid simple alcohols and polyhydric alcohols, solid carbohydrates, etc. Materials which are explosive per se, also may be used, e.g. nitrated organic materials such as trinitrotoluene, nitrostarch, nitrobenzene, nitric acid, cellulose nitrate, single, double and triple base smokeless powders and the like. However, according to the present invention, these usually are not really necessary.

It has previously been suggested, e.g. in the patent mentioned above and in U.S. Patent 3,121,036, that the inclusion of finely divided metal, such as aluminum, as a sensitizer in compositions of this type is often desirable and advantageous. It is well known that the sensitivity and the power of the explosive compositions may be adjusted or improved in various ways by incorporating suitable quantities or proportions of various reducing materials or fuels. Metals such as aluminum, boron, magnesium and the like have been suggested before and they are particularly important and essential in the present case. However, the basis of the present invention is the discovery that these metals may be made far more useful by special treatment. Of the metals named, aluminum is ordinarily the most economical and the most satisfactory, but this aspect of the invention contemplates the use of the other reactive metals such as those named above.

A principal object of this invention is to use a suitably lyophobic surfaced metal, in suitable particulate form, to control the sensitivity of the high ammonium nitrate explosive composition. However, additional metal, especially aluminum, may also be used, above and beyond sensitivity requirements, in such a manner as to augment the energy of the blasting agent. Such additional metal is frequently desirable to improve oxygen balance. In addition to or in lieu of aluminum, the other metals already mentioned, such as boron and magnesium, and particularly the latter, are very suitable for this latter purpose, provided their chemical activity as well as their lyophobic qualities are appropriate, i.e. coated magnesium can be used. In some experiments, untreated magnesium has been found to be overactive chemically and hence unsuitable.

A further object of this invention is to control directly the density of the slurry composition by the incorporation therein of suitably treated metal of appropriate particle size and character. This latter aspect is applicable also to non-slurry blasting materials of high inorganic nitrate composition, which contain aluminum. By choice of a suitable kind of aluminum, i.e., one of suitable particle size and density, and particularly one which has relatively high surface area and an irregular, e.g. wrinkled or fluffy structure, a considerable percentage by volume of void spaces may be included. When the aluminum or other metal is hydrophobic, for use in slurries having aqueous menstruum, this provides for the inclusion of gases, e.g. air, and has the quality of adding considerable bulk to the mass without increasing its weight proportionally. By this means the overall density of the slurry may be kept below a desired maximum value. For typical ammonium nitrate-water-aluminum compositions, which may include small amounts of other ingredients, this density value in terms of grams per cc. is generally not greater than about 1.5 and preferably not

much above 1.4. In most applications it is desirable that explosives of this general nature have a density that does not exceed about 1.45.

Without increasing the aluminum proportions, and by including gases so as to provide compressible pockets for hot spots, the sensitivity of explosives of this general type may be considerably increased. The sensitivity effect is substantially inversely proportional to the density. It is desirable for many purposes to control the overall slurry density; the range may vary rather widely consistent with requisite energy in the explosive mass, and a highly satisfactory range is generally between about 1.1 and 1.60. Without the lyophobic coating treatment, slurry type explosives will often have densities above 1.60 or even higher. In most cases the highly dense compositions are very difficult to detonate. By coating the metal particles or partially coating, surface activity may be controlled as desired and materials not ordinarily detonable may become so even if their density is relatively high.

The selective use of metals for optimum sensitization in the production of low density slurry compositions, with the consequent inclusion of voids in the form of tiny and numerous pockets for gases which, on detonation, can create hot spots as described above, constitutes a double advantage for the present invention.

