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2,716,056

## BLASTING EXPLOSIVE AND PROCESS OF PRODUCING SAME

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No Drawing. Application March 17, 1952, Serial No. 277,058

Claims priority, application Great Britain June 18, 1951

13 Claims. (Cl. 52—13)

The present invention is concerned with improvements in or relating to gelatine blasting explosives containing a major proportion of crystalline salts and if desired other solid ingredients distributed through a lesser proportion of a viscous solution or jelly of nitrocellulose in a solvent comprising at least one explosive liquid nitric ester and more especially at least one explosive liquid nitric ester and an aromatic nitro compound.

Since the nitroglycerine is one of the most expensive constituents in gelatine blasting explosives, whenever the blasting performance of the explosive permits, it is the practice to include a high proportion of crystalline salts, especially ammonium nitrate or other power producing salts in the composition, and other salts such as flame-quenching salts, oxidising salts, and plant tissue materials are frequently present also, but the extent to which the proportion of the nitroglycerine in the explosive composition can be minimised has hitherto been limited in practice more by the difficulty of maintaining a suitably plastic consistency sufficient for the extrusion of the composition for cartridge purposes than by the diminution in sensitiveness to initiation of the explosive, and obviously the higher the proportion of the salts and other solid ingredients the more important it is to maintain sufficient plasticity to enable the explosive to be extruded. To a certain extent economy in nitroglycerine can also be effected by partially replacing it by a liquid aromatic nitro compound, in particular a liquid nitrotoluene.

In British specification No. 586,224, which corresponds to U. S. Patent No. 2,454,643, there has been proposed a method of improving the plasticity of blasting explosives comprising a preponderating proportion of freely water-soluble salts distributed in a less proportion of a viscous solution or jelly of nitrocellulose in a solvent comprising at least one explosive liquid nitric ester by incorporating the water-soluble salts into the viscous solution or jelly in the presence of free moisture and of at least one compound of polyethylene glycol ether structure having in its molecule at least 8 carbon atoms joined together and also at least 2 ethenoxy groups joined together. The amount of the aforesaid compound of polyethylene glycol ether structure used is stated to be from 0.02 to 0.5% of the weight of the whole composition. Although the inclusion of the aforesaid compounds enables the percentage of nitroglycerine to be substantially reduced it has now been found that it is not possible to make this reduction when aromatic nitro compounds such as liquid nitrotoluene are present.

In British specification No. 596,279, which corresponds to U. S. Patent No. 2,545,270, there has been proposed a method of improving the plasticity of blasting explosives comprising a preponderating proportion of freely water-soluble salts distributed in a less proportion of a viscous solution or jelly of nitrocellulose in a solvent comprising a liquid explosive nitric ester by incorporating the water-soluble salts into the said viscous solution or jelly in the presence of free moisture and of at least one nitro-aryl-

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glycerol mono-ether or nitro-aryl-glycidyl mono-ether soluble in the explosive nitric ester and that has an aryl group containing 1 or 2 nitro groups for a single ring compound or between 1 and 3 nitro groups for a naphthyl compound, whether with or without lower alkyl substitution in the aromatic portion, the aforesaid ether being capable of assisting emulsification in the explosive liquid nitric ester of a saturated aqueous solution of the freely water-soluble salt that has to be present in the greatest proportion by volume. The aforesaid nitro-aryl-glyceryl mono-ethers or nitro-aryl-glycidyl mono-ethers likewise appear to be much less effective when aromatic nitro compounds are present.

According to the present invention the method for the production of blasting explosives of the kind comprising a preponderating proportion of crystalline salts distributed in a lesser proportion of a viscous solution or jelly of nitrocellulose in a solvent comprising a liquid explosive nitric ester comprises forming a mixture of said crystalline salts and said viscous solution or jelly in the presence of a tri ester of ortho-phosphoric acid wherein one esterifying radical is a para-tertiary-octyl-aryl group and the other two esterifying radicals are alkyl groups each containing up to 12 carbon atoms.

The said para-tertiary-octyl-aryl group is preferably a para-tertiary-octyl-phenyl group or nuclearly substituted alkyl derivative thereof, preferably a methyl derivative.

Examples of para-tertiary-octyl-aryl dialkyl esters of phosphoric acid effective for the purposes of the invention include

Para-tertiary-octyl-phenyl di-methyl phosphate  
Para-tertiary-octyl-phenyl di-ethyl phosphate  
Para-tertiary-octyl-phenyl di-n-propyl phosphate  
Para-tertiary-octyl-phenyl di-n-butyl phosphate  
Para-tertiary-octyl-phenyl di-n-amyl phosphate  
Para-tertiary-octyl-phenyl di-n-octyl phosphate  
Para-tertiary-octyl-phenyl di-n-nonyl phosphate  
Para-tertiary-octyl-phenyl di-n-lauryl phosphate  
Para-tertiary-octyl-phenyl di-isopropyl phosphate  
Para-tertiary-octyl-phenyl di-isobutyl phosphate  
Para-tertiary-octyl-phenyl di-sec-octyl phosphate  
Para-tertiary-octyl-phenyl monomethyl monoethyl phosphate

The amount of the aforesaid tri ester of phosphoric acid employed may advantageously be in practice from 0.15 to 0.5% of the weight of the whole explosive composition.

The aforesaid esters of phosphoric acid are powerful surface active agents and it is found that by their use the percentage of nitroglycerine in the explosive composition may be quite substantially reduced even when a nitro-aromatic compound is present in the liquid explosive solvent for the nitrocellulose without adversely affecting the extrudability of the composition.

In putting the invention into effect the aforesaid ester of phosphoric acid may be conveniently added to the aromatic nitro compound and the latter may then be dissolved in the nitroglycerine whereupon the nitrocellulose may be mixed with the resulting explosive liquid and the remainder of the ingredients introduced in known manner.

The required surface active tri active esters of phosphoric acid may be obtained from para-tertiary-octyl-aryl phosphoryl dichloride by reaction with a monohydric aliphatic alcohol in a quantity sufficient to react with both chlorine atoms or with a quantity sufficient to react with one chlorine atom and thereafter with another of said alcohols in a quantity sufficient to react with the other chlorine atom. Reference is made to co-pending applications, Serial Number 225,054, filed May 7, 1951, and Serial Number 276,684, filed March 14, 1952, both

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assigned to a common assignee, wherein is set forth method for obtaining the required surface active tri esters of phosphoric acid as noted heretofore.

Attention is also directed to co-pending application, Serial Number 235,908, filed July 9, 1951, common assignee. Example 1 of this application sets forth a para-tertiary-octyl-phenoxy-phosphoryl dichloride and indicates that the same has a boiling point of 142° C. at 0.8 mm. pressure and a boiling point of 190–192° C. at 10 mm. pressure.

The reaction is preferably carried out in the absence of moisture at raised temperature and results in the evolution of hydrogen chloride. In some cases better yields are obtained by effecting the reaction in presence of a tertiary nitrogen base as an acceptor for hydrogen chloride at ordinary or only slightly raised temperatures. Pyridine may be used for this purpose.

The aromatic nitro compound may be, for example, orthonitrotoluene or a mixture of nitrotoluenes or dinitrotoluenes that will not crystallise out from solution in the liquid explosive nitric ester, for example a dinitrotoluene oil. The liquid explosive nitric ester may if desired include in admixture with trinitroglycerol other liquid explosive nitric esters, for example, ethylene glycol dinitrate, as is commonly the case in the manufacture of low-freezing explosives.

The invention is illustrated by the following examples in which the parts and percentages are by weight.

#### Example 1

0.20 part para-tertiary-octyl-phenyl di-ethyl phosphate are mixed with 3 parts ortho-nitrotoluene and the resulting liquid is dissolved in 21 parts of a nitrated mixture of glycerol and ethylene glycol in the proportions 80–20. 1.1 parts of nitrocellulose are mixed with the resulting liquid and when gelatinisation is substantially completed there is incorporated a mixture of the following ingredients in known manner:

	Parts
Ammonium nitrate .....	56.9
Sodium nitrate .....	12.0
Oat husk meal .....	2.0
Waxed woodmeal .....	0.5
Woodmeal .....	1.0
Sulphur .....	2.0
Starch .....	0.5
Chalk .....	0.3

The ingredients are mixed in a McRoberts mixer. The product is a gelatine explosive that can be extruded satisfactorily through an ordinary cartridging machine as used for cartridging explosives.

When in a comparative trial the para-tertiary-octyl-phenyl di-ethyl phosphoric ester is omitted from the composition it is found that this resulting composition has no plastic properties and cannot be extruded through a cartridging machine as aforesaid.

The addition of at least one compound of polyethylene glycol ether structure having in its molecule at least 8 carbon atoms joined together and also at least 2 ethanox groups joined together in accordance with the method of British specification No. 586,224, U. S. Patent No. 2,454,643, or the addition of at least one nitro-aryl glycerol mono-ether or nitro-aryl glycidyl mono-ether in accordance with the method of British specification No. 596,279, U. S. Patent No. 2,545,270 does not confer plastic and extrusion properties.

In order to give plastic properties to this composition it is necessary to add for instance 5 parts of the said nitrated mixture of glycerol and ethylene glycol and 1 part of the said ortho-nitrotoluene.

#### Example 2

The para-tertiary-octyl-phenyl di-ethyl phosphate included in the composition produced in accordance with Example 1 is replaced by 0.2 part of para-tertiary-octyl-

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phenyl-di-isopropyl phosphate. The resulting composition has the same plastic and extrusion properties as the composition of Example 1.

The explosive compositions of Examples 1 and 2 also have substantially the same consistency and the same sensitivity to initiation and capability for transmitting their initiation with cartridges separated in file (as determined by a double cartridge test) as the following composition free from phosphoric esters and containing 30 parts of a liquid mixture consisting of 26 parts of a nitrated mixture of glycerine and ethylene glycol in the ratio of 80:20 and 4 parts ortho-nitrotoluene.

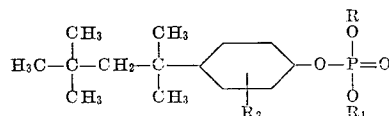
	Parts
Nitrated mixture of glycerine and ethylene glycol in the ratio 80–20 .....	26
Ortho-nitrotoluene .....	4
Nitrocellulose .....	1.1
Ammonium nitrate .....	47.6
Sodium nitrate .....	16.0
Woodmeal .....	2.5
Sulphur .....	2.0
Starch .....	0.5
Chalk .....	0.3

Insofar as this explosive composition is concerned it will be readily appreciated that it is not possible when not including the para-tertiary-octyl-aryl dialkyl phosphate in the compositions of the invention of Examples 1 and 2 simply to modify these compositions by employing 30 parts of said liquid mixture and proportionately less of the other ingredients as the composition has to be oxygen balanced and the proportion of said liquid mixture to be absorbed for the desired plasticity and extrudability to be obtained has to be arranged in large measure in accordance with the solids of the composition by choosing the particular one or more types of meal which have to be present.

The nitrocellulose used in Examples 1 and 2 is the variety known as blasting soluble nitrocellulose which is the product of nitration of purified cotton cops by the pot process to a nitrogen content of 11.95 to 12.2%. The product is at least 95% soluble in ether alcohol solution and has a viscosity of 100–1300 CGS. units in solution of 3 grams in 100 millilitres acetone (95% at 20° C).

What we claim is:

1. A method for the production of blasting explosives of the kind comprising a preponderating proportion of freely water-soluble inorganic nitrates distributed in a lesser proportion of a viscous solution of nitrocellulose in a solvent comprising a liquid explosive nitric ester which comprises forming a mixture of said freely water-soluble inorganic nitrates and said viscous solution in the presence of tri-ester of ortho-phosphoric acid having the general formula:



wherein R and R<sub>1</sub> are alkyl radicals containing up to 12 carbon atoms and R<sub>2</sub> is a radical selected from the group consisting of hydrogen and alkyl radicals.

2. A method as claimed in claim 1 wherein said solvent includes an aromatic nitro compound.

3. A method as claimed in claim 2 wherein the aromatic nitro compound is ortho-nitrotoluene.

4. A method as claimed in claim 2 wherein the aromatic nitro compound is di-nitrotoluene oil.

5. A method as claimed in claim 1 wherein R<sub>2</sub> is a hydrogen.

6. A method as claimed in claim 1 wherein R<sub>2</sub> is an alkyl radical.

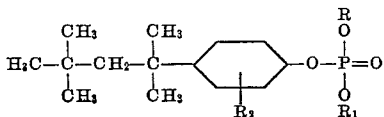
7. A method as claimed in claim 6 wherein the said alkyl radical is a methyl group.

8. A method as claimed in claim 1 wherein the amount

of the aforesaid tri ester of phosphoric acid is from 0.15 to 0.5% of the weight of the whole explosive composition.

9. A method as claimed in claim 1 wherein the aforesaid ester of phosphoric acid is added to the aromatic nitro compound, the latter is dissolved in the liquid explosive nitric ester, the nitrocellulose is mixed with the resulting explosive liquid and the freely water-soluble inorganic nitrates and any other ingredients are then added.

10. Blasting explosives of the kind comprising a preponderating proportion of freely water-soluble inorganic nitrates distributed in a lesser proportion of a viscous solution of nitrocellulose in a solvent comprising a liquid explosive nitric ester which explosives include a tri-ester of ortho-phosphoric acid having the general formula:



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wherein R and R<sub>1</sub> are alkyl radicals containing up to 12 carbon atoms and R<sub>2</sub> is a radical selected from the group consisting of hydrogen and alkyl radicals.

11. Blasting explosives as claimed in claim 10 which include an aromatic nitro compound.

12. Blasting explosives as claimed in claim 10 wherein the quantity of the aforesaid tri ester of phosphoric acid is between 0.15 and 0.5% of the weight of the whole of the explosive composition.

13. Blasting explosives as claimed in claim 10 wherein R<sub>2</sub> is hydrogen.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

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