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CELLULOSE FABRIC AND PROCESS OF MAKING SAME

Raymond S. Babiarz, 315 Marsh Road, Wilmington, Del., and Alton D. Hicks, 123 Lea Road, New Castle, Del.

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This invention relates to textile finishing and more particularly to the finishing of cellulose fibrous materials such as cotton and the like, providing certain altered and improved characteristics.

Many processes have been utilized heretofore in the treatment of cotton fabrics in an attempt to improve the chemical and physical properties of the material. For example, various treatments have been employed in an attempt to provide increased water resistance, flame resistance, to impart a wool-like hand, crease resistance, etc., and in all such cases it has been part of the problem to insure retention of the properties through repeated laundering or dry cleaning operations.

The prior processes dealing with chemical modifications of cellulose generally have been unsatisfactory in many respects. The attainment of improved properties in many cases has been attended by serious impairment of strength, lack of durability, and high cost of processing, etc., and consequently such processes have not had the widespread applicability desired by the textile art.

With the process of the present invention, however, it has been discovered that cellulosic fabrics can be treated in a novel manner to provide a remarkable improvement in the crease resistance of the fabrics as well as increase in resilience, mildew resistance, and other desirable properties to a marked degree, and such properties are maintained at a high level throughout the use of the treated fabrics.

The finishing process of the invention is effective on all weights and constructions of cellulose and regenerated cellulose fabrics, including cotton and linen goods, and viscose rayon, suitable for clothing, dresses, drapes, and the like, inclusive of high twist and tightly woven fabrics. It may also be applied to the individual yarn strands themselves as well as to woven or knitted fabrics.

Another improved characteristic of the finish of the present invention is the fact that the altered characteristics may be attained without appreciable impairment in the strength of the treated cloth.

The present invention has been found particularly applicable to the resultant products of the processes covered by Ford et al. Patent 2,482,755 and Babiarz et al. Patent 2,709,638. The first mentioned patent relates to a flameproof cellulose material comprising a cellulose-acid nitrogen complex derived, for example, from the reaction of cellulose with orthophosphoric acid and urea in prescribed amounts. The second patent describes a cellulose-acid sodium complex producing fabrics having wool-like characteristics in certain respects, particularly the hand of the material. The cellulose-acid sodium complex is derived generally by the substitution of sodium for the nitrogen in the complex of the 2,482,755 patent, by reaction of the nitrogenous complex with a caustic solution in a manner similar to the well-known mercerizing treatment.

In either of the above cellulose-acid complex materials the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent, i.e. for example, either a nitrogen substituent or sodium as previously mentioned, is linked to the cellulose at a hydroxyl group position of the cellulose molecule. The process of the invention comprises treating any of the above materials with a solution containing metal ions and subsequently further treating the material to cause the formation in situ of an insoluble compound of the metal in the cellulose fibers.

In a typical case, starting with a cotton fabric which has been first impregnated with an aqueous solution of orthophosphoric acid and urea, and then heated to effect reaction between the cellulose, the acid and the urea, the material then being in the form of a cellulose-acid-nitrogen complex, is impregnated with an aqueous solution of a zirconium salt, e.g. zirconium sulfate, and then subsequently treated with a sodium silicate solution, whereby an insoluble compound is formed in situ in the cellulose fibers by reaction of the silicate solution with the zirconium. Other appropriate standard treatments such as rinsing, drying, etc., may be applied, and the finished product exhibits the remarkable characteristics mentioned above, particularly a marked improvement in crease resistance, mildew and rot resistance, and moisture regain, and a decrease in porosity.

The processes of the present invention will now be described in greater detail.

One method of procedure, utilizing the cellulose-acid-nitrogen complex involves the following steps. The cellulose fabric is sized with the acid-urea mixture as described in the aforementioned Patent 2,482,755, and then frame dried, cured at an elevated temperature, washed in hot water and again frame dried. Then a solution of a metallic compound, e.g. an aqueous solution of a metallic salt, containing metal ions, namely either aluminum, tin, zirconium, or titanium, or a combination of such ions, is applied to the fabric by a conventional padding operation. The treated fabric is maintained in the wet state for approximately twenty minutes in order to promote the reaction with the metal.

The fabric at this point is usually still acid, having a pH of about 4.0 or even lower, and it is essential to raise the pH toward neutrality in order to effectuate the next step of the process, i.e. formation in situ of the insoluble compound of the metal in the cellulose fibers. Any one of several insolubilizing agents, including water itself, may be used for this purpose.

The fabric may be rinsed with water to remove excess reactants, and in some cases it may be found possible and even practical to continue the water rinse to such an extent that the pH of the fabric will be thereby raised sufficiently toward neutrality that the formation of the insoluble compound in the fibers will be carried to completion without the need for further treatment. This has been found feasible for example when using aluminum salts. Certain other salts, such as for example magnesium sulphate, require treatment with an additional agent on the alkaline side to raise the pH to the required level for the insolubilization to occur. Even where the water rinse may be employed alone to cause insolubilization other agents may be used to speed up the reaction.

The water rinsing step may be dispensed with and the fabric treated with any other agent causing the formation in situ of an insoluble product. Such agents are, for example, sodium silicate, sodium tetraborate, disodium phosphate, sodium benzoate, organic amines such as triethanolamine, etc., and the pH of the material is thereby raised toward neutrality to the desired level. It is even possible to apply a dilute caustic to the fabric by spraying or the like so long as the required pH is maintained, but it is easier to employ the previously mentioned reactants for this neutralizing step.

The insolubilizing agent is applied in an amount and for a length of time sufficient to cause the formation in situ of the insoluble compound of the metal in the cellulose fibers. The fabric is then again water rinsed, drawn out and frame dried, and subsequently a suitable softener can be applied and it can be tinted, dried, Sanforized, etc., as desired.