In experimenting with various types and grades of aluminum powder leading up to the present invention, it was found that certain "sub-grade" aluminum powders in some cases gave appreciably better results than virgin metal powders. Thus the powdered or granulated aluminum obtained by grinding thin, narrow aluminum strips, e.g. of U.S. Government surplus radar jamming materials known as "chaff," was found in many cases to give a particularly effective and satisfactorily sensitive composition when included in suitable proportions in high inorganic nitrate slurry compositions. At first, it was postulated that the coating itself might have been a contributing chemical ingredient of the explosive composition, perhaps by augmenting either the oxidizing or the reduction effect, in the presence of the inorganic nitrate. It was soon discovered, however, that the finely divided metal, from whatever source, may be rendered high effective, or relatively ineffective, depending on the extent to which it is wet by the aqueous menstruum. It was found that metal which originally did not have the desired surface active or hydrophobic properties could be treated in very simple fashion to control sensitivity of the composition with considerable success. The sensitivity of the blasting agent in which the finely divided metal, granulated or powdered appropriately is incorporated is found to be readily controllable by coating or partly coating the metal to make it water repellant or partly water repellant.

It further appears that the same concept is applicable to non-aqueous compositions, i.e., those which contain some continuous liquid menstruum other than water, such, for example, as oil, alcohol, ketones and other hydrocarbon derivatives. The metal is treated to resist in appreciable degree the wetting of its surface by any of these slurrying agents, i.e., it should be made lyophobic.

Hence, another object of this invention is to control the sensitivity and power of various liquid-containing explosives, which also contain aluminum or equivalent metal, particularly slurried or plastic mixes which are based mainly on inorganic oxidizers such as ammonium nitrate, sodium nitrate, etc., or combinations thereof. As suggested above, the compositions also may include other oxidizing materials such as the perchlorates along with the inorganic nitrate.

A further object of the invention is to enhance the power obtained from such combined ingredients by increasing the rate of combustion of the metallic powder materials included therein. As will be explained more fully below, this appears to be accomplished, at least in part, by setting up a system that will produce prodigious numbers of "hot spots" or explosion initiators.

Apparently the phenomenon of initiation of detonation often, perhaps generally, involves the creation of "hot spots." It is known that small masses or inclusions of gas subjected suddenly to extremely high pressures will create extremely high temperatures, e.g. of the order of some thousands of degrees K. When a detonator is set off adjacent to a gas bubble, it causes gas compression, as far as any air inclusions or sealed off air bubble regions are concerned. The hot spots thus created are sufficient in number and high enough in temperature, owing to adiabatic compression, to initiate rapid combustion or chemical reaction of adjacent reactive material. If this material happens to include a particle of high energy fuel, such as a particle of combustible metal, aluminum for example, in direct contact with a strongly oxidizing material such as ammonium nitrate or other inorganic nitrate at a temperature in excess of say 1000° C., the reaction becomes extremely fast. When a sufficient number of such hot spots are simultaneously created, and when the physical nature of the composition is such that their effect can be transmitted at high velocity to other sites of similar character, the powerful explosion ensues. The use of a continuous and relatively incompressible liquid phase, whether of water or some other liquid, probably greatly facilitates transmission of the high pressure started by the detonator, augmented if need be by a suitable booster.

Applying these evident phenomena to the use of metallic particles in the presence of oxidizers, such as high energy metal, e.g. aluminum in finely divided form in contact with inorganic nitrates, etc., is a further object of the present invention. It is designed to provide for an optimum or near optimum number and distribution of hot spots or initiation sites. It is designed to establish great numbers of extremely small gas bubbles in direct contact with the metal and in the presence of the potent nitrate or nitrate-perchlorate oxidizer. This is accomplished by taking steps to exclude liquid, particularly water but other polar liquids also, from at least part of the surface of the metallic particles.

In turn, the exclusion of liquid, by surface phenomena, from the metallic particles is preferably and most simply accomplished, according to the present invention, by treating the metal particles with suitable coating materials. The applied coatings may be extremely thin, perhaps approaching mono-molecular layers in thickness in some cases, and still be effective. According to one aspect of the present invention, the metallic particles, e.g. aluminum powders, are treated with small quantities of surface active or coating materials that will render them hydrophobic when water is the liquid. In general, the coating materials should prevent the particles from becoming so wet with the slurry liquid as to exclude the needed tiny gas particles or bubbles, e.g. small pockets or bubbles of air. Oil coatings on the metal are not desirable. Although they will prevent wetting with water, they are ineffective because the oil itself wets the metal. This has the effect, apparently, of destroying the desired gas pockets or rendering them ineffective.

