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3,161,551 AMMONIUM NITRATE-CONTAINING EMULSION SENSITIZERS FOR BLASTING AGENTS Richard S. Egly, West Terre Haute, and Albert E. Neckar, Terre Haute, Ind., assignors to Commercial Solvents Corporation, New York, N.Y., a corporation of

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Our invention relates to blasting agents. More particularly our invention relates to sensitizers for blasting agents in emulsion form.

Oxygen supplying salts such as ammonium nitrate, sodium nitrate, and potassium nitrate are widely employed 15 as constituents of blasting agents. Ammonium nitrate is considered a blasting material alone; however, it is too insensitive by itself to be initiated readily or to sustain sufficient propagation. It is necessary therefore, in order to be able to use ammonium nitrate as a blasting agent, to incorporate other materials with the ammonium nitrate for sensitization. To produce highly efficient ammonium nitrate blasting agents, sensitizers must be used which not only provide complete sensitization of each ammonium nitrate particle by covering the entire surface area of the particle but also fill all spaces in between each particle to give added density to the blasting agent both thereby providing increased blast hole pressure, increased power, more complete control, uniformity, and predictability for each blasting operation. In addition, in order to enable 30 ammonium nitrate to be used under conditions where water is present such as in wet bore holes, it is necessary that the sensitizer provide maximum resistance to water. Water resistance is necessary because the sensitiveness of the ammonium nitrate is altered by the presence of water 35 thus adversely altering the uniformity of its performance.

None of the known compositions previously used as sensitizers for oxygen supplying salts such as ammonium nitrate have proven entirely satisfactory for broad general use due to their failure to concurrently satisfy the require- 40

ments previously named.

The object of our invention is to produce improved sensitizers for use with oxygen-supplying salts, such as ammonium nitrate, which not only intimately cover each particle of ammonium nitrate and complete fill spaces in between the various particles of ammonium nitrate so as to give greater density to the blasting agent but have good resistance to water thereby enabling them to be used under

conditions wherein water is present.

We have now found that the foregoing objects are accomplished by forming water in oil emulsions containing from about 50 to about 70% by weight of ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a liquid organic sensitizer which has low solubility in water. The term "oil" as used herein is synonymous with liquid organic sensitizers. Emulsions having the above composition, when thoroughly mixed with ammonium nitrate in amounts of about one part by weight of emulsion to about 4 to 0.5 parts by weight of ammonium nitrate, produce sensitized blasting agents having an oxygen balance of from about +10% to about -10%. These blasting agents can then be satisfactorily employed under a wide variety of situations including those calling for a water resistant blasting agent.

The term "oxygen balance" is well known in the explosive art and is defined as 100 times the ratio obtained by dividing the difference between the weight of oxygen actually present and the weight of the oxygen needed to completely oxidize the elements of the composition by the total weight of the composition.

The emulsions of our invention can be formed by any

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suitable means. One such means consists of forming a mixture of from about 4 to about 20 parts by weight of an aqueous solution of ammonium nitrate containing from about 60 to about 75% ammonium nitrate by weight with one part by weight of a sensitized liquid organic compound having a low solubility in water which contains small amounts of an emulsifier capable of forming water in oil emulsions and agitating the thus formed mixture until the desired water in oil emulsion is obtained. The organic compounds which can be utilized in our invention must of themselves be sensitizers for oxygen supplying salts, they must be liquid, and they must have a low solubility in water, generally less than 5%. The thus defined organic compounds can be individually used in the emulsion or mixtures of two or more of them may be utilized. Included among these organic compounds are hydrocarbon fuel oils, tall oil, long chain fatty acids such as oleic acid, nitroalkanes such as 2-nitropropane, aromatic hydrocarbons such as benzene, nitro-substituted 20 aromatic hydrocarbons such as nitrobenzene, etc., and the like. It is necessary, as above stated, to use small amounts of an emulsifier in order to form an emulsion of desired stability. Any emulsifier which is hydrophobic in nature and will form water in oil emulsions is suitable for use in our invention. Among the emulsifiers which are operative in our invention are included the oxazolines such as 4,4-bis(hydroxymethyl)-1-heptadecyl-2-oxazoline and 4-methyl-4-hydroxymethyl-1-heptadecyl-2-oxazoline, salts of long chain fatty acids such as calcium oleate, magnesium oleate, aluminum oleate, and calcium stearate, sorbitan esters such as polyoxyethylenesorbitanmonooleate, and sorbitan sesquioleate, and ethylene oxide condensates of fatty acids. Generally we have found that about 1-3% by weight of emulsifier provides suitable stable emulsions. However, it is sometimes necessary in order to provide an emulsion stable over long periods of time to utilize up to 5% by weight of emulsifier.

While aqueous ammonium nitrate and liquid organic sensitizers are meant to compose the major part of our emulsions, we can include from about 1 to about 25% of additives to increase the sensitivity of the emulsion, lower the freezing point, increase the density, increase the viscosity, and add oxidizing or reducing potential to the emulsion composition. Additives which can be used for these purposes include tris(hydroxymethyl)nitromethane, sodium nitrate, urea, hydroxyethylcellulose, urea nitrate, etc.,

One of the important features of my new invention is the fact that it can be used in wet bore holes without being placed in a sealed bag or cartridge. Thus, solid ammonium nitrate can be dropped into the hole and the sensitized emulsion can be poured into the hole to completely cover the ammonium nitrate particles and fill the spaces in between each particle. One important feature of the emulsion is that the continuous phase of the emulsion is an organic compound with little solubility for or in water thus aiding prevention of contact of water with the ammonium nitrate to be sensitized. Another important feature of our invention is that our sensitizing emulsion compounds are heavier than water thus causing them to force water out of wet bore holes thereby further preventing contact of water with the ammonium nitrate to be sensitized.