Use of aluminum, tin, zirconium or titanium salts as described above has resulted in a great and unexpected alteration in the properties of the treated material, providing an improved fabric having a wide variety of uses. The treated material has greatly improved crease resistance, flame resistance, resilience, mildew resistance and other stable, enhanced characteristics, all with no change in color of the fabric. By such treatment cellulose fabrics may now be utilized under service conditions where and for purposes which hitherto would have been impossible or impractical.

Other metals can be employed in the process and product of this invention with enhancement of various desireable properties of the fabric. Such metals are silver, chromium, copper, nickel, iron, cobalt, calcium, barium and zinc. Except for calcium, barium and zinc, when using the other metals from the latter group it may be found that the resultant fabric has acquired a characteristic color different from that of the untreated material. Thus where a color change is to be avoided such metals must not be used. On the other hand, where a particular color change may be desired, one of such metals may be selected accordingly.

A second mode of procedure for the invention is as follows: The cellulose material is sized with the acid-urea mixture, frame dried, cured, and then treated with sodium hydroxide in a prescribed manner, drawn out and dried. At this point the cellulose-acid-sodium complex has been formed, rather than the cellulose-acid-nitrogen complex of the previous process. All subsequent steps may be the same as mentioned above.

The product of the first process will yield a finished width similar to resin treated fabrics. The product of the second process, on the other hand, depending on the particular fabric, may be treated such that it will lose as high as 10 and even 20% in both warp and filling dimensions which will result in a heavier, denser, and more wool-like fabric.

The following properties are among some of those which have been noted in materials after treatment with the processes of the present invention:

(1) Increase in weight depending on selection of metal: Approximately 25% for tin, and about 10% for aluminum—this general level of weight increase persists throughout numerous washings and dry cleanings.

(2) Slower rate of burning when exposed to a flame: In certain cases good durable flame resistance is achieved.

(3) In certain cases a water repellent effect is achieved and is durable to washing and dry cleaning.

(4) Measurements indicate the following effects of this treatment on a fabric:

a. Moisture regain-increased.
b. Porosity-decreased.
c. Vapor permeability unchanged.

Porosity affects the thermal qualities, that is, the lower the porosity the greater the wind resistance and, therefore, the warmer the fabric. Moisture regain and vapor permeability are related to the comfort of the fabric.

In effect, the above combination makes the fabric warmer by virtue of its lower porosity but not uncomfortable since it has the ability to hold greater moisture contents (higher moisture regain) and its ability to discharge water vapor (vapor permeability) has not been impaired.

(5) Mildew and rot resistance of high degree: Fabrics treated with most metals showed resistance to mildew rot, however, fabrics treated with Ti, Al, Zr, and Sn showed very little change in tensile strength properties when buried in the soil for six weeks as compared to untreated fabrics which disintegrated completely in less than two weeks.

(6) Ordinary cotton dyes such as vats, naphthol, and directs, and so forth, no longer have affinity for cellulosic fabrics treated according to this process. The treated fabrics now have affinity for cationic dyes such as "Sevron" (du Pont). Fabrics already containing cellulosic colors, however, are not impaired by this process.

(7) Improved resilience: Fabrics measure approximately 135° in each direction, warp and filling, for the angle of recovery as measured by the Monsanto Wrinkle Recovery Tester. This is much better than most resin treated fabrics currently on the market.

(8) Resistance to wrinkling: Subjective evaluations indicate high degree of resistance to wrinkling, approaching in magnitude the effect achieved by some synthetic fabrics.

(9) All the properties enumerated are durable to repeated launderings and dry cleanings.

As is already known, the pretreatment with acid and the nitrogen-containing compound should not be of such characteristic as to destroy or damage the fabric and for example it is known that strong halogen acid, or for example nitric acid, should not be used.

As disclosed in both of the aforementioned patents a wide variety of acids and nitrogen-containing compounds can be used to obtain the cellulose complex material. Any acid which will not destroy the fabric may be used. The acid must be polybasic, i.e. having at least two replaceable acid hydrogens providing for linking both with the cellulose molecule and the basic substituent, i.e. nitrogen, sodium, or the like as the case may be.

Examples of such acids are phosphoric acid, metaphosphoric acid, pyrophosphoric acid, ortho, meta- and pyrophosphorus acids, phosphamic acid, phosphotungstic acid, sulfuric acid, sulfamic acid, phytic, and similarly relatively strongly effective acids. Also weaker acids may be used, such as malonic, phthalic, citric, pyroantimonic, dihydroxydiphenic, molybdic, tungstic, vanadic, telluric, selenic, and fluosilicic. In fact any soluble dibasic acid, organic or inorganic, substantially non-volatile, which will react with the cellulose at the hydroxyl groups may be used and various polycarboxylic acids are suitable for the purpose.

Metal salts and organic substituted salts of the acids having free acidity for combination both with the cellulose and the nitrogen supplied from the nitrogen-containing compound may also be used.

Cellulose-acid-nitrogen complexes made with the acids themselves, and especially with orthophosphoric, sulfuric or sulfamic acid are preferred.

As already indicated, the cellulose-acid-nitrogen complex which may be treated according to the present invention may also be formed by the use of a variety of nitrogen-containing compounds. In general such compounds should be at least partially water soluble and should be basic toward the acid used. Urea is highly effective and other bases may be employed such as dicyandiamide, biuret, acetamide, cyanoacetamide, guanidine bicarbonate, aminoguanidine carbonate, biguanide, guanidine, or mixtures thereof.

The strength of the base is desirably varied according to the particular acid being used, the more strongly basic nitrogen-containing compounds being preferred where the stronger acids are used at the same time. Various bases may be used in combination or conjointly.

