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PRODUCTION OF DETONATABLE EXPLOSIVE EMULSION PREPARATIONS

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The present invention relates to improvements in detonatable explosion emulsion preparations and more particularly to a water-in-oil emulsion of water, an emulsifier, and an explosive component.

Heretofore, water has been added to gelatinous explosives together with glue, dextrin, and starch, the latter three components being used to bind the water added. Also of interest have been emulsions of liquid nitric acid esters and water, but only with a view to solving the delicate transportation problems attendant explosive materials. A particular possibility is known for the safe transportation of nitroglycerin, i.e. explosive oil generally of the nitric acid ester type, by conducting the nitroglycerin through a pipe line in the form of an emulsion produced with water. This conventional technique using a water emulsion with nitroglycerin, as demonstrated by extensive tests, is no longer in such a condition that dangerous detonation may be propagated. Unfortunately, however, these emulsions may only be kept stable under quite specific flow conditions, as for example, those which exist in a flow pipe positioned at an incline.

Therefore, many attempts have been made to improve upon explosive preparations whereby the same will be safe when transported, yet will provide the needed detonating properties at the end point of use. One attempt in this connection has been to increase the stability of emulsions of water with nitroglycerin by the incorporation of certain emulsifiers and even through the further inclusion of emulsifying auxiliary agents. Nevertheless, independently of the type of production procedure, the nitroglycerin-water-emulsion must possess as a prime condition, the ability to be safely transported in a manner that the preparation no longer possesses an explosive character, i.e. such preparation must no longer be capable of propagating a detonative conversion initiated at a given place. The various known emulsions include both oil-in-water and water-in-oil type emulsions.

It is an object of the present invention to provide a detonatable explosive emulsion preparation which is safe to transport in its prepared condition, yet will be capable of exerting the explosive force desired at the point of end use.

Other and further objects of the invention will become apparent from a study of the within specification and accompanying examples.

It has been found in accordance with the present invention that a detonatable explosive emulsion preparation may be provided which comprises a water-in-oil emulsion of water, an emulsifier, and an explosive component, whereby safety in transport will be possible as well as effective explosive force at the point of controlled detonation. The water-in-oil emulsion may contain up to 72% water whereas the emulsifier may be present in an amount of from about 0.05 to 5% by weight based upon the total emulsion preparation, and preferably in an amount of about 1% by weight.

A stabilizer for the explosive component may be optionally included in the emulsion preparation, as for example collodion cotton (normally used for explosives)

or polyvinylacetate, e.g., with about 20 monomers in the chain.

The explosive component of the preparation may be in the form of a liquid or a fused compound, such at nitroglycerin or trinitrotoluene.

The emulsifier used in the preparation in accordance with the invention may be an ionic or non-ionic substance. Specifically, the ionic substance may be a metal salt of a long-chain fatty acid, and more particularly a member selected from the group consisting of alkaline earth-, magnesium-, aluminum- and zinc-salts of paraffin fatty acids, oleic acid, paraffin oxy-fatty acids, abietic acid, and mixtures thereof. On the other hand, the non-ionic emulsifier may include a member selected from the group consisting of glycerin-stearates, abietic acid derivatives, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long-chain fatty acids and higher alcohols, and mixtures thereof.

In its broadest aspects, therefore, the present invention contemplates an aqueous emulsion capable of detonation in which the aqueous phase is emulsified in the form of fine droplets in the explosive component. The water-in-oil emulsion is produced actually with the aid of emulsifiers of water and liquid or fused explosive components. Regardless of the fact that the explosive component may be liquid or solid, suitably, the explosive component must be fusible, e.g. a fusible oil or a fusible solid. The particular emulsion preparation may be carried out in the conventional manner using the emulsifiers as they are added for the production of water-in-oil emulsions of the normal type. The specific ionic emulsifier substances which may be used include the alkaline earth-, magnesium-, aluminum- and zinc-salts of the paraffin fatty acids, oleic acid and the long-chain oxy-acids such as the lithium, calcium, magnesium, aluminum and zinc salts of stearic acid, palmetic acid, oxy-stearic acid, oleic acid, and other long-chain carboxylic acids, etc. The non-ionic emulsifier substances may include, as aforesaid, glycerin stearates, abietic acid, and abietic acid derivatives, such as alkyl esters and metal salts, polyglycol-ether of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, and esters of long-chain fatty acids with higher alcohols, such as lanolin, etc.

It will be appreciated that while the water-in-oil emulsions of the foregoing type may contain up to 72% water, with the emulsifier substance concentration ranging between 0.05 and 5%, preferably about 1%, based upon the emulsion, it is still possible to vary within a wide range the qauntity of water actually contained in the emulsion. Naturally, the stability of the water-in-oil emulsion is improved by the addition of a stabilizer, such as, for example collodion-cotton.

The following examples are set forth to establish the differences with respect to explosive properties of water-in-oil type emulsions (type W/O) as opposed to the known oil-in-water emulsion of nitroglycerin (explosive oil)/water (type O/W), it being understood that these examples are by way of illustration and not limitation.

EXAMPLE 1

A water-in-oil emulsion is produced from 50 cc. nitroglycerine (explosive oil) representing a mixture of 60 parts nitroglycerin and 40 parts nitroglycol, 55 cc. water and 0.5 gram zinc-oxy stearate. As stabilizer, 0.5 gram collodion-cotton are added. This aqueous emulsion is capable of detonation and exhibited in the lead-lock test according to Trauzl in a quantity of 10 grams, a bulging of 225 cubic centimeters, the emulsion being detonated with a priming cap #8. It is quite clear from this ex-

ample that the foregoing water-in-oil emulsion absolutely possesses the character of an explosive.

In contrast thereto, an analogously composed emulsion, to which had been added, in place of the zinc oxy stearate and collodion-cotton, corresponding quantities of sodium-cetyl sulphate and methyl cellulose as emulsifying agent so as to present an emulsion of the oil-in-water type, could no longer be detonated with a priming cap #8. Accordingly, this preparation did not exhibit any bulging of the lead-block as was the case with the emulsion preparation in accordance with the invention, and therefore the oil-in-water emulsion of the conventional type cannot be considered an explosive.

EXAMPLE 2

Using a water-in-oil emulsion of 75 cc. nitroglycerin explosive oil), 25 cc. water, 0.5 gram of partially acetylated polyvinyl alcohol, and 1 gram collodion-cotton, a lead block bulging of 410 cubic centimeters was obtained in accordance with the procedure of Example 1.

EXAMPLE 3

In accordance with the procedure of Example 1, a water-in-oil-emulsion of 50 cc. nitroglycerin (explosive oil), 50 cc. water, 0.5 gram magnesium-oleate, and 0.3 gram collodion-cotton showed a lead-block bulging of 220 cubic centimeters.

EXAMPLE 4

Using the procedure of Example 1, a water-in-oil emulsion of 75 cc. nitroglycerin (explosive oil), 25 cc. water, 0.5 gram calcium-stearate and 2 grams collodion-cotton, a lead-block bulging of 415 cubic centimeters was obtained.

EXAMPLE 5

In accordance with the procedure of Example 1, using a water-in-oil emulsion of 45 cc. nitroglycerin (explosive oil), 55 cc. water, 0.5 gram zinc stearate, and 2 grams collodion-cotton, a lead-block bulging of 215 cubic centimeters was obtained.

EXAMPLE 6

In accordance with the procedure of Example 1, using a water-in-oil emulsion of 40 cc. nitroglycerin (explosive oil), 60 cc. water, 0.5 gram polyglycol monostearyl ether (Peregal O) and 2 grams collodion-cotton, a lead-block bulging of 110 cubic centimeters was obtained.

EXAMPLE 7

In acordance with the procedure of Example 1, using a water-in-oil emulsion of 35 cc. nitroglycerin (explosive oil), 65 cc. water, 0.5 gram long-chain fatty acid of a higher alcohol (lanolin) and 1 gram collodion-cotton, a lead-block bulging of 75 cu. centimeters was obtained.

EXAMPLE 8

In accordance with the procedure of Example 1, using a water-in-oil emulsion of 30 cc. nitroglycerin (explosive oil), 70 cc. water, 0.6 gram zinc-12-oxy-stearate and 1 gram collodion-cotton, a lead-block bulging of 25 cu. centimeters was obtained.

EXAMPLE 9

At 90 degrees C., various TNT—H_2O-emulsions were produced using an addition of 0.5% collodion-cotton and 1% calcium stearate. The trinitrotoluene (TNT)-water emulsions so prepared were poured into cardboard tubes having an inside diameter of 30 mm. After cooling, stable solid emulsions were obtained which were placed on lead slabs of 6 mm. thickness and tested by ignition with pressed tetryl (trinitrophenylmethylnitramine) at a dosage of 25 grams to determine the detonation capacity of the particular emulsions. The following table indicates the results obtained:

Table

TNT, percent	H_2O, percent	Detonation capacity and/or brisance (Shattering power)
77.5	21	Lead slab completely ruptured.
63.5	35	Lead slab barely ruptured.
46.5	52	Lead slab strongly crushed-in.
30.5	68	Lead slab barely crushed-in.

Accordingly, the great advantage of the emulsions capable of detonation, as produced in accordance with the present invention, is the fact that the consistency of the mixtures of ingredients may be varied almost at random. By the particular selection of the amounts of the two liquids, to be emulsified, and the quantity of the stabilizer desired, preparations may be obtained which are pourable, creamy, foamy, syrupy, pulpy, gelatinous, pasty, fat-like or wax-like, brittle or massive solid masses. Because of these characteristics, the emulsion preparations produced in accordance with the invention are capable of detonation under the desired conditions but are safe in transport, rendering them widely applicable in explosion practice. The emulsion preparations in accordance with the invention have characteristics of impact (percussion) sensitiveness, and friction sensitiveness which may be varied within wide limits depending upon the amount of water added to the emulsion. These properties could not have been expected, since nitroglycerin is an explosive oil which is present in the emulsion as an undivided phase. Hence, a gelatin preparation of 100 cc. nitroglycerin (explosive oil) (60/40), 1 gram collodion-cotton and 0.5 gram zinc-12-oxy stearate may be detonated under a drop hammer according to Kast (Post's "Chemisch-Techniscke Analyse," 3rd Ed. (1909), vol. II, No. 3) using a 2 kg. weight and a dropping height of 60 centimeters. If half the volume quantity of the nitroglycerin (explosive oil) present in the gelatin is replaced by water so as to form an oil-in-water emulsion, no explosive detonation is obtained even with a 10 kg. weight and a dropping height of 60 centimeters.

It will be appreciated from the foregoing that by reason of the particular water-in-oil emulsion of water, an emulsifier, and an explosive component, in accordance with the invention, a safely transportable mass is obtained which is still able to be detonated under reasonable detonating conditions at the point of end use, using normal detonation impact values.

What is claimed is:

1. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier, and nitroglycerine, and additionally containing a stabilizer selected from the group consisting of collodion cotton and polyvinyl acetate, said water being present in an amount between about 21 and 72% by weight, said emulsifier being present in an amount between about 0.05 and 5% by weight and said stabilizer being present in an amount between about 0.3 and 2 grams per 100 cc. of the mixture of the water and nitroglycerine present, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

2. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier, and nitroglycol, and additionally containing a stabilizer selected from the group consisting of collodion cotton and polyvinyl acetate, said water being present in an amount between about 21 and 72% by weight, said emulsifier being present in an amount between about 0.05 and 5% by weight and said stabilizer being present in an amount between about 0.3 and 2

grams per 100 cc. of the mixture of the water and nitroglycol present, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

3. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier, and trinitrotoluene, and additionally containing a stabilizer selected from the group consisting of collodion cotton and polyvinyl acetate, said water being present in an amount between about 21 and 72% by weight, said emulsifier being present in an amount between about 0.05 and 5% by weight and said stabilizer being present in an amount between about 0.3 and 2 grams per 100 cc. of the mixture of the water and trinitrotoluene present, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

4. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier, and nitroglycerine, said water being present in an amount between about 21 and 72% by weight and said emulsifier being present in an amount between about 0.05 and 5% by weight, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

5. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier, and nitroglycol, said water being present in an amount between about 21 and 72% by weight and said emulsifier being present in an amount between about 0.05 and 5% by weight, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

6. Detonatable explosive emulsion preparation which consists essentially of a water-in-oil emulsion of water, an emulsifier and trinitrotoluene, said water being present in an amount between about 21 and 72% by weight and said emulsifier being present in an amount between about 0.05 and 5% by weight, and said emulsifier being selected from the group consisting of glycerine-stearates, alkyl esters of abietic acid, metal salts of abietic acid, polyglycol ethers of ethylene oxide, adducts of higher fatty amines and ethylene oxide, polyvinyl alcohols, esters of long chain fatty acids and higher alcohols, mixtures of the foregoing, and metal salts of long chain fatty acids.

References Cited by the Examiner

UNITED STATES PATENTS

1,999,828 4/1935 Wiggam ---------- 149—101 X

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