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Stabilized emulsion explosive.

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Description

This invention relates to a stabilized emulsion explosive; more particularly, it relates to explosives containing "water-in-oil" emulsions and ammonium nitrate (AN) and ANFO prills.

The term "water-in-oil" means a dispersion of droplets of an aqueous solution or water-miscible melt (the discontinuous phase) in an oil or water-immiscible organic substance (the continuous phase). The term "emulsion" hereinafter shall refer to a water-in-oil emulsion. The term "explosive" means both cap-sensitive explosives and non-cap-sensitive explosives commonly referred to as blasting agents.

The water-in-oil emulsion explosives in accordance with the present invention contain a water-immiscible organic fuel as the continuous phase and an emulsified inorganic oxidizer salt solution or melt as the discontinuous phase. (The terms "solution" and "melt" are hereinafter used interchangeably.) Added to and mixed uniformly throughout this emulsion are AN prills or AN prills in the form of ANFO, a mixture of generally about 94% ammonium nitrate prills and about 6% of an organic liquid hydrocarbon fuel. The resulting ANFO mixture will be referred to herein as "ANFO prills".

The present invention is based on the addition of a surfactant to the AN prills or the dissolution of a surfactant in the liquid organic fuel of the ANFO prills prior to the addition of the liquid fuel to the ammonium nitrate prills. It has been found that the use of a surfactant in this manner imparts greatly increased stability to the resulting emulsion and AN or ANFO prills mixture. By "stability" is meant that the emulsion phase of the emulsion and AN or ANFO prills mixture remains a stable emulsion, i.e., does not appreciably break down or experience crystallization of the discontinuous oxidizer salt phase over a given period of time.

An inherent problem with emulsion explosives, however, and particularly with emulsion and prill mixtures, is the relative instability thereof, due to the fact that they comprise a thermodynamically unstable dispersion of supercooled solution or melt droplets in an oil-continuous phase. It has now been found that, if the liquid fuel component of the ANFO prills contains a dissolved surfactant of the types described below or, if such a surfactant is added to AN prills, the stability of the resulting emulsion and AN or ANFO prills mixture is greatly enhanced over a similar mixture not containing a surfactant so dissolved in the fuel portion or added to the AN prills. For optimum performance, the selection of a surfactant may be based on the type of AN prill and coatings involved as well as the type of emulsifier system used.

In summary, the present invention relates to a method for stabilizing a detonable mixture of emulsion and AN or ANFO prills. If the mixture involves ANFO prills, the steps comprise dissolving a surfactant in a liquid organic fuel prior to adding the fuel to AN prills, adding the fuel containing the dissolved surfactant to the AN prills to form ANFO prills and blending the ANFO prills with an emulsion to form a stable explosive composition. If AN prills are used, the steps include adding the surfactant to the prills and then mixing them with the emulsion. The present compositions comprise stabilized emulsion explosives having a mixture of AN or ANFO prills and emulsion wherein the AN prills contain a surfactant and the ANFO prills comprise a mixture of AN prills and a liquid organic fuel in which a surfactant is dissolved.

The AN prills may be any of those used in the industry for manufacturing explosives. Typically, they are porous, low density prills that enhance the sensitivity of the explosive composition by contributing air voids or pockets to the composition. Ground or high density prills, however, may also be used. AN prills generally have a surface coating to retard caking due to the hydroscopicity thereof. The types of coating include inorganic parting agents, such as talcs and clays, and organic crystal habit modifiers, such as alkyl naphthalene sulfonates. As stated above, certain coatings are found to destabilize or poison an emulsion. The use of the surfactant in accordance with the present invention greatly enhances stability of the emulsion/prill mixture, even when the prills contain the destabilizing coatings.

The surfactant may be selected from lecithin; phosphatidylethanolamine, phosphatidylinositol and phosphatidylcholine derivatives; esters; amides; imides; carboxylates; amines; polyamides; alcohols; polyols; ethers and combinations thereof. Thus, the surfactants may be amphoteric, cationic, non-ionic and anionic. A preferred surfactant is lecithin. Natural fluid lecithin is most commonly derived from soybean plants and consists of a mixture of organic materials including soybean oil and phosphatidylcholine, phosphatidyl ethanolamine and phosphatidylinositol derivatives. Lecithin is generally considered an amphoteric surfactant since it has both negative and positive functional groups. The negative charge comes from underivatized sites on phosphate groups, while the positive charge comes from quaternary amines or protonated primary amines.

