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PROCESS FOR THE ACETYLATION OF REGENERATED CELLULOSE FIBERS AND PRODUCT RESULTING THEREFROM

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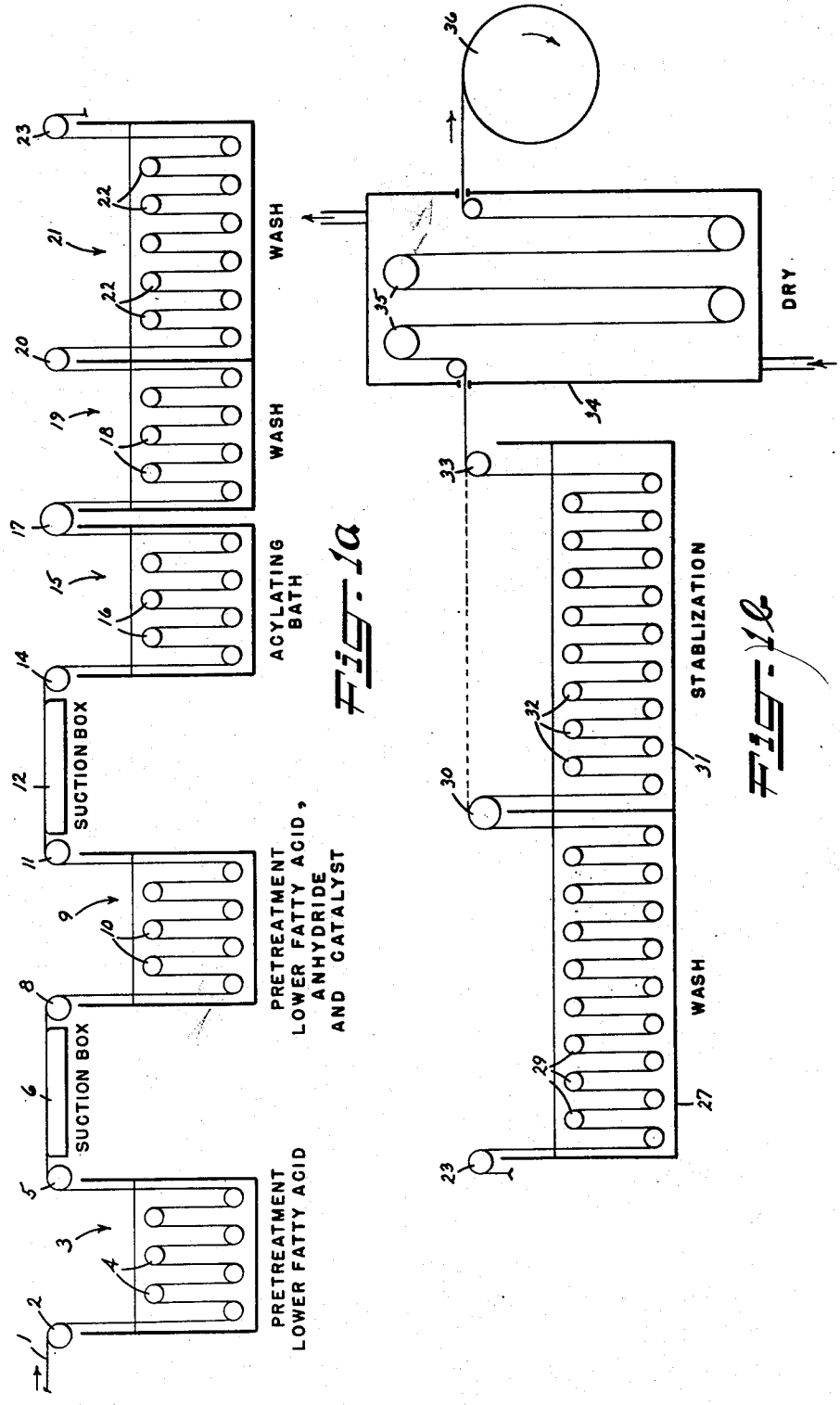


Fig. 1a

Fig. 1b

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PROCESS FOR THE ACETYLATION OF REGENERATED CELLULOSE FIBERS AND PRODUCT RESULTING THEREFROM

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3 Claims. (Cl. 8—121)

This invention relates to improved surface-esterified cellulosic yarns and a new process for producing them, and particularly to such a process that is readily adaptable to continuous operation.

