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# METHOD OF MAKING A BLASTING AGENT HAVING VARIABLE DENSITY

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## ABSTRACT OF THE DISCLOSURE

An elastomeric filamentary tackifying composition having variable cohesive and adhesive properties capable of preventing migration of uniformly disposed particulate constituents having widely varying densities; one example of which comprises powdered polacrylamide, water and an alcohol in desired proportions. It is especially effective in combinations where the said constituents are a high density particulate blasting composition with a low density particulate bulking agent.

Our present invention is an improved tackifying agent and compositions containing said agent and having the characteristics of being pourable and also selectively variable in density; and further discloses a unique method of making uniform, free flowing, non-segregating, dry mixtures of particulate materials having widely differing densities. More particularly, it relates to pourable blasting agents and/or explosive compositions containing inorganic oxidizing salts fuel, a filamentary or stringy tackifying agent and a light weight particulate bulking agent.

These compositions have to be mixed in a particular manner and can be formulated to any desired density (specific gravity) between .03 and 1.27.

In recent years the concepts of "sound wall" blasting and "presplitting" or "pre-shearing" have come into wide acceptance and use in the mining and construction industries. These methods are designed to retain the rock walls contiguous to a blast in a relatively undamaged condition. Both methods comprise the simultaneous detonation of light explosive charges in closely spaced drill holes. The pre-splitting concept creates a fracture plane between the wall rock and the rock to be blasted away, while the sound wall method utilizes the same concept to remove the last selvage of rock adjacent to the walls. The presplit or fracture plane is created by drilling axially parallel 2½" or 3" diameter holes on more or less two foot centers in the plane of the back slope. Explosive charges used to blast these holes are either a continuous series of coupled small diameter dynamite cartridges, or dynamite cartridges taped at intervals on detonating cord. The holes are detonated simultaneously prior to the main blast, either by electric blasting caps or a detonating cord trunk line. An explosive charge having a density of approximately .25 pound per foot of bore hole is satisfactory, in most instances.

Ammonium nitrate/fuel blasting agents have replaced dynamite in most other dry explosive applications, but, until this invention, not in pre-splitting/or sound wall blasting. This has been due to the fact that no ammonium nitrate/fuel product of the low densities required and that could be poured, blown or otherwise loaded into 1½" and larger drill holes was available. To illustrate: pourable

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ammonium nitrate/fuel oil (AN/FO) has a poured density of about 2.5 pounds per lineal foot in a 3" diameter drill hole, and is therefore ten times too dense for presplitting applications. By comparisons, the pourable variable low density (VLD) AN/Fuel compositions of this invention are easily formulated to densities of .25 pound per lineal foot in a 3" diameter drill hole. For the first time we have extended the cost savings inherent in AN/Fuel blasting agents, to pre-split and sound wall blasting. Many other potential applications for these VLD products are evident, among which are: open pit mine slope control, permissible low heat blasting agents for coal mining, and dry explosive forming.

The improvement embodied in this invention is the composition and the method for suspending particulate low density organic and inorganic bulking beads; for example, pre-expanded polystyrene foam beads or expanded vermiculite group micas; in a uniform, stable, free flowing and non-segregating mixture with the more dense ammonium nitrate/fuel particles.

To achieve the desired characteristics, it is not enough merely to wet-out the ammonium nitrate particles with fuel and mix in the bulking agent. Such mixtures drastically segregate the heavier AN/Fuel particles to the bottom of the mixer, leaving the low density bulking agent "floating" on top. Moreover, even if a perfectly uniform mixture of this type could be devised, upon being poured down a drill hole the light bulking agent particles would winnow out and strong stratifying or segregation would take place, resulting in alternate layers of bulking agent and the AN/Fuel, and the detonation would not propagate.

In order to obtain the desired non-separating, pourable, low density characteristics, the mixture also has to contain a tackifying agent of a unique type. The tackifying agent is tacky enough or of such adhesive and cohesive quality as to hold the particles of differing densities together, and yet not so strongly as to detract from the substantially free flowing characteristic of the mix when being poured. By the phrase "tackifying agent" we define a viscidulous substance that is adhesive and also elastically filamentary to such a degree as to permit the high and low density agglomerated and subdivided particles to tumble over one another during pouring as in normal flow of particulate materials, while the viscid tackifying agent elongates into fine filament until the forces involved are sufficient to effect separation thereof, yet it is sufficiently adhesive to preclude stratifying and separation of the particles by reason of density variations. A tackifying agent combining ethylene glycol/polyacrylamide, and water was found to be ideal for this purpose.

Together with the AN/Fuel and bulking agent, said tackifier forms a lightly tacky and stringy mixture which strongly resists segregation of the particles having widely varied constituent densities and are indefinitely stable.

A quality of these mixtures is that their detonation propagation sensitivity is not adversely affected by the addition of large amounts of bulking agent, and in fact are, under certain desired conditions an improvement over conventional AN/FO. This is indeed surprising when it is realized that many of the formulas tested contained between 15% and 30% by weight of bulking agents which accounted for more than 90% of the volume of the mixture. All VLD (variable low density) formulas tested propagated completely in a 1-inch I.D. steel pipe, 6 feet long, when primed with ¼ stick (about 40 grams) of 1" diameter high velocity gelatin dynamite. The spatially separated (by reason of the bulking agent) AN/Fuel particles detonate as though they are air propagating, and with a remarkable degree of reliability. The blasting agent types of VLD mixes are not cap sensitive. Cap sensitive mixtures can be made by utilizing an explosive fuel.

In making the VLD mixes it was found that a tumbling mixing action was very effective; it produced uniform results and did not break down fragile particles, such as the expanded vermiculite. One mixer found to be effective comprised a rotating cylindrical, flat bottomed aluminum drum mounted with its axis of rotation at about 60° to horizontal. A fixed polyethylene clad scraper in near spaced relation to the walls and bottom of the rotating drum during mixing, aids in the tumbling action, and cleans the mixer when the charge is dumped.

An illustrative mixing procedure for the lightest weight bulking agents wherein the constituent parts are given in weight percentage, is as follows: Into the mixer drum, first pour 12.5% of pre-expanded polystyrene foam beads as a bulking agent having a bulk density of .8 lb. cubic foot approximately. With the drum rotating, about 1% of ethylene glycol is slowly added to the agitated polystyrene to wet it out uniformly. This addition serves to completely dissipate any static electrical charge on the beads. The tumbling mass wets out very uniformly in about 1 minute, and while continuing the mixing, about .36% of polyacrylamide powder is sprinkled on. After another minute of mixing, the polyacrylamide powder has become uniformly mixed, adhering to the "wet-out" surface of the polystyrene beads. While continuing the mixing, 1.34% of water is slowly added or sprayed on. The polyacrylamide is rapidly dissolved by the water and in 1½ or 2 minutes the combination with the ethylene glycol is evident. The mixture on the surface of the polystyrene foam beads becomes stringly or filamentary and tacky and the beads start to agglomerate and tumble in 1½" to 2" diameter clumps as the gel becomes stronger. At this point, a premix of about 81.4% of porous ammonium nitrate prills with about 3.4% of ethylene glycol as fuel absorbed into and/or adsorbed onto the prills is added slowly and uniformly across the top of the agglomerating and tumbling polystyrene clumps, and mixing is continued. As the AN/EG particles fall through the lightly agglomerated polystyrene/tackifying agent clumps, they tend to break the clumps back down into single tacky particles. As the mixture tumbles together, the AN/EG particles also become coated with the tackifying agent. In the resulting mixture, the particles adhere mutually to one another, precluding further migration of the higher density AN/EG particles with respect to the bulking agent. By the time the AN/glycol addition is completed the mix is substantially uniform and ready for packaging. A 100 pound mix takes about 10 minutes to complete and the resulting mixture is uniform, non-segregating and pourable.

The above described VLD mix is slightly tacky but is dry to the touch. It will pour freely through a 2" funnel opening and has a density of 0.085. It pours readily into 2½ and 3-inch drill holes, with no separation of particles due to density differentials and at a poured density of about .20 lb. and .25 lb. per foot, respectively. A 1½" I.D. steel pipe, 6 feet long, loaded with this mixture and primed with a 2 inch long charge of high velocity gelatin dynamite, completely fragments the pipe upon detonation. Tests in 2½" and 3" drill holes 30 feet deep, were top primed with ½ and ¼ sticks of 2" x 8" high velocity gelatin dynamite. The holes propagated completely, and gave very satisfactory presplitting results. The mixtures do not set-up in storage and pour equally as well in warm and below freezing temperatures. Laboratory samples stored for over two years in glass and plastic containers show no change from the original characteristics. They do not adhere to polyethylene or polyethylene-lined bags.



