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DISCOLORATION-RESISTANT REGENERATED CELLULOSE ARTICLES

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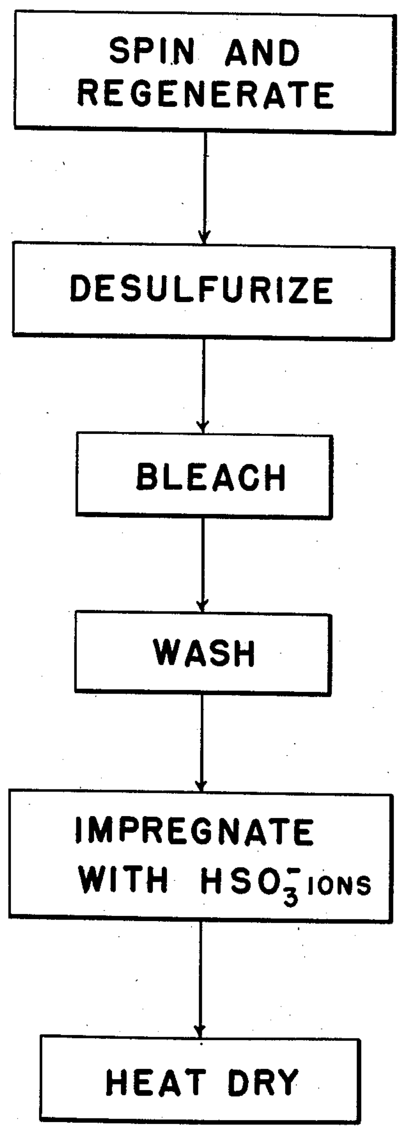

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DISCOLORATION-RESISTANT REGENERATED CELLULOSE ARTICLES

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This invention relates to regenerated cellulose articles and their manufacture, and more particularly to regenerated cellulose fibers and their manufacture from cellulose, which articles do not become yellow when subjected to higher temperatures in the presence of moisture.

While this invention will be described with reference to fibers which include continuous filaments as well as staple fibers, it is to be understood that it is equally applicable to films, ribbons, bands, casings, and the like, and the term "article" as used above and hereinafter is intended to be inclusive.

It has long been noted that bleached regenerated cellulose articles derived from viscose lose some whiteness when dried in accordance with the conventional drying practice in which such products are subjected to air drying at elevated temperatures and rather high humidity. Such discoloration is characterized by a tendency of the white rayon product to acquire a yellow tinted appearance; this tendency is particularly noticeable and undesirable when the rayon material is subjected to a succeeding drying or heating treatment occurring perhaps during the use of the material. For example, rayon goods used in fabricating surgical or sanitary articles are subjected to steam sterilization before use. White wearing apparel, such as certain types of undergarments now manufactured, are woven from white yarn and sold without further treatment except for steam sterilization. Under ordinary conditions of manufacturing rayon, such articles may be acceptably white upon delivery to the user but are noticeably discolored if they are subjected to temperature and humidity such as encountered in a steam sterilization treatment. The same is true, to a certain extent, of pastel colored articles.

A primary object of the present invention is to provide white or partially regenerated cellulose articles having resistance to discoloration. It is a specific object to render bleached undyed viscose rayon fiber and filaments resistant to the discoloration normally resulting from a humid and hot atmosphere such as developed in drying and sterilization treatments. An important object is to produce regenerated cellulose articles, particularly fibers, characterized by extraordinary freedom from discoloration at the completion of normal manufacturing processes. A further object is to provide an inexpensive treatment for regenerated cellulose articles by which the foregoing objects may be accomplished.

In originating the present invention, it has been discovered that color formation as the result of exposure of regenerated cellulose articles to a heated humid atmosphere may be almost completely prevented by previously drying the articles from a wet condition obtained by absorption of an aqueous solution containing HSO_3 ions. This solution may be applied conveniently within normal operations for manufacturing viscose filament or staple by including in the finally applied finish solution a suitable ingredient for supplying the HSO_3 ions. For HSO_3 ions to exist in such a solution, it is necessary for the pH to be maintained in the range of 3 to 7, preferably from about 4 to 6. When it is desired to have a finish material carried on the finally dried fibers or filaments, such material may be included as an ingredient in the solution containing the hydrogen sulfite ions. It is, of course, essential that the finish material be chemically stable within the aforementioned pH range.

