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## PROCESS OF MAKING CHLOROFORM-SOLUBLE CELLULOSE ACETATE.

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This invention relates to processes of making chloroform-soluble cellulose acetate, especially processes in which the cellulose is given a pretreatment prior to the main or final acetylation. One object of the invention is to provide a low cost process of this kind, which will yield cellulose acetate that can be made by subsequent operations into clear, flexible, transparent films. Another object is to provide a process of wide applicability to celluloses from different sources. Still another object is to provide a process in which an improved catalyst is used that stimulates acetylation without degrading the product and serves both during the pretreatment and the main or final acetylation. A further object is to provide a process in which the amount of cellulose sulf-acetates or other sulfur compounds in the product is reduced to the minimum. Other objects will hereinafter appear.

We have found that a process meeting the above requirements can be carried out by using a mixed catalyst of sulfuric acid and phosphoric acid in the right proportions, the same catalyst serving both for the pretreatment and for the final acetylation, an appreciable acetylation being accomplished during the pretreatment. The phosphoric acid is at least equal in weight to the sulfuric acid and may even weigh several times as much. We have found that this mixed catalyst functions better than sulfuric acid alone. The operations are under better control, the tendency to degrade the cellulose is less, the formation of sulf-acetates is minimized and the final transparent films are more brilliant.

In the preferred form of our invention the cellulose is pretreated with enough glacial acetic acid to thoroughly wet it, said acid containing an amount of said mixed catalyst that is less than 10% of the weight of the cellulose. The pretreatment is carried on until from 1 to 3.5% of acetyl is combined with the cellulose. The length of time varies with different kinds of cellulose and with different temperatures, being shorter at the upper temperatures. The latter are preferably under 40° C., at which temperature pretreatments of 2 to 4 hours generally suffice.

In the preferred form of our invention the final acetylation is brought about by adding simply enough acetic anhydrid to the complete pretreatment mixture. No further catalyst has to be added. The reaction proceeds until the pretreated cellulose is converted into fully chloroform-soluble cellulose acetate. This acetylation is conducted in our preferred process at 35° to 60° C. Less care is required to avoid degradation (as evidenced by brittleness of the final films) if temperatures in the lower part of this range are employed.

We also prefer to cool down the pretreated mass before the acetic anhydrid is stirred into it, so that the heat evolved during such addition will not raise the reaction mass to a dangerous temperature. The acetic anhydrid may be added rapidly or slowly at intervals. For uniformity we prefer to add it so that each part of the cellulosic material will receive its quota of anhydrid at about the same time as every other part.

It is one of the features of our process that it may be applied successfully to many different kinds of cellulose, such as high grade clean cotton fibers, cotton fiber tissue paper, such as is especially prepared for esterification, surgical cotton wool, cotton linters, and even carefully prepared and bleached sulfite wood pulp. These are merely illustrations of its wide applicability.

We shall now give one specific example, but it will be understood that our invention is not limited to the details thus given, except as indicated in the appended claims. Fifty parts by weight of cellulose, say cotton linters which have been purified in the usual way, say by a boil in dilute caustic soda and a short bleach, are mixed with 490 parts of glacial acetic acid containing 3½ parts of mixed catalyst. The latter is composed of 2.6 parts by weight of phosphoric acid (95% strength) and .9 parts of sulfuric acid (98% strength). The pretreatment mass, thus obtained, is kept at 38° C. for 4 hours. The ingredients may be brought to this temperature after mixing, or they may be preheated to this temperature and then mixed, the latter giving a more easily regulatable treatment.

At the end of the pretreatment the mass is brought to a lower temperature, say room temperature or even 15° C. This can be

done by artificial cooling, or by allowing the heat from the mass to pass into the atmosphere. The time of cooling is not of critical importance and 2 or 3 hours has been found convenient.

Into the cooled pretreatment mass there is next stirred 150 to 170 parts by weight of acetic anhydrid (85% strength). This corresponds to about 127 to 144 parts by weight of the actual anhydrid. The addition of the anhydrid causes the reaction mass to increase in temperature. This operation is conducted so that the reaction mass finally reaches a temperature within the range hereinabove named, say 42° C. If the reaction mass does not reach the required temperature from the evolution of heat within, it may be heated by external means so as to bring the mass gradually up to the required point. The reaction, with the reagents kept thoroughly mixed, is carried out until the fibers disappear and a clear reaction solution or dope is obtained. Then a test is made of a sample to make certain that the product is fully soluble in chloroform.

The chloroform-soluble cellulose acetate thus obtained may be hydrolyzed to the acetone-soluble form in any of the known ways, such as by adding a mixture of water, mineral acid and acetic acid to the reaction mass and allowing the hydrolysis to proceed at the appropriate temperatures, as is well known. Or the chloroform-soluble cellulose acetate may be obtained from the reaction mixture by precipitating in water and washing, or by spray drying methods; and then the solid chloroform-soluble cellulose acetate, thus obtained, may be hydrolyzed by treatment with appropriate aqueous acid solutions, as hitherto described in the art.

The films produced by subsequent hydrolysis of the chloroform-soluble cellulose acetate and final solution in acetone are strong, flexible and brilliantly transparent and their flexibility is very durable under prolonged tests at the usual testing temperatures. Analysis indicates that the amounts of cellulose sulf-acetate and other deleterious cellulose-sulfur compounds are very low in our product.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In the process of making cellulose acetate, pretreating the cellulose with glacial acetic acid containing a mixed catalyst of sulfuric and phosphoric acids in which the latter acid is at least equal to the weight of the former, mixing acetic anhydrid into the pretreated mass to complete the acetylation, and conducting the reaction until the product is chloroform-soluble, the same mixed catalyst serving both in the pretreatment and the final acetylation.

2. In the process of making cellulose acetate, pretreating the cellulose with glacial acetic acid containing a mixed catalyst of sulfuric and phosphoric acids in which the latter acid is from one to five times the weight of the former, said mixed catalyst being less than 10% of the weight of the cellulose, and said pretreatment being conducted until between 1 and 3.5% of acetyl has been combined with the cellulose, mixing acetic anhydrid with the pretreated mass to complete the acetylation, said acetylating reaction being carried on until the product is chloroform-soluble, the same mixed catalyst serving both in the pretreatment and the final acetylation.

3. In the process of making cellulose acetate, pretreating the cellulose with glacial acetic acid containing a mixed catalyst of sulfuric and phosphoric acids in which the latter acid is from one to five times the weight of the former, said mixed catalyst being less than 10% of the weight of the cellulose, and said pretreatment being conducted at a temperature below 40° C. until between 1 and 3.5% of acetyl has been combined with the cellulose, cooling the mass to at least room temperature, stirring in acetic anhydrid to complete the acetylation, said acetylation being conducted at a temperature between 35° and 60° C. until the product is chloroform-soluble, the same mixed catalyst serving both in the pretreatment and in the final acetylation.

Signed at Rochester, New York, this 19th day of Aug., 1927.

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