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MANUFACTURE OF CELLULOSE ACETATE

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This invention relates to an improved process of manufacturing cellulose acetate which is particularly adapted for operation as a continuous process although, if desired, it may be operated as a batch process.

In its broad aspects the process consists in softening the fibers of cellulosic material by pretreatment such as with acetic acid or a mixture of acetic acid and other agents, such as an oxidizing agent, followed by the treatment of the cellulosic material in a bath containing acetic anhydride, an inert diluent which is a non-solvent of cellulose acetate and cellulose and which is a diluent for acetic acid and acetic anhydride, such as toluene, and an acetylating catalyst. There results from this treatment, depending upon the time, temperature, concentration of reagents and like factors, a cellulose acetate of a definite solubility. Ordinarily, the treatment is allowed to continue until the resulting cellulose acetate is soluble in chloroform. However, by modified treatments cellulose acetate of other types and characteristics may be prepared. For example, cellulose acetate of different solubilities, such as products soluble in acetic acid, acetone, mixtures of alcohol and tetrachlorethane or chloroform, etc. may be prepared.

In the cellulose acetate industry it is customary to employ a cellulose which has been treated with caustic soda, washed, and dried to nearly bone dryness. In the preparation of cellulose acetate from such material, it is customary to subject the material to a pretreatment with acetic acid or acetic acid vapor. In typical commercial practice following this treatment a given amount of the material, say 100 parts, is acetylated by use of 350 to 400 parts each of glacial acetic acid and acetic anhydride, and 2 to 5 parts of sulfuric acid or other catalyst. In this process, the cellulose is commonly used either in the form of shredded cotton cellulose or shredded wood pulp cellulose. In this and following paragraphs when "parts" are designated parts by weight are meant.

In the present process, we prefer to employ the cellulose in the form of a strip, such as a strip of cotton cloth or a strip from a roll of cotton or wood pulp cellulose. By employing the cellulose in such form it is possible to conduct the process as a continuous process most advantageously, as will hereinafter be more readily apparent. However, it will be obvious that the process may be employed as a batch process and that the cellulosic material in the shredded form commonly employed may be used if desired. However, in view of our preference for employing a strip of cellulose material and for operating the process as a continuous one, such operation of the process will be hereinafter described as the preferred embodiment thereof.

In the practice of the process, a strip of cellulosic material is passed into a bath of acetic acid or a bath containing acetic acid and an oxidizing agent. Instead of treating the cellulosic material with a liquid bath, the reagents may be used in vapor phase if desired. We have found that a somewhat dilute acetic acid, such as 80 to 90 per cent. acetic acid, may be employed in this pretreatment step, but our preference is to employ approximately 100 per cent. acetic acid since the time of pretreatment is materially shortened thereby. As stated, we have found it advantageous to add an oxidizing agent to the pretreating bath and as such agent we prefer to employ nitric acid. Other materials such as halogens, chromic acid, manganese compounds and the like may also be employed. When an oxidizing agent of the character referred to is employed, this material is preferably used in small amounts, say two per cent. on the basis of the cellulosic material to be treated. While it is not definitely known why the addition of oxidizing agents to the pretreating bath is advantageous it appears that the speed of softening of the cellulose fiber is increased by the presence of the oxidizing agent.

The length of the tank containing the pretreating bath and the speed of passage of the cellulose material therethrough are so chosen that the cellulose will be in contact with the acetic acid long enough for the acetic acid to penetrate into substantially every fiber. The length of time depends upon the form of cellulose strip (tightness of twist of the cotton thread in the cloth, etc.), upon the temperature of the operation, upon the amount of secondary reagents present in the bath after the process has been in operation for some period, and the strength of the acetic acid. In actual practice, we have found that a period of approximately two hours is required for the pretreatment operation when a bath containing 250 parts of acetic acid of approximately 100 per cent. strength, per 100 parts of cellulose to be treated is employed, and the process is operated at a temperature of approximately 25° C. This temperature is the preferred temperature of operation but may be widely varied without serious disadvantage. For example,

the process may be successfully operated at a temperature of from 15° to 100° C.

Instead of employing a pretreatment bath of the character set forth above, we may use, if desired, acetic acid diluted with an inert solvent such as the discarded contents of the acetylating bath hereinafter described in detail or instead the distilled portion of same containing acetic acid. The ingredients other than acetic acid present in such discarded acetylating bath do not prevent the penetration of the acetic acid into the cellulose fiber and in some instances it may be found economical to use this discarded acetylating bath for the pretreatment.