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The hydrogen sulfite anions may be supplied to the aqueous solution for treating the rayon material by sulfurous acid; the sulfites; the anhydrous meta bisulfites (e. g. $Na_2S_2O_5$); or the acid sulfites (bisulfites) of the monovalent alkali metals, i. e., sodium, potassium, and lithium. A suitable solution of the anions may be obtained by bubbling SO_2 gas into a solution of a hydroxide of one of the monovalent alkali metals until the desired pH value is reached. It is necessary when using the acid or the non-acid sulfites to adjust the pH to a value within the range of 3 to 7. For example, when using the acid, sodium hydroxide may be added to a solution of the acid to adjust the pH; when using a non-acid sulfite, e. g., sodium sulfite, hydrochloric acid or some other non-oxidizing acid may be added. Such adjustment of pH tends to shift the acid or the sulfite toward the formation of a preponderance of the bisulfite which ionizes to provide acid sulfite anions.

The preferred material to add to a finish solution for rayon fibers or filaments is the bisulfite itself since it provides in an approximate manner the desired pH value. Because of its low cost, sodium bisulfite is likely to be most generally used in practicing this invention. Although the discoloration inhibitor may be applied in solution to rayon material in a dried or partly dried condition, it is conveniently applied to bleached and rinsed wet yarn or fibrous product derived from the spinning operation and the immediate after treatments. When the filaments or fibers are supplied in this condition it is found that optimum prevention of discoloration consistent with the economical use of the sodium bisulfite may be obtained by treating the rayon material with solutions of the bisulfite of about 0.4% concentration, although greater concentrations are entirely satisfactory from the standpoint of inhibiting discoloration. The strength of the solution required does not appear to be materially affected by the presence of a finish material therein as long as the pH of the solution is maintained within the above indicated operative range. Sodium bisulfite normally produces a solution having a pH of approximately 4.5. Since if for any reason the pH drops appreciably below this point, SO_2 gas is released into the atmosphere, the pH is preferably maintained at a level of approximately 5.0 by the addition of caustic or other alkali.

In practicing the invention in manufacturing rayon staple fiber, the fiber is carried progressively from the tow cutter as a blanket supported on a flat conveyor through such conventional after treatments as desulfurizing, bleaching, deactivating residual bleach solution, and rinsing. In preparation for receiving the finish solution, the blanket advances some distance while water drains therefrom and then it passes through squeeze rolls. The blanket as it issues from the squeeze rolls has a moisture content in the range of 175 to 300 percent based on the weight of the dry fiber. Thereafter the blanket advances under a shower of a liquid finish solution containing dissolved sodium bisulfite which may or may not contain other ingredients. The blanket of fibers is then prepared for drying in a conventional convection dryer by squeezing, such as by passing the blanket through squeeze rolls to reduce the moisture content to as low a level as practical, e. g., around 200 percent based on the weight of the dry fiber. The fibers are thus derived from the rolls in a moist condition in which they are damp with the solution containing hydrogen sulfite ions. Without other processing, the fibers are thereafter dried in a conventional manner, and while drying, the fibers may be conveniently retained in blanket form and supported on a conveyor.

The practice of the invention may in a similar manner be incorporated into the manufacturing of filaments. For example, in the manufacturing of tow or smaller strands by the known continuous systems, the step of cutting is omitted from the general steps mentioned hereinabove with respect to staple fiber. When filaments are collected in the form of cakes of yarn, as in pot spinning, the cakes are subjected, in a special machine well known to the trade, to the operations of deacidifying, desulfurizing, bleaching, rinsing, and applying the finish solution generally comprising an emulsion containing a textile lubricant. The cakes, just prior to the application of the sizing solution drain to about 250 percent moisture based on the weight of the dry cakes. Sizing solution containing preferably from 0.3 to 0.5 percent sodium bisulfite is then passed through the cakes which thereafter drain and subsequently are placed in a centrifugal extractor in which they are rotated to reduce the moisture content thereof to about 165 percent. Thereafter the cakes are dried in a conventional manner in the presence of the sodium bisulfite or other source of acid sulfite ions such as by drying the cakes while supported on cars in a conventional type dryer for 30 to 125 hours at a temperature of 100° to 200° F.

The accompanying drawing is a flow sheet diagram illustrating the practice of this invention. The viscose is spun and regenerated, that is, it is extruded through an appropriately shaped aperture to form a filament or film or other desired shaped body and is coagulated and regenerated in the preshaped form. Coagulation and regeneration may, of course, be effected in any conventional manner either in a single bath or a two-bath system as desired. The preshaped and regenerated body is then subjected to the usual or conventional after-treating operations such as desulfurizing, bleaching and washing. Such processing may be applied to the running filaments or sheet or, as in pot spinning, the filaments may be collected in the form of a cake and then subjected to these treatments. After thorough washing to remove the impurities, the body is then treated as by impregnating with the aqueous solution containing the bisulfite ions and thereafter dried at elevated temperatures.

Since, in practically all textile or industrial uses of rayon fibers, the fibers are preferably provided with an uncutous finish agent or surface conditioner for the fibers for one or more purposes, such as lubricating the fiber for passage through textile machinery, reducing the development of static electricity, or changing the inter-fiber cohesive forces, the discoloration inhibitor of this invention is preferably added with the finish agent for the reason that if separate solutions for each ingredient were used, the solution last applied would tend to wash out of the fibers the ingredient deposited in the fibers by the first applied solution. Thus, in order to supply the inhibitor and the finish material in proper quantity, the last solution to be applied to the fibers before drying contains both ingredients, if a finish material is required. It is, of course, essential that the finish material is one that will not be deleteriously affected by an acid environment in the pH range of 3 to 6. At present, finish materials are selected with respect to their stability within this pH range.

A number of fiber-finishing or surface-conditioning materials are found to be stable in solutions maintained at pH values within the range desired in the practice of this invention. These materials occur in sufficient variety to provide the essential functions required of finish materials, such as lubricity, preventing the development of static electricity, and the development of desired fiber

to fiber cohesive forces. Examples of materials which are useful in one or more of these functions and are stable in the presence of hydrogen sulfite anions are polyoxyethylene glycol monoether of sorbitan monolaurate containing about 20 ethylene oxide units per mole, sorbitan monopalmitate and polyoxyethylene glycol monoether of sorbitan containing about 16 ethylene oxide units per mole which are non-ionic in character; anionic material, such as lauryl sulfate and white mineral oil in the presence of a sulfated butyl oleate; and cationic substances, such as cetylethylmorpholinium ethosulfate.

The preferred method of applying the discoloration inhibitor is to subject regenerated cellulose fibers, which have been thoroughly washed to rinse them free of soluble impurities and, while in a wet condition, apply the final or finish solution. When the fibers are in the form of staple, the final solution may be applied by overhead shower devices; continuous filaments or strands may be drawn through a bath of the solution and in either case, the product passed through a wringer such as squeeze rolls. The final solution is ordinarily applied to cakes of rayon yarn by pumping through the walls thereof from a perforated tube extending centrally through the cakes. Whether by shower, or by bath, or by the cake treatment just described, the finish solution containing the soluble discoloration inhibitor passes through the body of the fiber to wet it with the finish solution, and to a substantial extent, though possibly not completely, to impregnate the individual fibers inwardly of their cross-sections.

The following examples are illustrative of the invention and the manner in which the sodium bisulfite functions as a discoloration inhibitor.

Example I

A cake of viscose rayon yarn wet with a finish solution having a pH of about 7.8 and containing sorbitan monolaurate and polyoxyethylene glycol monoether of sorbitan tristearate containing about 16 ethylene oxide units per mole was rotated about its axis in the conventional manner to reduce the moisture content thereof to about 175 percent based on its dry weight. While the yarn was still damp, 1000 yards were unwound from the cake and wound into two skeins of 500 yards each. One entire skein was dipped into a 1 percent solution of sodium bisulfite. This skein was rotated to reduce the moisture content in a manner described above with respect to the cake. Both skeins were then oven-dried for about 2 hours at 105° C. Thereafter one end of each skein was dipped in water and redried. After the second drying, the yarn of the skein which had not been dipped in sodium bisulfite had a yellowish appearance at the boundary zone which had existed between the wet and dry portions of the skein prior to the second drying. The skein which had been treated with sodium bisulfite showed no discoloration.

Example II

One of two cakes of viscose rayon yarn both of which weighed about 1500 grams (620 grams dry weight) and subjected to the same finish application and liquid extraction treatments as the cake of Example I was dipped in a 1 percent solution of sodium bisulfite; the dipped cake was then rotated to centrifugally remove and reduce the moisture of the cake to about 175 percent. Both cakes were then tunnel-dried about 95° C. for approximately 100 hours. The cakes were then rewetted by spraying the peripheral surface thereof with water using a paint spray gun until the yarn was moist to a depth of approximately ¼ inch from the outside surface of the cakes. The cakes were then redried. After the second drying, the cake which was not treated with sodium bisulfite exhibited yellowish discoloration within an interfacial zone between the rewetted outer portion and the dry inner portion existing after the rewetting treatment and prior to the second drying. The cake subjected to the sodium bisulfite treatment showed no discoloration whatever after the second drying.

Example III

The conditions of Example II were duplicated except that the cakes contained no finish ingredient. After the cakes were dried, they were examined visually for discoloration. The cake which was not treated with sodium bisulfite showed discoloration of the same nature as exhibited by the cake of Example II which had not been dipped in sodium bisulfite solution. The sodium bisulfite treated cake contained no discolored yarn.

Example IV

A lot of bleached scoured rayon staple fiber having no finish ingredient therein was divided into four 150 grams samples. One sample (1) was simply wetted with plain water. A second sample (2) was wetted with a finish solution containing about .03 percent polyoxyethylene glycol monoether of sorbitan monolaurate containing about 20 ethylene oxide units per mole with the pH thereof at about 7.5. A third sample (3) was wetted with solution containing about .03 percent polyoxyethylene glycol monoether of sorbitan monolaurate containing about 20 ethylene oxide units per mole and about .05 percent of sodium bisulfite with the pH at about 6.5. All three samples were centrifuged to remove excess liquid and the oven-dried in the following stages: 10 minutes at 250° C., 10 minutes at 235° C., and 20 minutes at 220° F. The three samples were examined for brightness at the end of the drying cycle and then reexamined for brightness at the end of a steam heating treatment conducted at 15 pounds pressure for 30 minutes. At each observation, the samples were examined for two color characteristics, i. e., (1) brightness and (2) yellowness factor in accordance with the method as practiced with the aid of a machine manufactured by the Henry H. Gardner Company known as the Color Difference Meter. The machine and the method are described in a bulletin published by this company dated June, 1950 and entitled "Description and Instructions for Hunter Color and Color-Difference Meter." In this method of color measurement, separate scales of measurement for brightness and yellowness factors are employed in which the values indicated by numbers ranging from 0 to 100 increase with increases in the characteristics being measured. The color data obtained by this method is as follows:

Sample	1	2	3
	Brightness		
After Drying	94.0	91.4	93
After Steam Treatment	86.5	88.4	89.5
	Yellowness Factor		
After Drying	2.98	3.22	2.28
After Steam Treatment	6.42	5.41	2.49

From the above data, it may be observed the sample 3 did not lose brightness to nearly as great an extent nor increase in yellowness nearly as much as did samples 1 and 2 which had not been subjected to the sodium bisulfite treatment.

Example V

Rayon yarn cakes **1**, **2**, **3**, **4**, **5**, **6**, **7**, and **8** produced by the centrifugal bucket spinning method were divided into four different groups (A, B, C, and D) of test cakes. Each group comprises two cakes, a control cake and a sodium bisulfite treated cake, which were processed under identical conditions of purification (e. g., washing, desulfiding, bleaching), finish application, and drying except that the finish solution for the control cake of each group did not contain sodium bisulfite. The groups differ with respect to each other in the purification procedure which was followed. As the exact nature of the purification procedure is not a part of the present invention the details thereof are herein omitted. Of cakes **5**, **6**, **7**, and **8**, each had been treated with sodium bisulfite contained as an ingredient at 0.3 percent concentration in an aqueous finish solution also containing approximately 1.9 percent concentration of a mixture comprising 75 parts white mineral oil and 25 parts sulfated butyl oleate. The pH of the finish solution for the control cakes **1**, **2**, **3**, and **4** was maintained at 6.5 to 7.0 by a buffer agent. The pH of the finish solution for the bisulfite treated cakes **5**, **6**, **7**, and **8** was maintained at 3.5 to 4.0. After drying in a convection type dryer for 95 hours at approximately 145° F., the cakes reached a moisture content of 5 percent or less. Thereafter yarn samples from the cakes were examined in a Spectrophotometer manufactured by General Electric Company for whiteness values as indicated on this machine which were as follows:

Group	A	B	C	D
Control Cakes	1	2	3	4
Whiteness	78	77	81	84
Sodium Bisulfite Treated Cakes	5	6	7	8
Whiteness	82	83	85	88

According to the above data, the sodium bisulfite treated cake for each group was observed to have 4 units greater whiteness than the control cake of the same group.

It may thus be concluded that rayon yarn may be dried from a condition of wetness caused by wetting the yarn with a solution containing sodium bisulfite or other source of bisulfite ions to increase the whiteness of the yarn without any other change in the manufacturing process than modification of the liquid treatment applied to the yarn just before drying. Because of the superior whiteness of the bisulfite treated yarn, it is possible to dye rayon textiles or fabrics more uniformly to light colors and to obtain purer colors, particularly in the light shades or tints. Moreover, such textile material is more color stable through subsequent dry cleaning, sterilizing treatments, and the like. Color stability, of course, is most apparent with respect to undyed goods which is desirably maintained in as white a condition as possible.

Various changes and modifications may be made in practicing the invention without departing from the spirit and scope thereof and, therefore, the invention is not to be limited except as defined in the appended claims.

We claim:

1. Process for manufacturing discoloration-resistant cellulosic articles comprising washing a preshaped regenerated cellulose article free of soluble impurities, saturating the article with a solution having a pH in the range of 3 to 6 and containing hydrogen sulfite ions and then drying the article in the presence of the hydrogen sulfite ions.

2. Process for manufacturing discoloration-resistant cellulosic articles comprising washing a preshaped, bleached, regenerated cellulose article free of soluble impurities while wet but substantially free of loosely held water, saturating the article with a solution having a pH in the range of 3 to 6 and having dissolved therein a compound from the group consisting of bisulfites of the monovalent alkali metals, sulfurous acid, and sulfur dioxide, squeezing most of the loosely held solution from the article, and then drying it in the presence of said compound.

3. Process for manufacturing discoloration-resistant cellulosic pellicles comprising washing a preshaped, bleached, regenerated cellulose pellicle free of soluble impurities while wet but substantially free of loosely held water, saturating the pellicle with a solution having a pH in the range of 3 to 6 and having dissolved therein a

compound from the group consisting of bisulfites of the monovalent alkali metals, sulfurous acid, and sulfur dioxide, drying the pellicle from a condition of wetness caused by said solution, and heat treating the pellicle with steam.

4. Process for manufacturing discoloration-resistant rayon fibers comprising washing fully regenerated fibers of viscose rayon free of soluble impurities, saturating the fibers with a solution having a pH in the range of 3 to 6 and having dissolved therein a compound from the group consisting of bisulfites of the monovalent alkali metals, sulfurous acid and sulfur dioxide, then squeezing the solution from the fibers loosely held thereby, and drying the fibers.

5. Process as defined in claim 4 in which said solution contains an unctuous fiber finish ingredient that is chemically stable within said pH range.

6. Process for manufacturing discoloration-resistant rayon fibers comprising washing fully regenerated fibers of viscose rayon free of soluble impurities, saturating the fibers with a solution having a pH in the range of 3 to 6 and having dissolved therein sodium bisulfite of at least 0.1 percent concentration and an unctuous fiber finish ingredient that is chemically stable within said range, then squeezing loosely held portions of the solution from the fibers, and drying the fibers.

7. As an article of manufacture, a shaped regenerated cellulosic article having a high resistance to discoloration when subjected to high temperatures and humidities and comprising the dried product of preshaped regenerated cellulose impregnated with an aqueous solution having a pH in the range of 3 to 6 and containing at least 0.1% of a substance selected from the group consisting of bisulfites of the monovalent alkali metals, sulfurous acid and sulfur dioxide.

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