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METHOD OF ACCELERATION OF GELATINIZATION OF CELLULOSE NITRATE AND LIQUID NITRIC ESTERS AND THE PRODUCT THEREOF

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This invention relates to the acceleration of the gelatinization of cellulose nitric esters and liquid nitric esters, particularly glycerine trinitrate and mixtures of glycerine trinitrate with its freezing point depressants, such as the glycol nitric esters, polymerized glycerine nitric esters, nitric esters of chlorhydrins, etc., and to the products resulting therefrom.

The present application is a division of our copending application, Serial Number 705,622, filed January 6, 1934.

The object of our invention is to gelatinize cellulose nitric esters by means of liquid nitric esters with the aid of more efficient gelatinization accelerators than any heretofore known or used; thus making a more satisfactory product and obtaining greater speed, economy, and flexibility in the production of compositions which involve this process, as for example, smokeless powder, blasting gelatins, gelatin dynamites and plastics.

In the manufacture of explosives such as blasting gelatin, gelatin dynamites, semi-gelatins, smokeless powders, etc., which contain cellulose nitrate and liquid nitric esters such as nitroglycerine, glycol nitrates, dinitrochlorhydrin, etc., it is the usual practice to gelatinize the cellulose nitrate by adding it in the fibrous form, to the liquid nitric ester or mixture of two or more nitric esters, contained in a mixer provided with an agitator. The mixer may or may not be provided with means for satisfactorily applying heat. The choice of liquid nitrates, cellulose nitrate and degree of gelatinization have heretofore determined whether or not heat was necessary. While nitroglycerine and ethylene glycol dinitrates are solvents of cellulose nitrates of the class used in the manufacture of gelatinized explosives as above described, the solvent action of nitroglycerine is very slow and that of ethylene glycol dinitrate, although faster, is still relatively slow.

To hasten the solution of the cellulose nitrate heat is usually provided. Complete gelatinization of all the cellulose nitrate fibres is very difficult to obtain. The fibres tend to form aggregates of more or less incompletely gelatinized cellulose nitrate. The surfaces of these aggregates are covered with a film of gelatinized material which prevents the penetration of liquid nitric ester to the interior of the aggregate in sufficient amount to effect complete gelatinization. Even with excessive periods of mixing it is difficult to break down all of these aggregates. The result is a distribution throughout the finished explosive of gelatinized, partly gelatinized and ungelatinized cellulose nitrate. The sensitiveness to detonation, the velocity of detonation, and the length of time the product may be stored before it becomes unsatisfactory to use, are adversely affected.

Increasing the time of gelatinization or elevation of the temperature of the reacting materials, while of some benefit, does not overcome the trouble and either prolongation of the time of mixing or elevation of the temperature introduces additional hazards. Acetone, alcohol-ether mixtures and similar solvents of relatively low boiling point have been tried but are not desirable due to their unfavorable effect on sensitivity and keeping properties of the explosives in storage.

We are aware that U. S. Patent No. 1,640,712, issued to Moran, claims glycols as accelerators in the gelatinization of cellulose nitrate with nitroglycerine mixtures. However, we have found that fully substituted glycols, such as ethoxyethyl acetate (cellosolve acetate) are much more efficient than the glycols themselves. The most effective substituents are the monovalent hydrocarbon residues, acyl groups (and monovalent inorganic acid radicals). Compounds of this type may be represented as derived by the etherification or etherification and esterification of all of the hydroxyls of a polyhydric alcohol.

The derivation of these products may be more clearly illustrated by considering a polyhydric alcohol, such as glycol or glycerine, to have at least one of its hydroxyl groups replaced by an alkoxy group, and all of any of the remaining hydroxyls replaced by a monobasic organic acid radical or an inorganic acid radical. By alkoxy group we mean a saturated acyclic monohydric alcohol from which the hydroxylic hydrogen atom has been removed, and having the formula (C_nH_{2n+1})—O. For example, in our preferred accelerator, namely, ethylene glycol ethyl ether acetate, or β-ethoxyethyl acetate, the polyhydric alcohol, ethylene glycol, has one hydroxyl group replaced by the ethoxy group, and the one remaining hydroxyl group replaced by the monobasic organic acetate radical.

These compounds are by definition fully substituted and contain no free hydroxyl groups.

Our improved process of gelatinization may be carried out in different ways. We may add the accelerator to the liquid nitric esters or a mixture of liquid nitric esters and cellulose nitrate in the mixing bowl; we may choose to mix the cellulose nitrate and the accelerator to form a solution before admixing the liquid nitric esters;

or we may elect to mix the accelerator and liquid nitric ester and then add the cellulose nitrate. We prefer to stir the mixture during and subsequent to the addition of the cellulose nitrate. We may elevate or reduce the temperature by adding or subtracting heat during the mixing, depending on the selection of materials, the degree of gelatinization desired, and the time available for carrying out the process.

The quantity of accelerator required for this gelatinization is small, usually ranging from 0.1 to 5% of the explosive composition.

As an illustration of the efficacy of accelerators of the type herein disclosed we give the following example:

Example I

To a mixture of 1.5 parts cellulose nitrate and 100 parts low-freezing nitroglycerine, 1 part of β-ethoxyethyl acetate (cellosolve acetate) was added, and the mixture stirred until gelatinized. This required 10 minutes. To reach the same degree of gelatinization without the accelerator 85 minutes were required.

As cited above the esterification may be carried out with inorganic acids as well as organic. Thus, in the case of etherified nitrates, such as cellosolve, or ethoxyethyl nitrate, we may choose to add the cellosolve to the glycerine or glycol mixture and carry out the nitration of the ether simultaneously with the nitration of the glycerine or glycol mixture.

Example II

A mixture of 89 parts by weight of glycerine, 10 parts ethylene glycol, and 1 part cellosolve was nitrated at 5.0–5.5° C. employing 511 parts of mixed acid having the composition—

	Percent
Sulfuric acid	54.30
Nitric acid	45.33

The nitrated mixture was washed and neutralized in the cutomary manner. 91.5 parts of this oil were used for gelatinizing 8.5 parts of nitrocellulose. The gelatinization test was carried out at 30° C. Gelatinization took place in 4½ minutes, whereas a similar gelatin, made without any accelerator, required 17 minutes to gelatinize.

Among the accelerators of the character described we may specifically mention as contemplated and satisfactory forms β-ethoxyethyl acetate (cellosolve acetate), ethylene glycol diethyl ether and ethoxyethyl nitrate (cellosolve nitrate).

The invention is not limited to the particular species named but includes within its purview such satisfactory substitutes as fall within the terms or the spirit of the appended claims.

Having described our invention, what we claim is:

1. The process of gelatinizing cellulose nitric esters with liquid nitric esters which comprises bringing about the gelatinization in the presence of an accelerator comprising ethylene glycol diethyl ether.

2. The process of gelatinizing cellulose nitric esters with liquid nitric esters which comprises bringing about the gelatinization in the presence of an accelerator comprising β-ethoxyethyl acetate (cellosolve acetate).

3. The process of gelatinizing cellulose nitric esters with liquid nitric esters which comprises bringing about the gelatinization in the presence of an accelerator comprising ethoxyethyl nitrate (cellosolve nitrate).

4. An explosive composition comprising nitrocellulose gelatinized with a liquid nitric ester in the presence of 0.1% to 5.0% of an accelerator comprising β-ethoxyethyl acetate (cellosolve acetate).

5. The process of gelatinizing cellulose nitric esters with liquid explosive nitric esters which comprises bringing about the gelatinization in the presence of an accelerator comprising at least one of the group of compounds derivable from a polyhydric alcohol having not more than 3 hydroxyl groups by replacing at least one of the hydroxyl groups by an alkoxy group containing not more than 4 carbon atoms, and replacing all of any remaining hydroxyls by a monobasic acid radical taken from the group consisting of the radicals of paraffin acids containing not more than 4 carbon atoms, and nitric acid radical.

6. A process as in claim 5, wherein all the hydroxyls of the polyhydric alcohol are replaced by alkoxy groups.

7. A process as in claim 5, wherein the acid radicals are those of paraffin acids containing not more than 4 carbon atoms.

8. A process as in claim 5, wherein the acid radical is the nitrate radical.

9. A composition of matter comprising a cellulose nitric ester gelatinized with a liquid explosive nitric ester in the presence of a minor proportion of an accelerator comprising at least one of the group of compounds derivable from a polyhydric alcohol having not more than 3 hydroxyl groups by replacing at least one of the hydroxyl groups by an alkoxy group containing not more than 4 carbon atoms, and replacing all of any remaining hydroxyls by a monobasic acid radical taken from the group consisting of the radicals of paraffin acids containing not more than 4 carbon atoms, and nitric acid radical.

10. A composition of matter containing an accelerator as in claim 9, wherein all the hydroxyl groups of the polyhydric alcohol are replaced by alkoxy groups.

11. A composition of matter containing an accelerator as in claim 9, wherein the acid radicals are those of paraffin acids containing not more than 4 carbon atoms.

12. A composition of matter containing an accelerator as in claim 9, wherein the acid radicals are the nitrate radical.

13. An explosive composition comprising nitrocellulose gelatinized with a liquid nitric ester in the presence of an eccelerator comprising ethylene glycol diethyl ether.

14. An explosive composition comprising nitrocellulose gelatinized with a liquid nitric ester in the presence of an accelerator comprising ethoxyethyl nitrate (cellosolve nitrate).

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