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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 product resulting therefrom.

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 dinitrate are solvents of cellulose nitrates of the class used in the manufacture of gelatinized explosives as above described, their solvent action is very 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 because of their volatility; with resultant proneness to form explosive gaseous mixtures with air, and toxic poisoning effect on the workmen.

We have discovered that the alkyl and aryl ethers of the polyhydric alcohols are exceedingly efficient in the gelatinization of mixtures of cellulose nitrate and liquid nitric esters, such as glycerine trinitrate. This series of compounds may be defined by the general formula $R-O-R'$ in which R is a polyhydric alcohol residue, or an esterified polyhydric alcohol residue, and R' is a monohydric alcohol residue. In this class of compounds we mean to include the alkyl, aryl, and mixed alkyl-aryl ethers of the polyhydric alcohols as well as alkyl, aryl and mixed alkyl-aryl ethers of esterified polyhydric alcohols. Etherification may be either complete, or partial, leaving one or more free hydroxyl groups. The partially etherified polyhydric alcohol may have one or more of its hydroxyl groups replaced by an ester group, such as chloride, nitrate, acetate, benzoate, etc. These ethers of the polyhydric alcohols include the alkyl and aryl ethers of the glycols, such as ethylene, propylene, trimethylene, and butylene glycol; the alkyl and aryl ethers of glycerine, erythrite, pentaerythrite, xylite, arabite, adonite, dulcitol, mannitol, sorbitol, etc.

The quantity of the ethers of the polyhydric alcohols required to accelerate the gelatinization of cellulose nitrate with liquid nitric esters is exceedingly small. By one method of carrying out a gelatinization test at 70-80° F. we have found that if 1.5 parts of cellulose nitrate are added to 100 parts of a low freezing nitroglycerine it requires 85 minutes for the mass to attain a certain degree of plasticity. If, however, 1 part of monoethyl ether of ethylene glycol is added to a duplicate mixture in a similar test, this same degree of plasticity is attained in ten minutes. 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, for example, that monoethyl ether of ethylene glycol is more than twice as efficient as the glycol itself.

Our improved process of gelatinization may be carried out in different ways. We may add the accelerator to the liquid nitrate esters or a mixture of liquid nitrate 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 nitrate esters; or we may elect to mix the accelerator and liquid nitrate 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. In the case of ether nitrate esters, such as monoethyl ether of ethylene glycol, we may choose to add the ether to the glycerine or glycol mixture and carry out the esterification of the ether simultaneously with the nitration of the glycerine or glycol mixture.

Among the accelerators of the character described we may specifically mention, as contemplated and satisfactory forms, monomethyl ether of ethylene glycol; monoethyl ether of ethylene glycol acetate; monoethyl ether of ethylene glycol nitrate; hexamethyl sorbite; pentaethyl sorbite; pentamethyl mannite; monomethyl glycerine; diethyl glycerine; trimethyl glycerine; monotolyl glycerine; ditolyl glycerine; monomethyl glycerine diacetate; dimethyl monochlorhydrin.

Prior, during or after the gelatinization, we may add, for example, in the manufacture of gelatin dynamites, other ingredients, such as oxygen carrying inorganic salts, as ammonium or sodium nitrate; a carbonaceous combustible material,

such as wood pulp and sawdust; nitrohydrocarbons; sulphur; chalk; zinc oxide; sodium chloride; etc.

Having described our invention, what we claim is:

1. The process of gelatinizing cellulose nitric esters with liquid nitric esters in the presence of an accelerator comprising a pentaethyl sorbite.
2. The process of gelatinizing cellulose nitric esters with liquid nitric esters in the presence of an accelerator comprising a pentamethyl mannite.
3. A composition comprising a cellulose nitric ester gelatinized with a liquid nitric ester in the presence of a minor proportion of an accelerator comprising an alkyl ether of a hexahydric alcohol, said ether having at least five ether groups.
4. A composition comprising a cellulose nitric ester gelatinized with a liquid nitric ester in the presence of a minor proportion of an accelerator comprising a pentamethyl sorbite.
5. The process of gelatinizing cellulose nitric esters with liquid nitric esters, which comprises bringing about said gelatinization in the presence of an accelerator comprising an alkyl ether of a hexahydric alcohol, said ether having at least five ether groups.
6. A composition comprising cellulose nitric ester gelatinized with liquid nitric ester in the presence of an accelerator comprising a pentaethyl sorbite.
7. A composition comprising cellulose nitric ester gelatinized with liquid nitric ester in the presence of an accelerator comprising a pentamethyl mannite.

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