When working with the heavier mineral or inorganic bulking agents such as, vermiculties, hydro-biotites, perlite, pumicite and expanded shales and particularly the more absorbent ones, the foregoing sequential mixing procedure is followed, except, that the first and last steps may be reversed. That is, the mix is started with the AN/Fuel, and add sequentially the ethylene glycol, polyacrylamide, water, and is completed with the addition of the dry bulking agent. By increasing the percentage of polyacrylamide, the strength of the tackifying agent is increased to accommodate heavier particles. These inorganic bulking agents are generally 6 lbs./cubic foot and may be heavier. The strength of the tackifier may also be adjusted by varying the relative proportions of the 3 ingredients, ethylene glycol, polyacrylamide and water.

A continuous mixing process can also be used with the VLD mixes. The trough and impellers of a continuous mixer ideally should be coated with polyethylene or other substance not adhesively related to the tackifier. Clearance between the scraper and drum wall and other members should be such that they will be wiped continuously. The order of addition of ingredients is as previously described, with the option that the polystyrene/glycol/polyacrylamide may be made up as a premix, and activated in the mixing trough by spraying on water.

While the illustrative mix contains ethylene glycol both in the tackifying agent and as a fuel, and polystyrene foam as the bulking agent, many suitable and useful variations of these ingredients can be made. Alcohols and polyhydric alcohols, for example: methanol, diethylene glycol, propylene glycol and glycerol, can be used interchangeably, alone or in combination, as a substitute for ethylene glycol both in the tackifier and as fuels. A variety of hydrocarbon fuels can be used with the porous ammonium nitrate prills, as well as a number of explosive nitric/ester fuels such as glycerol dinitrate and ethylene glycol dinitrate.

In formulating variations from the basic ingredients described, there are a number of requisites to observe.

Firstly, the tackifying agent must be of a suitable stringly-tacky character. While many other water soluble polymers and natural gums are available that will form tacky, thick and even rubbery gels, none was found that also had the stringy characteristics. When particles coated with the glycol/polyacrylamide/water tackifier are pulled apart, the gel strings out into extremely fine, strong and elastic filaments, similar to certain nitro cellulose/nitroglycerin gel characteristics. It is this characteristic that is so effective in actively holding the particles of the mixture together and yet retaining the pourability. Therefore, we employ the term "filamentary tackifying agent" to distinguish over one that is merely tacky or adhesive.

Secondly, there must be a mutual affinity or adhesion between the tackifier and both the AN/Fuel and bulking agent. The glycol/polyacrylamide/water system does not adhere well to polyethylene or wax, and consequently polyethylene foam or heavily waxed AN particles are not held together as required.

Thirdly, the ingredients must be mutually compatible. Diesel fuel oil and other liquid hydrocarbon fuels will "deflate" expanded polystyrene foam beads, but can be used with the solvent resistant expanded styrene-acrylonitrils copolymer (SAN) beads. On the other hand, nitroglycerin and nitroglycol dissolve the SAN beads while not affecting the polystyrene beads.

One of the formula variations evaluated was the substitution of pre-expanded SAN beads as the bulking agent while using DFO as the fuel with porous ammonium nitrate prills. Despite the larger size of the SAN beads (up to ⅜" diameter) the mixtures were equally dry, pourable, non-segregating and of closely similar densities to the polystyrene foam VLD compositions. Attempts to also use DFO as the wetting agent for the SAN beads were unsuccessful, since without the glycol, polyacrylamide and water are ineffective as a tackifying agent.

Table I lists a range of typical formulas and their density characteristics.

TABLE I

| | Tamped #1 | Poured at— #2 | #3 | #4 | #5 | #6 | #7 | #8 |
|---|---|---|---|---|---|---|---|---|
| PSF | 0.6 | 0.6 | 5.00 | 10.0 | 15.0 | 30.0 | | |
| SANF | | | | | | | 12.5 | 12.5 |
| AN | 86.0 | 86.0 | 90.10 | 84.3 | 78.5 | 61.0 | 80.6 | 80.6 |
| EG$_1$ | 11.6 | 11.6 | 3.75 | 3.5 | 3.3 | 2.5 | | 3.3 |
| DFO | | | | | | | 3.3 | |
| EG$^2$ | 0.4 | 0.4 | 0.40 | 0.8 | 1.2 | 2.4 | 1.0 | 1.0 |
| PA | 0.8 | 0.8 | 0.20 | 0.30 | 0.40 | 0.8 | 0.5 | 0.5 |
| H$^2$O | 0.6 | 0.6 | 0.55 | 1.1 | 1.6 | 3.3 | 2.1 | 2.1 |
| Total | 100.0 | 100.0 | 100.00 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Density | 1.27 | 0.97 | .25 | .15 | .087 | .039 | .13 | .12 |
| Lbs./ft. 3" hole | 3.9 | 3.0 | 0.82 | 0.48 | 0.27 | 0.13 | 0.44 | 0.40 |