Other preferred surfactants include polyamine derivatives (such as polyethylene polyamine) of polyisobutenyl phenol. This surfactant is cationic in the presence of ammonium ions.

Another preferred class of surfactants are derivatives of polyisobutenyl succinic anhydride (PIBSA) and alkanolamines. One such surfactant is a 2:1 derivative of trishydroxymethyl aminomethane and PIBSA.
Although this surfactant is a mixture of ester, imide, amide and oxazoline derivatives, the majority of surfactant molecules are nonionic in nature.

The surfactant may be added directly to the AN prills, such as by spraying, in trace amounts up to 5% or more, by weight of the prills. It may also be added to the fuel portion of ANFO prills. The fuel portion of the ANFO prills is comprised of those immiscible organic fuels described below. Prior to adding the fuel to the AN prills, the surfactant is dissolved in the organic fuel in an amount of from about 2 to about 100%, by weight of the organic fuel. This fuel solution is then added to the AN prills generally in an amount of from about 2 to about 10%, by weight of the ANFO prills. The ANFO prills then may be added to the emulsion to form the emulsion explosive composition. The amount of the emulsion may vary from about 10 to about 90%, by weight of the total composition, and the ANFO prills from about 90 to about 10%.

The immiscible organic fuel forming the continuous phase of the emulsion is generally present in an amount of from about 3 to about 15%, preferably from about 4 to about 8%, by weight of the emulsion. The actual amount used may be varied depending upon the particular immiscible fuel(s) used and upon the presence of other fuels, if any. The immiscible organic fuels may be aliphatic, alicyclic and/or aromatic and may be saturated and/or unsaturated, so long as they are liquid at the formulation temperature. Preferred fuels include tall oil, mineral oil, waxes, paraffin oils, benzene, toluene, xylenes, mixtures of liquid hydrocarbons generally referred to as petroleum distillates, such as gasoline, kerosene and diesel fuels, and vegetable oils, such as corn oil, cotton seed oil, peanut oil and soybean oil. Particularly preferred liquid fuels are mineral oil, No. 2 fuel oil, paraffin waxes, microcrystalline waxes and mixtures thereof. Aliphatic and aromatic nitro-compounds and chlorinated hydrocarbons may also be used. Mixtures of the above may be used.

The emulsifiers may be selected from those conventionally employed and are generally used in an amount of from about 0.2 to about 5%. Typical emulsifiers include sorbitan fatty esters, glycerol esters, substituted oxazolines, alkylamines or salts thereof, derivatives thereof and the like. More recently, certain polymeric emulsifiers, such as a bis-alkanolamine or bis-polyol derivative of a bis-carboxylated or anhydride derivatized olefinic or vinyl addition polymer, have been found to impart better stability to emulsions under certain conditions.

In addition to the immiscible liquid organic fuel, solid or other liquid fuels or both may be employed in selected amounts. Examples of solid fuels which may be used include finely divided aluminum particles; finely divided carbonaceous materials, such as gilsonite or coal; finely divided vegetable grain, such as wheat; and sulfur. Miscible liquid fuels, also functioning as liquid extenders, are listed below. These additional solid and/or liquid fuels may generally be added in amounts of up to about 25%, by weight.

The inorganic oxidizer salt solution forming the discontinuous phase of the emulsion generally comprises inorganic oxidizer salt in an amount of from about 45 to about 95%, by weight of the emulsion, and water and/or water-miscible organic liquids in an amount of from about 0 to about 30%. Preferably, the oxidizer salt is primarily ammonium nitrate, but other salts may be used in amounts of up to about 50%. The other oxidizer salts are selected from ammonium, alkali and alkaline earth metal nitrates, chlorates and perchlorates. Of these, sodium nitrate (SN) and calcium nitrate (CN) are preferred.