The following are representative emulsions coming with-65 in the scope of our invention.

(A)

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	P	ercent
70	Ammonium nitrate	. 60.9
	Water	26.1
	Fuel oil	11.0
	1-heptadecyl-4,4-bis(hydroxymethyl)-2-oxazoline	2.0

3 (B)

Ammonium nitrate	60.0	
Water	16.2	
Benzene	20.8	
1-heptadecyl-4,4-bis(hydroxymethyl)-2-oxazoline		
Hydroxyethylcellulose	0.5	

The following table shows the oxygen balance of blasting agents using the above-described emulsifiers with ammonium nitrate.

Table 1

AN:Emulsion Ratio	Emulsion A	Emulsion B
0.5 1.0 2.0 3.0 4.0	-9.78 -2.33 +5.11 +8.83	-6. 49 +0. 14 +4. 11

Now having described our invention, what we claim is: 1. A blasting agent comprising a mixture of from about 0.5 to 4 parts by weight of a solid inorganic oxygen supplying salt for an explosive and about 1 part by weight of an emulsion containing from about 50 to about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic compound having a solubility of less than 5% in water and from about 1 to 5% of a hydrophobic emulsifier capable of forming a water in oil emulsion, the said mixture having an oxygen balance ranging from about +10% to about -10%.

2. A blasting agent comprising a mixture of from about 0.5 to about 4 parts by weight of a solid oxygen supplying salt selected from the group consisting of ammonium nitrate, sodium nitrate, and potassium nitrate and about 1 part by weight of an emulsion containing from about 50 to about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic compound selected from the group consisting of hydrocarbon fuel oil, long-chain fatty acids, nitroalkanes, aromatic hydrocarbons, and nitrosubstituted aromatic hydrocarbons, said sensitizing liquid organic compound having a solubility of less than 5% in water, and from about 1 to about 3% of a hydrophobic 45 emulsifier selected from the group consisting of oxazolines, salts of long-chain fatty acids, sorbitan esters, and ethylene oxide condensates of fatty acids, the mixture having an oxygen balance ranging from about +10% to about -10% .

3. The composition of claim 2 wherein the oxygen supplying salt is ammonium nitrate.

4. The composition of claim 2 wherein the emulsifier is an oxazoline selected from the group consisting of 4,4yl-4-hydroxymethyl-1-heptadecyl-2-oxazoline.

5. A sensitizer in emulsion form for blasting agents comprising from about 50 to about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic com- 60 pound having a solubility of less than 5% in water and from about 1 to about 5% of a hydrophobic emulsifier capable of forming a water in oil emulsion.

6. A sensitizer in emulsion form of the water-in-oil type for blasting agents comprising from about 50 to 65

about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic compound selected from the group consisting of hydrocarbon fuel oil, long-chain fatty acids, nitroalkanes, aromatic hydrocarbons, and nitro-substituted aromatic hydrocarbons, said sensitizing liquid organic compound having a solubility of less than 5% in water, and from about 1 to about 3% of a hydrophobic emulsifier selected from the group consisting of oxazolines, salts of long-chain fatty acids, sorbitan esters, and ethylene oxide condensates of fatty acids.

7. The composition of claim 6 wherein the emulsifier is an oxazoline selected from the group consisting of 4,4bis(hydroxymethyl)-1-heptadecyl-2-oxazoline and 4-meth-

15 yl-4-hydroxymethyl-1-heptadecyl-2-oxazoline.

8. A blasting agent comprising a mixture of from about 0.5 to 4 parts by weight of a solid oxygen supplying salt selected from the group consisting of ammonium nitrate, sodium nitrate and potassium nitrate and about 1 part by weight of an emulsion containing from about 50 to about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic compound selected from the group consisting of hydrocarbon fuel oil, long chain fatty acids, nitroalkanes, aromatic hydrocarbons and nitro-substituted aromatic hydrocarbons, said sensitizing liquid organic compound has a solubility of less than 5% in water, and from about 1 to 5% of a hydrophobic emulsifier capable of forming a water-in-oil emulsion, the said mixture having an oxygen balance ranging from about +10% to about -10%.

9. A sensitizer in emulsion form for blasting agents comprising from about 50 to about 70% ammonium nitrate, from about 15 to about 35% water, and from about 5 to about 20% of a sensitizing liquid organic compound selected from the group consisting of hydrocarbon fuel oil, long chain fatty acids, nitroalkanes, aromatic hydrocarbons and nitro-substituted aromatic hydrocarbons, said sensitizing liquid organic compound has a solubility of less than 5% in water, and from about 1 to about 5% of a hydrophobic emulsifier capable of forming a water-in-oil emulsion.

10. The compound of claim 8 wherein the aromatic hydrocarbon is benzene.

11. The compound of claim 9 wherein the aromatic hydrocarbon is benzene.

12. The compound of claim 8 wherein the nitrosubstituted aromatic hydrocarbon is nitro benzene.

13. The compound of claim 9 wherein the nitro-sub-50 stituted aromatic hydrocarbon is nitro benzene.

14. A blasting agent as defined in claim 1 wherein said emulsion contains from about 1 to about 25% tris(hydroxymethyl) nitromethane.

15. A sensitizer as defined in claim 5 further includbis(hydroxymethyl)-1-heptadecyl-2-oxazoline and 4-meth- 55 ing from about 1 to about 25% tris(hydroxymethyl)nitromethane.

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