Nov. 24, 1959 L. KÄSTLI 2,913,769

PROCESS OF PUFFING DRY REGENERATED CELLULOSE AND CELLULOSE ACETATE TEXTILE FIBERS BY GENERATING OXYGEN IN SITU AND PRECIPITATING BARIUM SULPHATE WITHIN THE FIBERS

Filed July 6, 1953 2 Sheets-Sheet 1

FIG. 1

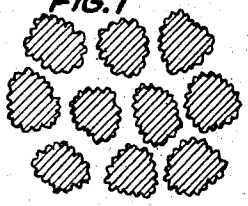


FIG. 4

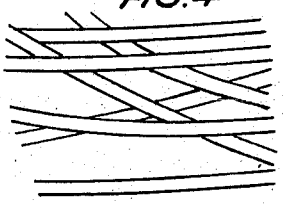


FIG. 4a

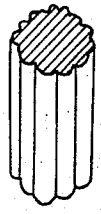


FIG. 2

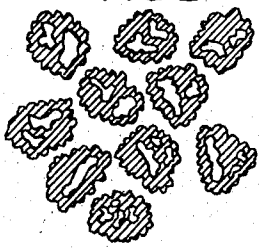


FIG. 5

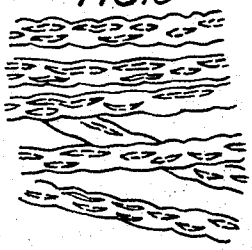


FIG. 5a

FIG. 3

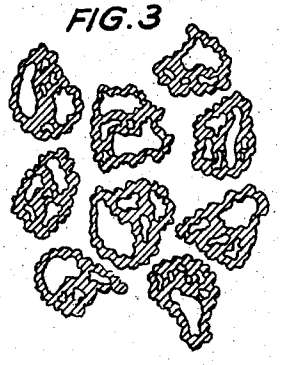


FIG. 6

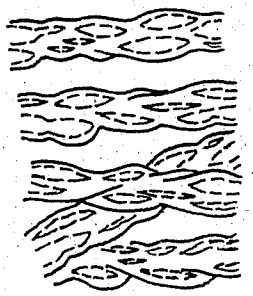


FIG. 6a

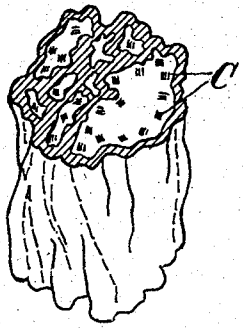


FIG. 7

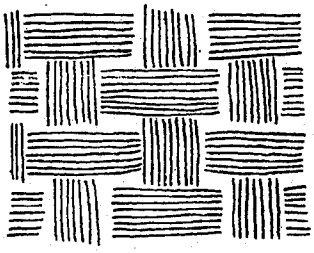
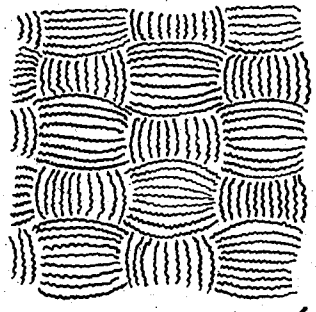


FIG. 8



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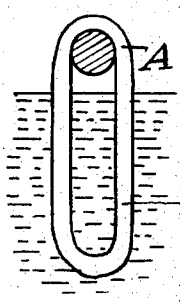

