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GELATINE BLASTING EXPLOSIVE COMPOSITIONS CONTAINING WATER-SOLUBLE SALTS

Stanley Fordham, Saltcoats, Scotland, and John L. Moilliet, Styal, England, assignors to Imperial Chemical Industries Limited, a corporation of Great Britain

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6 Claims. (Cl. 52-13)

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The present invention relates to the production of new or improved blasting explosives of the kind comprising a preponderating proportion of freely water-soluble salts distributed through a lesser proportion of a viscous solution or jelly of nitrocellulose made with a solvent comprising at least one explosive liquid nitric ester, and is particularly applicable to the production of gelatine blasting explosives required to contain not less than 60 per cent of their weight of freely water-soluble salts, especially when other ingredients insoluble in the gelatinised nitrocellulose solvent are also to be included.

In order to minimize the cost of gelatine blasting explosives it is customary to include salts of explosive or oxidising character, frequently in association with oxidisable ingredients insoluble in the gelatinised nitrocellulose solvent, and the explosive or oxidising salts commonly employed are freely soluble in water, for instance ammonium nitrate, alkali metal nitrates or alkaline earth metal nitrates. Water soluble perchlorates are sometimes used instead of nitrates. In the manufacture of safety explosives it is necessary to minimise the proportion of explosive nitric ester, and this constituent is largely replaced by a self explosive salt, which is usually ammonium nitrate, while there are also included ingredients of a flame quenching or cooling character. These, too, are frequently water-soluble salts.

It is to be expected that as the proportion of the salts and other ingredients insoluble in the gelatinised nitrocellulose solvent can be increased only by decreasing the proportion of the gelatinised nitrocellulose solvent, explosive compositions containing a preponderating proportion of salts, with or without other undissolved ingredients, are liable to possess insufficient plasticity to enable them easily to be cartridged by extrusion, and may be so lacking in cohesiveness that they have not the character of a gelatine.

It is an object of the invention to provide gelatine blasting explosives of the kind described having improved plasticity, and it is a cognate object of the invention to enable the proportion of the gelatinised nitrocellulose solvent required to bind the undissolved ingredients of a gelatine blasting explosive as aforesaid to be reduced without rendering it incapable of cartridging by extrusion.

It has been proposed in specification Number 460,576 to include in a gelatinous or semi-gelatinous explosive a small proportion, preferably 2-6 per cent of a finely divided substantially non-carbonaceous plastic clay or clay-like mate-

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rial as therein defined which, both alone and in the form of a mixture with any carbonaceous ingredients contained in the explosive, has a low absorbency for nitroglycerine. The plasticity of the explosive composition is thereby increased, and gelatine explosives containing a preponderating proportion of water-soluble salts and other undissolved ingredients of increased plasticity or better flame-quenching characteristics may thereby be obtained, or the proportion of the liquid nitric ester in the composition may be reduced. The use of clay is specially advantageous in the manufacture of safety explosives, since apart from its plasticising effect it has a pronounced flame-quenching or cooling effect, but the desensitising effect of this diluent is greater than that of an equal weight of crystalline salts.

It is also known from U. S. Patent Number 1,966,090 that gelatinisation of nitrocellulose by means of a liquid nitric ester can be accelerated by the use of a small proportion of certain derivatives of aliphatic alcohols having at least two hydroxyl groups, these derivatives containing at least one unsubstituted hydroxyl group and one ether group and that gelatine explosive compositions containing, if desired, a preponderating proportion of salts such as sodium nitrate and ammonium nitrate of more thoroughly gelatinized character may thereby be obtained. The derivatives of which the employment is proposed include for example, diethylene glycol, ethylene glycol monoethyl ether, diethyleneglycol monobutyl ether, and the like.

We have now found that the plasticity of blasting explosives comprising a preponderating proportion of freely water-soluble salts distributed in a lesser proportion of a viscous solution or jelly of nitrocellulose in a solvent comprising at least one explosive liquid nitric ester can even more effectively be improved by incorporating the water-soluble salts into the said viscous solution or jelly in the presence of at least one compound (soluble in an explosive liquid nitric ester) of polyethylene glycol ether structure having in its molecule at least eight carbon atoms joined together and also at least two ethenoxy groups joined together, provided that free moisture is present when the salts are mixed in, said compound being capable of assisting emulsification in said explosive liquid nitric ester of a saturated aqueous solution of whichever freely water-soluble salt is to be present in the greatest proportion by volume.

In other words, the compound of polyethylene glycol ether structure used to carry out the

method of the present invention is soluble in the explosive liquid nitric ester, has in its molecule at least eight carbon atoms joined together and also at least two ethenoxy groups joined together, and is capable of assisting emulsification in said explosive liquid nitric ester of a saturated aqueous solution of whichever freely water-soluble salt is to be present in the greatest proportion by volume.

According to the present invention, therefore, the 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 comprises incorporating the water-soluble salts into the said viscous solution or jelly in the presence of free moisture and of at least one compound of polyethylene glycol structure as herein defined.

It is believed that there is a casual relationship between emulsifying properties of the aforesaid compounds and their beneficial effect on plasticity of the explosives containing a preponderating proportion of freely water-soluble salts, independent of any effect they may have on the gelatinisation of the nitro-cellulose, since the presence of moisture, although only in small amounts is necessary for this beneficial effect to be obtained, and many of the compounds that give it are soluble only to a slight extent in the liquid nitric ester and have no palpable effect on the gelatinisation of the nitrocellulose.

The polyethenoxy chain of the compound may terminate in a free hydroxyl group, or an esterified or etherified hydroxyl group, such as a nitric ester group or a methoxyl group. Suitable compounds are conveniently prepared by condensing phenols, alcohols, amines or amides having at least eight carbon atoms directly joined together with suitable proportions of ethylene oxide. The best effects are usually obtained when at least three molecular proportions of ethylene oxide are condensed with one molecular proportion of the phenol, alcohol, etc.

The suitability of the compounds may readily be ascertained by shaking together a layer of the explosive liquid nitric ester with a smaller layer of a saturated solution of the freely water-soluble salt that is to be present in the greatest volume proportion in the explosive composition, in presence of a small amount of the compound and observing whether the breaking of the emulsion is markedly delayed in comparison with that in a control test carried out without the compound.

Only very small proportions of the aforesaid compounds are required in the explosive composition to exert a substantially plasticising effect, and the use of higher proportions than are necessary does not usually result in a correspondingly increased beneficial effect on the plasticity. Hence the increased plasticity may be attained without the introduction of sufficient diluent material to reduce the sensitiveness to initiation of the explosive appreciably. The amounts of the aforesaid linear compounds of polyethylene glycol structure used is advantageously from about 0.02 to about 0.5 per cent of the weight of the whole composition.

While moisture must be present during the mixing of the water-soluble salts with the gelatinised nitrocellulose solvent, the amounts ordinarily associated with the freely water-soluble salts, which are frequently hygroscopic or deli-

quescent compounds, for instance ammonium nitrate, and with the other ingredients, for instance the explosive liquid nitric ester, is often sufficient for the purpose. The moisture is most effective for the purpose of the invention when it is associated with the surfaces of the crystals of the water-soluble salt and in this case about 0.1 to 0.25 per cent on the weight of the explosive is amply sufficient, but if the water-soluble salts are very dry and the water can only find its way into contact with their crystal surfaces as a result of their being mixed into a moist jelly a somewhat higher proportion may be required. If vegetable carbonaceous ingredients are present, any moisture they may contain up to their natural humidity content is not to be reckoned as free moisture. If the natural moisture content of the salts is insufficient, as may be the case if they have been freshly dried, the necessary amount of water may be introduced, either directly by addition to the viscous solution or jelly or indirectly by moistening at least the salt that is to be used in the greatest volume proportion before the salts are introduced into the said viscous solution or jelly.

The aforesaid compounds may be introduced into the viscous solution or jelly along with the salts or the salt that is to be used in the greatest volume proportion; or into the nitrocellulose solvent before the gelatinisation of the nitrocellulose; or during the gelatinisation of the nitrocellulose; or after the gelatinisation of the nitrocellulose but before the incorporation of the water-soluble salts.

Owing to the increase in plasticity attained according to our invention it is possible to formulate explosive compositions capable of cartridgeing by extrusion that contain a lower proportion of explosive liquid nitric ester and a higher proportion of materials insoluble in the gelatinised nitrocellulose solvent than has hitherto been possible, and the production of inexpensive gelatine explosive compositions is thereby facilitated.

It will be understood that mixtures of linear compounds each with differing numbers of ethenoxy groups associated with the remainder of the molecule, such as are frequently obtained in condensations between ethylene oxide and phenols, alcohols, amines or amides having at least eight carbon atoms, may be used.

In the case of some mixtures of the compounds of polyethylene glycol ether structure, the interfacial tension between the liquid explosive nitric ester phase and the air phase is sufficiently low to enable aerated gelatine explosive compositions to be obtained easily when the ingredients are mixed together with mechanical action, and this is especially the case when the average number of ethenoxy groups per molecule in the mixture of the compounds is between three and four approximately. When explosive compositions of less aerated character are desired they may be used mixtures of the compounds in which the average number of ethenoxy groups per molecule is somewhat higher, e. g. from about 4 to 6 or more. The exact line of demarcation between the number of ethenoxy groups tending to yield strongly aerated gelatines and the number per molecule yielding more normally aerated gelatines varies somewhat according to the group to which the poly ethenoxy groups are attached.

The invention is illustrated by the following examples. In the case of Examples 1-8 the gela-

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tine explosive chosen as the standard of plasticity has the composition:

	Per cent
Nitroglycerine (containing approximately 0.5 per cent moisture)	34.4
Blasting soluble nitrocellulose	0.8
Woodmeal (oven dried)	4.0
Ammonium nitrate (containing 0.1-0.5 per cent moisture)	36.8
Sodium nitrate (containing approximately 0.1 per cent moisture)	24.0

Blasting soluble nitrocellulose is the product of nitration of purified cotton cops by the pot process to a nitrogen content of 11.95 to 12.25 per cent. The product is at least 95 percent soluble in an ether-alcohol solution, and has a viscosity of 100 to 300 c. g. s. units in solution of 3 gms. in 100 ml. acetone (95 per cent) at 20° C.

The nitroglycerine is first mixed by hand with the woodmeal and the nitrocellulose, and the salts are later mixed into the resulting jelly containing the suspended woodmeal in a McRoberts mixer for about half an hour.

The resulting gelatine explosive can be cartridged easily by extrusion and is slightly aerated. Its density is approximately 1.5, and it can be initiated by means of a commercial detonator such as a No. 6 lead azide or mercury fulminate detonator.

Example 1

The ingredients were as follows:

	Per cent
Nitroglycerine (containing approximately 0.5 per cent moisture)	28.0
Blasting soluble nitrocellulose	0.8
Woodmeal (oven dried)	4.0
Polyethylene glycol mono-cetyl ethers containing an average of 4.3 ethenoxy groups per molecule	0.4
Ammonium nitrate (0.1-0.5 per cent moisture)	42.8
Sodium nitrate (approximately 0.1 per cent moisture)	24.0

The polyethylene glycol cetyl ethers were mixed into the jelly formed from the nitroglycerine and the nitrocellulose containing the woodmeal in suspension, in the McRoberts mixer. The moist salts were then introduced while the mixer was kept running for about 30 minutes. The resulting gelatine explosive was easily cartridged by extrusion and the cartridges were satisfactorily sensitive to commercial blasting detonators, for instance No. 6 lead azide or mercury fulminate detonators, both when freshly prepared and after storage for six months. The power of the explosive was slightly lower than that of the explosive containing 34.4 per cent nitroglycerine, and its density was approximately 1.3.

Example 2

The ingredients were as follows:

	Per cent
Nitroglycerine, as used in Example 1	30.0
Blasting soluble nitrocellulose	0.8
Woodmeal, as in Example 1	4.0
Polyethylene glycol mono-cetyl ethers containing an average of 17 ethenoxy groups per molecule	0.4
Ammonium nitrate, as used in Example 1	40.8
Sodium nitrate, as used in Example 1	24.0

The procedure was the same as in Example 1.

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The resulting explosive was less strongly aerated and of somewhat higher density than that produced according to Example 1, and could be cartridged by extrusion. The cartridges were also of satisfactory sensitiveness to initiation both when fresh and on storage for six months.

Example 3

The composition and the procedure were the same as in Example 1, except that instead of polyethylene glycol mono-cetyl ethers there were used polyethylene glycol mono beta - naphthyl ethers containing an average of three ethenoxy groups per molecule. The properties of the resulting explosive were very similar to that of the explosive prepared according to Example 1.

Example 4

The ingredients were as follows:

	Per cent
Nitroglycerine, as in Example 1	29.9
Blasting soluble nitrocellulose	0.8
Woodmeal, as in Example 1	4.0
Polyethylene glycol mono beta - naphthyl ethers having an average of 4.5 ethenoxy groups per molecule	0.4
Ammonium nitrate, as in Example 1	40.9
Sodium nitrate, as in Example 1	24.0

The product was less strongly aerated than that prepared according to Example 3 and had a density of approximately 1.5. It could be cartridged easily by extrusion and had satisfactory sensitiveness to initiation when fresh and after storage for six months.

Example 5

The ingredients and the procedure were the same as in Example 4 except that the polyethylene glycol mono beta-naphthyl ethers contained an average of 6 ethenoxy groups per molecule. The resulting explosive was very similar to that obtained in Example 4.

Example 6

The ingredients were as follows:

	Per cent
Nitroglycerine, as in Example 1	29.4
Blasting soluble nitrocellulose	0.8
Woodmeal, as in Example 1	4.0
Nitric acid ester of polyethylene glycol mono beta-naphthyl ether containing 5 ethenoxy groups in the molecule	0.4
Ammonium nitrate, as in Example 1	41.4
Sodium nitrate, as in Example 1	24.0

The procedure was otherwise similar to that described in Example 1.

Example 7

The ingredients were as follows:

	Per cent
Nitroglycerine, as in Example 1	26.0
Blasting soluble nitrocellulose	0.8
Woodmeal, as in Example 1	4.0
Polyethylene glycol monoethers of oleo ethanolamide having an average of 3.4 ethenoxy groups per molecule	0.4
Ammonium nitrate, as in Example 1	44.8
Sodium nitrate, as in Example 1	24.0

The procedure was otherwise the same as in Example 1, and the density of the resulting gelatine explosive was similar.

Example 8

The ingredients were as follows:

	Per cent
Nitroglycerine, as in Example 1.....	27.0
Blasting soluble nitrocellulose.....	0.8
Woodmeal, as in Example 1.....	4.0
Polyethylene glycol monododecyl ethers hav- ing an average of 3 ethenoxy groups per molecule	0.4
Ammonium nitrate, as in Example 1.....	43.8
Sodium nitrate, as in Example 1.....	24.0

The procedure was otherwise similar to that described in Example 1 and the properties of the resulting gelatine explosive were closely similar.

Example 9

This example illustrates the production of a safety gelatine explosive of plasticity similar to that of a gelatine made in known manner. In each case the water-soluble salts are mixed in a McRoberts mixer into the nitroglycerine jelly containing the remaining ingredients.

The explosive prepared in known manner has the composition:

	Per cent
Nitroglycerine-nitroglycol mixture (4:1) containing approximately 0.5 per cent moisture	27.2
Blasting soluble nitrocellulose.....	0.7
Oat husk meal (oven dried).....	3.3
Sodium chloride (approximately 0.1 per cent moisture)	22.4
Ammonium nitrate (0.1-0.5 per cent mois- ture)	44.0
China clay.....	2.4

Example 10

The safety gelatine composition made in accordance with the invention had the composition:

	Per cent
Nitroglycerine-nitroglycol mixture (4:1) containing approximately 0.5 per cent moisture	22.0
Blasting soluble nitrocellulose.....	0.7
Oat husk meal (oven dried).....	3.3
Sodium chloride (approximately 0.1 per cent moisture)	22.4
Ammonium nitrate (0.1-0.5 per cent mois- ture)	49.0
China clay.....	2.4
Polyethylene glycol mono beta-naphthyl ethers containing an average of 4.5 ethe- noxy groups per molecule.....	0.2

The density of the explosive was about 1.6, and it cartridged easily by extrusion. The explosive was satisfactorily sensitive to initiation by a number 6 mercury fulminate detonator when fresh and also after six months storage.

We claim:

1. A method of improving the plasticity of blasting explosives which contain at least sixty per cent by weight of water soluble explosive inorganic oxidizing salts, which comprises incorporating the said salts into a viscous explosive nitric ester-nitrocellulose solution in the presence of from 0.02 to 0.5 per cent by weight of the entire composition of polyethylene glycol ethers containing at least eight carbon atoms joined together and at least two ethenoxy groups joined together, in the presence of from 0.1 to 0.25 per cent by weight of the entire composition of moisture.

2. A method as claimed in Claim 1 wherein the moisture is associated with the surfaces of the crystals of the salt.

3. An explosive composition comprising at least sixty per cent by weight of water soluble explosive inorganic oxidizing salts, a less proportion of an explosive liquid nitric ester, a small amount of nitrocellulose dissolved therein, from 0.02 to 0.5 per cent by weight of polyethylene glycol ethers of at least eight carbon atoms joined together and of at least two ethenoxy groups joined together, and from 0.1 to 0.25 per cent by weight of the entire composition of moisture.

4. An explosive composition as claimed in claim 3, wherein the polyethylene glycol ethers are polyethylene glycol monocetyl ethers containing at least two ethenoxy groups per molecule.

5. An explosive composition as claimed in claim 3, wherein the polyetheylene glycol ethers are polyethylene glycol mono betanaphthyl ethers containing at least two ethenoxy groups per molecule.

6. An explosive composition as claimed in claim 3, wherein the polyethylene glycol ethers are polyethylene glycol mono ethers of oleoethanolamide containing at least two ethenoxy groups per molecule.

STANLEY FORDHAM.
JOHN L. MOILLIET.

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