After the desired period of treatment of the cellulosic material in the pretreatment bath the cellulose strip is passed between press rolls and the excess of pretreating liquid is pressed out and returned to the pretreatment bath. The pretreated cellulose strip is then subjected to an acetylation treatment. This involves passing the strip of cellulose material into a bath containing an inert diluent which is a non-solvent of cellulose acetate or cellulose, such as toluene, acetic anhydride, acetic acid (carried over from pretreatment bath and formed by the acetylation), and an acetylating catalyst, such as nitrosyl-sulfuric acid. Other catalysts such as sulfuryl chloride, a mixture of concentrated nitric and sulfuric acids, a mixture of nitrous and sulfuric acids, and the like may be employed in place of the nitrosyl-sulfuric acid. Only small amounts of such catalysts are needed. Other non-solvents of cellulose acetate and cellulose such as benzene, carbon tetrachloride and the like or their mixtures may be employed as the inert diluent provided they are miscible with but without action on acetic acid and acetic anhydride, but we prefer to employ toluene. We designate such liquids by the term "inert diluents."

The proportions of ingredients in the acetylating bath may be varied considerably. We prefer, however, to employ a bath in which at least 50 per cent. of the volume thereof consists of an inert diluent, preferably toluene. In actual practice, we have found it advantageous to employ, for each 100 parts of cellulose treated, a bath containing from 200 to 500 parts of acetic anhydride and 400 to 1,000 parts of toluene. Of this bath only a part will be used up or removed by the acetylated cellulose. Acetic acid will be present in an amount depending upon the amount formed by reaction and the amount carried over from the pretreating bath. The amount of catalyst employed is small, for example about ½ per cent. on the basis of the cellulose to be treated. The time of treatment of the material in the acetylating bath at a temperature of 25° C. is ordinarily about 14 hours. The product obtained under such conditions is completely soluble in chloroform.

By employing somewhat more of the catalyst, say about one per cent., and operating the process at a somewhat higher temperature, say 50° C. the operation can be carried out in from 1 to 2 hours. In this case, acetylation takes place so rapidly that in the first stage of the operation cooling may be desirable.

While the acetylation operation may be conducted in a single bath as described above, we prefer to employ a plurality of acetylation baths and pass the strip successively through the baths. When such procedure is followed, we prefer to use acetylating baths of varying proportions, the concentration of the acetic anhydride in the several baths progressively increasing and the concentration of acetic acid preferably decreasing. We have found that by such a treatment a product of superior qualities is produced.

In practising the process wherein two acetylation baths are employed, we have found it advantageous to use in the first bath an acetylating mixture consisting of approximately 400 parts of toluene, or other inert diluent, 200 parts of acetic anhydride, and approximately ½ part of nitrosyl-sulfuric acid. The strip of cellulose (100 parts) is treated in such a bath at a temperature of approximately 40° C. for approximately two hours after which the strip is passed through press rolls to remove the excess of treating liquid. The strip is then passed through a second acetylating bath containing approximately 350 parts of acetic anhydride, 800 parts of an inert diluent such as toluene, and approximately ½ part of nitrosyl-sulfuric acid. The strip is treated in the second acetylating bath at a temperature of approximately 40° C. for approximately four hours, after which the strip is passed through press rolls to remove as much of the acetylating bath as practicable. The resulting material is chloroform soluble. As is well known, in the process of acetylation one molecule of acetic acid is formed and left in the acetylating bath from each molecule of acetic anhydride used in the acetylation.

If it is desired to render such a cellulose acetate soluble in acetone, the strip is passed into a bath in which partial hydrolysis will occur whereby the material is rendered acetone soluble. This bath may consist of hot dilute acetic acid or of other materials commonly used for this purpose. This step of the process is conventional and any suitable known method may be employed. Following the hydrolysis treatment, the cellulose acetate strip is preferably passed through tanks carrying clear water (or water containing a small amount of alkali) wherein the material is thoroughly washed. It is then dried preferably by passing the strip over heated drums. The resulting material may be rolled up for storage or passed directly to tanks where it is dissolved in acetone and clarified by filtration, following which the solution thus prepared may be delivered to spinning cells to produce cellulose acetate filaments.