NOTE.—Abbreviations: PSF=Polystyrene foam, 1.1 #/cu. ft.; SANF=Styreneacrylonitrile foam, 1.0 #cu. ft.; AN=Pourous ammonium nitrate prills; DFO=Diesel fuel oil saturating the prills; EG$_2$=Ethylene glycol used to wet out the foam beads; PA=Polyacrylamide powder (Polyhall M295 of Stein Hall manufacture); EG$_1$=Ethyleneglycol saturating the prills.

It should be noted that when the AN prills are crushed or ground, tamped densities in excess of 1.25 are obtainable.

The rounded shaped and non-porous, non-absorbent surfaces of the polystyrene and copolymer expanded foam beads are important advantages over other bulking agents. They mix ideally and required very small amounts of wetting agent to coat their surfaces completely. This in turn facilitates the uniform distribution of the polyacrylamide powder on their surfaces and its ready activation by the water. All commercially available sizes of the expanded foam beads (1/32" to 1/2") function equally well in the VLD mixes. The uniform smaller size beads tend to make denser mixes, and the amount of water, ethylene glycol and polyacrylamide may be varied somewhat to accommodate to differing particle size distribution. Weaker filamentary tackifying systems prevent clumping of the smaller particles.

Many other low density foamed plastics are available, such as polyurethane, phenolic, polyethylene, etc. However none of these is presently available in the rounded, non-absorbent, particulate form so ideally suitable for VLD mixes but could never-the-less be substituted if desired. These have to be chopped or diced, and in this form present open cells at the surface which absorb the wetting agent and prevent uniform distribution of the polyacrylamide. This adverse characteristic can be overcome by using much larger quantities of wetting-out liquid and correspondingly more of the polyacrylamide. Very satisfactory VLD compositions were made using diced polyurethane foam. These had characteristics approaching the foam bead types, were generally of a more moist consistency and required some variations in mixing procedures. Preparation and ingredient costs were higher.

A number of inorganic, relatively low density, particulate bulking agents are also available that are suitable for the VLD blasting agent compositions. Expanded vermiculite group micas and "popped" perlite have bulk densities of between 5 and 10 pounds per cubic foot. Pumicite and expanded shales are heavier, generally weighing over 15 lbs. per cubic foot. Perlite is the only one of these that has relatively rounded particles, and is also relatively non-absorbent.

While the extremely low densities attainable with the plastic foams cannot be achieved with these inorganic bulking agents, very satisfactory VLD mixes can be made at poured densities of .35 and higher. For example, 15% of expanded vermiculites having a bulk density of 8 lbs./cubic foot will form a VLD mix having a poured density of .45, and a loading density of 1.35 lbs. per foot in a 3" drill hole. An identical poured and loading density can be obtained using only 2% of polystyrene foam beads having a bulk density of .8 lbs/cubic foot.

Like the organic bulking agent mixes, propagation characteristics are excellent. A 15% expanded vermiculite mix will propagate completely in a 1" steel pipe, and shoot at a velocity of about 9,000 feet per second in a 3" steel pipe. As the expanded vermiculite is extremely absorbent and somewhat fragile, it was found advantageous to use the second mixing method, i.e., using the AN/Fuel as the starting point of the mix, adding the vermiculite last and mixing only until uniform. This mixture is homogenous and can be packaged immediately. However, it does not obtain maximum filamentary tackifying cohesive properties between the particles until it ages for a short time of one to two hours. Like the polystyrene bulking agent VLD mixes, samples employing vermiculite stored for over two years show no setting-up or other changes from the original properties. Perlite formulations using either of the two mixing methods with slightly higher polyacrylamide contents are satisfactory.

Additional VLD formulas are listed in Table II, and show the wide variations possible in composition and densities.

TABLE II

| | #1 | #2 | #3 | #4 | #5 | #6 | #7 |
|---|---|---|---|---|---|---|---|
| VMC | 0.0 | 2.5 | 7.5 | 12.5 | | | |
| PP | | | | | 12.5 | | |
| PSF | | | | | | 12.5 | |
| PUF | | | | | | | 5.0 |
| AN | 94.6 | 90.0 | 82.6 | 77.4 | 77.2 | 76.8 | 82.1 |
| DFO | 5.4 | 4.5 | 2.7 | | | | |
| EG$_1$ | | | 3.5 | 6.0 | 6.0 | | 3.4 |
| GD | | | | | | 6.5 | |
| EG$_2$ | | 1.8 | 1.8 | 1.5 | 1.5 | 1.5 | 4.8 |
| PA | | 0.2 | 0.4 | 0.6 | 0.8 | 0.7 | 1.4 |
| H$_2$O | | 1.0 | 1.5 | 2.0 | 2.0 | 2.0 | 3.3 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Poured density | .85 | .79 | .63 | .51 | .55 | .085 | .25 |
| Lbs./ft. 3" hole | 2.50 | 2.35 | 1.85 | 1.47 | 1.63 | 0.25 | 0.82 |

NOTE.—Abbreviations: VMC=Expanded #3 vermiculite; PP=Expanded perlite; PUF=Polyurethane foam, diced; DFO=Diesel fuel oil saturating the prills; GD=Glycerol or glycol dinitrate.

Oxygen balanced VLD compositions are much more readily attained with the inorganic bulking agents as they do not act as fuels in the detonation. However, the organic bulking agent VLD compositions detonate very effectively as much as 15% and more on the negative side of theoretical oxygen balance, and without the black smoke characteristic of oxygen negative detonations. While AN/FO blasting agents become markedly less sensitive as fuel is increased and they become more oxygen negative, there is no corresponding decrease in sensitivity as these organic bulking agent VLD compositions become theoretically more oxygen negative.

With an increase in bulking agent content, there is a regular decrease in velocity of detonation, brisance, and temperature of the reaction, and it is theorized that the reactions depart from the calculated values and are actually much less oxygen negative than would be predicted on the basis of theory.

In underground mining operations, fume class #1 explosives and blasting agents are mandatory. A number of methods are available to oxygen balance the organic bulking agent VLD compositions above 5% content which are normally negative. These entail one or more of the following methods: (1) substitution of an alternate oxidizer for part of the ammonium nitrate, which would have more available oxygen—such as sodium nitrate, calcium nitrate, potassium nitrate and certain perchlorates common in the art, and many other common oxidizers; (2) replacing all or part of the porous ammonium nitrate prills with a non-absorbent variety of ammonium nitrate such as agrictultural prills or kettle grained ammonium nitrate—this would eliminate the absorbed portion of the fuel (60% to 80%) leaving only a coating film which would shift the oxygen balance strongly toward the positive side; (3) substitution of a more nearly oxygen balanced fuel for the strongly negative fuels—such as nitroglycerin or ethylene glycol dinitrate. This latter concept is illustrated in Formula No. 6 of Table II, in which the nitroglycerin is largely absorbed in porous ammonium nitrate prills.

Many other variations in composition are possible and will be apparent to one skilled in the art.

What is claimed is:

1. The method for making a variable density detonatable composition having an inorganic nitrate oxidizer and fuel as a blasing agent, a tackifying agent and a bulking agent, which comprises:

while continuously mixing, sequentially adding:

a constituent selected from between a particulate bulking agent and a particulate blasting agent;

ethylene glycol sufficient to wet-out the surfaces of said constituent;

powdered polyacrylamide to uniformly adhere to said ethylene glycol;

water to form an elastomeric filamentary tackifying agent with said ethylene glycol and polyacrylamide substantially as and for the purposes described; and



the other of the first named constituents and continuing the mixing until uniform dispersal is achieved and wherein said particulate bulking agent is selected from organic bulking agents of discrete beads, chopped, diced, or shredded foams, selected from the group of polystyrene foam, styrene-acrylonitrile copolymer foam, polyethyelne, polyurethane and other suitable plastic foams and combinations thereof, or a mineral bulking agent of particulate expanded vermiculites, hydrobiotites, jeffersites, perlites, pumicites and shales and combinations thereof, as well as functional admixtures with said organic foams, and said particulate blasting agent is inorganic oxidizer salt selected from the group of particulate ammoniums, sodium, potassium and calcium nitrates, particulate ammonium, sodium and potassium chlorates and perchlorates and combinations thereof in combination with the fuel component which is absorbed and adsorbed with respect to the ozidizer salts and is selected from the group of liquid and liquifiable hydrocarbons, alcohols, polyhydric alcohols, nitric esters, and combinations thereof.


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