Certain generalizations apparently may be made at this point. Fine aluminum powders are more effective as sensitizers than coarse powders, other things being equal, but they may increase the composition density so much as to offset or more than offset the sensitizing effect. Uncoated aluminum powder of smooth surface character is generally somewhat better, because more lyophobic, than uncoated rough surfaced aluminum. An example of the latter is the so-called reclaimed product obtained by burning the paper off paperbacked aluminum foil. The smooth surfaced granules appear to be more hydrophobic. The reclaimed material is otherwise a good source for particulate aluminum but the burning makes it particularly receptive to wetting with water. Virgin aluminum, ground to appropriate particle size, is somewhat effective without coating but not as satisfactory as when coated with a water repellant material.

As aqueous ammonium nitrate slurries containing aluminum stand for a period of time, they appear to lose sensitivity, apparently because more and more of the aluminum surface becomes wet. This tendency to progressive surface wetting may be offset, at least to some extent, by including in the mix a thickening or gelling agent such as guar gum, starch or the like to take up the water. Thickened compositions of this type are found to retain higher sensitivity for longer periods of time.

Various coating agents may be used to impart the desired lyophobic properties to the particulate metal. Among these are normally solid fatty acids such as stearic acid, palmitic acid, etc. and their derivatives such as, for example, calcium stearate, stearamide, etc., gilsonite, high melting point waxes applied dry (but not liquid waxes or oils), asphaltic materials, finely divided polyolefins such as polyethylene, polypropylene, etc., which are water repellant to a degree, silicone greases (which are frequently repellant to oils and other liquids as well as water) and the like and mixtures thereof.

In order to facilitate study of a large number of materials, to determine probable suitability for use in aluminum-containing slurries of the general type described above, a rather simple screening procedure was developed. Granulated or powdered metal was mixed with water after separate treatment of a portion with each coating material. For example, a small quantity of ground or comminuted aluminum, 2 to 10 cc. in volume, was mixed into a beaker partly filled with water and rapidly stirred. When readily wetted, the metal particles generally fell to the bottom in a compact mass; otherwise, in most cases, it remained suspended, in part at least, as a frothy flotation. Uncoated aluminum particles, in general, tended to quickly settle to the bottom of the beaker, whereas aluminum powder or granules coated even sparsely with most of various agents mentioned above, i.e., stearic acid, powdered waxes of high melting point, powdered gilsonite and the like, showed good hydrophobic properties and did not sink readily. An exception was ground virgin aluminum which had high specific gravity and sometimes sank even after coating. This screening test was not conclusive but it generally made it possible to quickly eliminate some coating agents.

In general, the surface active materials were applied to the aluminum by first dissolving them in a suitable solvent, such as carbon tetrachloride and thereafter mixing the particulate aluminum into the solution. This was followed by drying off the solvent. In this manner gilsonite, various waxes, silicone greases, etc. were applied successfully. Oil coated aluminum particles also remained in flotation on the water but were not successful in actual explosion tests. Finely powdered agents such as gilsonite were also applied dry with good results.

After the screening tests a number of specific examples of the more promising materials were compounded which are recited below:

EXAMPLE 1

An aqueous composition was prepared comprising 37.8 parts by weight of ammonium nitrate, 10 parts of sodium nitrate, 7 parts of sodium perchlorate, and 15 parts of water. In general, the water dissolved these salts completely especially when temperature was raised moderately. A small amount of an inhibitor to prevent excessive reaction between finely divided aluminum and water was included, 0.2 part by weight in this instance. To the solution or slurry described above, its condition depending somewhat on temperature, a mixture of additional dry ingredients was added. This dry mixture was composed of the following constituents: aluminum, 12 parts by weight, sulfur 6, gilsonite 1.5, and a guar gum thickening agent, 0.5. The guar gum in this instance contained a cross-linking agent designed to facilitate its gelling and thickening. Such a material is available un-

der the trade name EXFC-50. Ten further parts of sodium nitrate, in addition to that in the solution, were included in the dry ingredients in this specific example.

