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AMMONIUM NITRATE EMULSION BLASTING AGENT AND METHOD OF PREPARING SAME

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ABSTRACT OF THE DISCLOSURE

An emulsion blasting agent is provided having an aqueous solution component forming a discontinuous emulsion phase; a carbonaceous fuel component forming a continuous emulsion phase and preferably characterized with a gas occlusion temperature between about 70° F. and about 190° F.; and an occluded gas component dispersed within the emulsion and forming a discontinuous emulsion phase. The emulsion is generally prepared with a prescribed carbonaceous fuel component, ammonium nitrate, water, occluded gas and an emulsifying agent. The formed emulsion, which may include added optional ingredients, is usually characterized with a pH in the range of about 2 to about 8 and is found to have unexpected stability and explosive performance characteristics.

This invention relates to an emulsion type blasting agent having an aqueous solution component forming a discontinuous emulsion phase; a carbonaceous fuel component forming a continuous emulsion phase and preferably characterized with a gas occlusion temperature between about 70° F. and about 190° F.; and an occluded gas component dispersed within the emulsion and forming a discontinuous emulsion phase. More particularly, the present invention relates to an emulsion type blasting agent having four basic components and prepared by a method wherein a particularly characterized carbonaceous fuel component, aqueous solution component and an emulsifying agent are combined in prescribed amounts with occluded gas to form an emulsion system having a pH between about 2 and about 8, and having unexpected stability and explosive performance characteristics.

Slurry type blasting agents have been formulated heretofore with normally insensitive ingredients such as inorganic nitrates, water and carbonaceous fuels. Such slurry type blasting agents are generally difficultly detonable, if at all and require, for detonability, addition of a sensitizing ingredient such as TNT, nitrostarch, smokeless powder, or aluminum. Aqueous slurries of this general nature also suffer a severe tendency for component separation and poor water resistance with a consequent deterioration in detonability. Gelling agents which are frequently added to inhibit component separation and improve water resistance generally increase the cost of such slurries without materially contributing to the explosive characteristics.

It has now been found that, although the present emulsion type blasting agent contains normally insensitive ingredients as principal components, by the practice of the present invention there results a composition having unexpectedly high sensitivity and explosive velocity with high water resistance and good storage stability. The prepared emulsion is also found to have little or no tendency for component separation even in the absence of conventional gelling agents.

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Generally stated, the present invention provides a new emulsion type blasting agent having an aqueous solution component forming a discontinuous emulsion phase, a carbonaceous fuel component forming a continuous emulsion phase, and preferably characterized with a gas occlusion temperature between about 70° F. and about 190° F., and an occluded gas component dispersed within the emulsion and forming a discontinuous emulsion phase. These components are combined by a method which forms, with a water-in-oil type emulsifying agent, an emulsion system having at least about 4% by volume of occluded gas at 70° F. and atmospheric pressure, and a density below about 1.45 grams per cc. at about 70° F. and an emulsion pH within the range of about 2 to about 8.

The preferred emulsion type blasting agent of the present invention includes four principal components forming three emulsion phases. These principal components are (1) an aqueous solution component forming a discontinuance emulsion phase, (2) a carbonaceous fuel component forming a continuous emulsion phase, (3) an occluded gas component forming a discontinuous emulsion phase, and (4) a water-in-oil type emulsifying agent component.

A first component of the present emulsion system is an aqueous solution component forming a discontinuous emulsion phase. The aqueous solution component is basically formed of ammonium nitrate dissolved in water but may also include other water soluble, emulsion compatible materials.

The aqueous solution component generally includes as a basis for the prepared emulsion, 100 parts by weight of ammonium nitrate. While commercially available "fertilizer grade" ammonium nitrate is suited for use in the composition of the present invention, other grades of ammonium nitrate may also be used. Preferably, the ammonium nitrate, prior to being dissolved, is in particulate form, that is, in the form of prills, pellets or granules having a size that will pass a No. 8 USS screen since it is found that such a size rapidly dissolves in water during formation of the aqueous solution component.

The aqueous solution component may include from about 10 to about 60 parts by weight of water as based on 100 parts by weight of ammonium nitrate. In the preferred embodiment, however, the aqueous solution component includes from about 18 to about 44 parts by weight of water to form an internal or discontinuous phase of the emulsion system.

Although the aqueous solution component forming the discontinuous emulsion phase is generally present as a solution of water and ammonium nitrate, one of the preferred embodiments of the invention may include an aqueous solution component formed of ammonium nitrate and a water soluble emulsion compatible inorganic oxidizer salt such as sodium nitrate. It is generally found that the presence of a material such as sodium nitrate permits a greater quantity of oxidizer salt to be dissolved in solution at a given temperature while influencing the final density of the emulsion.

Other water soluble emulsion compatible materials which may be substituted or additionally included with the sodium nitrate in forming the aqueous solution component include inorganic oxidizing materials such as sodium salts illustrated by sodium chlorate, and sodium perchlorate; calcium salts illustrated by calcium nitrate, calcium chlorate, and calcium perchlorate; potassium salts illustrated by potassium nitrate, potassium chlorate, and potassium perchlorate; ammonium salts illustrated by ammonium chlorate, and ammonium perchlorate; lithium salts illustrated by lithium nitrate, lithium chlorate, and lithium perchlorate; magnesium salts illustrated by

magnesium nitrate, magnesium chlorate and magnesium perchlorate; aluminum salts illustrated by aluminum nitrate, and aluminum chlorate; barium salts illustrated by barium nitrate, barium chlorate, and barium perchlorate; zinc salts illustrated by zinc nitrate, zinc chlorate, and zinc perchlorate; and organic materials illustrated by ethylene-diamine-dichlorate, and ethylene-diamine-di-perchlorate; and mixtures of these various additives as well as other emulsion compatible water soluble materials. These water soluble, emulsion compatible materials may be generally added in an amount from 0 to about 55 parts by weight and preferably to about 36 parts by weight as based on 100 parts by weight of ammonium nitrate. As in the case of ammonium nitrate, these materials desirably have a particle size that will pass a No. 8 USS screen to effect rapid formation of the aqueous solution phase.