Foremost among the problems in surface-acylation of fibrous cellulosic materials is that of retaining the fibrous form and/or the inherent strength of the cellulosic starting material in the acylated product. It is very difficult to control the reaction and if uncontrolled it results in substantial loss of tensile strength and in extreme cases in complete disintegration of the cellulose. In the absence of suitable precautions, the material loses its fibrous structure and cannot be maintained in the form of a yarn.

It is the primary object of this invention to produce a surface-esterified regenerated cellulose yarn containing 6 to 22 percent acyl groups with tensile strengths of at least 2.5 gms. per denier dry and at least 1.45 gms. per denier wet with dry and wet extensibilities of at least 15 percent.

It is another object of the present invention to provide a process for acylation that avoids localized reaction which would result in an irregular rate of acylation, and disintegration of the cellulose which are characteristic of previous processes of acylation of fibrous cellulose material.

It is another object to provide a process whereby cellulosic filaments, yarns, fabrics and other materials are obtained which have affinities for a larger variety of dyestuffs and, when in the form of fabrics, have improved resistance to moisture as compared to the cellulose starting materials.

It is another object to provide a process whereby it is possible to carry out the surface-acylation in a shortened time and retain the wet strength of the acylated material.

Other objects and advantages will appear hereinafter.

In the drawing, which is illustrative of the invention,

Figure 1*a* is a diagrammatic side view of a system for carrying out the process of the invention continuously, and

Figure 1*b* is a continuation of the system showing the final stages of washing and drying.

The process of the present invention comprises the acylation of filaments, fibers or yarns of regenerated cellulose in the wet gel condition by which is meant the regenerated cellulose prior to the first drying that is normally given to it. The regenerated cellulose may be that formed by the viscose process, the cuprammonium cellulose process, or any in which the regenerated cellulose is obtained in a swollen, wet gel condition. For example, the viscose process generally involves the extruding of cellulose xanthate into an acid coagulating and regenerating bath in the form of a shaped article followed by washing the article to remove the acid bath and further processing including desulfurizing, washing and drying. The present process may be applied to the freshly formed regenerated cellulose yarn at any time before the initial drying. It may be applied to the yarn which has only been washed

after coagulation and regeneration to remove the acid coagulating bath and has not had the impurities, such as sulfur, sulfides and small quantities of xanthates, removed from the yarn. The use of wet gel yarn has been found to result in a product having a higher tensile strength than that obtained from yarn that has once been dried and then rewet before surface acylation.

In accordance with this invention, regenerated cellulose yarn in the wet gel condition and having an adjusted water content is impregnated with a lower fatty acid, such as glacial acetic acid. The fatty acid used may correspond to the ester desired to be produced or it may in all cases be merely glacial acetic acid. The fatty acid serves to reduce the amount of water present on the yarn while maintaining it in a swollen gel condition in which it is highly susceptible to rapid acylation. This is followed by an addtional pretreatment with enough organic acid anhydride corresponding to the ester to be produced to eliminate any residue of water. After this pretreatment, the fatty acid content of the impregnated yarn is adjusted to predetermined limits, the yarn is passed through an acylating bath, the acylated yarn is washed to remove all the excess treating liquids, and is subsequently dried.

It has been found that to introduce a given amount of acyl groups into cellulosic material with a minimum loss of strength and extensibility of the yarn, it is necessary to control the amount of water that is on the yarn at the time it is introduced into the stage of pretreatment with the lower fatty acid, such as glacial acetic acid. It is also necessary to control the amount of acid that is present on the yarn when it is introduced into the acylation bath. If the water content or the acid content of the yarn at the respective stages mentioned is too high, then the physical properties, especially the tensile strength, of the yarn are severely damaged by the acylation process. If the water content or the acid content at these stages is too low, then the amount of acylation is too low to modify the physico-chemical character of the yarn, especially in respect to resistance to moisture and dye affinities.

The moisture content of the wet gel yarn at the time of introduction into the initial fatty acid pretreating bath must be within the limited range of 35 to 60 percent by weight of the wet gel yarn. The amount of water is preferably in the range of 50 to 60 percent. The rate and extent of the reaction can be controlled by varying the amount of water in the yarn. The moisture content of the yarn, which on leaving the normal liquid-treatment stages, such as those of the viscose process may and usually does contain 80% or more water, may be adjusted to the desired amount by partially dehydrating. Careful control is maintained at this point to insure that the moisture is uniformly distributed throughout the filaments or fibers of the yarn.

