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PROCESS FOR CRYSTALLIZING ORGANIC EXPLOSIVE COMPOUNDS

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The present invention relates to a process for the preparation of explosive compounds which normally exist in the form of crystalline solids. The invention has particular application to the preparation of pentaerythritol tetranitrate, tetranitraniline, erythritol tetranitrate, mannitol hexanitrate, tetryl and trimethylene trinitramine.

The process of my invention may be adequately illustrated by a discussion of its application in the preparation of pentaerythritol tetranitrate. The art is familiar with various processes for the formation of the crude pentaerythritol tetranitrate. An early method comprised the direct nitration of pentaerythritol in strong nitric acid followed by precipitation of the nitrated product with sulfuric acid. A safer method of nitration was disclosed in U. S. Patent 1,660,651 to Marshall and Bergeim in which process pentaerythritol was dissolved in sulfuric acid and the resulting ester was added to nitric acid. An additional method of preparation comprised the nitration of pentaerythritol with mixed sulfuric and nitric acids.

The crude pentaerythritol tetranitrate formed by the processes of the prior art was rendered impure and consequently unstable by the presence of occluded or included matter comprised chiefly of the acids used in nitration. A standard method of purification and stabilization was employed. After separation from the bulk of the waste acid by drowning in water and filtration, the crude product was washed substantially free from acid by means of successive treatments with water and dilute alkali solution. Further purification was effected by dissolving the washed product in acetone, neutralizing any traces of residual acid and precipitating the purified product from solution by drowning the acetone solution in a larger amount of water in the presence of means for agitation of the system. The solid product was then recovered by filtration and dried. The resulting substance was in extremely finely divided form, being almost clay-like in consistency. Whether the agitation during final drowning was slow or fast, the product was still so fine that 99% passed a 150-mesh screen.

The extreme fineness of the petaerythritol tetranitrate was undesirable in view of the prospective uses for which the material was intended. Pentaerythritol tetranitrate may be employed in fuse manufacture, in commercial blasting explosives, and in explosives adapted to military purposes. Specifications for pentaerythritol tetranitrate to be used in the manufacture of fuse have usually stipulated that the material must consist largely of crystals so coarse that they will fail to pass through the 150-mesh screen. This enhances the free-flowing property of the material which was desirable from the standpoint of handling and processing. Coarse crystals were also desirable in order that the particles would not be so fine as to work through and penetrate the cover of the fuse. Apart from the manufacture of fuse, the extremely fine material was so difficult to handle or charge for any purpose that graining was necessary.

One of the chief objects of my invention is to provide an improved process for the preparation of explosive compounds which normally exist in the form of solid crystals. Another object is a process for the preparation of normally solid crystalline explosive compounds in the form of relatively coarse crystals. An additional object is a process for the formation of pentaerythritol tetranitrate in relatively coarse crystals. Other objects will be apparent from the detailed description of my invention which follows.

I have discovered that, upon the gradual addition of cold water, either in liquid form or as ice, to a solution of a normally crystalline explosive compound in an inert organic solvent, relatively coarse crystals of such compound are formed. For instance, upon the addition of cold water or ice to a solution of pentaerythritol tetranitrate in acetone, the crystals of pentaerythritol tetranitrate precipitated are much larger than those formed in the process of the art in which the acetone solution of the explosive is drowned in a larger body of water. My process comprises a reversal of the drowning process of the art, with the formation of a substantial proportion of crystals which fail to pass through a 150-mesh screen. The best results are obtained by the gradual addition of ice to the acetone solution, as illustrated in the example.

Example

The neutralized acetone solution consisting of 90 lbs. of pentaerythritol tetranitrate in 300 lbs. of acetone was run into an empty drowning tub. The initial temperature of the solution was 90° F. Thirty-five pounds of cracked ice was added and the mixture stirred until the ice was completely melted. This procedure was repeated until 100 lbs. of ice had been added. At this point, the temperature had fallen to 50° F., and most of the pentaerythritol tetranitrate had been precipitated in the form of coarse crystals. Enough water was added to bring the total volume of wa-

ter equal to 100 gallons. The pentaerythritol tetranitrate was then completely precipitated and could be handled in the usual way. The following table presents a wet screen analysis of the product.

	Per cent
On 48 mesh	8
100 mesh	43
150 mesh	8
Thru 150 mesh	41

If a coarser product is desired the fines may be separated and reworked by the same process. In this way my invention permits the manufacture of pentaerythritol tetranitrate in crystals coarse enough to meet any specification desirable. The invention provides a product sufficiently coarse for handling without graining.

It is to be understood that the scope of the invention is not to be limited by the above example. The temperatures may be varied at will within limits of safety and practicability. Under the above conditions I prefer to maintain the initial temperature between 85 and 90° F. and cool to between 50 and 55° F. The proportions of acetone and water and ice may be varied between suitable limits. I prefer to dissolve 80 to 90 lbs. of pentaerythrite tetranitrate in 300 lbs. of acetone. Any suitable equivalent solvents may be used.

The scope of my invention is also not to be limited by the illustrated application to the preparation of pentaerythritol tetranitrate. As stated in the foregoing, this is merely a preferred embodiment of the invention, chosen as a fitting illustration of the principles involved therein. The process may be applied in the preparation of any explosive material which normally exists in the form of a crystalline solid, provided that the stabilities and solubilities of the materials in the particular solvents and cooling means employed do not hinder such application. For example, the process of my invention may be applied to the preparation of coarse crystals of tetranitroaniline, erythritol tetranitrate, mannitol hexanitrate, tetryl and trimethylene trinitramine.

Acetone has been employed as the solvent in the foregoing illustration. It is to be understood however, that in a particular application of the process of my invention, any neutral organic solvent medium may be used whose properties render it suitable for the purification of the particular substance under consideration. It is necessary that the solvent medium be miscible in water or whatever equivalent of water is used as a precipitant. It is likewise desirable that the solvent be compatible with the explosive substance. For instance, solvents such as ethyl alcohol, methyl alcohol, acetone and the like possess these properties.

Although I have described my invention in detail and have therefore utilized certain specific terms and language therein, it is to be understood that the present disclosure is illustrative rather than restrictive and that changes and modifications may be resorted to without departing from the spirit or the scope of the claims appended hereto.

I claim:

1. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in a neutral organic solvent medium miscible with water, establishing a temperature of from 80 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of cold water thereto.

2. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate produce containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in a neutral organic solvent medium miscible with water, establishing a temperature of from 80 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of ice thereto.

3. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in acetone, establishing a temperature of from 80 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of cold water thereto.

4. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in acetone, establishing a temperature of from 80 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of ice thereto.

5. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises dissolving pentaerythritol tetranitrate in acetone to form approximately a 26 to 30% solution therein, establishing an initial temperature of 85 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of cold water thereto.

6. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises dissolving pentaerythritol tetranitrate in acetone to form approximately a 26 to 30% solution therein, establishing an initial temperature of 85 to 90° F. in said solution, gradually cooling said solution to between 50 and 55° F. by the gradual addition of ice thereto.

7. The process for the formation of a coarse, crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises dissolving approximately 90 pounds of pentaerythritol tetranitrate in 300 pounds of acetone, establishing an initial temperature of approximately 90° F. in said solution, adding 35 pounds of cracked ice thereto, stirring the mixture until the ice is melted, adding more ice repeatedly in approximately the same amount until the temperature has fallen to approximately 50° F.

8. The process for the formation of a coarse crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen,

which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in a neutral organic solvent miscible with water, establishing an elevated temperature in said solution, and gradually cooling and diluting said solution by the gradual addition of cold water thereto.

9. The process of claim 8 wherein the gradual cooling is effected by the gradual addition of ice.

10. The process or the formation of a coarse crystalline pentaerythritol tetranitrate product containing a substantial proportion of crystals which fail to pass through a 150-mesh screen, which process comprises forming a substantially neutral solution of pentaerythritol tetranitrate in acetone, establishing an elevated temperature in said acetone solution, and gradually cooling and diluting said solution by the gradual addition of cold water thereto.

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