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PROCESS FOR THE MANUFACTURE OF SOLUTIONS OF CELLULOSE IN SULFURIC ACID

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This invention relates to the manufacture of solutions of cellulose in sulfuric acid.

It is known to dissolve cellulose in mineralic acids, such as sulfuric acid, phosphoric acid, hydrochloric acid and other acids or mixtures thereof, and to work up these solutions into fibers, films or similar structures of this kind. In this case the cellulose is first thoroughly swollen with a weaker acid near the dissolving concentration and finally completely dissolved with an acid of higher concentration.

Furthermore it is known that cellulose in these strongly acid solutions is easily decomposed, and that the production and working up of these solutions is therefore connected with considerable difficulties.

It is an object of the present invention to provide a method of dissolving cellulose in sulfuric acid, which is free from these disadvantages.

This and other objects will become apparent from the following specification.

The present invention relates to the manufacture of solutions of cellulose in strong sulfuric acid, whereby the cellulose is first impregnated or wetted with a weaker acid (wetting acid) and then dissolved in a strong acid (dissolving acid).

The process comprises impregnating the cellulose with only 2½–3 times its weight of wetting acid and adding so much of dissolving acid of a concentration above 90%, that the total amount of sulfuric acid used for complete solution (calculated as monohydrate) amounts to not more than 5 times, preferably 4 times and less, the weight of cellulose.

It has always been endeavoured in the art to dissolve in the strong acids as much cellulose as possible, but in spite of this in no case there were reached concentrations higher than 1 kg. cellulose in 8 liters strong acid, as the concentrations of the acids applied and the working methods did not admit the dissolution of larger quantities of cellulose.

When wetting the cellulose with an amount of acid just being sufficient, it is difficult to impregnate evenly the entire cellulose. When working too slowly and when using a swelling acid, the latter being near the dissolving concentration, part of the cellulose takes up the total amount of sulfuric acid, whereas the other part remains dry. Also when mixing and kneading continuously such an uneven cellulose-sulfuric-acid-mixture, an even distribution of the sulfuric acid in the cellulose mass can never be obtained. On the other hand it is unpractical to use the wetting acid in too weak a concentration, since solutions of high cellulose contents are required, for which then correspondingly higher amounts of dissolving acid are necessary. Most suitable for that purposes are concentrations between 55–59% H_2SO_4.

Though it is possible when working quickly and with not too large quantities, to evenly impregnate the cellulose being suitably distributed with 2,5–3 times its quantity of 55–59% acid, if said acid is added to the mass all at once while stirring violently, it is generally to be preferred to employ a larger surplus of wetting acid and to squeeze it off again as quickly as possible. When squeezing off the acid, care has to be taken, that the cellulose, though completely impregnated, has not yet reached the maximum degree of swelling, which may be brought about by adapting the concentration of the wetting acid to the swelling capacity of the employed cellulose material. The right concentration is easily determined in every case by some pretests. The right degree of pressing the cellulose can be, for instance, brought about by impregnating the cellulose bredth with wetting acid of the right concentration on a continuous belt conveyer and immediately squeezing off the acid between press rolls.

While hitherto 10 times the weight of wetting acid has been used for the impregnation of the cellulose, it may be attained, when working properly and adjusting properly the concentration to the kind of cellulose material, that the weight of the cellulose pulp amounts to only 3 times, sometimes 2,5 times that of the cellulose.

In order to cause dissolution of the cellulose, it is necessary to employ an extremely high concentration of the dissolving acid which hitherto was unusual, for instance 90–96% H_2SO_4. Also sulfuric acid monohydrate may be employed, while cooling, without causing a harmful decomposition of the cellulose. The amount of the dissolving acid required depends on the concentration. Solutions containing 4–5 parts H_2SO_4 (monohydrate) for one part cellulose are relatively easy obtained, provided the concentration of the acids was properly chosen and the mass properly cooled. The high cellulose contents of the solutions are quite useful for the manufacture of filaments and films, when working up the solutions, because large quantities of sulfuric acid and precipitating agents can be safed in this way. Especially useful is also, that these solutions are relatively stable.

It is evident that the cellulose solutions according to the present invention are so extremely viscous, that the viscosity cannot be determined any more according to known methods. The spinning of the solutions, however, with known devices, for instance by using spinning nozzles of an inner width of 0.09 mm, is easily feasible. An increased pressure, however, has to be applied to extrude the solutions through the nozzles. 50–60 atmospheres are completely sufficient in most cases.

Example I

475 grams cellulose (air dry) are brought together at 0° in a mixing vessel with 1500 grams sulfuric acid of 95% H_2SO_4 and are then homogenized in a suitable device adapted for kneading, while cooling continuously. There are added to the cellulose pulp 1060 grams sulfuric acid of 96% H_2SO_4, which are also very well pre-cooled. After a short time there is obtained a clear solution which can be spun or worked up in a manner known per se into filaments, films and the like; it contains

	Percent
Cellulose	14.7
H_2SO_4	62.7
Water	22.6

Example II

Cellulose (air dry) is impregnated at 0° in the form of plates or directly from the continuous belt conveyer in sulfuric acid of 59% H_2SO_4 in such a way, that always 400 grams cellulose are brought together with 3000 grams sulfuric acid of 59% and squeezed down to 1000 grams in the usual way by means of cell filters or pressrolls. The cellulose thus treated is brought together, while continuously cooling, after it has been loosened up in a mixing vessel adapted for kneading or otherwise suitable with 1080 grams sulfuric acid of 91% H_2SO_4, whereby the sulfuric acid must be pre-cooled very well. After a short time a solution is obtained, which may be worked up according to Example I.

Example III

550 grams cellulose (air dry) are impregnated at 0° with 3000 grams sulfuric acid of 59% and shortly afterwards squeezed down to 1550 grams. This mass is homogenized, while cooling, in a crusher or kneading device and thereto are added 250 grams oleum of 25% SO_3. A pasty clear solution, in which the sulfuric acid amounts to less than double the amount of cellulose, is obtained.

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