The dry materials just described were mixed into the solution at a temperature of 45° C. The original solution was essentially saturated at this temperature and the added materials were suspended in a slurry.

The resulting slurry was poured into cardboard containers of various sizes, from 2 inches in diameter to 6 inches in diameter, all charges being 6 diameters long. The material was then cooled to 25° C. and the charges were detonated while unconfined except for the minor confinement of the cardboard container. For detonation, boosters of Composition B and pentolite were employed. These were usually about one and one-half inches in diameter. 3C boosters were used for charges 3 inches in diameter or greater. For 2 and 2½ inch diameters, the boosters were size 2A. For smaller diameters, pentolite was used and was generally satisfactory.

The composition of Example I was varied by treating the metal with various agents as will be next explained. This was done for improving the sensitizing effectiveness of the particulate aluminum.

Example I-A.—Ten pounds of aluminum (reclaimed by grinding paper backed foil from which the paper had been burned) were treated with 45 grams of stearic acid dissolved in alcohol. The mixture was stirred well and thereafter the alcohol was allowed to evaporate. When the sample was completely dry, 12 parts of the coated aluminum were mixed with 6 pairs of sulphur, 1½ parts of gilsonite, and ½ part of a thickening agent. The latter was a guar gum containing a self cross-linking agent marketed under the trade name EXFC-50. Ten parts of sodium nitrate were also included in the dry mix. These dry ingredients were then mixed with the slurry suspending aqueous solution which, as noted in Example I, was made up of 37.8 parts by weight of ammonium nitrate, 10 parts of sodium nitrate, 7 parts of sodium perchlorate, 15 parts of water and 0.2 part of the inhibitor. When mixed, the combined ingredients gave a plastic flowable slurry with a density of 1.39 grams per cc. The mixture was detonated satisfactorily in a 3-inch diameter cardboard tube with a 3C booster (360 grams Composition B) but it failed in a 2½-inch diameter charge. By comparison, the uncoated aluminum mixed in exactly the same fashion detonated only in a 5-inch diameter charge with a 3C booster and failed in a 4-inch diameter charge.

Example I-B.—Fifty grams of gilsonite, select grade, were dissolved in one liter of carbon tetrachloride and the solution was sprayed on 20 pounds of aluminum recovered from paper back foil as in Example I. Mixing was continued during the spraying until all the solution was exhausted. This coated material was then thoroughly dried and incorporated in a slurry explosive in the same manner as Example I-A. This mixture detonated in a 2½ inch diameter charge, using a 2A booster (approximately 140 grams Composition B) and failed in a 2-inch diameter charge with the same booster. Mix density was 1.42 grams per cc. at 25° C.

Example I-C.—Reclaimed aluminum similar to that used in Examples I-A and I-B was stirred vigorously in a Waring Blendor with powdered dry gilsonite in a ratio of 4 grams of gilsonite per pound of aluminum. This material was then stirred into a slurry composition in the same fashion as in the above examples at 65° C. The density of the mixture was 1.43 grams per cc. at 25° C. At this temperature a 2½ inch diameter charge detonated with a 2A booster but a 2-inch diameter charge failed to detonate.

Example I-D.—Example I-C was repeated, substituting dry stearic acid for gilsonite in the same proportion. The coated material was then incorporated into a slurry in the same manner as in the preceding examples. The final density was again 1.43 grams per cc. at 25° C. and a 2½

inch diameter charge at this temperature detonated with a 2A booster while a 2-inch diameter charge failed to detonate.

As previously suggested, it was found that a wax coating applied in the same general manner as gilsonite was ineffective when slurries were mixed at a temperature above the melting point of the wax. As long as the mixing temperature was held below the wax melting point, for example around 45° C., wax was found to be an effective coating agent. Apparently, the wax must not melt so as to completely cover the aluminum particles as it probably prevents entrapment of gas particles or tiny bubbles to produce the hot spots mentioned above.