The acetylation solution removed from the strip during the process is recovered for re-use in the process. At times it will be found desirable to recover the mixture of the inert diluent and acetic acid in pure form. For this reason, we prefer to employ toluene as the inert diluent because this material can be very readily recovered in pure form, as can the acetic acid when toluene is used. This recovery can be inexpensively accomplished by distillation without appreciable loss by making use of the fact that toluene and acetic acid form a constant boiling mixture, the composition of which varies with the pressure at which the mixture is distilled. In other words, by simply distilling off part of the material at one pressure, say atmospheric pressure, at which the constant boiling mixture contains about 30 per cent. acetic acid, and then reworking part by distilling at another pressure, say at a pressure of three atmospheres, at which the constant boiling mixture contains about 50 per cent. of acetic acid, it is possible to separate these materials so that the acetic acid can be either sold as glacial acetic acid or re-

covered for reuse in the process. Actually, there is some accumulation of acetic acid in the process, so that it will be necessary to dispose of a part of it. The points at which the distillation cuts are made will depend upon the composition of the exhausted acetylation bath. However, this will be apparent to those skilled in the art.

If desired the constant boiling mixture carrying toluene and acetic acid recovered by the distillation process referred to above can be employed as the pretreating material with or without an oxidizing agent, instead of acetic acid alone. It has been demonstrated in actual tests that under some conditions of operation it may be found advantageous to follow such procedure.

A modification of the process can be carried out without the use of an inert diluent by using the pretreatment step of softening with acetic acid, partially acetylating the moving cellulosic material in a mixture of acetic acid and acetic anhydride and catalyst to give a lower cellulose acetate, say one having an acetyl content of 20 per cent. to 30 per cent. calculated as acetic acid, then passing the moving strip of partially acetylated cellulose into a second bath containing a catalyst and rich in acetic anhydride and before acetylation is complete passing it through press rolls so set that sufficient acetic anhydride and catalyst will be left in the cellulosic strip to complete the acetylation but not sufficient acetic acid and excess acetic anhydride to bring the cellulose acetate into solution. The strip of cellulosic material can be loosely rolled up and allowed to mature until the acetylation is complete. After partial hydrolysis to render it acetone soluble it will then be washed with water to remove the acid. It will be noted that the same principle is used in this modification as when the inert diluent is used, i. e., the acetylation of a moving cellulosic material by acetic anhydride in the presence of an acetylating agent under conditions such that the cellulose acetate produced does not go into solution in the mixture of acetic acid and acetic anhydride used for acetylation but remains in its original form.

The term "inert diluent" as employed in the specification and claims is intended to include materials which when present in the acetylating bath prevent the solution of the cellulose acetate or cellulose by the acetic acid or acetic anhydride and which are inert with respect to acetic acid and acetic anhydride though miscible therewith, i. e. soluble in them.

The term "acetylating catalyst" as employed in the specification and claims is intended to cover nitrosyl-sulfuric acid, sulfuryl chloride, a mixture of concentrated nitric and sulfuric acids, a mixture of nitrous and sulfuric acids, and similarly acting catalysts as described above. While the materials referred to are termed "catalysts" there is some evidence that the materials themselves are not the actual activating catalysts but instead act with the acetylating mixture to form a new compound which is the true catalyst. However, in a broad sense they may be considered as catalysts and are so considered herein.

As stated above, we prefer to operate the process by passing a strip of cellulosic material through the various baths, rolls, driers, etc. described above and this may be accomplished by regulating conditions so that the strip may move continuously throughout the process. However, the movement may be intermittent. For example, the strip may be moved forward for a desired distance and then stopped for a desired period of time. It will be understood that the term "moving" is intended to include both of these types of movement.

While we have described in detail the preferred embodiment of our invention it is to be understood that the details of procedure may be variously modified without departing from the spirit of the invention or the scope of the subjoined claims.

We claim:

1. The process of manufacturing cellulose acetate which comprises passing a moving strip of cellulose, prior to acetylation thereof, through a treating bath comprising acetic acid and an oxidizing agent, passing said strip out of said bath, and thereafter successively passing the moving strip into, through, and out of a plurality of separate baths, each containing an acetylating mixture, to convert the cellulose to cellulose acetate.

2. The process of manufacturing cellulose acetate which comprises passing a moving strip of cellulose, prior to acetylation thereof, through a treating bath comprising acetic acid and an oxidizing agent comprising nitric acid, passing said strip out of said bath, and thereafter successively passing the moving strip into, through, and out of a plurality of separate baths, each containing an acetylating mixture, to convert the cellulose to cellulose acetate.

3. The process of manufacturing cellulose acetate which comprises passing a moving strip of cellulose, prior to acetylation thereof, through a treating bath comprising acetic acid, an oxidizing agent, and an inert diluent, passing said strip out of said bath, and thereafter successively passing the moving strip into, through, and out of a plurality of separate baths, each containing an acetylating mixture, to convert the cellulose to cellulose acetate.

4. The process of manufacturing cellulose acetate which comprises subjecting a moving strip of cellulose to the action of a treating bath comprising acetic acid and an oxidizing agent, moving said strip out of said bath, pressing the excess of said treating mixture out of said strip, and passing said strip into, through, and out of a separate bath comprising an acetylating mixture containing acetic anhydride and an inert diluent.

5. The process of manufacturing cellulose acetate which comprises treating a moving body of cellulose with acetic acid of greater than 80 per cent. strength, and thereafter moving the body of material through a series of independent acetylating baths, each comprising an acetylating mixture containing acetic anhydride, an inert diluent, and an acetylating catalyst.

6. The process of manufacturing cellulose acetate which comprises subjecting cellulose to the action of a bath comprising acetic acid of greater than 80 per cent. strength, removing the material from said bath, thereafter treating the material in a separate bath comprising an acetylating mixture containing acetic anhydride, an acetylating catalyst and an inert diluent, removing said material from said second named bath, thereafter treating the partially acetylated material in a third bath comprising an acetylating mixture containing acetic anhydride, an acetylating catalyst, and an inert diluent, removing said material from said third named bath, pressing out the excess acetylating mixture, and permitting the resulting material to stand for completion of acetylation.

7. The process of manufacturing cellulose acetate which comprises treating a moving body of cellulose with acetic acid of greater than 80 per cent. strength, and thereafter moving the body of material through a series of independent acetylating baths, each comprising an acetylating mixture containing acetic anhydride, toluene and an acetylating catalyst.

8. The process of manufacturing cellulose acetate which comprises treating a moving body of cellulose with acetic acid of greater than 80 per cent. strength, and thereafter moving the body of material through a series of independent acetylating baths, each comprising an acetylating mixture containing acetic acid, acetic anhydride, toluene, and nitrosyl-sulfuric acid.

9. In a process of manufacturing cellulose acetate the improvement in acetylating treatment which comprises successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing acetic acid, acetic anhydride and an inert diluent, in which series of baths the concentration of the acetic anhydride progressively increases and the concentration of the acetic acid progressively decreases.

10. The herein described process of manufacturing cellulose acetate which comprises passing a moving strip of cellulose through a bath containing acetic acid of greater than 80 per cent. strength and an oxidizing agent comprising nitric acid, pressing out the excess of treating mixture from the strip, passing the treated strip through a succession of acetylation baths each containing acetic acid, acetic anhydride, toluene, and nitrosyl-sulphuric acid, the toluene in each of said baths constituting more than 50 per cent. of the bath, and the concentration of the acetic acid in said baths progressively decreasing and the concentration of acetic anhydride progressively increasing, pressing out the excess of acetylating mixture from the strip, and passing the thus treated strip through a hydrolyzing bath for partial hydrolysis of the material to render it soluble in acetone.

11. In a process of manufacturing cellulose acetate the improvement in acetylating cellulose without putting it into solution which comprises the steps of treating such material with acetic acid, removing the excess acetic acid from the material, and thereafter successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing acetic anhydride, an inert diluent, and an acetylating catalyst, the excess acetylating mixture being removed from the material after treatment thereof in one of said series of acetylating baths and prior to treatment thereof in the next of said series of said acetylating baths.

12. The process of manufacturing cellulose acetate which comprises acetylating cellulose to render the material chloroform-soluble by successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing an acetylating mixture comprising acetic anhydride, an inert diluent and an acetylating catalyst, and effecting partial hydrolysis of the material to render it soluble in acetone.

13. In a process of manufacturing cellulose acetate, the improvement in acetylating cellulose without putting it into solution which comprises successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing acetic anhydride, an inert diluent, and an acetylating catalyst, to produce a substantially completely acetylated cellulose.

14. In a process of manufacturing cellulose acetate, the improvement in acetylating cellulose without loss of its fibrous character which comprises successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing acetic anhydride, an inert diluent and an acetylating catalyst, and permitting the resulting material to stand for completion of acetylation, and treating the acetylated material in a hydrolyzing bath for partial hydrolysis of the material to render it soluble in acetone.

15. In a process of manufacturing cellulose acetate, the improvement in acetylating cellulose without putting it into solution which comprises successively introducing the material to be treated into and removing the material from a plurality of separate acetylating baths, each containing acetic anhydride, an inert diluent, and a catalyst, to produce a substantially completely acetylated cellulose, said catalyst being selected from the group consisting of nitrosyl-sulfuric acid, sulfuryl chloride, a mixture of concentrated nitric and sulfuric acids, and a mixture of nitrous and sulfuric acids.

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