Water is preferably employed in amounts of from about 1 to about 30%, by weight of the emulsion. It is commonly employed in emulsions in an amount of from about 9 to about 20%, although emulsions may be formulated that are essentially devoid of water. Water-miscible organic liquids may at least partially replace water as a solvent for the salts and such liquids also function as a fuel for the composition. Moreover, certain organic compounds also reduce the crystallization temperature of the oxidizer salts in solution. Miscible solid or liquid fuels may include urea, alcohols, such as sugars and methyl alcohol, glycols, such as ethylene glycol, amides, such as formamide, amines, amine nitrates and analogous nitrogen-containing fuels. As is well known in the art, the amount and type of water-miscible liquid(s) or solid(s) used may vary according to desired physical properties.

Chemical gassing agents preferably comprise sodium nitrite, which reacts chemically in the composition to produce gas bubbles, and a gassing accelerator, such as thiourea, to accelerate the decomposition process. A sodium nitrite/thiourea combination begins producing gas bubbles immediately upon addition of the nitrite to the oxidizer solution containing the thiourea, which solution preferably has a pH of about 4.5. The nitrite is added as a diluted aqueous solution in an amount of from less than 0.1 to about 0.4%, by weight, and the thiourea or other accelerator is added to the oxidizer solution in a similar amount. In addition to or in lieu of chemical gassing agents, hollow spheres or particles made from glass, plastic or perlite may be added to provide density reduction. These solid density control agents also may effect the stability of emulsion explosives of the present type. It has been found that certain surfactants function better with a particular solid density control agent.
The emulsion according to the present invention may be formulated in a conventional manner. Typically, the oxidizer salt(s) and other water-soluble constituents are first dissolved in the water (or aqueous solution of water and miscible liquid fuel) at an elevated temperature of from about 25 to about 90° C or higher, depending upon the crystallization temperature of the salt solution. The aqueous solution, which may contain a gassing accelerator, is then added to a solution of the emulsifier and the immiscible liquid organic fuel, which solutions are preferably at the same elevated temperature, and the resulting mixture is stirred with sufficient vigour to produce an emulsion of the aqueous solution in a continuous liquid hydrocarbon fuel phase. Usually this may be accomplished essentially instantaneously by rapid stirring. (The compositions may also be prepared by adding the liquid organic to the aqueous solution.) Stirring should be continued until the formulation is uniform. When gassing is desired, which could be immediately after the emulsion is formed or up to several months thereafter when it has cooled to ambient or lower temperatures, the gassing agent and other advantageous trace additives are added and mixed homogeneously throughout the emulsion to produce uniform gassing at the desired rate. The solid ingredients, if any, may be added, together with the gassing agent and/or trace additives and stirred throughout the formulation by conventional means. Packaging and/or further handling should quickly follow the addition of the gassing agent, depending upon the gassing rate, to prevent loss or coalescence of gas bubbles. The formulation process also can be accomplished in a continuous manner as is known in the art.

It is advantageous to predissolve the emulsifier in the liquid organic fuel prior to adding the organic fuel to the aqueous solution. This method allows the emulsion to form quickly and with minimum agitation. However, the emulsifier may be added separately as a third component, if desired.

Once the emulsion is formed, the AN prills, to which a surfactant has been added, or the ANFO prills, which comprise AN prills and liquid organic fuel in which a surfactant has been dissolved, are then added to the emulsion and mixed uniformly throughout by conventional means.

Reference to the following Table further illustrates the present invention. Mixes 1, 3, 5 and 7 do not contain a surfactant “stabilizer” according to the present invention, while corresponding mixes 2, 4, 6 and 8, respectively, do. By comparing the detonation results between mixes 1 and 2, 3 and 4, and so on, the stabilizing effect of the surfactant is readily apparent.
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a) Sorbitan monooleate.
b) A polymeric emulsifier as described in US Patent 4,931,110.
c) Glass microballoons from 3M Company.
d) Organic microballoons from Expancel Company.
e) Ammonium nitrate prill with a talc/Petro AG coating.
f) Ammonium nitrate prill with a clay coating.
g) Ammonium nitrate prill containing both internal and external surfactants which are known emulsion poisons.
h) Liquid soya lecithin.
i) Imide derivative of PIBSA and polyethylene polyamine.
emulsion to form an explosive composition, characterized in that a surfactant is added to the AN prills prior to blending the prills with the emulsion or is dissolved in the liquid organic fuel prior to adding the fuel to the AN prills in forming ANFO prills.

2. A method as claimed in claim 1 wherein the surfactant is selected from lecithin; phosphatidylcholine, phosphatidyethanolamine and phosphatidylinositol derivatives; esters; amides; imides; carboxylates; amines; polyamines; alcohols; polyols; ethers and combinations thereof; lecithin being preferred.

3. A method as claimed in claim 1 or claim 2 wherein the liquid organic fuel is selected from tall oil, mineral oil, waxes, benzene, toluene, xylene, petroleum distillates, such as gasoline, kerosene and diesel fuels, and vegetable oils, such as corn oil, cottonseed oil, peanut oil and soybean oil; and is preferably No. 2 fuel oil.

4. A method as claimed in any of claims 1 to 3 wherein the ammonium nitrate prills have a clay or talc coating.

5. A method as claimed in any of claims 1 to 4 wherein the emulsion comprises an organic fuel as a continuous phase, an emulsified inorganic oxidizer salt solution or melt as a discontinuous phase, an emulsifier, and optionally, a density reducing agent.

6. A method as claimed in claim 5 wherein the emulsifier is selected from a bis-alkanol amine or bis-polyol derivative of a bis-carboxylated or anhydride-derivatized olefinic or vinyl addition polymer, sorbitan fatty esters, glycerol esters, substituted oxazolines, alkylamines or salts thereof, and derivatives thereof.

7. A blasting composition characterised in that it comprises ANFO prills stabilized by a method as claimed in any of claims 1 to 6 and an emulsion comprising an organic fuel as a continuous phase, an emulsified inorganic oxidizer salt solution or melt as a discontinuous phase, an emulsifier and, optionally, a density reducing agent.

8. A blasting composition as claimed in claim 7 wherein the surfactant is present in an amount of from about 2 to about 100%, by weight of the liquid organic fuel.

9. A stabilized emulsion explosive composition comprising a mixture of emulsion and ANFO prills and further comprising an emulsion in an amount of from 10 to 90%, by weight of the total composition, and ANFO prills in an amount of from 90 to 10% and comprised of ammonium nitrate prills in an amount of from 90 to 98%, by weight of the ANFO prills, a liquid organic fuel in an amount of from 10 to 2% of the ANFO prills, and characterized in that it comprises a surfactant in an amount of from about 2 to 30% of the liquid organic fuel and dissolved therein.

Patentansprüche


2. Verfahren nach Anspruch 1, bei welchem das Tensid ausgewählt wird aus Lezithin, Phosphatidylcholin, Phosphatidyethanolamin- und Phosphatidylinositolderivativen, Estern, Amidcn, Imiden, Carboxylaten, Aminen, Polyaminen, Alkoholen, Polyolen, Ethern und deren Kombinationen, wobei Lezithin bevorzugt ist.

3. Verfahren nach Anspruch 1 oder 2, bei welchem der flüssige organisches Brennstoff ausgewählt wird aus Tallöl, Mineralöl, Wachsen, Benzol, Tolukol, Xylol, Erdöldestillaten, wie Benzin, Kerosin und Dieselbrennstoffen, sowie pflanzlichen Ölen, wie Maisöl, Baumwollsamenöl, Erdnußöl und Sojabohne-
nöI, wobei Nr. 2 BrennstoffsöI bevorzugt ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei welchem das Ammoniumnitratgranulat einen Ton- oder Taktumüberzug besitzt.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei welchem die Emulsion einen organischen Brennstoff als kontinuierliche Phase, eine emulgierter anorganische Oxidationssalzlösung oder -schmelze als diskontinuierliche Phase, einen Emulgator und wahlweise ein Dichtereduzierungsmittel enthält.


7. Sprengstoffzusammensetzung, dadurch gekennzeichnet, daß sie AN-DK-Granulat, stabilisiert durch ein Verfahren gemäß einem der Ansprüche 1 bis 6, enthält sowie eine Emulsion, die einen organischen Brennstoff als kontinuierliche Phase, eine emulgierter anorganische Oxidationssalzlösung oder -schmelze als diskontinuierliche Phase, einen Emulgator und wahlweise ein Dichtereduzierungsmittel aufweist.

8. Sprengstoffzusammensetzung nach Anspruch 7, bei welcher das Tensid anwesend ist in einer Menge von etwa 2 bis etwa 100 Gew.-% bezogen auf den flüssigen organischen Brennstoff.


Revidierungen

1. Procédé pour stabiliser un mélange, apte à la détonation, constitué d’une émulsion et de pastilles de AN ou de ANFO, comprenant l’addition facultative d’un combustible organique liquide à des pastilles de AN pour former des pastilles de ANFO et le mélange des pastilles de AN ou de ANFO à une émulsion pour former une composition explosive, caractérisé en ce qu’un surfactant est ajouté aux pastilles de AN avant le mélange des pastilles à l’éMulage ou bien est dissous dans le combustible organique liquide avant addition du combustible aux pastilles de AN lors de la formation de pastilles de ANFO.

2. Procédé suivant la revendication 1, dans lequel le surfactant est choisi entre la léctihine, des dérivés phosphatidylocholines, de phosphatidythanolamine et de phosphatidylinositol ; des esters, des amides ; des imides, des carboxylates ; des amines ; des polyamines ; des alcools ; des polyols ; des éthers et leurs associations ; la léctihine étant préférée.

3. Procédé suivant la revendication 1 ou 2, dans lequel le combustible organique liquide est choisi entre le tall oil, une huile minérale, des cires, le benzène, le toluène, le xylène, des distillats de pétrole tels que l’essence, le kérosène et les combustibles diesels, ainsi que des huiles végétales, telles que l’huile de maïs, l’huile de graines de cotonnier, l’huile d’arachide et l’huile de soja, et est de préférence le fuel oil n° 2.

4. Procédé suivant l’une quelconque des revendications 1 à 3, dans lequel les pastilles de nitrate d’ammonium portent un revêtement d’argile ou de talc.

5. Procédé suivant l’une quelconque des revendications 1 à 4, dans lequel l’émulsion comprend un combustible organique comme phase continue, une solution ou masse fondue d’un sol comburant inorganique émulsionnée comme phase discontinue, un émulsionnant et, facultativement, un agent de réduction de densité.
6. Procédé suivant la revendication 5, dans lequel l'émulsionnant est choisi entre un dérivé de bis-alcanol-amine ou de bis-polyol d'un polymère d'addition oléfinique ou vinyle bi-carboxylé ou transformé en dérivé avec un anhydride, des esters gras de sorbitanne, des esters de glycérol, des oxazolines substituées, des alkylamines ou leurs sels, et leurs dérivés.

7. Composition de sautage caractérisée en ce qu'elle comprend des pastilles de ANFO stabilisées par un procédé suivant l'une quelconque des revendications 1 à 6 et une émulsion comprenant un combustible organique comme phase continue, une solution ou masse fondu d'un sel comburant inorganique émulsionnée comme phase discontinue, un émulsionnant et, facultativement, un agent de réduction de densité.

8. Composition de sautage suivant la revendication 7, dans laquelle le surfactant est présent en une quantité d'environ 2 à environ 100 % en poids du combustible organique liquide.

9. Composition explosive en émulsion stabilisée constituée d'un mélange d'une émulsion et de pastilles de ANFO, comprenant une émulsion en une quantité de 10 à 90 % en poids de la composition totale, et des pastilles de ANFO en une quantité de 90 à 10 % constituées de pastilles de nitrate d'ammonium en une quantité de 90 à 98 % en poids des pastilles de ANFO et d'un combustible organique liquide en une quantité de 10 à 2 % des pastilles de ANFO, et caractérisée en ce qu'elle comprend un surfactant en une quantité d'environ 2 à 30 % du combustible organique liquide, dissous dans ce combustible.