In the case of gilsonite, a quantity of this material was dissolved in carbon tetrachloride and applied in proportions of 1 to 10 grams per pound of aluminum. In all cases it was found to be an effective coating agent. A number of charges were made using various mixture in this manner. Except for the wax coating mentioned above, it was found feasible to mix the coating ingredients with the aluminum at a temperature of 65° C. This is in general range of the temperature often preferred for field mixing of slurries, particularly in cold weather operations. All the charges which were prepared were detonated, or detonation was attempted, at 25° C.

The results of all the findings are indicated in Table I. These results verify that aluminum sensitization of slurry-type blasting agents depends to a very large degree on the extent to which it is wet by water or other liquid. For hot solutions, i.e., mixes made around 65° C. or higher, select grade gilsonite dissolved in carbon tetrachloride was found to be a very suitable coating from the standpoint of effectiveness, ease of application and economy. However, silicone resins, particularly silicone greases, were also very satisfactory. Paraffin wax was suitable at lower mixing temperatures only. Gilsonite has a melting point of approximately 135° C. which gives adequate protection to the coated aluminum at high operating temperatures.

It was speculated that residual solvent might be hazardous and therefore differential thermal analyses were run on various mixtures. For this purpose aluminum granules coated with gilsonite that was first dissolved in carbon tetrachloride were tested. No effective residual solvent was observed in any case, except that with double-base

smokeless powder (20 percent nitroglycerine and 80 percent nitrocellulose) employed as coating agents, there appeared to a definite exothermic reaction at about 68° C. In this case appreciable quantities of carbon tetrachloride were found to be present. Processing can easily be done with low residual solvent and hence is not expected to cause any difficulty, even with the double-base smokeless powder materials mentioned. In other cases residual solvent, if any remained, appeared to have no effect whatsoever.

Coated aluminum powders obtained from various sources were tested, including the reclaimed materials named above. Many which were quite unsatisfactory when uncoated were found to be highly effective sensitizers with only a very light coating. The data of Table II includes granulated or powdered aluminum from various sources. The aluminum indicated at "B" is of a particular manufacture which has been obtained by comminuting the reclaimed paper backed aluminum foil mentioned above. On the other hand, aluminum designated RR39 was obtained by pulverizing a radar "chaff" in the form of slender aluminum foil strips originally obtained from the U.S. Government as a surplus war material. Uncoated aluminum of the paper backed foil type, reclaimed by burning was particularly susceptible to moisture retention and, when used uncoated, was found to have a marked tendency to depress the sensitivity of compositions containing it. This is, however, an economical source for aluminum. By coating, according to this invention, the cost of the metal component may be sharply reduced as compared to aluminum from most other sources.

The contrast between the various types of aluminum, when used without coating at all, was very marked indeed. The "chaff" particles gave very high sensitivity, due apparently to the fact that they had been previously coated. However, when the reclaimed aluminum from paper backed foil was coated with gilsonite to render it hydrophobic, according to the principles of this invention, it showed a remarkable increase in sensitivity. Results are summarized in Tables I and II. In the last column of the table, D indicates a successful detonation and F a failure. Sensitivity varies roughly inversely as d_c (critical diameter).

