

UNITED STATES PATENT OFFICE

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PROCESS FOR PRODUCING CELLULOSE ESTERS

No Drawing. Application filed August 25, 1928, Serial No. 302,138, and in Germany September 30, 1927.

This invention relates to a process for producing cellulose esters.

The object of the invention is to effect esterification of the cellulose in a more expeditious and effective manner.

It has been known that the reaction in the esterification of cellulose is a slow one; and in order to improve same in the case of acetyl cellulose it has been proposed to first convert the cellulose by a pretreatment into hydro-cellulose by treating the cellulose with very dilute sulphuric acid (3% sulphuric acid) and then drying and heating the cellulose. The resulting hydro-cellulose was then acetylated by treating it with acetic anhydride in the presence of sulphuric acid. According to said known treatment the sulphuric acid was too weak to bring about a swelling action of the cellulose fibre, i. e., too weak to act as a swelling means for the fibres; but the heating of the fibres when dry was required to convert the cellulose into hydro-cellulose, i. e., to effect a hydrolyzation of the cellulose. This hydrolyzation, however, is undesirable as it changes the cellulose structurally in a manner to effect a certain destruction or disintegration in the cellulose which is undesirable in the treatment, since it results in a substantially useless or a very inferior product for the production of artificial silk, films, etc. This process was therefore given up.

We have discovered that the esterification of cellulose can be accomplished in a rapid and uniform manner if instead of hydrolyzing the cellulose fibres (such for example as cotton fibres) as heretofore proposed, the fibres are pretreated so as to cause them to swell, and while in the swollen state they are subjected to the action of the reagent or reagents. The object of the swelling action is to bring about a physical change in the fibres such as to render the material thereof more readily accessible to the reagent.

The swelling should be carried out preferably without hydrolyzation, and in any event without substantial hydrolyzation, it being desirable where an acid swelling agent is used for the pretreatment, to effect the swelling in such manner as to avoid, if possible, any hy-

drolyzation of the fibres. It is also important that the swollen condition of the fibres is maintained until the esterifying reagent is applied, and that undesirable coagulation of the swollen fibres should not take place before the esterifying reagent is applied.

Further objects and advantages of the invention will more fully appear from the following description of some preferred methods of carrying out the invention.

As suitable swelling agents there may be used such of the known or usual swelling agents as are of an acid character or of a so-called neutral character; as distinguished from those of an alkaline character. For example there may be used concentrated mineral acids such as sulphuric, phosphoric, nitric, hydrochloric or the like, either separately or in mixtures; also salts having swelling properties, such for example as zinc chloride, calcium thiocyanate, etc. While these salts are not in a strict technical sense exactly neutral, yet for the purpose of this invention they may be regarded as neutral in comparison to the acid swelling agents and to the alkaline swelling agents such as caustic and Schweitzer's solution. Alkaline swelling agents are to be avoided because if they are used, then when the swollen fibres are treated with the esterifying mixture, which is acid, there will take place a momentary coagulation, and hence a destruction of the desired swollen state of the fibres. Alkaline swelling agents are therefore not usable unless some means should be provided whereby this resulting undesirable coagulation could be overcome.

The character and strengths of the various swelling agents, the duration of treatment of various kinds of cellulosic fibres thereby, etc., to effect swelling without detrimental effect to the particular fibres treated, are now all well understood and need not be detailed. Those skilled in the art also now known that when acid swelling agents are used on cellulosic fibres, that if the swelling action is permitted to continue after the swelling of the fibres has taken effect, the undesirable hydrolyzation may take place; and care should be taken to stop the action of the

acid swelling agent in time to avoid, if possible, any hydrolyzation of the fibres.

As is known, the strength of the agent, the character of the fibres, and other factors and conditions will come into consideration in determining the permissible length of the swelling treatment in each case, so that no fixed rule can be laid down.

After the desired swelling of the fibres has taken place the excess of swelling agent in the fibres should be removed and the fibres subjected to the esterifying mixture while the fibres are in the swollen state. The excess swelling agent may be removed from the fibres in any suitable way as by means of pressing out, centrifuging or the like.

In cases where the presence of the swelling agent may have an unfavorable influence on the esterifying mixture or on the reaction of this mixture upon the fibres, the fibres after having been swollen can be washed out so that the residue of swelling agent is reduced to an uninjurious quantity or is removed altogether. The swelling agent can be washed out by water or organic solvents as for instance alcohol, glacial acetic acid, or acetone. The washing means can be removed in any suitable manner as for example by squeezing out or centrifuging the fibres, etc.; but drying must be avoided.

The esterification of the swollen fibres is carried out in known manner as for example with concentrated organic acid, acid anhydrides, acid chlorides or reagents having a similar action, and if necessary or desirable utilizing therewith a catalizer. After the reaction has taken place the mass is poured into water or into a precipitating bath and the converted cellulose is isolated. The primary esters that are formed may also be converted into the more readily soluble secondary products in well known manner by means of partial saponification or transformation. The products that are obtained may be dissolved in the usual solvents, for example, acetone, chloroform, pyridin, etc.; and out of this solution artificial silk, films or lacquers can be produced. The production of moulded structures may also be effected by means of direct coagulation of the said mass.

As the materials to be treated, one may use any suitable cellulosic material or cellulosic-containing substance capable of being acted upon by the reagents. For example, cellulosic fibres such as cotton may be used or other cellulosic material preferably in the form of finely divided fibrous material; but moderately reduced material may also be utilized such as wood splinters or the like, capable of being acted upon by the reagents; also paper pulp may be used.

Examples

1. Previously bleached cotton waste is introduced into sulphuric acid of 62%

strength in the cold state, and is left therein for several minutes until swollen. The sulphuric acid is then drawn off and the surplus acid is pressed out, the remaining substance (swollen fibres) being then introduced into the esterifying mixture which may consist of 6 parts of acetic acid anhydride and 6 parts of glacial acetic acid, these parts being by weight with relation to the unit of weight of the dry cellulosic fibre. The temperature is maintained below about 40° C. by means of cooling. The reaction sets in very rapidly and is concluded in a quarter of an hour, whereupon the product can be isolated by precipitation in water.

2. Cleaned or purified loose cotton is allowed to swell for a quarter of an hour in nitric acid of 70% strength, whereupon most of the acid is removed by pressing. The residue of the nitric acid is then removed from the fibres by washing by means of glacial acetic acid, whereupon the mass is pressed out again. Thereupon the esterifying mixture is caused to act on the mass while in the swollen state. This mixture may consist of 4 parts of acetic acid anhydride, 4 parts of glacial acetic acid and 0.15 parts of concentrated sulphuric acid, these parts being by weight with relation to the unit of weight of the dry cotton. The temperature is kept below about 30° C. and the reaction is completed in two hours. The esterified cellulose is now removed by precipitation in the usual manner.

As heretofore stated, coagulation or drying of the swollen goods should be avoided prior to the esterifying reaction and care should be taken to avoid detrimental hydrolyzation.

By the use of the term "neutral character" as used in the specification and claims to characterize the swelling agents, we wish to be understood as using the term in its broader sense, i. e., as meaning swelling agents which are substantially neutral in character, as contrasted with the decided acid or sour character of the acid swelling agents and as contrasted with the decided alkaline character of what are generally known as alkaline swelling agents, such for example as caustic acid and Schweitzer's solution. Also, by the term "suitable swelling agent" as used in the claims, we wish to be understood as including swelling agents of acid and neutral character as herein mentioned, and also any other swelling agents of an acid or neutral character having similar action for the purpose.

Thus while we have described our improvements in detail and with respect to certain preferred forms, we do not desire to be limited to such details or forms since, as will be understood by those skilled in the art after understanding our invention, many changes and modifications may be made and the invention embodied in widely different forms

without departing from the spirit and scope thereof in its broader aspects, and we desire to cover all modifications, forms and embodiments coming within the scope of any one or more of the appended claims.

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

1. Process of producing cellulose esters which comprises producing a swelling action in the cellulose without substantial production of hydrocellulose, and while it is in the swollen condition and not alkaline in reaction, treating said cellulose with a reagent to esterify it.

2. Process of producing cellulose esters which comprises swelling the cellulose without substantial production of hydrocellulose by treating it with a non-alkaline swelling agent and while swollen treating said cellulose with a reagent to esterify it.

3. Process of producing cellulose esters which comprises treating the cellulose without substantial production of hydrocellulose with a non-alkaline swelling agent until the material is swollen, removing the excess swelling agent from the cellulose and thereupon treating said swollen material with a reagent to esterify it.

4. Process of producing cellulose esters which comprises treating the cellulose without substantial production of hydrocellulose with a swelling agent to swell the same and thereupon treating the swollen cellulose with a reagent to esterify it.

5. Process of producing cellulose esters which comprises treating the cellulose without substantial production of hydrocellulose with a swelling agent to swell the same, removing the excess swelling agent from the cellulose and thereupon treating the swollen cellulose with a reagent to esterify it.

6. Process of producing cellulose esters which comprises treating the cellulose without substantial production of hydrocellulose with a non-alkaline swelling agent until the material is swollen, washing the swollen cellulose and thereupon treating said cellulose with a reagent to esterify it.

7. Process of producing acetyl cellulose esters which comprises treating the cellulose without substantial production of hydrocellulose with a swelling agent to swell the same, removing the excess swelling agent from the cellulose, then washing the cellulose to remove an additional amount of the swelling agent therefrom, and thereupon treating the swollen material with a reagent to acetylyze it.

8. As a product of manufacture, a cellulose ester made according to the process of claim 1.

9. Process of producing acyl cellulose which comprises treating cellulose with a strong mineral acid to swell the material

without substantial production of hydrocellulose, and while it is in swollen condition, treating said material with a reagent to acylyze it.

10. Process of producing acetyl cellulose which comprises treating cellulose with a strong mineral acid to swell the material without substantial production of hydrocellulose, and while it is in swollen condition, treating said material with a reagent to acetylyze it.

In testimony whereof we have signed our names to this specification.

GEORGES HEBERLEIN.
ALBERT BODMER.

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CERTIFICATE OF CORRECTION.

Patent No. 1,858,993.

May 17, 1932.

GEORGES HEBERLEIN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 95, for "known" read know; page 3, line 51, claim 7, strike out the word "esters"; and that the said Letters Patent should be read with these correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of July, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.