The curing temperature and other process details in obtaining the complex, such as concentrations and strength of acid, pH, range of acid content on the treated cloth, and other details are disclosed in the aforementioned patents. Briefly the curing temperature of the acid-nitrogen complex is from about 250 to 400° F. and the corresponding length of curing time from about thirty minutes to about one minute, time and temperature being correlative factors. For a single application of the acid-nitrogen containing solution with a substantially 100% solution pick-up by weight of the fabric in the dry state, the concentration of orthophosphoric acid, for example, may run between 2% and 16% by weight of the solution, and even up to about 30% acid may be used if desired.

The pH of the solution as applied is not critical. During curing of the acid-nitrogen complex the pH on the cloth may be from about 2 to about 7 pH and preferably from about 3 to 6 as determined by indicator solutions.

The preferred range of urea to orthophosphoric acid in the treating solution is of from 1 to 4 mols of urea to 1 mol of acid, although one may go as high as 10 mols of urea to 1 mol of acid, although economically the latter ratio is perhaps undesirable. In the case of the use of phospheric acid the quantity of acid content in the fabric, after baking, washing and drying, may range upwardly to an amount sufficient to provide a content of 5% phosphorus in the complex which in terms of phosphoric acid is 15%, but the quantity of acid in the complex may range downwardly to about 1.5% which would provide a content of 0.5% phosphorus in the complex. The nitrogen content may range from about 0.5% to 6.0%, usually from about 1.4% to about 4.0%, by weight of the fabric in the dry state.

It has been found that the esterification or phosphorylation of the cellulose molecule effects a consequent impairment, to a degree at least, of the tensile strength, and possibly other mechanical or physical properties, of the fabric. Thus there is, in effect, a compromise aspect of the process, and the above indicated preferred ranges of phosphorus in the complex provide a sufficient degree of esterification without appreciable detriment to fabric strength or other properties.

The preparation of the cellulose-acid-sodium complex is described in detail in the 2,709,638 patent, and may be summarized as the impregnation of the cellulose-acid-nitrogen complex with an aqueous solution containing from 0.25% to 50% of caustic soda at a temperature between about 14° F. and room temperature up to 140° F., the solution being retained in contact with the fabric for a sufficient time to reduce the nitrogen content of the complex to between 0.25% and 1%, thus substantially replacing the nitrogen substituent in the complex with sodium.

The caustic soda treatment may be effected at room temperature and for example a 30% caustic soda solution is suitable and treatment for a period of time of the order of about 45 seconds is appropriate to cause the sodium for nitrogen substitution in the cellulose complex. The treatment with caustic soda may be effected in any one of a variety of ways adapted to apply the caustic to the fabric, including immersion of the fabric in the caustic soda solution, padding the solution on the cloth, or printing the solution on the cloth, and such treatment may be applied while the fabric is either slack or under tension. These and other details are outlined in the above patent and need not be elaborated upon here.

The solution of the metal salt may vary in strength over a wide percentage range but from both an economic as well as a practical standpoint the concentration preferred should be in the range of about 1 to about 15%, and room temperature is normally advisable although the temperature itself does not appear to be critical. Where the metal salt solution is padded on the fabric, the higher metal concentrations are preferred, and when large liquor to cloth ratio are encountered satisfactory results can be obtained with the lower concentrations.

The salt solution may be applied in any of the well-known ways, as for example, those described above for application of the caustic soda solution. The cellulose material is maintained in contact with the salt solution for approximately twenty minutes at room temperature and then is removed and the pH of the treated fabirc raised toward neutrality in one of the ways previously described in order to effect insolubilization of the metal in the fibers, i.e. by a water rinse alone in some cases, or by treatment with one of the other aforementioned insolubilizing agents, or a combination of such steps.

The material is subjected to what is referred to as "control neutralizing" with one of the insolubilizing agents

described above for a period varying up to about thirty minutes, usually about fifteen minutes, and at an elevated temperature from about 80 to about 150° F. although room temperature is permissible with a corresponding increase in length of time of treatment. The sodium salt of a weak acid such as sodium silicate is preferred because the pH on the fabric must be maintained within prescribed limits, depending upon the particular metal involved, so that the insoluble compound will be formed in the fibers.

In the case of those metals which exhibit amphoteric behavior, i.e. Al, Zr, Sn and Ti a pH must be maintained which insures that the metal will be in its cationic state, so that an insoluble compound will be formed, rather than in its anionic state, in which a soluble product would be formed. In other words when using, for example, an aluminum salt with a subsequent sodium silicate treatment, it is desired that insoluble aluminum compounds be formed rather than soluble sodium aluminate during the neutralizing step.

While the exact theory of operation of this process is not definitely known, there is convincing evidence that a chemical reaction takes place when the metal salt solution is applied to the phosphorylated cloth or fibers and that the metal at least in part replaces the sodium, nitrogen or other basic substituent in the cellulose molecule complex, and by virtue of the respective valences, it may be possible that, for example, three sodium atoms are replaced by one aluminum atom. Evidence shows that the metal solution reacts with the cellulose fabric in proportionate amounts related to the quantity of acid present in the complex molecule.

Upon subsequent treatment with the insolubilizing agent such as sodium silicate, sodium may replace aluminum in the molecule although, because of the unique properties of the finished product it is not definitely known whether there is an actual chemical bond remaining between the aluminum and the complex or whether the aluminum is replaced in the molecule and forms for example aluminum hydroxide which by virtue of the previous bond of the aluminum with the cellulose complex is consequently intimately dispersed within the cellulose fibers. In any event, the finished product containing the insoluble metal compound has unusual durability.

Similar treatments of pure cotton, i.e. exposure to such metallic salts, followed by rinsing and neutralizing in the same manner, result in either complete removal of the salt during rinsing or a spotty surface precipitate after neutralizing which has little or no durability and none of the properties exhibited by the product of the present invention.

Work thus far has demonstrated that a large number of compounds in a wide variety of combinations can be produced by the above technique. For instance, it is possible to apply progressive treatments with the same or different metal salts or neutralizing agents, the only limit being steric hindrance, and there will be an additive or step-wise increase in the above mentioned properties of the fabric. Since it may be observed that certain metals tend to enhance certain of the properties in a characteristic manner, it may be desirable to treat with two or more different metal solutions either simultaneously or in successive steps to achieve optimum results.