The initial pretreatment with glacial acetic acid replaces a large part of the water. Further pretreatment for the purpose of removing any remaining moisture may be accomplished in a number of ways. The yarn may be impregnated with a bath containing a mixture of a lower fatty acid, such as glacial acetic acid, a fatty acid anhydride, such as acetic anhydride, and a small amount of an acid adapted to serve as a catalyst during the subsequent acylation. For example, the yarn may be first impregnated with a glacial acetic acid bath, the excess liquid removed and then impregnated with a second bath containing glacial acetic acid and from about 2 to 10 percent by weight of the acid anhydride and a small amount of catalyst such as perchloric acid on the order of about 0.005 to 0.05 percent by weight. The preferred catalyst is perchloric acid but any other acylation promoting catalyst may be used such as sulfuric acid or phosphoric acid. The excess acetic acid

is then removed to bring the acetic acid within the range of 35 to 60%, preferably 40 to 50%, by weight of the yarn by passing the yarn over a suction box or by subjecting the yarn to various other treatments such as vibrating the yarn. The yarn may be exposed to each pretreatment bath for a period of 30 to 240 seconds. The temperature of the pretreatment baths depends on the rate of reaction desired and the extent of acylation desired in the final product, but it is preferably within the range of 20 to 30° C.

The yarn, passing to the acylation bath, should contain from 35 to 60 percent, preferably from 40 to 50 percent, by weight of organic acid. If the fatty acid content of the yarn is above 60%, esterification is no longer restricted to the surface or outer peripheral zone of the individual filaments thereof but instead it permeates practically to the core thereof and causes marked reduction of strength, increases the cross-sectional swelling of the filaments instead of reducing it, and tends to cause cementation of the filaments together in the yarn.

The acylation bath comprises 75 to 95 percent by weight of an organic non-solvent diluent, 5 to 25 percent by weight of the appropriate organic acid anhydride, and 0.05 to 0.1 percent by weight of a catalyst for promoting acylation. The preferred ranges for the bath when acetylating are 75 to 80 percent of the diluent, 20 to 25 percent of acetic anhydride and 0.05 to 0.1 percent of the catalyst. The bath may be maintained at a temperature between 35 to 65° C. and preferably at about 45° C. The yarn may be treated with the acylation bath for from 15 to 120 seconds, preferably from 30 to 60 seconds, the time depending on the degree of acylation desired. The bath is generally used in a ratio of about 50 parts of bath per part of cellulose in the yarn.

The organic diluent must be a non-solvent for the cellulose ester or such a slow-acting solvent that it does not appreciably affect the cellulose ester during the period of contact during acylation, i. e., the organic diluent for the fatty acid anhydride, such as acetic acid, is substantially inert to the cellulose ester. Benzene is the preferred diluent but other substances may be used such as ethyl acetate, butyl acetate, etc., toluene, xylene, ether, petroleum ether and the like.

While it is preferred to use perchloric acid as the acylation promoting catalyst, any of the known acylation catalysts may be employed such as sulfuric or phosphoric acids, trifluoroacetic acid, and boron trifluoride. Sulfuric acid reacts with cellulose under certain conditions and is therefore sometimes less desirable. Perchloric acid does not react with cellulose and is a very rapid acting catalyst.

The yarn is thoroughly washed after acylation, such as by treatment consecutively with cold and hot alcohol such as isopropanol followed by washing with water. The yarn may then be washed with water to insure the removal of all the treating liquid. After washing, the yarns, if produced with sulfuric acid as the catalyst, may be stabilized by heating in water containing approximately 20 parts of codium acetate per million parts of solution at about 90° C. The yarn is then dried by any suitable means.

In the single figure of the drawing, there is shown as an example a schematic arrangement of apparatus for the acylation of yarn in a continuous manner. The numeral 1 indicates a regenerated cellulose wet gel yarn containing between 35 and 60 percent by weight of water supplied continuously from some source. The yarn passes from its source around a roll 2 into a bath 3 maintained at 25° C. containing a lower fatty acid, such as glacial acetic acid. The yarn is maintained in the bath for a period, such as 60 seconds, by passing about a series or rolls 4. The yarn passes out of the bath over a roller 5 and over a suction box 6 which removes excess liquid from the yarn. The yarn then passes over a roller 8 into a second bath 9 maintained at 25° C. comprising a lower fatty acid, such as glacial acetic acid, an organic acid anhydride and a small amount of a catalyst, such as perchloric acid. The yarn is maintained in the bath for a period, such as 60 seconds, by passing around a series of rolls 10 and then passes out of the bath over a roller 11 and over a suction box 12 which reduces the fatty acid content carried by the yarn to a value between 35 and 60% by weight. The yarn then passes over a roller 14 and into an acylation bath 15 maintained at 45° C. containing a diluent, such as benzene, a fatty acid anhydride, such as acetic anhydride, and a small amount of a catalyst, such as perchloric acid. The yarn is maintained in the bath for a period, such as 60 seconds, by passing over a series of rolls 16. The yarn passes out of the bath over a roller 17 and into a bath 19 such as of isopropanol, wherein it is maintained for a period, such as five minutes, by passing about rollers 18 and is washed free of the acylation bath. From this bath, it passes over roller 20 into another washing bath 21, such as of isopropanol, maintained at 75° C. where it remains for a period, such as 30 minutes by passing about rollers 22. From this bath it passes over roller 23 into water bath 27 where it is thoroughly washed. It is maintained in the water bath by passing over a series of rollers 29 which maintain the yarn in the water bath for the desired length of time. From this bath, it may pass over a roller 30 into water bath 31 maintained at 90° C. containing sodium acetate for stabilizing the yarn if sulfuric acid is used as the catalyst. The yarn may be maintained in bath 31 for one hour by passing about rollers 32. The yarn is then passed over a roll 33 and through a heating chamber 34 about rolls 35 where hot air is blown on the yarn and the yarn is thoroughly dried. From the drying chamber, the yarn passes to a collecting device 36. If a catalyst other than sulfuric acid is used, the yarn may by-pass bath 31, and instead proceed directly from roll 30 to the drier 34.

The following examples illustrate the new process.

Example I

A 12-gram skein of so-called "green" viscose yarn, that is yarn still in the wet gel state, containing 46.1 percent by weight of water was immersed in 800 parts by weight of glacial acetic acid at 25° C. for 1 minute. The yarn was then centrifuged for 2 minutes and then immersed for one minute in 800 parts by weight of glacial acetic acid at 25° C. containing 5 percent by weight of acetic anhydride and 1 part by weight of perchloric acid per 5,000 parts by weight of the mixture of acetic acid and acetic anhydride. The skein of yarn was then centrifuged for three minutes. This pretreated yarn which contained 40.2 percent by weight of acetic acid was immersed in 800 parts by weight of an acetylation bath, which was composed of 600 parts by weight of benzene, 200 parts by weight of acetic anhydride, and 0.8 parts by weight of 100 percent perchloric acid. The time of the acetylation reaction was 1 minute and the temperature was 45° C. The acetylated yarn was removed from the acetylation bath at the end of the reaction and immersed in isopropyl alcohol for 5 minutes. It was then washed in hot (75° C.) isopropyl alcohol for 30 minutes, washed in cold water 4 to 6 times. The skein of acetylated yarn was then centrifuged and dried at 65° C. for 12 to 15 hours. The yarn had a dry tensile strength of 2.72 gms. per denier, and a wet tensile strength of 1.59 gms. per denier; a dry extensibility of 15.8, and a wet extensibility of 17.3 percent. The yarn analyzed 9.09 percent acetyl, or 12.69 percent acetyl calculated as percent acetic acid.

The same procedure as described in Example I was followed with other yarns having various water contents and various acetic acid contents as indicated in the table below in which the acyl content is given and the properties of the yarn are tabulated. For convenience of comparison, Example I above is included in the table. The wa-

ter content given in the second column of the table refers to the percentage of water at the beginning of the pretreatment. The acetic acid content given in the third column of the table is that at the time of introduction of the yarn into the acylation bath.

Examples I to IX

Ex. No.	Water Content, Percent	Acetic Acid Content, Percent	Acetyl Content, Percent	Tenacity		Extensibility	
				Dry, g./d.	Wet, g./d.	Dry, Percent	Wet, Percent
I	46.1	40.2	9.09	2.72	1.59	15.8	17.3
II	56.65	40.2	9.94	2.56	1.46	15.3	16.4
III	36.4	40.2	6.35	2.69	1.55	15.3	17.5
IV	52.0	59.87	7.43	2.81	1.56	19.2	19.5
V [1]	52.0	78.1	8.09	2.18	1.05	17.4	17.3
VI	52.0	40.62	8.17	2.98	1.78	19.9	21.5
VII	52.0	35	7.45	2.58	1.42	18.4	20.7
VIII	59.0	58.7	15.78	2.77	1.45	16.8	17.7
IX [1]	59.0	76.5	15.48	2.42	1.12	15.7	15.2

[1] It is to be noted that Examples V and IX are outside the scope of the invention. They show what happens when the acetic acid content exceeds 60% as the yarn is introduced into the acylation stage.

Since it is obvious that many changes and modifications can be made in the above-described process without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the above-described details except as set forth in the appended claims.

I claim:

1. A process for the acetylation of regenerated cellulose fibers with retention of their fibrous structure comprising successively impregnating regenerated cellulose fibers in their swollen, wet gel state and containing between 35% and 60% by weight of water with (1) glacial acetic acid and (2) a mixture containing between about 2% and 10% by weight of acetic anhydride, a small amount by weight of an acetylation catalyst and the balance glacial acetic acid, said successive impregnations effecting the substitution of acetic acid for substantially all of the water contained by the wet gel fibers while maintaining the fibers in a swollen state, removing the excess acetic acid solution to provide the fibers with an acetic acid content between 35% and 60% by weight, then immersing the swollen fibers for from 15 seconds to 150 seconds in an acetylating bath maintained at a temperature between 35° C. and 60° C., said bath comprising by weight, between 5% and 25% acetic anhydride, between 0.05% and 0.1% of an acetylation catalyst and between 75% and 95% of an organic diluent for the acetic anhydride, the organic diluent being substantially inert to cellulose acetate, washing the acetylated fibers and finally drying the acetylated fibers.

2. A process of the acetylation of regenerated cellulose fibers with retention of their fibrous structure comprising successively impregnating regenerated cellulose fibers in their swollen, wet gel state and containing between 50% and 60% by weight of water with (1) glacial acetic acid at a temperaure of between 20° C. and 30° C. for from 30 seconds to 240 seconds and (2) a mixture containing between about 2% and 10% by weight of acetic anhydride, between about 0.005% and 0.05% by weight of perchloric acid and the balance glacial acetic acid for from 30 seconds to 240 seconds, said mixture being maintained at a temperature of between 20° C. and 30° C., said successive impregnations effecting the substitution of acetic acid for substantially all of the water contained by the wet gel fibers while maintaining the fibers in a swollen state, removing the excess acetic acid solution to provide the fibers with an acetic acid content between 40% and 50% by weight, then immersing the swollen fibers for from 30 seconds to 60 seconds in an acetylating bath maintained at a temperature of about 45° C., said bath comprising, by weight, between 20% and 25% of acetic anhyride, between 0.05% and 0.1% perchloric acid and between 75% and 80% of an organic diluent for the acetic anhydride, the organic diluent being substantially inert to cellulose acetate, washing the acetylated fibers and finally drying the acetylated fibers.

3. As an article of manufacture, a regenerated cellulose fiber acetylated only at its surface and outer peripheral zone formed by successively impregnating a swollen wet gel regenerated cellulose fiber containing between 35% and 60% by weight of water with (1) glacial acetic acid and (2) a mixture containing between about 2% and 10% by weight of acetic anhydride, a small amount by weight of an acetylation catalyst and the balance glacial acetic acid, said successive impregnations effecting the substitution of acetic acid for substantially all of the water contained by the wet gel fibers while maintaining the fibers in a swollen state, removing the excess acetic acid solution to provide the fibers with an acetic acid content between 35% and 60% by weight and then immersing the swollen fibers in an acetylating bath maintained at a temperature between 35° C. and 65° C., said bath comprising, by weight, between 5% and 25% of acetic anhydride, between 0.05% and 0.1% of an acetylation catalyst and between 75% and 95% of an organic diluent for the acetic anhydride, the organic diluent being substantially inert to cellulose acetate, and washing and finally drying the acetylated fiber, said fiber having an acetyl content of between 6% and 22%, a dry tenacity of at least 2.5 grams per denier, a wet tenacity of 1.45 grams per denier and a wet and dry extensibility of at least 15%.

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