FIG. 9a

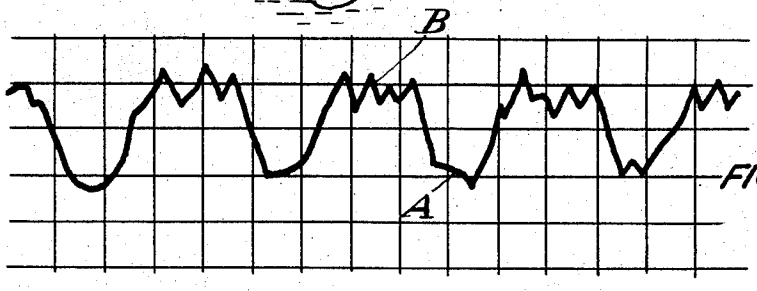

FIG. 9

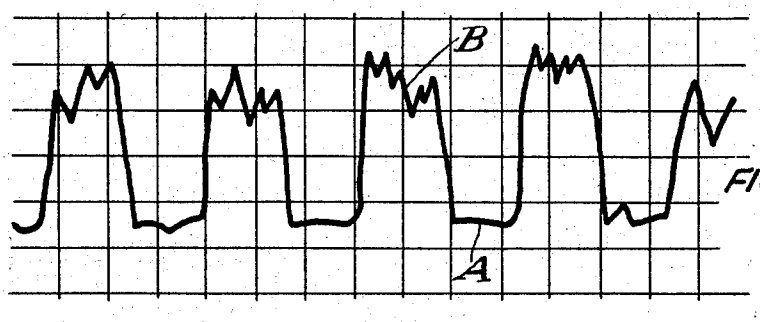

FIG. 10

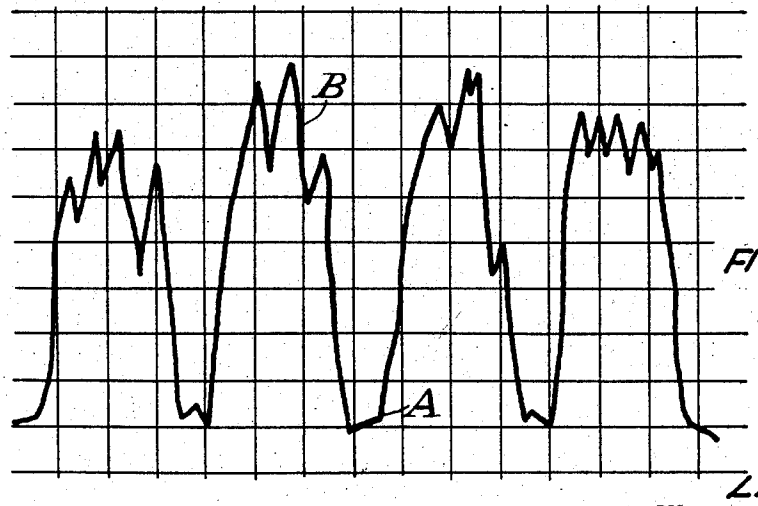

FIG. 11

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PROCESS OF PUFFING DRY REGENERATED CELLULOSE AND CELLULOSE ACETATE TEXTILE FIBERS BY GENERATING OXYGEN IN SITU AND PRECIPITATING BARIUM SULPHATE WITHIN THE FIBERS

Leo Kästli, St. Gall, Switzerland

Application July 6, 1953, Serial No. 366,310

Claims priority, application Great Britain April 8, 1948

3 Claims. (Cl. 18—48)

This invention relates to a process for the preparation of inflated, expanded, artificial fibrous articles as disclosed in my earlier application Ser. No. 27,263, filed May 15, 1948, and now abandoned, of which the present application is a continuation-in-part.

A primary object of the present invention is the provision of means affording sequential treatment of dried and finished articles made from artificial fibers, fibrous sheets, ribbons and like cellulosic textile fibers to obtain hollow spaces within the microfibrillae of the fibers of such articles, such treated fibrous articles showing markedly improved qualities, remaining in a porous and spongy state and indicating concomitant significant alteration of the physical properties.

A further object of the invention is to provide means conducive to improved fiber structures with enhanced heat-insulating properties, increased volume, softer and fuller touch, wavy or curly grained exterior surfaces, increased opaqueness, subdued luster and improved absorptive capacity for dyes, water-repellents, crease-proofing agents, shrink-proofing agents and the like without substantially having any deleterious effect on the original fibrous material or any diminution of the desirable physical properties inherent in the original fibrous material from which such articles are made.

Another object of the invention is to provide means facilitating efficient and speedy treatment of a large variety of types of artificial fibrous materials, such as viscose rayon, acetate rayon, nitrocellulose rayon, cuprammonium rayon, alginate rayon, protein fibers, zein fibers and the like to thereby markedly enhance desirable properties of such materials without the use of complicated and elaborate apparatus.

An additional object of the invention is to provide means facilitating treatment of artificial fibrous material which is normally difficulty swellable or only slightly swellable in water to thereby enhance the physical properties of such material in a manner not heretofore known in the art to which this invention relates.

Several methods are known for generating hollow spaces in artificial fibers such as viscose rayon, in order to make them more like vegetable or animal fibers which normally contain such hollow spaces in their microfibrillar structure. All the known methods start with a modified spinning solution, e.g., viscose spinning solution. The solution may contain finely divided gas bubbles in suspension or a dissolved substance, e.g., sodium acid carbonate which liberates a gas in the spinning process. The spinning solution may also contain suspended, powdered solids which are afterward dissolved out of the threads, thereby creating hollow spaces.

These known processes are complicated and add to the difficulties of spinning. The fibers thus produced, are unsatisfactory in several respects: either the hollows are too large, so that the threads are tubular and readily collapsible (cellular silk), or they are too small and of little efficiency. The strength of such fibers is considerably diminished.

According to the present invention hollow spaces are produced in ready-made and finished textile fibers, such as rayon and other fibrous articles. This process may also be applied to any fiber capable of swelling in water. It is, therefore, not limited to the treatment of viscose rayon, but is applicable also to the treatment of cuprammonium rayon, protein fibers and even natural fibers, e.g., cotton. The material to be treated may be in the form of a hank, a fabric or a ready-to-use article, such as a ribbon, film, sheet or the like. It is not necessary to start with a specially prepared spinning solution nor to change anything in the spinning process. The process of the present invention may, therefore, be readily practiced by the dyer or finisher.

The proposed process contemplates the treatment of artificial fibrous articles with certain aqueous solutions in which they swell. At least one of the treating solutions should contain a substance which may generate a gas by catalyzed decomposition.

This is not a double reaction as in the case of sodium acid carbonate. In the case of viscose rayon and other fibrous articles, the catalyst may be introduced as a solution into finished articles having the form of ribbons, films, sheets or the like. It is also advantageous to treat the material first with the catalyst solution, and then with the gas-generating solution although the reverse order of treatment also yields the desired results.

It has been found that hydrogen peroxide is eminently suitable as a gas-generating substance. The following description is based on the use of hydrogen peroxide without, however, intending to limit the process of the invention thereto.

Hydrogen peroxide may be decomposed by a series of manganese compounds as catalysts, e.g., manganous hydroxide, manganous manganite, potassium permanganate and the like with attendant evolution of gaseous oxygen.

The catalysts must, of course, be soluble in water in order to penetrate the fibers. Compounds of metals having several stages of oxidation, such as lead, manganese, chromium, copper and the like are particularly suitable for the purposes of the invention.

The catalyst may also be formed only in the interior of the material to be treated in such a way that a non-catalytic substance as, for example, manganous sulfate, manganous chloride, manganous nitrate and the like in aqueous solution, is introduced by swelling into the interior of the material, whereupon it is transformed into a catalyst by chemical reaction, for example by treatment with alkali metal hydroxide and oxidizing agents.

Another method of producing bubbles and hollow spaces in the material to be treated involves saturating said material with concentrated hydrogen peroxide which contains a non-catalyatic water-soluble manganese salt (e.g., manganous sulfate, manganous chloride, manganous nitrate) as a stabilizer. By after-treatment in an alkali metal hydroxide bath the manganese salt is transformed in the interior of the material into a catalytic manganese compound and the hydrogen peroxide is decomposed simultaneously.

The shape, size and distribution of the gas bubbles to be introduced, are determined by the nature and the physical condition of the material to be treated, e.g., the degree of swelling, and also by the rate of gas generation. The latter may be varied as desired and in an exactly reproducible manner by regulating the concentration of the solution, the temperature, the pH value and particularly by the addition of compounds which per se do not catalyze the decomposition of the peroxide. As a rule, the process may be satisfactorily executed at ordinary room temperature, but, if necessary, it may be accelerated by heating or retarded by cooling. The ad-

dition of neutral substances, especially in high concentration, to the solutions influences not only the rate of gas generation, but also the physical properties of the treated articles. Thus alkaline substances increase swelling, while substances such as sodium sulfate and sodium chloride and other substances which have high osmotic pressure decrease and equalize swelling of the fibers.

This invention contemplates the introduction, into finished artificial fibers, ribbons, sheets, films and the like, of hollow spaces of any desired number, size and distribution. Under controlled conditions the gas bubbles do not break through the surface of the material. The surface is only bulged outwardly at irregularly distributed points so that a wavy or curly, grained appearance is imparted to the surface of the material. Under the microscope it appears that the gas is generated between the microfibrillae which are the components of the individual fibers, although they are normally invisible to the naked eye. The gas forces the fibrillae apart without tearing them. For this reason the strength of the treated articles is not appreciably diminished, since the effective cross-sectional area is not decreased by the gas bubbles, but only expanded and bloated out into a wider perimeter.

If a single application of the treatment does not produce the desired effect, the process may be repeated. In this way, extremely marked effects may be created under very mild conditions.

Fibers, such as viscose rayon and the like, which are treated in this manner have their volume considerably increased. Accordingly, it follows that they have a higher covering power and produce, for a given weight, denser and softer tissues. Their heat-insulating capacity is much improved, partly because of the gas enclosed in the hollow cavities and partly because more air remains entrapped between the threads on account of their wavy surface. The numerous internal, curved interfaces cause diffusion of reflected light, thereby producing a pleasant delustering effect.

The delustration obtained by the gas bubbles alone is quite considerable but may be increased even further by precipitating a water-insoluble solid substance such as barium sulfate in the interior of the material simultaneously with the formation of the hollow cavities therewithin by the interaction of barium chloride with a soluble sulfate. Microscopic study shows that the precipitate forms on the newly-created internal surfaces defined by the hollow spaces. The described delustering effect, therefore, is made possible by the introduction of hollow spaces into the fibers of the treated material. The precipitate, e.g., barium sulfate, formed on the surface of the treated material cannot be washed off the material as in the case of externally-applied delustering agents. This new method of delustration also gives the material additional weight.

Fibers treated according to this invention, are more easily penetrated by dye baths and, in consequence are more easily dyed than untreated fibers. Differential absorption of dyes is substantially eliminated by the practice of the present invention. A tissue which normally dyes in stripes will generally dye evenly after treatment. Treated fabrics may be dyed in clear, pastel-like shades unobtainable in the case of conventional, untreated lustrous rayon.

Not only dyes, but also other agents generally employed in the treatment of fabrics for water-proofing, crease-proofing, shrink-proofing, etc., are more readily absorbed by the treated material after application of the process of the present invention than has been heretofore possible. Especially for water-proofing, the increased volume of the threads results in increased density of the tissue as a whole and enhances the water repellency of material treated in this manner.

The use of neutral manganese compounds instead of potassium permanganate has the advantage that the former are stable and that the material treated therewith is not affected chemically, which is not the case with potassium permanganate.

A further embodiment of the invention involves impregnation of the material to be treated, preferably regenerated cellulose, with a neutral or slightly acid solution of a manganese compound in concentrated hydrogen peroxide, whereupon the decomposition of the hydrogen peroxide is effected with an alkali metal hydroxide solution.

It has been found that the position of the bubbles in the material, and more particularly their distribution between the center and the outer portions of the fibers, as well as the size and number of the gas bubbles may be influenced at will by special conditions, such as the character of the material to be treated, concentration and temperature of the solutions, addition of inert salts as stabilizers for the hydrogen peroxide solution and time of treatment of the solutions on the starting material.

By suitable modification of the process it is also possible to produce hollow spaces in materials which are not at all, or only slightly swellable in water. Such materials must be swollen in suitable solvents. The swelling agent and the catalyst may be incorporated either separately or together. The catalyst may also be incorporated in the material to be treated by heating the aqueous solution of the catalyst up to the softening point of the material.

The artificial fibrous starting materials may be impregnated, according to one mode of practice of the invention, with an aqueous solution containing

2 gms. $KMnO_4$, and
150 gms. NaCl

per liter, freed from excess solution and subsequently treated in a second bath consisting of 30% H_2O_2 containing

300 gms. $Na_2SO_4 \cdot 10H_2O$
300 gms. $Mg\ SO_4 \cdot 7H_2O$

per liter, for from 1 to 2 minutes at room temperature. Thereafter the resulting product is thoroughly rinsed and dried.

The process may be used for treating glossy or lustrous rayon, or opaque rayon in form of strands, fabrics, knitted goods, and the like.

If in the first treating bath NaCl is replaced by $BaCl_2$ for the treatment of lustrous rayon, an opaque product is obtained, the $BaSO_4$ content of which depends on the concentration of the $BaCl_2$ solution employed.

If sheet materials like foils or films are treated according to the process of the present invention, the concentration of $KMnO_4$ to be used need only be approximately 0.5%. The concentration of $KMnO_4$ may be varied to achieve a corresponding variation in the final appearance of the treated material.

The treatment according to the process of the invention results in a profound irreversible change of the structure of the hydrated cellulosic fibers or films or other material so treated.

This structural transformation results in the following substantial improvements and distinctive features inherent in the practice of the present invention:

(1) The regular surface of the fibers or films is expanded by the enclosed coarse bubbles into a wavy structure whereby special luminous, lustrous effects are imparted to the treated articles.

(2) The entrapment of coarse bubbles in the material results in a loosening of the internal structure of the material which, in combination with the wavy surface, gives a softer and fuller touch or "hand" to the treated material.

(3) The volume of the treated material is increased to an amount of from 100% to 260% of the original

volume (see Viviani diagrams in Figs. 9, 10 and 11 of the drawing in the application).

(4) The increase in volume of the treated material results in improved heat insulating properties. If the difference in the heat loss of a metallic body insulated with cotton or normal rayon is 41%, then the difference in heat loss after insulation with rayon which was after-treated by the process of the present invention is only 26%.

(5) The water-absorptive capacity of the treated material is up to 100% greater than that of untreated material, which fact makes material treated in the described manner highly advantageous for the manufacture of underwear and the like.

(6) The capacity of absorbing dyes is also enhanced and shades of greater intensity may be obtained with smaller amounts of dyes.

(7) Fabrics which normally dye unevenly dye more evenly after being subjected to the treatment of the invention.

(8) Although it is known to produce opaque rayon by precipitating barium sulfate onto the fiber, the process of the present invention provides a substantial improvement resulting from the simultaneous production of hollow spaces and the deposit of barium sulfate in said spaces in the interior of the fibers, which deposit is resistant to washing and rubbing and may amount to as much as one-fourth of the weight of the starting material. This deposit of barium sulfate in the hollow spaces within the fibers, e.g., on the wall of the fiber where air is excluded, produces an additional light-refractive effect which results in substantially increased opaqueness.

The known processes hitherto described for treating textiles with H_2O_2 and catalysts are directed only to obtaining a bleaching effect or destruction of the material, whereas treatments for producing hollow spaces in the fibers in order to change the structure of the finished textile products such as fabrics, films, sheets, knitted goods and the like have been completely unknown heretofore.

The hollow fibers of the prior art are characterized by formation through the introduction of small hollow spaces during the spinning process without alteration of the cross-sectional area of the fibers, or by the formation of tube-like collapsed structures, whereas the fibers obtained by applicant's process contain expanded bubbles which are separated from each other by partition walls.

When ribbons and films are after-treated in this manner the bubbles formed are visible to the naked eye. In the treated fibers and fabrics the increase in volume and the change in the refraction of light are easily recognized but the changes in structure and surface can only be properly detected by microscopic examination. In order to illustrate the structural and surface changes of fibers and fabrics treated according to the practice of the present invention, reference is made to the annexed drawings, wherein:

Fig. 1 is a cross-sectional view of a dry and finished viscose rayon thread;

Fig. 2 shows the same thread after treatment in cross section;

Fig. 4 is a longitudinal view of the same thread of Fig. 1;

Fig. 4*a* is an enlarged sectional view of a single fiber of the thread of Fig. 4;

Fig. 5 shows a side elevational view of the threads of Fig. 2, and

Fig. 5*a* illustrates a section of a single fiber;

Figs. 3, 6 and 6*a* show, respectively, cross-sectional, and side elevational views of the microfibrillae forced apart and further an enlarged sectional view of a fiber or thread whose surface is weavy without being damaged or split open;

Figs. 7 and 8 show photomicrographs of viscose fibers as they appear subsequently to treatment steps;

Fig. 9*a* illustrates diagrammatically the use of the Viviain apparatus to which reference is made in the description; and

Figs. 9 to 11 represent curves relating to testing of the regularity of the cross-section of a thread during treatment stages.

Reference is now made to the attached drawings.

The Viviani apparatus, which is generally used for testing the regularity of cross-section of a thread, has supplied the curves of Figs. 9, 10 and 11 for a hank of viscose rayon which had been treated according to this invention on approximately only two-thirds of its circumference (Fig. 9*a*). In the curves, A represents the untreated portion, and B represents the treated portion of the hank. Three different strengths of treatment are represented. In Fig. 9, the increase of volume is 30% to 40%; in Fig. 10, 50% to 70%; and in Fig. 11 up to 160%. The curves show that the increase in volume is very regular. The thermal resistance and heat insulating properties of the treated product are increased proportionally to the increase in volume.

Fig. 7 shows the magnified image of a viscose tissue, Fig. 8 the same tissue after treatment. The increased density of the fabric is very apparent.

The following examples will illustrate several ways of carrying out this invention without, however, limiting the latter thereby.

Example 1

Viscose rayon in the form of a hank or fabric is steeped in a solution of 2 grams potassium permanganate and 150 grams sodium chloride in 1 liter of water. After removing excess solution, this material is soaked in a solution of 300 grams sodium sulfate and 300 grams magnesium sulfate in 1000 cc. of 30% hydrogen peroxide.

After not more than approximately 2 minutes, the process of decomposition in the internal fibrous structure of the material is interrupted in a bath containing 1% acetic acid, and the treated material is thoroughly rinsed and dried. The proportion of material to be treated to the treating bath is preferably approximately 1:20.

Example 2

Viscose rayon fabric is steeped in a saturated solution of barium chloride containing 2 grams potassium permanganate per liter and then centrifuged. Afterwards, the fabric is drawn through a solution of 150 grams sodium sulfate, 150 grams magnesium sulfate and 500 cc. hydrogen peroxide (40%) in 500 cc. water. After washing and drying the denier of the threads has increased from 100 to 125, i.e., 25 grams barium sulphate have been incorporated in 100 grams of thread. The increase in volume is such, that the original 100 denier thread now has the volume of a normal 250 denier thread while the absorptive capacity has increased similarly at least 100%. In the same manner all other viscose materials like rayon films, sheets, ribbons and the like may be treated.

Example 3

Viscose ribbons in form of hanks are pre-treated for approximately 5 minutes with an aqueous solution containing 1% manganous sulfate. After removal of the excess liquid the ribbons are treated for approximately 2 minutes with 2% sodium hydroxide solution and thoroughly rinsed with water. The ribbons are treated further in a third bath with a 20% solution of hydrogen peroxide for approximately 2 minutes and then dipped into a 1% to 2% acetic acid bath, washed and dried. The proportion of the material to be treated to the treating baths should be 1:20. The ribbons treated in this manner have a grained surface and a higher volume while their weight remains constant. The change in structure is extremely apparent since the original ribbons had a plain, glossy, smooth surface.

Example 4

Viscose films in the form of sheets or cut in ribbons are treated with an aqueous solution containing 1% manganous sulfate and 40% hydrogen peroxide. After draining off of the treating liquor the films are aftertreated in 1% to 4% sodium hydroxide solution, then in acetic acid containing 1 gm. in 1000 ml., and finally rinsed and dried. The proportion of the films to the treating baths should be approximately 1:20. The films are completely grained and have a greatly increased volume while their weight remains constant.

Example 5

A hank of cellulose acetate is swollen in a mixture of 30 parts acetone and 70 parts water, then dipped into a 1% solution of potassium permanganate and thereafter treated for 2 minutes with a 30% hydrogen peroxide solution which is stabilized with magnesium sulfate and then washed and dried. Under the microscope it can be determined that the fibers have increased in volume and contain bubbles.

Example 6

Cellulose acetate silk is treated for approximately 5 minutes in a 1% solution of potassium permanganate at a temperature of about 80° C., then rinsed with water and treated with a stabilized 30% hydrogen peroxide solution not longer than approximately 2 minutes. The treated filaments of the material are expanded by bubbles.

Example 7

Viscose rayon in the form of a hank or fabric is steeped for from 1 to 2 minutes in a solution of 50 cc. lead acetate (spec. gravity 1.6) in 1 liter of water. After draining and squeezing out the excess liquid, the rayon is drawn slowly through a solution of 200 cc. hydrogen peroxide (30%), 30 cc. caustic soda (20%) and 30 cc. sodium silicate (spec. gravity 1.44) in 470 cc. of water, the immersion time being approximately 1 to 2 mintues. The lead acetate is then washed out with a solution of ammonium acetate (10% to 20%). Finally, the rayon is washed and dried.

Example 8

Cuprammonium rayon in the form of a hank or fabric is stepped for approximately 5 minutes in a solution of 2 grams of potassium permanganate and 10 grams of crystalline sodium sulfate in 1 liter of water. After removal of the excess liquid, the material is treated further with a 40% solution of hydrogen peroxide. After not more than approximately 1 minute, the process of decomposition in the internal structure is interrupted by treatment in a 1% acetic acid bath and the material is then subjected to thorough washing, scrooping and drying. The proportion of treated fibrous material to the treating bath is preferably 1:20. The volume of the cuprammonium rayon treated in the above-described manner is thus substantially increased.

Example 9

Nitrocellulose rayon in the form of hanks or skeins is steeped at room temperature for approximately 3 minutes in a solution of 0.2 potassium permanganate and 2% sodium sulfate and subsequently treated, after centrifuging or drying in any other suitable manner, for not more than approximately 2 minutes with a 20% solution of hydrogen peroxide. After thorough washing the treated expanded nitrocellulose rayon, having hollow cavities introduced into its microfibrillar structure, is scrooped and dried.

Example 10

Artificial silk derived from casein is steeped in a solution of 0.05% potassium permanganate and 1% sodium sulfate for approximately 2 minutes, after which it is dried or centrifuged and subsequently treated for not more than approximately 2 minutes in a 20% solution of hydrogen peroxide containing 1% sodium sulfate.

Example 11

Alginate rayon.—Approximately 40 cc. of a 20% solution of lead acetate is treated with a sufficient amount of a 20% solution of caustic soda (approximately 160 cc.) to dissolve the lead hydroxide formed in the reaction and then water is added to make up a total volume of approximately 1000 cc. Alginate rayon is steeped for approximately 1 minute in the alkaline sodium plumbate solution resulting from the above-described reaction and subsequently treated with a 10% solution of hydrogen peroxide containing a small amount of acetic acid. Finally, the artificial fibrous material is thoroughly washed, scrooped and dried.

Since certain modifications may be made in the process of the present invention without departing from the scope thereof, it is intended that all matter contained in the foregoing specificaion and shown in the accompanying drawings be interpreted merely as illustrative and not in a limiting sense.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. The process of treating dry textile fibers composed of a material selected from the group consisting of regenerated cellulose and cellulose esters of acetic acid; comprising the steps of first impregnating said material with an aqueous solution of alkali metal permanganate saturated with barium chloride, and subsequently subjecting said material for not more than two minutes to the action of an aqueous solution of hydrogen peroxide containing at least one compound selected from the group consisting of sodium sulfate and magnesium sulfate until oxygen bubbles are generated within said fibers under controlled conditions so that the gas bubbles do not break through the surface of the fibers and enlarged hollow spaces are formed within the microfibrillae of said fibers and barium sulfate is precipitated within said hollow spaces.

2. The process of claim 1, wherein said alkali metal permanganate is potassium permanganate, the solution thereof being maintained at a concentration of said potassium permanganate of approximately 0.2%.

3. The process of claim 2, wherein said hydrogen peroxide treatment is carried out with a concentration thereof amounting to about 40%.

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