The aqueous solution component of the present emulsion system may be formed by heating the water with the ammonium nitrate and when included, the water soluble emulsion compatible material until a solution is formed. Heating to form the aqueous solution component may be at a temperature of about 110° F. to about 120° F. and may be effected prior to or during formation of the finally prepared emulsion. Regardless of how the solution is formed, when the aqueous solution component is dispersed to form the discontinuous emulsion phase, it is generally desirable for optimum explosive properties that the water soluble materials form a saturated aqueous solution with excess solid water soluble materials dispersed therein such that a crystalline phase appears in the finally prepared emulsion when detonated.

The crystalline phase of the present emulsion generally results on cooling the finally prepared emulsion and appears in the aqueous solution component when at a temperature of about 70° F. and desirably at that temperature at which the emulsion may normally be detonated. It is generally found that the presence of crystals in the aqueous solution component increases the effective blasting potential of the present emulsion system.

Soluble carbohydrate materials exemplified by mannose, glucose, sucrose, fructose, maltose, and molasses may be added to the aqueous component to serve as supplemental fuels if desired. Other related water soluble fuels may also be similarly added to the aqueous solution component.

A second component of the present emulsion system is a carbonaceous fuel component forming a continuous or external emulsion phase and in a preferred embodiment, characterized with a gas occlusion temperature between about 70° F. and about 190° F. and preferably with a gas occlusion temperature between about 95° F. and about 130° F. Such a carbonaceous fuel component is broadly defined as one of the type which is non-water soluble and forms a water-in-oil type emulsion with the aqueous solution component when a water-in-oil type emulsifying agent is present.

The gas occlusion temperature may be defined as a temperature at which the emulsion system, when substantially free of occluded gas at a temperature above 70° F., will demonstrate the ability to occlude gas when cooled and agitated. The gas occlusion temperature may also be defined as that temperature below which gas or atmospheric air will become entrapped within the emulsion system as evidenced by a sudden decrease in the density of the emulsion-occluded gas system. Conversely, the gas occlusion temperature is that temperature at which an aerated emulsion of low density, upon heating to a temperature above about 70° F., will lose occluded gas to the atmosphere when the emulsion-occluded gas system is agitated in some manner to expose new surfaces of the emulsion to the atmosphere. Deaeration as described is accompanied by a sudden increase in the density of the emulsion-occluded gas system.

The consistency of the carbonaceous fuel component for the external emulsion phase is usually important for retention of the occluded gas component which is necessary to provide the desired sensitivity in the product emulsion. If the consistency at ambient use and storage conditions is too thin, the occluded gas component will tend to agglomerate or will be expelled from the emulsion. On the other hand, the carbonaceous fuel component used must be sufficiently fluid at manufacturing temperatures to permit formation of the emulsion. Thus, although the finally prepared emulsion may have a solid or near solid external phase, it appears usually necessary that the external emulsion phase be liquid or sufficiently fluid when the emulsion is prepared in the first instance. The carbonaceous fuel component should therefore have the ability to provide this desired consistency differential with variations in temperature.

It is generally found that when the gas acculsion temperature is lowered to below about 70° F., the prepared emulsion will either experience a tendency to lose occluded gas in normal storage and use, or the occluded gas will tend to agglomerate resulting in a product having decreased blasting potential. It is recognized, however, that such emulsions may be prepared with occluded gas provided the storage and use temperatures are maintained very low, i.e., substantially below about 70° F.

It is also generally found that gas occlusion temperatures below about 190° F. are most useful for preparing the present emulsion as it is generally desirable from a convenience stand-point to work with water emulsions at temperatures below the boiling point thereof. The preferred gas occlusion temperature in the range of about 95° F. to about 130° F., therefore avoids both gas agglomeration in normal storage and use and is most practical for commercially preparing the present emulsion blasting composition.

The carbonaceous fuel material selected for use in the present emulsion system will generally depend upon the physical form desired in the final product. The firmness of the emulsion system may be varied depending on which carbonaceous fuel material is used and especially upon the physical consistency of the fuel. The carbonaceous fuel material selected is also found to influence the explosive characteristics of the prepared product since the occluded gas component is primarily retained in the fuel component as a discontinuous phase of the emulsion system.

The carbonaceous fuel component preferably includes an all wax component, a wax and an oil component, a wax and a polymeric material component, or a wax and a polymeric modified oil component. The fuel component may thus include hydrocarbons whether paraffinic, olefinic, naphthenic, aromatic, saturated or unsaturated and which are suitable for use as the fuel component.

Waxes which may be used in the carbonaceous fuel component include waxes derived from petroleum such as petrolatum wax, microcrystalline wax, and paraffin wax; mineral waxes such as ozocerite, and montan wax; animal waxes such as spermacetic; and insect waxes such as beeswax, and Chinese wax. The most desirable waxes are those which have melting points of at least 80° F. and which are readily compatible with the formed emulsion. Preferably, these waxes have a melting point in the range of about 100° F. to about 160° F.

With the addition of any given amount of wax in the carbonaceous fuel component, the thickening effect produced may be that of the wax plus a wax modifier such as a viscous oil or polymeric material. It is found that a quantity of at least about 2% and preferably at least about 5% by weight of the carbonaceous fuel component should desirably constitute wax or insufficient occlusion of gas results in the finally prepared emulsion.