Organic materials such as softeners and waterproofing agents are also applicable, each compound imparting its own characteristic properties to the fabric.

The present process can be used on a wide variety of cellulose derivatives, the basic requirement being the presence of a cation acceptor in the cellulose molecule, such as the polybasic acids of phosphorous, sulfur, and polycarboxilic acids mentioned above. It is possible, of course, that more than one of the acid hydrogens of the polybasic acid may be replaced by the basic substituents such as sodium or nitrogen and it is contemplated as being within the scope of the invention that the "control neu-

tralizing" steps of the process can in some cases even utilize an acid such as orthophosphoric acid which thus forms insoluble metal phosphates and thus replaces the metal in the complex molecule with hydrogen rather than sodium as previously described. The fabric must be treated further to raise the pH of the fabric to substantial neutrality before drying, the requirement of the board aspect of the invention being that insolubilizing anions are provided which will combine with the metal to form the insoluble compound in the fibers.

Example I

A 45"—64/60—4.65 cotton fabric in the pure state, desized, scoured and bleached, was impregnated with the following solution, squeezed, dried and then baked for four minutes at 320° F.

Phosphoric acid (75%)	lbs.	150
Dicyandiamide	lbs.	85
Urea	lbs.	300
Syntholite	ozs.	10

100 gallons with water.

The solution was prepared by first heating together the phosphoric acid, dicyandiamide, and about 150 lbs. of water. When the violent reaction has subsided the urea and the remainder of the water was added to bring the volume up to 95 gallons. Finally, 10 ozs. of Syntholite (Synthron, Inc., Ashton, R.I.), a polyoxyalkylated condensation product type wetting agent, were added to promote the wettability of the fabric and the volume brought up to 100 gallons with water.

The fabric prepared according to the foregoing was then treated with caustic sode as described in the outlines of the process. In this case, the caustic soda was applied on the mercerizing frame using a 48° Tw. (24%) solution. The fabric was thoroughly washed with hot water while under tension in the mercerizing machine. It was then given an additional cold water wash in rope form to remove excesses of alkali.

Approximately 200 yards of the wet fabric from the above caustic operation was then treated in a 100 gallon solution containing 2% stannic chloride (technical grade $SnCl_4.5H_2O$) and 3% hydrochloric acid (37%) for approximately twenty minutes at room temperature. This treatment was carried out in a Rodney Hunt type of vessel and the fabric received the usual rope passage through the machine. After the metal treatment the fabric was rinsed in an excess of water at room temperature in the same vessel. Next, the fabric was passed into another Rodney Hunt machine containing 100 gallons of a 2% sodium silicate solution (Star Brand, 42° Bé., Philadelphia Quartz Company), and the treatment continued for approximately fifteen minutes at 120° F. Finally the fabric was rinsed in the same vessel in an excess of water at 120° F. soaped for about ten minutes in 0.5% soap solution at 180° F. and rinsed in warm water to remove the soap. The drying was accomplished in a regular tenter frame. Subsequently it was softened by padding on about 2% of Moropol (Moretex Chemical Products, Spartanburg, S.C.) a nonionic polyethylene emulsion, frame dried, and sanforized for shrinkage control.

The fabric finished at around 36 inches finished width, had unusually high crease resistance, good strength, and a thick, yet soft wool-like hand. Soil burial tests indicated a high degree of mildew resistance. All properties were durable to washing and dry cleaning.

Example II

A 41"—136/60—3.60 cotton pure white broadcloth fabric was treated with the phosphoric acid dicyandiamide and urea solution as in Example I, dried and baked for three minutes at 340° F.

Approximately 200 yards of the cured fabric was then treated in a 100 gallon solution of 2% stannic chloride and 3% hydrochloric acid as described in Example I. All subsequent treatments were the same as in Example I.

The fabric finished at around 38" finished width, had a smooth silky hand with high crease resistance and satisfactory strength. All properties were durable to washing and dry cleaning.

Example III

An all linen fabric, scoured off and bleached was treated in accordance with the details set forth in Example II.

The finished fabric had unusual crease resistance for a linen fabric with a satisfactory strength. It had an appreciable weight increase over the untreated fabric. In addition, it had a slower rate of burning and its mildew resistance was quite good. All properties were durable to washing and dry cleaning.

Example IV

A 39"—80/80—4.00 cotton print cloth in the dyed state was impregnated with the following solution, squeezed, dried and baked for three minutes at 330° F.

	Lbs.
Diammonium phosphate (anhydrous)	80
Monosodium phosphate (anhydrous)	70
Urea	300
Isopropyl alcohol	8

100 gallons with water.

The ingredients for the above were simply added to a portion of the water in a mixing vessel and some steam heat supplied to effect more rapid solution. Water was added to bring to total volume. The isopropyl alcohol was used to promote more effective wettability of the fabric.

The dried and baked fabric was then subjected to a caustic soda treatment on the mercerizing frame as described in Example I.

50 yards of wet fabric was then fed into a conventional jig for a series of wet operations. The first of these consisted of a 30 minute treatment at room temperature in the following solution:

	Lbs.
Stannic chloride	5
Hydrochloric acid	6

30 gallons total volume.

At the end of thirty minutes the bath was dropped and the fabric was given an overflow rinse in plain water at room temperature for approximately five minutes. It was then treated in a sodium silicate bath containing five lbs. silicate per 30 gallons water at 120° F. After approximately ten minutes treatment this bath was dropped and the fabric given another overflow rinse with plain water at 140° F. for about ten minutes. Finally the fabric was removed from the jig, squeezed, frame dried, softened and Sanforized in the usual way.