Table I.—Summary of coating tests on aluminum

Sample No.	Aluminum	Treating Agent	Mix Soln. Temperature, ° C.	Density, g./cc.	d_c (inches)
IA1	Braman "B" ¹	Stearic Acid, 45 gm./4,500 gm.	45	1.28	2½ D
IA2	Braman "B"	Stearic Acid, 10 gm./4,500 gm.	45	1.25, 1.39	3 D
IB1	Braman "B"	Paraffin, 45 gm./4,500 gm.	45	1.27	2½ D
IB2	Braman "B"	Paraffin, 10 gm./4,500 gm.	45	1.347 (35° C.)	2½ D
IC1	Braman "B"	Armeen T, 45 gm./4,500 gm.	45	1.525	2 F
IC2	Braman "B"	Armeen T, 10 gm./4,500 gm.	45	1.370 (33° C.)	4 F 10
	M-30 ¹	None	45	1.355 (34° C.)	5 D
S2B2A	R.R39 Chaff	Lacquer Stripped with Acetone.	45	1.450	5 D
S2B2A	R.R39 Chaff	do.	45	1.345	6 F
S2B1	Braman "B"	Calcium Stearate, 45 gm./4,500 gm.	45	1.362	5 F
S2B2B	Braman "B"	Coated with Lacquer from S2B2A.	45	1.377 (37° C.)	6 F
S2B2B	Braman "B"	do.	45	1.37	3 F
S2B2B	Braman "B"	Coated with SPDN in Acetone.	45	1.35	4 F
S2B3	Braman "B"	Untreated	45	1.387 (33° C.)	5 D
	R.R39	Untreated	45	1.317 (37° C.)	4 F
S2D IA	Braman "B"	Paraffin, 2 gm./4,500 gm.	45	1.38 (34° C.)	2½ D
S2D IB	Braman 10% "B"	Uncoated	45	1.37	4 F
	MD-44 2%	Paraffin, 10 gm./4,500 gm.	45	1.436 (35° C.)	2 F 1½
S2D IC	Braman 10% "B"	Uncoated	45	1.405 (34° C.)	5 F
	MD-44 2%	Paraffin, 2 gm./4,500 gm.	45	1.342 (34° C.)	4 F
S2D ID	R.R39	Sieved. Sample is +325 mesh	45	1.37 (31° C.)	2 D
S2D IE	M-30	Paraffin, 10 gm./4,500 gm.	45	1.32 (33° C.)	1½ D
S2D IF	Braman "B"	Mold Release Sprayed on	45	1.36 (32° C.)	1 F
S2D IG	Braman "B"	Vistanex LMMS, 10 gm./4,500 gm. (polyisobutylene-heavy liquid).	45	1.35 (33° C.)	2½ D
S2E IIIA	Braman "B"	Stearic Acid, 10 gm./4,500 gm.	45	1.395 (33° C.)	2 F
S2E IIIB	M-30	Stearic Acid, 20 gm./4,500 gm.	45	1.495 (35° C.)	2½ D
S2E IIIC	MD-44	do.	45		4 D
					3 F

Table I.—Summary of coating tests on aluminum—Continued

Sample No.	Aluminum	Treating Agent	Mix Soln. Temperature, ° C.	Density, g./cc.	d _c (inches)
82E V	I-30 ¹	Paraffin, 2 gm./4,500 gm.	45	1.335 (35° C.)	2 D 1½ F
82F IA	Braman "B"	None	45	1.44 (37° C.)	5 D
82F IB	Braman "B"	do	45	1.41 (35° C.)	4 F
82F IC	Braman "B"	Paraffin, 10 gm./4,500 gm.	45	1.35 (37° C.)	2½ D 2 F
82G IA	I-30	Gilsonite Select, 10 gm./4,500 gm.	65	1.31 (53° C.)	2½ D 2 F
82G IB	I-30	Vistanex LMMS, 10 gm./4,500 gm.	65	1.32 (51° C.)	4 D 3 F
82G IC	Braman "B"	Gilsonite Select, 10 gm./4,500 gm.	65	1.39 (42° C.)	4 D 3 F
82G ID	Braman "B"	Vistanex LMMS, 10 gm./4,500 gm.	65	1.38 (42° C.)	3 F 4 F

¹ In general, "Braman B" and M-30 aluminums were from reclaimed foil, originally paper backed from which the paper had been burned. MD-44 was an atomized molten aluminum, fine silvery beads. I-30 was from ground virgin foil which had not been burned.

Table II.—Effect of coatings on flotation of aluminum powder

Aluminum Sample	Coating	Percent Settled Before Stirring	Temperature, ° C.	Percent Settled After Stirring
Braman	Plain	<10	50	80-90
Braman	Gilsonite, 2 g./10 lb.	<1	45	40
Braman	Gilsonite, 10 g./10 lb.	<1	50	10-20
Braman	do	<1	45	10
Braman	Vistanex LMMS, 10 g./10 lb.	0	45	30
M-30	Plain	<10	43	70
M-30	Gilsonite, 10 g./10 lb.	0	45	<10
I-30	Plain	0	45	<10
I-30	Gilsonite, 10 g./10 lb.	0	45	<5
RR39	Plain	0	45	<1
RR39	Gilsonite, 10 g./10 lb.	0	45	<1
MD-44 ¹	Plain	95	45	100
MD-44 ¹	Gilsonite, 10 g./10 lb.	95	45	99
Braman	Stearic Acid, 2 g./10 lb.	0	45	10
M-30	do	0	45	10-20
MD-44	do	95	45	99
Braman	Stearic Acid, 0.5 g./10 lb.	0	45	20
Braman	Stearic Acid, 1.0 g./10 lb.	0	45	10-20

¹ Aluminum was too dense to be supported on water.

The coating material if finely powdered may also be applied as a dry coating, i.e., without solvent, in many cases. Thus by mixing dry stearic acid powder or finely powdered gilsonite directly with the particulate metal, a suitable lyophobic surface condition may be obtained on the metal. This condition is one obtained artificially which is more lyophobic than the normal untreated metal. Very small quantities of the coating agent will suffice in most cases. As a rule, it is not necessary that the entire surface of the metal be coated. It is adequate, and in some cases at least probably better, to apply merely enough coating so that the metal particles will establish sites for occluded gas, e.g. oxygen or nitrogen, etc., from the ambient atmosphere, sufficient to establish the very small but numerous hot spots to support and promote the detonation. The extent to which the liquid menstuum supports detonation by effective transmission of the shock wave or waves of detonation has not been accurately determined but such effective transmission appears to be involved in many cases, particularly in aqueous slurries containing enough water to establish a reasonably continuous phase. Preferred coating materials include the normally solid waxes, gilsonite, long chain fatty acids and derivatives which are solid such as stearic acid, calcium stearate, stearamide, silicones and silicone greases, and mixtures thereof.

It should be emphasized that the surface of the metallic particles should not be coated or wet with any liquid constituent of the slurring agent, whether water, oil, molten wax, etc., to such an extent as to preclude the entrapment of small pockets or bubbles of gas with the consequent establishment of numerous and mutually cooperating hot spots. These appear to greatly aid in detonation, al-

though they probably do not affect propagation, once effective detonation has been started.

It will be obvious that many variations in the process of preparing the material and in the particular ingredients used, as well as their proportions, may be made within the spirit and purpose of the invention. The proportions of the main ingredients may vary widely, e.g. 40 to 90 percent by weight of ammonium nitrate, preferably at least 50 percent, 0 to 20 percent or more of sodium nitrate, 5 to 25 percent of water (or other liquid such as ethylene glycol may be substituted for part and perhaps all of the water), 0.1 to 25 percent, but preferably 0.5 to 20 percent of finely divided metallic aluminum or other active metal, for most uses, 0.02 to 5 percent of coating material, preferably 0.1 to 3 percent (based on the weight of the aluminum or other metal), and preferably a thickener in proportions of 0.1 to 3 percent. The latter is not always necessary. A very useful range of aluminum is between 5 and 18%. Under appropriate conditions the slurry may be made of thick, mudlike consistency, with undissolved ammonium nitrate and/or sodium nitrate, perchlorate, etc., forming a very substantial part of the suspended solids, and particulate metal in such quantity as to render other thickening unnecessary. The liquid menstuum need not be completely continuous but it is often desirable to have it substantially so. In general the slurry is sufficiently liquid to flow freely by gravity.

Obviously, other fuels and sensitizers including explosives, such as TNT, cellulose nitrate, smokeless powders, etc., and/or non-explosives such as solid carbohydrates, cellulose materials such as sawdust, and organic liquids readily miscible with water such as alcohols, glycols, ketones, aldehydes, and carboxylic acids may be added,

so long as they are consistent with the required properties of the metallic particles, as regards liquid repellancy and gas entrapment. However the preferred fuels include solids such as sulfur and coal and other carbonaceous materials finely subdivided, as well as liquid fuels such as the alcohols, ketones, aldehydes, amines and amides that are liquid at normal temperatures and have fuel value. Formamide, in particular is a very suitable fuel.

It is intended by the claims which follow to cover all the above variations that come within the spirit and purpose of this invention, as far and as broadly and fully as the prior art properly permits.

What is claimed is:

1. A slurry explosive composition containing not more than about 25% by weight of a liquid solvent, at least 40 percent by weight, based on the total composition, of an inorganic oxidant and 0.1 to 25 percent of an active metal in finely divided solid state, said metal having an artificially produced lyophobic surface in sufficient measure substantially to increase its normal repellancy to the liquid solvent, the quantity of metal and its surface condition being sufficiently effective to substantially increase the detonation sensitivity of the total composition.

2. Composition according to claim 1 wherein the lyophobic surface is produced by a coating material selected from the group which consists of normally solid waxes, gilsonite, long chain aliphatic carboxylic acids, their metallic and nitrogen based salts, and their esters, silicones and silicone greases, and mixtures thereof.

3. Composition according to claim 1 wherein the liquid is predominantly water in proportions of 5 to 25 percent by weight of the total composition.

4. Composition according to claim 1 wherein the metal is aluminum.

5. Composition according to claim 1 wherein the metal is magnesium.

6. Composition according to claim 1 wherein the metal is boron.

7. Composition according to claim 1 wherein the metal is at least partly coated with a water repellent substance to increase its lyophobic properties.

8. A slurry blasting composition which comprises at least 50 percent by weight, based on the total composition, of ammonium nitrate, enough water to form a slurried suspension of said ammonium nitrate, but not to entirely dissolve it at normal temperatures, and 0.1 to 25 percent of finely divided metallic aluminum, said aluminum being coated with 0.02 to 10 percent, based on its own weight, of a hydrophobic coating material sufficient to prevent its being wetted entirely by said water.

9. Composition according to claim 8 containing 5 to 25 percent of water.

10. Composition according to claim 8 which also contains a thickener.

11. Composition according to claim 10 wherein the thickener comprises 0.1 to 3 percent by weight, based on the total composition, of guar gum.

12. Composition according to claim 8 which also includes ethylene glycol.

13. A composition which comprises:

0 to 90 percent, by weight, of ammonium nitrate

0 to 20 percent of sodium nitrate

5 to 20 percent of water

0 to 70 percent of inorganic perchlorate

1/2 to 25 percent of finely divided aluminum, said aluminum being coated with a water repellent coating agent in sufficient quantity to prevent substantial wetting of its surface,

0.1 to 3 percent of a thickener and

0 to 15 percent of a fuel selected from the group which consists of sulfur, solid carbonaceous materials, and liquid alcohols, ketones, aldehydes, amines and amides, and mixtures thereof.

14. Composition according to claim 13 which contains 1 to 10 percent of ethylene glycol.

15. Composition according to claim 13 wherein the coating agent comprises stearic acid compounds.

16. Composition according to claim 13 wherein the coating agent comprises gilsonite.

17. Composition according to claim 13 wherein the coating agent comprises wax applied dry so as not to wet the entire aluminum surface.

18. The process of making a relatively insensitive slurry blasting composition of high inorganic nitrate content, which comprises first treating a high energy particulate metal with a coating agent to render it substantially lyophobic and thereafter adding the so-treated metal to the slurry in proportions of 0.1 to 25 percent to sensitize said composition.

19. Process according to claim 18 wherein the metal is aluminum.

20. Process according to claim 18 wherein the coating agent is selected from the group which consists of waxes, gilsonite and long chain aliphatic carboxylic acids, their metallic and nitrogen based salts, and their esters, and mixtures thereof.

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