A petroleum oil of any desired viscosity may be used as a component of the carbonaceous fuel and may include oils having viscosities varying from a thin liquid to those

which are so thick that they do not flow at ordinary temperatures. Brookfield viscosities at 85° F. for typical petroleum oils appear in the range of about 160 to about 5,000 centipoises and preferably to about 3,100 centipoises.

Non-volatile, water-insoluble polymeric or elastomeric materials of the group consisting of natural rubber, synthetic rubber and polyisobutylene may be included in the carbonaceous fuel component of the present emulsion. Copolymers of butadiene-styrene, copolymers of isoprene-isobutylene, or copolymers of isobutylene-ethylene and copolymers of related materials as well as terpolymers thereof may also be usefully employed to modify the fuel component and improve same in retaining occluded gas over a prolonged period of time. Other polymeric materials may also be employed for this purpose as desired.

The carbonaceous fuel component is generally added in an amount from about 4 to about 45 parts by weight per 100 parts by weight of ammonium nitrate. In the preferred embodiment, the carbonaceous fuel component is added in an amount of about 5 to about 17 parts by weight per 100 parts by weight of ammonium nitrate.

Supplementary fuels such as saturated fatty acids, higher alcohols having a chain length of at least about 6 to more than about 18 carbon atoms, and the like may be found suitable for use in the carbonaceous fuel component of the emulsion system.

Supplementary fuels of the saturated fatty acid type which are suitable for use in the carbonaceous fuel component include octanoic acid, decanoic acid, lauric acid, palmitic acid, behenic acid and stearic acid.

Supplementary fuels of the higher alcohol type which are suitable for use in the carbonaceous fuel component include hexyl alcohol, nonyl alcohol, lauryl alcohol, cetyl alcohol and stearyl alcohol.

Other immiscible, carbonaceous materials useful as supplementary fuels in the carbonaceous fuel component include the vegetable oils such as corn oil, cottonseed oil and soybean oil.

The present emulsion system may also include as an optional fuel ingredient a finely divided non-water soluble solid particulate fuel such as carbon, coal, graphite, sulfur, or the like, or it may contain a metallic powder which serves as a fuel such as aluminum, magnesium or related alloys thereof.

Other additives may be included in the carbonaceous fuel component, as desired, provided that this component retains the ability to form a water-in-oil type emulsion and, in the preferred modification, is characterized with a gas occlusion temperature of at least about 70° F. to about 190° F.

A third component of the present emulsion system is an occluded gas component forming a discontinuous emulsion phase. Sufficient gas, generally air, is introduced into the present emulsion system by any suitable means such as by using a gas inducing mixer, or by direct introduction of gas into the emulsion which is then subsequently blended. An example of a gas inducing mixer is a ribbon-type mixer, whereas the Votator scraped surface heat exchanger type unit by Girdler Company, Louisville, Kentucky, exemplifies suitable means for combining directly introduced gas with the emulsion.

The gas component is desirably added during cooling of the emulsion to a temperature below the gas occlusion temperature such that the prepared emulsion containing the four principal components retains from about 4% to about 47% by volume of gas at 70° F. and atmospheric pressure. Preferably, this emulsion retains from about 13% to about 33% by volume of gas at 70° F. and atmospheric pressure.

If desired, the various non-gas components being processed may be heated to drive off entrapped gas. By having an entrapped gas-free system during the pre-blending or blending stages in preparation of the present emulsion, a standardized composition results into which an exact amount of gas may be added to achieve a pre-determined

density, and thereby avoid wide variance in densities of the prepared composition.

The present emulsion system contains as a fourth component, a water-in-oil type surfactant or emulsifying agent in an amount of about 0.75 part to about 5 parts by weight per 100 parts by weight of ammonium nitrate and in the preferred embodiment, from about 1.3 parts to about 3 parts by weight per 100 parts by weight of ammonium nitrate. Additional amounts of emulsifying agent may be added, if desired, since the surplus emulsifying agent may serve as a supplemental fuel for the blasting composition.

Suitable emulsifying agents found useful herein are the water-in-oil type and include those derivable from sorbitol by esterification with removal of one molecule of water. Such sorbitan emulsifying agents may include sorbitan fatty acid esters such as sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate and sorbitan tristearate. The mono- and glycerides of fat-forming fatty acids are also useful as water-in-oil type emulsifying agents.

Other water-in-oil type emulsifying agents which may be used include polyoxyethylene sorbitol esters such as the polyoxyethylene sorbitol beeswax derivative materials. Water-in-oil type emulsifying agents such as the isopropyl ester of lanolin fatty acids may also prove useful as may mixtures of higher molecular fatty alcohols and wax esters. Various other specific examples of water-in-oil type emulsifying agents include polyoxyethylene (4) lauryl ether, polyoxyethylene (2) oleyl ether, polyoxyethylene (2) stearyl ether, polyoxyalkylene oleyl/laurate, oleyl acid phosphate, substituted oxazolines and phosphate esters, to mention but a few. Mixtures of these various emulsifying agents as well as other water-in-oil type emulsifying agents may also prove useful.

The pH of the present emulsion system is generally either equivalent to or incident to the pH of the aqueous solution component taken either as aqueous ammonium nitrate solution, as the water soluble emulsion compatible oxidizer material in solution, or a combination thereof. Generally, the pH of the prepared emulsion is between about 2 and about 8, and preferably about 3.5 and about 7. When emulsions are prepared above pH 8, it is found that ammonium nitrate decomposes in the emulsion and when emulsions are prepared more acidic than pH 2, acid corrosive problems are encountered.