The resulting fabric had a dense full hand, rather high resilience. Its mildew resistance was excellent. It also showed an appreciable gain in weight due to the process. The finished width measured approximately 34 inches. All properties were durable to washing and dry cleaning.

Example V

Another portion of the 39—80/80—4.00 cotton print cloth in the dyed state was converted to the cellulose-acid-nitrogen complex in accordance with the details prescribed in Example IV. The dried and baked fabric was also subjected to a caustic soda treatment on the mercerizing frame as described in Example I.

50 yards of the wet fabric from the previous caustic treatment was then subjected to a treatment in 100 gallons of a 4% magnesium chloride solution for 15 minutes at room temperature. It was then rinsed in an excess of water followed by treatment in ½% sodium carbonate at room temperature for 15 minutes. The fabric was

again rinsed in an excess of water, squeezed, and dried. It was finally finished off by applying a softener, frame drying and Sanforizing.

The resultant fabric exhibited a definite increase in weight. It had a dense wool-like hand with improved resistance to wrinkling. Exposure to a flame indicated a reduced rate of burning. All properties were durable to washing and dry cleaning.

Example VI

A 39"—80/80—4.00-cotton print cloth in the dyed state was converted to a cellulose-acid-nitrogen complex as described in Example IV.

After mercerizing 50 yards of the wet fabric was again charged into a jig and treated with stannic chloride and hydrochloric acid as in Example IV. The overflow rinse followed. This time the alkaline treating agent used to produce the insoluble tin compound in the fabric was disodium phosphate, 5 lbs. per 30 gallons of water. The treatment lasted for ten minutes at 120° F. and was followed by the usual overflow rinse of ten minutes at 140° F.

Finishing proceeded in the conventional manner by tenter framing, softening and Sanforizing to finishhed dimensions.

The resulting fabric had all the desirable characteristics described in Example IV.

Example VII

Another 50 yards portion of the dyed cotton print cloth of Example IV was treated in accordance with the method described in that example. The procedure was carried through the conversion to a cellulose-acid-nitrogen complex, caustic soda, and stannic chloride treatments. After the conventional overflow rinse following the latter step the alkaline agent this time was borax at a concentration of 5 lbs. per 30 gallons of water for ten minutes at 120° F. The final overflow rinse followed and the fabric was finished off in the usual manner.

The resulting fabric was again similar to that of Example IV with all the desirable features present to substantially the same extent.

Example VIII

A 41"—88/50—3.30 printed fabric was converted to a cellulose-acid-nitrogen complex according to Example I. This included sizing with the phosphoric acid, dicyandiamide and urea solution followed by drying and baking. Treatment with 42° Tw. caustic followed according to previous descriptions.

After thorough rinsing to remove alkali from the previous operation 50 yards of the wet fabric was charged into an open beck containing 100 gallons of a 5% commercial grade titanium sulfate solution (using Titanium Sulphate Cake, Titanium Pigment Corporation). The material was worked in this solution for approximately twenty minutes at room temperature. The bath was then dropped and the fabric rinsed in running water. It was then subjected to an alkaline treatment with 2% sodium silicate for fifteen minutes at 140° F. after which the bath was again dropped and the fabric thoroughly rinsed in plain water.

The fabric was then drawn out of the beck, scutched, and frame dried. It was then padded with a 2% solution of Sapamine WL (an acid salt of a complex amino organic compound—Ciba Co.) squeezed and slack dried. Finally the fabric was pin framed on an overfeed pin tenter to a finished width of 35 inches.

The resulting fabric had a soft, dense and wool-like hand with high resilience. It had a substantial increase in density and weight, mildew resistance was excellent. All the desirable properties were durable to washing and dry cleaning.

Example IX

50 yards of the 41"—88/50—3.30 printed fabric was carried through the same treatments as described in Example VIII including the formation of the cellulose-acid-nitrogen complex followed by the caustic treatment and then the treatment in an open beck containing 100 gallons of a 5% commercial grade titanium sulfate solution. After the usual rinse in overflowing water, the fabric this time was subjected to a treatment in 2% sodium stannate ($Na_2SnO_3.3H_2O$, C.P.) for fifteen minutes at 120° F. An additional treatment in 2% sodium silicate for fifteen minutes at 120° F., followed by rinsing in warm water completed the process. The fabric was also softened using Sapamine WL and pin framed to finished width as in Example VIII.

The resulting fabric had all the desirable properties described in Example VIII including a soft, dense wool-like hand with high resistance to creasing. It also showed a substantial increase in density and weight with excellent mildew resistance. In addition to all these properties the fabric this time also exhibited good flame resistance with a minimum of afterglow. Although it would char only when exposed to a flame, the removal of the flame would also stop any further propagation of the charring. This was measured according to the specifications of the AATCC, "Evaluation of Fire Resistant Textiles, Standard Test Method 34—1952." All the properties described were durable to numerous washings and dry cleanings.

Example X

A 45"—64/60—4.65 fabric in the dyed state was converted to a cellulose-acid-nitrogen complex according to Example I. This included sizing with the phosphoric acid, dicyandiamide and urea solution followed by drying and baking. Treatment with 42° Tw. caustic followed according to previous descriptions.

After thorough rinsing to remove alkali from the previous operation, 50 yards of the wet fabric was charged into a vessel containing 3% zirconium sulfate (Titanium Alloy Manufacturing Company) and 2% solution of sulfuric acid (66° Bé.). Treatment was carried out for fifteen minutes at room temperature followed by rinsing in running water. It was then subjected to a treatment in 1% sodium stearate for fifteen minute at 140° F. followed by additional rinsing in water. Softening with 2% Sapamine WL followed by frame drying to finished width completed the process.

The resultant fabric had a full dense hand with substantial improvement in resistance to creasing. It also indicated the property of a slower burning rate when exposed to a flame. There was also a significant increase in the finished weight of the fabric. Furthermore this material exhibited a water repellent effect as measured by the spray method. This was done in accordance with "AATCC Resistance to Wetting (Spray Test), Standard Test Method 22—1952." All of these properties including the water repellent effect were durable to numerous washings and dry cleanings.

Example XI

Another portion of the 64/60 fabric was prepared as described in Example X. This included sizing with the phosphoric acid, dicyandiamide, and urea solution followed by drying and baking. Treatment with 42° Tw. caustic followed according to previous descriptions.

After thorough rinsing to remove the alkali from the previous operations, 50 yards of the wet fabric was charged into a vessel containing 100 gallons of 2% of manganese chloride solution. The treatment in this solution was carried out for fifteen minutes at 80° F. followed by rinsing in an excess of cold water. It was then treated in a 100 gallon solution of 1% sodium silicate for fifteen minutes at room temperature followed by additional rinsing in an excess of cold water: Softening by the application of 2% Sapamine WL on a padder

followed by frame drying and sanforizing completed the process.

The resultant fabric had a dense, resilient hand with improved resistance to wrinkling. It showed a moderate but definite increase in weight and exhibited a slower rate of burning than an untreated fabric. Furthermore this fabric exhibited a water repellent effect. All of these properties were durable to numerous washings and dry cleanings.

Example XII

A 40"—80/80—3.50-plain dyed fabric was converted into the cellulose-acid-nitrogen complex in accordance with Example IV.

50 yards of the previously sized, dried, and baked goods were then charged into a beck containing 100 gallons of a 5% solution of aluminum sulfate (iron free, crystalline, General Chemical Division of Allied Chemicals). The goods were worked in this solution for twenty minutes at room temperature after which the bath was dropped and the fabric rinsed in overflowing water. A 2% sodium silicate solution was then prepared and the fabric worked in it for fifteen minutes at 100° F., after which the bath was dropped and the fabric subjected to another overflow rinse in plain water.

The fabric was finished off by drawing out of the beck, scutching, frame drying, softening and sanforizing. Its final finished width was 36 inches.

The finished fabric had a smooth, soft hand with high resilience. Its weight increase was appreciably lower than the fabrics in previous examples. It also exhibited excellent mildew resistance. These properties were durable to numerous washings and dry cleanings.

Example XIII

Another 50 yard portion of the 80/80—3.50 fabric was treated in accordance with the details of Example XII. This included the conversion into the cellulose-acid-nitrogen complex followed by the treatment in 100 gallons of 5% aluminum sulfate at room temperature. After approximately twenty minutes treatment in this solution the fabric was rinsed thoroughly in an excess of cold water, squeezed, drawn out and without any further treatment in the wet state dried at a low temperature.

The fabric was finished off by softening with a solution containing a lubricant and some alkali to raise the pH of the fabric to approximately 7.0 followed by frame drying and sanforizing.

The resultant fabric had an improved resilient hand with improved resistance to wrinkling. It showed a definite increase in weight and exhibited slower burning properties. Resistance to mildew was improved. All properties were durable to washing and dry cleaning.

Example XIV

Still another 50 yard portion of the 80/80—3.50 fabric was treated in accordance with the details of Example XII in the formation of the cellulose-acid-nitrogen complex. The converted cellulose was then subjected to a fifteen minute treatment in a 100 gallon solution containing 2% aluminum sulfate and 10% urea. It was then squeezed and without any additional treatment in the wet state dried at low temperature.

The fabric was finished off by softening with a solution containing a lubricant and some alkali to raise the pH of the fabric to approximately 7.0 followed by frame drying and sanforizing.

The resultant fabric had all the desirable properties enumerated in Example XIII with equally satisfactory durability.

Example XV

A cotton fabric was converted to a cellulose-acid-nitrogen complex by treatment with the following solution, squeezing, drying, and baking—

	Pounds
Sulphamic acid	200
Urea	200

100 gallons with water.

50 yards of the fabric prepared according to the foregoing was thereafter treated with a metal salt, aluminum sulfate, and an alkaline agent, sodium silicate, and subsequently finished off exactly as in Example XII.

The resultant fabric had satisfactory strength, good flexible soft hand with high crush resistance. It also exhibited excellent mildew resistance. All properties were durable to washing and dry cleaning.

Example XVI

The cellulose of a cotton fabric was converted to a cellulose-acid-nitrogen complex by pretreatment with the following solution, squeezing, drying and baking for fifteen minutes at 300° F.

	Pounds
Phthalic anhydride	298
Urea	298
Mill ammonia (28%)	215
Guanidine carbonate	60

100 gallons with water.

The fabric prepared according to the above was subsequently treated with aluminum sulfate, sodium silicate and finished off in accordance with the descriptions of Example XII.

The finished results were generally comparable to those obtained in Example XII.

Example XVII

A 39"—80/80—4.00 plain dyed cotton fabric was treated in accordance with the details of Example I to form the cellulose-acid-nitrogen complex.

3000 yards of the baked fabric from the above operation was impregnated on a padder with following solution at room temperature, squeezed, and shelled up wet on a roll.

	Lbs.
Aluminum sulfate	100
Zirconium sulfate	150
Water	750
Total weight	1000

The wet fabric was retained on the shell in the wet state for approximately two hours. The pick up of the solution was calculated to be around 100%. At the end of this time the wet fabric was rolled off the shell and charged into an open beck where it was thoroughly rinsed in an excess of water at room temperature. It was then treated in a 3% sodium silicate solution for twenty minutes at 110° F., in the same vessel. This was followed by another rinsing with an excess of plain water, drawing out of the beck, scutching, and frame drying. The fabric was finished off in the usual way which included softening, drying and sanforizing.

The finished fabric exhibited a soft, pliable hand with rather high resilience. A high degree of mildew resistance was also indicated. There was an appreciable increase in the weight of this fabric. All properties were durable to washing and dry cleaning.

Example XVIII

A 39"—80/80—4.00 plain dyed cotton fabric was treated in accordance with procedure described in Example XVII. This included the formation of the cellulose-acid-nitrogen complex as well as the subsequent treatment with the metallic salt combination of aluminum and zirconium sulfates followed by exposure to a sodium silicate solution. After rinsing and drying the fabric was again impregnated with the same metallic salt solution of

aluminum and zirconium sulfates, retained in the wet state for two hours followed by a treatment in the beck with 3% sodium silicate solution. After rinsing the fabric was drawn out of the beck, scutched, frame dried, softened and sanforized.

The resultant fabric showed a higher degree of resilience than the one in Example XVII, along with a significant increase in weight. The hand remained soft and supple along with good strength. All the properties were durable to washing and dry cleaning.

Example XIX

An all rayon fabric was treated in accordance with the details set forth in Example XII. This included the conversion into the cellulose-acid-nitrogen complex as well as the formation of the aluminum compound in the fabric by treatment with aluminum sulfate and a sodium silicate. The fabric was finally finished off by softening and pin framing to width on an overfeed pin tenter.

The resultant fabric had a lively, crush resistant hand, with a small increase in its overall weight. Mildew resistance was quite high. All properties were durable to washing and dry cleaning.

Example XX

A 39 inch—80/80—4.00 cotton print fabric in the dyed state was converted to the cellulose-acid-nitrogen complex in accordance with the details described in Example IV. The dried and baked fabric was also subjected to a caustic soda treatment on the mercerizing frame as described in Example I.

The wet fabric from the previous caustic treatment was then subjected to a treatment in 5% silver nitrate for twenty minutes at room temperature. It was then rinsed in an excess of water followed by a treatment in 2% sodium oxalate for ten minutes at 130° F. The fabric was again rinsed in an excess of water, squeezed, and dried.

The resultant fabric showed a definite increase in weight. It also exhibited a significant sensitivity to light. Upon exposure to ordinary daylight, the fabric progressively changed color, reaching a deep grayish brown shade in a matter of a few hours. A pure fabric: i.e. one that was not converted to the cellulose-acid-nitrogen complex, treated with the same silver nitrate solution under the same conditions, rinsed and subsequently treated with sodium oxalate, rinsed and dried as described above, produced only a slight change in shade after prolonged exposure. Quantitative analysis revealed only a slight trace of silver on the pure fabric.

The broad aspects of this invention contemplate the use of the processes described above to introduce into the cellulose fibers, in an intimate association, by either chemical or physical bonding or both with the cellulose, a property-enhancing radical or substituent, either metal or non-metal, which selectively provides certain pronounced characteristics to the fabric, and which properties persist even after long periods of use and after repeated launderings or the like.

Although only certain embodiments of the invention have been shown and described herein, it is to be understood that other changes and additions can be made by those skilled in the art without departing from the scope and spirit of the invention.

We claim:

1. A process for imparting improved properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising reacting said material with a solution of a metallic compound and further treating said material to cause the formation in situ of an insoluble compound of such metal in the cellulose fibers.

2. A process for imparting improved properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising reacting said material with a solution of a metallic salt and further treating said material with a solution of an insolubilizing agent to cause the formation in situ of an insoluble compound of such metal in the cellulose fibers.

3. A process for imparting improved properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, selected from the group consisting of polycarboxylic acids and the acids of phosphorus and of sulfur, and having at least one of its acid hydrogens replaced by a basic substitutent, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of a metallic salt to introduce said metal into said complex; further treating said material with a solution containing an insolubilizing agent which combines with the metal in said complex.

4. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of a metallic salt to introducing said metal into said complex; further treating said material with a solution containing an insolubilizing agent which combines with the metal in said complex.

5. The crease-resistant cellulosic fibrous material produced by the process of claim 4.

6. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc to introduce said metal into said complex; further treating said material with a solution containing an insolubilizing agent which combines with the metal in said complex.

7. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc to introduce said metal into said complex; and further treating said material with a solution of a sodium salt of a weak acid.

8. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and

further treating said material with a sodium silicate solution.

9. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of an amphoteric polyvalent metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc; further treating said material with dilute alkali to raise the pH of the wet material toward neutrality.

10. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with a sodium tetraborate solution.

11. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of an amphoteric polyvalent metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with a disodium phosphate solution.

12. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a monovalent basic substituent selected from the group consisting of nitrogen containing radicals and sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with an aqueous alkaline solution.

13. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with an aqueous solution of an aluminum salt; further treating said material with a solution containing insolubilizing anions which combine with the aluminum on the material to form an insoluble compound in the cellulose fibers.

14. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by sodium, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of aluminum sulfate; further treating said material with a solution containing insolubilizing anions which combine with the aluminum on the material to form an insoluble compound in the cellulose fibers.

15. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a nitrogen containing radical, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with a solution containing insolubilizing anions which combine with the metal to cause the formation in situ of an insoluble compound in the cellulose fibers.

16. A process for imparting improved crease resistance and other desirable properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by nitrogen containing radical, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising the steps of reacting said material with a solution of an aluminum salt; further treating said material with a solution containing insolubilizing anions which combine with the aluminum to cause the formation in situ of an insoluble compound in the cellulose fibers; and washing said material again and then drying it to remove excess moisture.

17. A process for imparting improved crease resistance and other desirable properties to a fibrous phosphorylated cellulose material comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with a solution containing an insolubilizing agent which combines with the metal to cause the formation in situ of an insoluble compound in the cellulose fibers.

18. A process for imparting improved crease resistance and other desirable properties to a fibrous phosphorylated cellulose material comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with a sodium salt of a weak acid.

19. A process for imparting improved crease resistance and other desirable properties to a fibrous phosphorylated cellulose material comprising the steps of reacting said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with sodium silicate.

20. A process for imparting improved crease resistance and other desirable properties to a fibrous phosphorylated cellulose material comprising the steps of reacting said material with an aqueous solution of an aluminum salt and further treating said material with sodium silicate.

21. A process for imparting improved crease resistance and other desirable properties to a fibrous phosphorylated cellulose material comprising the steps of reacting said material with an aqueous solution of an aluminum salt and further treating said material with a solution containing an insolubilizing agent which combines with the aluminum on the material to form an insoluble compound in the cellulose fibers.

22. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal, and further treating said material with an insolubilizing agent to cause the formation in situ of an insoluble compound with the metal of the cellulose complex.

23. A process for selectively enhancing properties of

a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further treating said material with an insolubilizing agent to cause the formation in situ of an insoluble compound with the metal of the cellulose complex.

24. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further reacting said material with an insolubilizing agent.

25. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent selected from the group consisting of nitrogen containing radicals and sodium to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further reacting said material with an insolubilizing agent.

26. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent selected from the group consisting of nitrogen containing radicals and sodium to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further reacting said material with an aqueous alkaline solution.

27. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent selected from the group consisting of nitrogen containing radicals and sodium to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further reacting said material with a solution of a sodium salt of a weak acid.

28. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a basic substituent selected from the group consisting of nitrogen containing radicals and sodium to replace at least one hydrogen of said acid with said basic substituent, then reacting said material with a metal selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and further reacting said material with sodium silicate.

29. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a sodium containing material to replace at least one hydrogen of said acid with sodium, then reacting said material with aluminum, and further reacting said material with an aqueous alkaline solution.

30. A process for selectively enhancing properties of a fibrous cellulosic material comprising the steps of treating said material with a polybasic acid selected from the group consisting of polycarboxylic acids and acids of phosphorus and sulfur to introduce the acid radical into the cellulose molecule at a hydroxyl group position of said molecule, further treating said material with a nitrogen containing radical to replace at least one hydrogen of said acid with the nitrogen containing radical, then reacting said material with aluminum, and further reacting said material with an aqueous alkaline solution.

31. A process for imparting improved properties to a fibrous cellulose-acid complex material in which the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent, is linked to the cellulose at a hydroxyl group position of the cellulose molecule, the process comprising reacting said material with a solution of a metallic compound and further treating said material to raise the pH thereof toward neutrality to cause the formation in situ of an insoluble compound of said metal in the cellulose fibers.

32. A crease-resistant fibrous cellulose-acid complex material comprised of a polybasic acid linked to the cellulose at a hydroxyl group position of the cellulose molecule by replacement of one of the hydrogens of the acid, said acid having at least one other acid hydrogen replaced by a basic substituent, and an in situ formed insoluble compound in the cellulose fibers containing a metal substituent derived from said complex.

33. A crease-resistant fibrous cellulose-acid complex material comprised of the radical of a polybasic acid selected from the group consisting of polycarboxylic acids and the acids of phosphorus and sulfur, and having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble compound in the cellulose fibers comprised of a metal substituent derived from said complex.

34. A crease-resistant fibrous cellulose-acid complex material comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble compound in the cellulose fibers comprised of a metal substituent selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, and metal being derived from said complex.

35. A crease-resistant fibrous cellulose-acid complex material comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by sodium, and linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble compound in the cellulose fibers comprised of a metal substituent selected from the group consisting of

aluminum, tin, zirconium, titanium and zinc, said metal being derived from said complex.

36. A crease-resistant fibrous cellulose-acid complex material comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a nitrogen containing radical, and linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble compound in the cellulose fibers comprised of a metal substituent selected from the group consisting of aluminum, tin, zirconium, titanium and zinc, said metal being derived from said complex.

37. A crease-resistant fibrous cellulose-acid complex material comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by sodium, and linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble compound in the cellulose fibers comprised of aluminum hydroxide, the aluminum being derived from said complex.

38. A fibrous cellulose-acid complex material having improved properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical being linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of an insolubilizing agent and a metal in said complex.

39. A fibrous cellulose-acid complex material having improved properties comprised of the radical of a polybasic acid selected from the group consisting of polycarboxylic acids and the acids of phosphorus and sulfur, and having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical being linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of an insolubilizing agent and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

40. A fibrous cellulose-acid complex material having improved properties comprised of the radical of a polybasic acid selected from the group consisting of polycarboxylic acids and the acids of phosphorus and sulfur, and having at least one of its acid hydrogens replaced by sodium, said acid radical linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of an insolubilizing agent and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

41. A fibrous cellulose-acid complex material having improved crease resistance and other properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a nitrogen containing radical, said acid radical being linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of an aqueous alkaline solution and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

42. A fibrous cellulose-acid complex material having improved crease resistance and other properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent, and linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of a solution of a sodium salt of a weak acid and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

43. A fibrous cellulose-acid complex material having improved crease resistance and other properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical being linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of sodium silicate solution, and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

44. A fibrous cellulose-acid complex material having improved crease resistance and other properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, said acid radical linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of disodium phosphate, and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

45. A fibrous cellulose-acid complex material having improved crease resistance and other properties comprised of the radical of a polybasic acid, having at least one of its acid hydrogens replaced by a basic substituent selected from the group consisting of nitrogen containing radicals and sodium, linked to the cellulose at a hydroxyl group position of the cellulose molecule, and an in situ formed insoluble constituent in the cellulose fibers consisting of the reaction product of sodium tetraborate and a metal in said complex, said metal being selected from the group consisting of aluminum, tin, zirconium, titanium and zinc.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,991,146 July 4, 1961

Raymond S. Babiarz et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 68, for "fabirc" read -- fabric --; column 7, line 34, for "sode" read -- soda --; column 9, line 24, for "finishhed" read -- finished --; column 14, line 31, for "introducing" read -- introduce --; column 18, line 66, for "and", second occurrence, read -- said --.

Signed and sealed this 5th day of December 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC