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NITRATION OF ALCOHOLS

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1 Claim. (Cl. 260—467)

This invention pertains to the nitration of solid polyhydroxy alcohols.

The nitration of solid polyhydroxy alcohols presents certain difficulties which prevent the direct addition of said alcohols to a nitrating mixture of nitric and sulfuric acids. Thus, prior attempts to effect nitration in this manner have invariably been characterized by incomplete distribution of the mass of crystals of the solid polyhydroxy alcohol throughout the nitrating medium, due partly to the fact that the nitrated product separates in a solid phase as soon as formed. As a result of this incomplete distribution, there is a tendency for localized heating to occur, said heating, of course, presenting an explosion hazard. Likewise, incomplete distribution of the alcohol is attended by low yields, due to incomplete nitration of the material.

Because of the foregoing difficulties, many efforts have been made to develop a method of nitration which would give a high yield of the nitrated product without entailing hazardous or complicated steps in the procedure. Thus, Marshall in U. S. Patent 1,660,651 discloses a method for the nitration of solid polyhydroxy alcohols which is characterized by the dissolution of the solid alcohol in sulfuric acid of 90 to 95 percent strength, following which the resulting solution is added to concentrated nitric acid of 90 to 100 percent strength, nitration being effected at a temperature between 40° and 60° C. Although this method, in general, represents an improvement in the art, the yields of nitrated product obtained when operating in accordance therewith are not entirely satisfactory.

The object of the present invention is a process for nitrating solid polyhydroxy alcohols, said process permitting the attainment of yields of the nitrated product appreciably higher than those obtained by any process known heretofore. Another object is a process for the nitration of solid polyhydroxy alcohols, which process is characterized by safety as well as ease of operation. A further object is a process for producing a pure, granulated, solid, nitrated polyhydroxy alcohol, such as erythritol tetranitrate, for example. Still further objects will become apparent as the invention is described more fully hereinafter.

I have found that the foregoing objects are attained by effecting distribution of the solid polyhydroxy alcohol in a medium comprising water and a material which will act as a "diluent" or "stabilizer" when the aqueous solution of the polyhydroxy alcohol is nitrated. As such "dilu-

ent" or "stabilizer," I may employ sulfuric acid, acetic acid, phosphoric acid, and the like. Although the proportions of the water and diluent present in the medium employed for dissolution of the polyhydroxy alcohol may be varied rather widely, I prefer to restrict the water content to the minimum quantity which is essential for facile dissolution of the alcohol to be nitrated and yet is sufficient to prevent charring and decomposition of said alcohol, as well as to inhibit material chemical reaction thereof.

After the alcohol has been dissolved in such solution, it may be nitrated readily by reacting with a mixed acid composed of nitric and sulfuric acids to yield a crystalline product that may be purified easily.

The following example is cited as a specific embodiment of my process in order that it may be described more in detail. It is understood, of course, that this example is merely illustrative and is not intended to limit my invention.

Example

Twenty-one pounds of mesoerythritol were dissolved in 42 pounds of a mixture of sulfuric acid and water, the acid and water representing a sulfuric acid solution of 70% strength. The resulting solution was run into a stainless steel nitrator, wherein was present 276 pounds of a nitrating acid mixture composed of 27.5 parts of nitric acid and 72.7 parts of sulfuric acid, said mixture being agitated vigorously. The charge was cooled during the nitration reaction by passing cold water through the jacket of the nitrator. After nitration was complete, the charge was drowned in about 1300 pounds of cold water and the drowned charge neutralized by washing with a dilute sodium carbonate solution. The crude erythritol tetranitrate was then dissolved in a 50—50 mixture of acetone and ethyl alcohol, any occluded acidity being neutralized with aqueous sodium carbonate, and the resulting solution forced through a spray nozzle having a circular opening of 0.10 inch in diameter into a vessel containing water, which was vigorously stirred during the interval required for spraying the erythritol tetranitrate solution. The precipitated erythritol tetranitrate was then separated from the liquid by filtration, following which the material was dried. The finished product represented a yield which was 91 per cent of the theoretical and possessed a nitrogen content of 18.50 percent and a melting point of 61.3° C.

The dissolution of the solid polyhydroxy alcohol in the water-diluent mixture offers no par-

ticular difficulty. As stated hereinbefore, a sufficient volume of water should be present to effect ready solution of the alcohol. Likewise, the ratio of water to acid is maintained sufficiently high to prevent decomposition and charring or chemical reaction with the alcohol. Thus, I have found that, when sulfuric acid is employed as the diluent or stabilizer, it is permissible to employ an aqueous solution of sulfuric acid having a strength as high as about 80% sulfuric acid. However, I prefer to use a solution ranging from 60 to 70% sulfuric acid, because in this range it is certain that substantially no decomposition or carbonation of the alcohol will occur. Nor does the use of such mixture entail a substantial heat evolution, characteristic of sulfation.

Once the solid polyhydroxy alcohol has been dissolved in the water-acid mixture, nitration thereof may be effected readily by means of a mixed acid. The composition of the mixed acid may be varied rather widely, say to approximately equal parts of sulfuric and nitric acid, but I prefer to use an appreciable preponderance of sulfuric acid, because it facilitates suitable agitation of the charge during the nitration stage. I have found a mixed acid composed of about 70 parts sulfuric acid and 30 parts nitric acid very desirable. The nitration of the solid polyhydroxy alcohol solution, with the aforementioned conditions obtaining, does not require an exact temperature control, but instead proceeds even though the temperature varies over rather wide limits. Obviously, variations in the temperature affect the time cycle required for complete nitration of the alcohol.

The present process makes available a method for nitrating solid polyhydroxy alcohols which may be executed readily, which is free from the hazards characterizing heretofore known processes for the nitration of such materials. In addition, my process is characterized by an unusually high yield of the finished product.

It will be understood that the process is not limited to the nitration of erythritol, but rather is applicable, in general, to solid polyhydroxy

alcohols which may be dissolved in diluents, such as sulfuric acid, acetic acid, phosphoric acid, and the like. Hence, it is applicable to mannitol, arabitol, xylitol, sorbitol, dulcitol, and the like.

The term "diluent" or "stabilizer," as applied to the acids disclosed in the foregoing, is intended to denote the effect which said acids exert when the solution of alcohol is brought into contact with the mixed nitrating acids. Thus, their presence renders the aqueous alcohol solution compatible with the nitrating medium and avoids the violent reaction which otherwise would occur. Likewise, their presence serves as a medium for the absorption of heat evolved during the nitration reaction. Consequently, such meaning should be ascribed to these terms throughout the present description.

Although I have described my invention in detail, it will be understood by those skilled in the art that variations may be made without departing from the spirit or scope thereof. For example, it is not essential that the nitrated alcohol be reprecipitated from a solvent solution as set forth in the specific example. On the contrary, it may be desirable to employ the product after it has been washed with water and neutralized with the aqueous alkaline solution. This is permissible because the nitrated product crystallizes as it is formed, and the crystals may be purified by methods deemed standard for the purification of freshly-nitrated materials, that is to say, washing with water and dilute alkaline solutions. I intend, therefore, to be limited only in accordance with the following claim.

I claim:

A method of producing erythritol tetranitrate, which comprises dissolving erythritol in a water-sulfuric acid medium equivalent to a sulfuric acid solution not exceeding 80% strength, and treating the resultant erythritol-containing solution with a nitric-sulfuric acid mixture composed of from 50 to 80 parts of sulfuric acid and from 50 to 20 parts of nitric acid.

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