The present emulsion system may be prepared by combining the water with the ammonium nitrate and when included, the water soluble emulsion compatible oxidizer material to form an aqueous solution thereof. Conveniently, the aqueous solution may be rapidly effected by heating the water. Alternately, the aqueous solution component may result by simply combining all the materials in a container and heating same during formation of the emulsion. Other variations in preparing the aqueous solution component are also possible and may be employed.

The carbonaceous fuel component of the present emulsion may be prepared by combining the various fuel components and the emulsifying agent or these materials may be separately added and combined during formation of the emulsion.

When the aqueous solution component and the carbonaceous fuel component are separately prepared, they are combined to form an emulsion by any suitable mixing system which occludes sufficient quantities of the gas component into the emulsion. Alternately, the emulsion may be prepared by simple addition of the various components to a mixer with either little or no occlusion of gas. The gas is then occluded by a separate step after the emulsion is prepared.

The present emulsion is preferably formed from an external emulsion phase material having a consistency sufficiently thin for emulsion formation above the gas occlusion temperature. Thereafter, the consistency is thickened by cooling so that the occluded gas may be retained. Thus,

a carbonaceous fuel component forming the external emulsion phase appears in liquid form at emulsion preparation temperatures and as a paste or solid form at either storage or use temperatures.

It is desirable for the preferred embodiment of the present invention that the fuel component and the aqueous solution component be processed at a temperature either at or above the gas occlusion temperature. It is also found desirable that the materials in the aqueous solution component be in solution during formation of the emulsion. This will insure that the crystalline phase appear dispersed within the aqueous solution phase when the emulsion is cooled to a temperature below the solution saturation point. Thus, the crystalline phase should appear in the aqueous solution phase of the prepared emulsion when the emulsion temperature is about 70° F. and desirably at that temperature at which the emulsion may normally be detonated.

The temperature of emulsion formation as well as the gas occlusion temperature varies depending upon the materials being processed. It is generally found in the preferred embodiment that the temperature of emulsion formation is within the range of about 100° F. to about 135° F. and the gas occlusion temperature is within the range of about 95° F. to about 130° F.

In combining the components in one process of the present invention, it has been found that greater uniformity of the emulsion on storage may be obtained if the temperature during the mixing or emulsification step is kept above the melting point of the fuel blend, that is, from about 100° F. to about 160° F. However, the process of this invention may be performed outside these temperature limits, if desired.

The preferred process of the present invention generally involves forming an emulsion system by separately mixing the aqueous solution component with the carbonaceous fuel component containing a water-in-oil type emulsifying agent and other materials as may be desired. This preferred process is generally performed with heating and mixing, of the components at a temperature above the gas occlusion temperature. After the components have been combined to a substantially uniform consistency, the temperature is gradually lowered to the gas occlusion temperature with continued mixing. A sudden decrease in density is experienced about the gas occlusion temperature and after the requisite amount of gas has been occluded into the emulsion, the temperature may be lowered at any desired rate without further mixing. Should it be found that insufficient gas has been occluded into the emulsion, then the emulsion may be heated to the gas occlusion temperature for introduction of additional quantities of gas as desired.

Many variations exist for introducing the occluded gas component into the emulsion system. The most common method consists of simply mixing the emulsion in an open vessel. However, gas may be introduced by bubbling gas through an orifice, by the use of injectors, or by various other mechanical means. Chemical generation of gas in the emulsion is also possible. It is also noted that although the occluded gas is generally air, other gases may be used such as gaseous hydrocarbons, nitrous oxide, nitrogen, carbon dioxide, substantially pure oxygen, or the like.

In order to further illustrate the present invention, the following examples are given wherein all parts are by weight unless otherwise indicated:

EXAMPLE 1

An emulsion type blasting agent is prepared by combining as a wax component, 2.3 parts by weight of a friable oil-soluble crystalline wax having a melting point of about 121–124° F. and identified by the trademark Atlantic 342 by the Atlantic Refining Co.; as an oil component, 5.4 parts by weight of a highly refined mineral

oil identified by the trademark Atreol 34 also by the Atlantic Refining Co.; 5 parts by weight of a water-in-oil type emulsifying agent formed of mono- and diglycerides of fat forming fatty acids and identified by the trademark Atmos 300 by Atlas Chemical Industries, Inc.; 100 parts by weight of ammonium nitrate; 15 parts by weight of sodium nitrate and 28 parts by weight of water. These various materials are combined in a water jacketed mixer. Heat is applied to the mixer until the temperature of emulsion formation of about 114° F. is passed. Thereafter, the ingredients are actively mixed to form an emulsion of substantially uniform consistency. The prepared emulsion is slowly cooled to a gas occlusion temperature found to be 114° F. at which a sudden drop in density is noted during which time air is occluded into the emulsion by continued mixing in the open vessel. The temperature is continuously lowered to about 110° F. at which temperature mixing is stopped. The finally prepared emulsion, upon further cooling is found to have about 13.9% by volume, at 70° F. and atmospheric pressure, of occluded air a density of about 1.18 gms./cc. at 70° F. and a pH 4. At 70° F., the prepared emulsion is found to have a very soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F. is found to have a 3" x 12" cartridge detonation velocity of about 14,700 ft./sec.

EXAMPLE 2

An emulsion blasting agent is prepared by combining 2.4 parts by weight of the wax component of Example 1, 5.6 parts by weight of the oil component of Example 1, 3 parts by weight of a water-in-oil type emulsifying agent formed of oleyl acid phosphate, 100 parts by weight of ammonium nitrate, 16 parts by weight of sodium nitrate, and 29 parts by weight of water. In addition, 2 parts by weight of hollow, finely divided, low-density particles of glass identified by the trademark Micro-balloon by the Standard Oil Co. of Ohio is included as gas retaining particles. These various materials are combined according to the procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 114° F. and a gas occlusion temperature of 114° F. The prepared emulsion is also found to have about 14.2% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.15 gms./cc. at 70° F. and a pH 4. At 70° F., the prepared emulsion is found to have a soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 16,400 ft./sec.

EXAMPLE 3

An emulsion blasting agent is prepared by combining as a wax component, 3.4 parts by weight of a modified, highly cohesive microcrystalline wax having a melting point of about 114–119° F. and identified by the trademark Indra 2119 by Industrial Raw Materials Corp.; as an oil component, 3.4 parts by weight of a polymer modified, high viscosity lubricating oil identified by the trademark Molol-B by Witco Chemical Company, Inc.; 1.4 parts by weight of a water-in-oil type emulsifying agent formed of polyoxyethylene(2)oleyl ether and identified by the trademark Brij 92 by Atlas Chemical Industries, Inc.; 100 parts by weight of ammonium nitrate; and 27 parts by weight of water. The wax component and oil component are separately combined after which the water-in-oil emulsifying agent is added. The ammonium nitrate and water are separately combined. These two component mixtures are then formed into an emulsion at a temperature above the saturation temperature for the ammonium nitrate solution and according to the mixing procedure

of Example 1. The emulsion is found to have an emulsion formation temperature of about 115° F. and a gas occlusion temperature of about 111° F. The prepared emulsion is also found to have about 7.7% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.35 gms./cc. at 70° F. and a pH 5. At 70° F., the prepared emulsion is found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 14,900 ft./sec.

EXAMPLE 4

An emulsion blasting agent is prepared by combining 9.7 parts by weight of the wax component of Example 3, 1.8 parts by weight of a water-in-oil type emulsifying agent formed of sorbitan monooleate, 100 parts by weight of ammonium nitrate, 31 parts by weight of potassium nitrate, 35 parts by weight of water, and 20 parts by weight of finely divided carbon. These various ingredients are combined to form an emulsion according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 121° F. and a gas occlusion temperature of about 110° F. The prepared emulsion is also found to have about 19% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.17 gms./cc. at 70° F. and a pH 5. At 70° F., the prepared emulsion is found to have a soft character and when detonated by 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have 3" x 12" cartridge detonation velocity of about 17,400 ft./sec.

EXAMPLE 5

A series of emulsion blasting agents are prepared by the procedure of Example 1, each having one of the following water-in-oil type emulsifying agents substituted for Atmos 300; sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate and sorbitan tristearate. The emulsions are found to have emulsion formation temperatures of about 114° F.-116° F. and gas occlusion temperature of about 114° F. The prepared emulsions are also found to have about 15.3% to about 19.7% by volume of occluded air at 70° F. and atmospheric pressure, densities of about 1.10-1.16 gms./cc. at 60° F. and pH's about pH 4 to about pH 5. At 70° F., the prepared emulsions are found to have very soft to soft character and when each is detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at 70° F., are found to have 3" x 12" cartridge detonation velocities of about 13,900 ft./sec. to about 14,500 ft./sec.

EXAMPLE 6

An emulsion blasting agent is prepared using the ingredients of Example 1. Initially, a solution is formed by dissolving sodium nitrate and ammonium nitrate in water. Thereafter, a carbonaceous fuel component is prepared with the wax and oil components to which is added the water-in-oil emulsifying agent. The carbonaceous fuel component, at a temperature above the aqueous solution temperature, is stirred until a substantially uniform consistency is obtained. Thereafter, the prepared aqueous solution component and the carbonaceous fuel component, while both at a temperature above the saturation temperature for the aqueous solution, are blended with stirring and heating to a temperature above the emulsion formation temperature of about 114° F. The prepared emulsion is slowly cooled to a gas occlusion temperature found to be 114° F. at which a sudden drop in density is noted during which time air is occluded into the emul-

sion by continued mixing in the open vessel. The temperature is continuously lowered to about 110° F. at which temperature mixing is stopped. The finally prepared emulsion upon further cooling is found to have about 12.4% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.20 gms./cc. at 70° F. and a pH 4. At 70° F., the prepared emulsion is found to have a very soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have 3" x 12" cartridge detonation velocity of about 15,500 ft./sec.

EXAMPLE 7

An emulsion blasting agent is prepared by the procedure of Example 1, having an emulsifying agent formed of high molecular weight cationic polymeric fatty amine and identified by the trademark G-3570 by Atlas Chemical Industries, Inc. substituted for Atmos 300. The emulsion is found to have an emulsion formation temperature of about 114° F. and a gas occlusion temperature of about 114° F. The prepared emulsion is also found to have about 14% by volume of occluded gas at 70° F. and atmospheric pressure, a density of about 1.18 gms./cc. at 70° F. and pH about 6.5. At 70° F., the prepared emulsion is found to have a soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 14,000 ft./sec.

EXAMPLE 8

An emulsion blasting agent is prepared by combining 9.1 parts by weight of a viscous motor oil identified as RM-8670 by Industrial Raw Materials Corp., 1.8 parts by weight of the water-in-oil type emulsifying agent of Example 1, 100 parts by weight of ammonium nitrate, 29.1 parts by weight of sodium nitrate, and 36.4 parts by weight of water. In addition, 5.5 parts by weight of hollow, finely divided, low-density particles of glass identified by the trademark Microballoons by the Standard Oil Co. of Ohio is included as gas retaining particles. These various materials are combined according to the procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 106° F. and a consistency at 70° F. such that the gas entraining particles are held substantially uniformly throughout the prepared emulsion. The prepared emulsion is also found to have a density of about 1.15 gms./cc. at 70° F. and a pH 4. At 70° F., the prepared emulsion is found to have a very soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 16,400 ft./sec.

EXAMPLE 9

An emulsion blasting agent is prepared by combining as a wax component, 3.4 parts by weight of a modified, highly cohesive microcrystalline wax having a melting point of about 118-122° F. and identified by the trademark Indra 2126 by Industrial Raw Materials Corp.; as an oil component, 3.4 parts by weight of Atreol 34 of Example 1; 1.4 parts by weight of sorbitan monooleate water-in-oil type emulsifying agent; 100 parts by weight of ammonium nitrate; and 27 parts by weight of water. The wax component and oil component are separately combined after which the water-in-oil emulsifying agent is added. The ammonium nitrate and water are separately combined. These two component mixtures are then formed into an emulsion and mixed at a temperature above the saturation temperature for the ammonium nitrate solu-

tion and according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 113° F., a gas occlusion temperature of about 112° F., and about 12.3% by volume of occluded air at 70° F. and atmospheric pressure. The prepared emulsion is found to have a density of about 1.14 gms./cc. at 70° F. and a pH 4.5. The emulsion is also found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 17,300 ft./sec.

EXAMPLE 10

An emulsion blasting agent is prepared by combining as a wax component, 3.5 parts by weight of a modified, highly cohesive microcrystalline wax having a melting point of about 114–119° F. and identified by the trademark Indra 2119 by Industrial Raw Materials Corp.; 5.3 parts by weight of DNT; 1.4 parts by weight of sorbitan monooleate water-in-oil type emulsifying agent; 29.7 parts by weight of sodium nitrate; 100 parts by weight of ammonium nitrate; and 35 parts by weight of water. The wax component and DNT component are separately combined after which the water-in-oil emulsifying agent is added. The ammonium nitrate, sodium nitrate and water are separately combined and mixed. These two component mixtures are then formed into an emulsion at a temperature above the saturation temperature for the ammonium nitrate-sodium nitrate solution and according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 114° F. and a gas occlusion temperature of about 112° F. The prepared emulsion is also found to have about 19.6% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.15 gms./cc. at 70° F. and a pH 5. At 70° F., the prepared emulsion is found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 4" x 12" cartridge detonation velocity of about 16,600 ft./sec.

EXAMPLE 11

An emulsion blasting agent is prepared by combining as a wax component, 4.4 parts by weight of a modified, highly cohesive microcrystalline wax having a melting point of about 118–122° F. and identified by the trademark Indra 2126 by Industrial Raw Materials Corp.; as an oil component, 4.4 parts by weight of Atreol 34 of Example 1; 1.8 parts by weight of sorbitan monooleate water-in-oil type emulsifying agent; 15.3 parts by weight of particulate aluminum; 29.9 parts by weight of sodium nitrate; 100 parts by weight of ammonium nitrate; and 35.1 parts by weight of water. The wax, aluminum and oil are separately combined after which the water-in-oil emulsifying agent is added. The ammonium nitrate, sodium nitrate and water are separately combined and mixed. These two component mixtures are then formed into an emulsion at a temperature above the saturation temperature for the ammonium nitrate-sodium nitrate solution and according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 112° F. and a gas occlusion temperature of about 110° F. The prepared emulsion is also found to have about 22.3% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.15 gms./cc. at 70° F. and a pH 6. At 70° F., the prepared emulsion is found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a

temperature of about 70° F., is found to have a 4" x 12" cartridge detonation velocity of about 17,700 ft./sec.

EXAMPLE 12

An emulsion blasting agent is prepared by combining as a wax component, 3.6 parts by weight of a crystalline wax identified by the trademark Atlantic 342; as an oil component, 3.6 parts by weight of Atreol 34; 3.1 parts by weight of sorbitan monooleate water-in-oil type emulsifying agent; 100 parts by weight of ammonium nitrate; 15.4 parts by weight of sodium nitrate and 27.7 parts by weight of water. These various materials are combined in a water jacketed mixer. Heat is applied to the mixer until the temperature of emulsion formation of about 117° F. is passed. Thereafter, the ingredients are actively mixed to substantially uniform consistency. The prepared emulsion is slowly cooled to a gas occlusion temperature found to be 110° F. at which a sudden drop in density is noted during which time air is occluded into the emulsion by continued mixing in the open vessel. The temperature is continuously lowered to about 101° F. at which temperature mixing is stopped. The finally prepared emulsion, upon further cooling is found to have about 37.1% by volume occluded air at 70° F. and atmospheric pressure, a density of about 0.88 gms./cc. at 70° F. and a pH 4. At 70° F., the prepared emulsion is found to have a very soft character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by the No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 8" cartridge detonation velocity of about 12,280 ft./sec.

EXAMPLE 13

An emulsion blasting agent is prepared by combining as a wax component, 4.4 parts by weight Indra 2126 wax; 4.4 parts by weight of high molecular weight isobutylene polymer identified by the trademark Paratac by Arkansas Co., Inc.; 1.7 parts by weight of Atmos 300 water-in-oil type emulsifying agent; 100 parts by weight of ammonium nitrate; 29.8 parts by weight of sodium nitrate; and 35 parts by weight of water. The wax component and polymer component are separately combined after which the water-in-oil emulsifying agent is added. The ammonium nitrate, sodium nitrate and water are separately combined and mixed. These two component mixtures are then formed into an emulsion at a temperature above the saturation temperature for the ammonium nitrate-sodium nitrate solution and according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 118° F. and a gas occlusion temperature of about 112° F. The prepared emulsion is also found to have about 17.1% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.16 gms./cc. at 70° F. and a pH 5. At 70° F., the prepared emulsion is found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have a 3" x 12" cartridge detonation velocity of about 16,200 ft./sec.

EXAMPLE 14

An emulsion blasting agent is prepared by combining as a wax component, 5.2 parts by weight of a modified, highly cohesive microcrystalline wax having a melting point of about 114–119° F. and identified by the trademark Indra 2119 by Industrial Raw Materials Corp.; as an oil component, 3.4 parts by weight of bunker fuel oil; 1.7 parts by weight of Atmos 300 water-in-oil type emulsifying agent; 100 parts by weight of ammonium nitrate; 31 parts by weight of sodium nitrate; and 31 parts by weight of water. The wax component and oil component

are separately combined after which the water-in-oil emulsifying agent as added. The ammonium nitrate, sodium nitrate and water are separately combined and mixed. These two component mixtures are then formed into an emulsion at a temperature above the saturation temperature for the ammonium nitrate-sodium nitrate solution and according to the mixing procedure of Example 1. The emulsion is found to have an emulsion formation temperature of about 107° F. and a gas occlusion temperature of about 104° F. The prepared emulsion is also found to have about 16.9% by volume of occluded air at 70° F. and atmospheric pressure, a density of about 1.23 gms./cc. at 70° F. and a pH 5. At 70° F., the prepared emulsion is found to have a firm character and when detonated by a 3" x 3" cartridge of high velocity gelatin dynamite initiated by a No. 6 standard electric blasting cap after emulsion storage for 28 days at a temperature of about 70° F., is found to have 3" x 12" cartridge detonation velocity of about 15,820 ft./sec.

The sensitivity and detonation velocity of the present emulsion usually may be modified by addition of gas entraining particles of a size that will at least pass through a No. 8 USS screen such as, for example, microspheres formed of resinous materials, or hollow glass balls. Generally, about 1 part by weight of the gas entraining particles based on 100 parts by weight of ammonium nitrate is required to obtain an advantage and usually more than about 70 parts by weight per 100 parts by weight of ammonium nitrate fail to yield further advantage or improvement.

The gas entraining particles may be substituted in total or in part for the occluded air component. When the gas entraining particles are substituted in total for the occluded air component, it is necessary that the carbonaceous fuel component have a consistency such that the gas entraining particles be held substantially uniformly throughout the prepared emulsion when at normal use temperatures, i.e., about 70° F. It is recognized that the consistency of the carbonaceous fuel component in this instance may be thinner for holding the gas entraining particles than in the case when gas component is simply occluded in the emulsion. Generally because of the greater cost of these gas entraining particles as compared to air, it is desirable to include such particles in the present emulsion only as a supplemental material.

Preferably, the amounts of the principal components added to form the present emulsion are adjusted within the range specified to yield a mobile emulsion which has approximately an oxygen balance of about ± 10 percent. When an amount of finely divided solid fuel such as coal or aluminum is added, the oxygen balance of the emulsion may be as low as -20 percent and the finally prepared emulsion containing optional additives is preferably within the oxygen balance range of ± 10 percent.

The present emulsion is ordinarily detonated with the aid of a booster charge, and is thus non-cap sensitive to a standard No. 8 blasting cap when the emulsion is prepared with occluded air to a density of about 0.90 gms./cc. to about 1.40 gms./cc. at about 70° F. A standard No. 8 blasting cap generally possesses the explosive equivalent of about 2.00 grams of mercury fulminate.

The present emulsion are insensitive to usual mechanical shock and are capable of performing as powerful explosives but do not contain, unless optionally added, a sensitive high explosive material such as TNT and nitroparaffins. Materials such as DNT may also be optionally added if desired.

The present emulsion when prepared with occluded gas in the density range above 0.90 gm./cc. at about 70° F. may be safely manufactured, stored and shipped, and may be prepared in a processing plant and transported to the blasting site. Alternately, the present emulsion may be prepared at the site in a mobile unit.

The explosive velocity of the presently prepared blast-

ing agents is generally in the range of about 13,000 ft./sec. to about 20,000 ft./sec. Higher and lower explosive velocities may be prepared as desired by altering either the density or composition of the prepared emulsion.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

What is claimed is:

1. An emulsion blasting agent consisting essentially of an aqueous solution of ammonium nitrate forming a discontinuous emulsion phase; a carbonaceous fuel forming a continuous emulsion phase; an occluded gas dispersed within said emulsion and comprising at least 4% by volume, thereof at 70° F. and atmospheric pressure; and a water-in-oil type emulsifying agent; said carbonaceous fuel having a consistency such that said occluded gas is held in said emulsion at a temperature of 70° F.
2. The blasting agent of claim 1 wherein said occluded gas is substantially uniformly dispersed within said emulsion in gas entraining particles.
3. The blasting agent of claim 1 wherein said prepared blasting agent has a stability for at least 28 days at 70° F. storage temperature.
4. The blasting agent of claim 1 wherein: said aqueous solution is formed of:
 - (a) 100 parts by weight of ammonium nitrate;
 - (b) about 10 to about 60 parts by weight of water;
 - (c) up to about 55 parts by weight of at least a second water soluble, emulsion compatible oxidizing material in addition to said ammonium nitrate;
 said carbonaceous fuel is present in an amount from about 4 to about 45 parts by weight; said occluded gas is present in an amount from about 4% to about 47% by volume of said emulsion at 70° F. and atmospheric pressure; and said water-in-oil type emulsifying agent is present in an amount from about 0.75 to about 5 parts by weight.
5. The blasting agent of claim 1 wherein: said aqueous solution is formed of:
 - (a) 100 parts by weight of ammonium nitrate;
 - (b) about 18 to about 44 parts by weight of water;
 - (c) up to about 36 parts by weight of at least a second water soluble, emulsion compatible oxidizing material in addition to said ammonium nitrate;
 said carbonaceous fuel is present in an amount from about 5 to about 17 parts by weight; said occluded gas is present in an amount from about 13% to about 33% by volume of said emulsion at 70° F. and atmospheric pressure; and said water-in-oil type emulsifying agent is present in an amount from about 1.3 to about 3 parts by weight.
6. The blasting agent of claim 1 wherein ammonium nitrate in crystalline phase is present within the aqueous solution when said solution is at a temperature of 70° F.
7. The blasting agent of claim 4 wherein the water soluble, emulsion compatible oxidizing material is selected from the group consisting of sodium nitrate, sodium chlorate, sodium perchlorate, calcium nitrate, calcium chlorate, calcium perchlorate, potassium nitrate, potassium chlorate, potassium perchlorate, ammonium chlorate, ammonium perchlorate, lithium nitrate, lithium chlorate, lithium perchlorate, magnesium nitrate, magnesium chlorate, magnesium perchlorate, aluminum nitrate, aluminum chlorate, barium nitrate, barium chlorate, barium perchlorate, zinc nitrate, zinc chlorate, zinc perchlorate,

ethylene-diamine-dichlorate and ethylene-diamine-dipchlorate.

8. The blasting agent of claim 1 wherein at least 2% by weight of the carbonaceous fuel is a wax having a melting point above about 80° F.

9. The blasting agent of claim 8 wherein a petroleum oil is included in combination with the wax in the fuel phase.

10. The blasting agent of claim 8 wherein a tackifying polymeric material is included in combination with the wax in the fuel phase.

11. The blasting agent of claim 8 wherein the wax is selected from the group consisting of microcrystalline wax, and paraffin wax having a melting point of about 100° F. to about 160° F.

12. The blasting agent of claim 1 wherein a supplementary fuel is included.

13. The blasting agent of claim 1 wherein a non-water soluble solid particulate fuel is included.

14. The blasting agent of claim 13 wherein the non-water soluble particulate fuel is carbon, coal, aluminum, or magnesium.

15. The blasting agent of claim 1 wherein the water-in-oil type emulsifying agent is a sorbitan fatty acid ester selected from the group consisting of sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, and a mono- or diglyceride of a fat-forming fatty acid.

16. The blasting agent of claim 4 wherein about 1 to about 70 parts by weight of gas entraining particles are included.

17. The blasting agent of claim 16 wherein the gas entraining particles are glass microspheres having a particle size that will at least pass through a No. 8 USS screen.

18. A process for preparing an emulsion blasting agent which comprises:

(A) preparing with a water-in-oil type emulsifying agent an emulsion of:

(1) an aqueous ammonium nitrate solution as a discontinuous emulsion phase, and

(2) a liquid carbonaceous fuel as a continuous emulsion phase;

(B) thickening by cooling said liquid carbonaceous fuel to a consistency such that a gas may be occluded therein; and

(C) occluding at least 4% by volume at 70° F. and atmospheric pressure of a gas in the thickened emulsion.

19. The process of claim 18 wherein said aqueous solution has a pH in the range from about 2 to about 8.

20. The process of claim 18 wherein the occluded gas constitutes from about 4% to about 47% by volume at 70° F. and atmospheric pressure of the thickened emulsion.

21. The process of claim 18 wherein the occluded gas constitutes from about 13% to about 33% by volume at 70° F. and atmospheric pressure of the thickened emulsion.

22. The process of claim 18 wherein the emulsion is formed of:

(a) 100 parts by weight of ammonium nitrate;

(b) about 10 parts to about 60 parts by weight of water;

(c) up to about 55 parts by weight of at least a second water soluble, emulsion compatible oxidizing material in addition to said ammonium nitrate;

(d) about 4 parts to about 45 parts by weight of a carbonaceous fuel; and

(e) about 0.75 part to about 5 parts by weight of a water-in-oil type emulsifying agent.

23. The process of claim 18 wherein the temperature of emulsion formation for the mixed components is about 100° F. to about 120° F.

24. The process of claim 18 wherein the gas is occluded in the emulsion at a temperature of about 70° F. to about 190° F.

25. The process of claim 18 wherein the emulsion is formed of:

(a) an aqueous solution of 100 parts by weight of ammonium nitrate, and up to about 36 parts by weight of at least a second water soluble, emulsion compatible oxidizing material in addition to said ammonium nitrate, dispersed in from about 18 parts to about 44 parts by weight of water; and

(b) a carbonaceous fuel of about 5 parts to about 17 parts by weight of a carbonaceous fuel having a gas occlusion temperature from about 95° F. to about 130° F.; and

(c) about 1.3 part to about 3 parts by weight of a water-in-oil type emulsifying agent.

26. The process of claim 25 wherein said second water soluble, emulsion compatible oxidizing material is sodium nitrate.

27. The process of claim 22 wherein the fuel includes at least 2% by weight of wax having a melting point about 100° F. to about 160° F.

28. The process of claim 27 wherein a tackifying polymeric material is included in combination with the wax in the fuel phase.

29. The process of claim 22 wherein the water-in-oil type emulsifying agent is a sorbitan fatty acid ester selected from the group consisting of sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan tristearate.

30. The process of claim 22 wherein gas entraining particles having a particle size that will at least pass through a No. 8 USS screen are included in an amount from about 1 to about 70 parts by weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,447,978

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Harold F. Bluhm

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, lines 60 and 61, "substantilly" shpuld read -- substantially --. Column 4, line 18, "acclulsion" should read -- occlusion --. Column 6, line 19, before "glycerides" insert -- di --. Column 9, line 49, "60°" should read -- 70° --; line 66, before "temperature" insert -- saturation - .

Signed and sealed this 19th day of May 1970.

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents