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**PROCESS OF MAKING WOOL-LIKE CELLULOSIC
TEXTILE MATERIALS**

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This invention relates to the production of improved
cellulosic textile materials, and more particularly to novel
methods for obtaining such materials.

This application is a continuation in part of my co-
pending application Serial No. 512,307, filed May 31,
1955 (now abandoned).

In my copending U.S. application Serial No. 707,870,
filed January 9, 1958 (now U.S. Patent No. 2,980,490,
dated April 18, 1961), novel cellulose products exhibiting
improved flame resistance, mildew resistance, and wool-
like resistance to wrinkling are prepared by subjecting
relatively cheap cotton fabric materials to swelling and
metallation treatments. Briefly, a fibrous textile material,
including cotton, linen, rayon, etc., is subjected to swell-
ing and complexing in a suitable liquid medium contain-
ing a swelling agent such as a primary or secondary
amine, the swollen material is then separated from the
major portion of the first amine solution and is then
treated with a suitable organic ester of a metal such as
tetraisopropyl titanate. The cellulose material at this
point of the process is in very highly tenderized, swollen
state. When this ester-amine containing cellulose is im-
mersed in water, it regenerates into its original, strong
form and results in the improved product containing up
to 20–25% of the metal oxide or oxides of the metal-
lating agent or mixtures of such agents. Following the
metallation, excess reagents are removed from the product
by a washing treatment with an anhydrous solvent, such
as an alcohol or hydrocarbon. This prevents hydrolysis
of the excess metal ester present and production of an
undesirable dusty product as well as reagent loss. In
the washing and treating steps, anhydrous solvents em-
ployed must be protected from moisture and to secure
an economically attractive operation must be recovered.
In addition, a 100% utilization and complete reaction of
the metal ester with the cellulose is not realized.

It has now been found that a desired, more complete
100% utilization of such metal ester can be readily
achieved in such process and that simplification of han-
dling and recovery of solvents and other liquids em-
ployed in the metallation can be effected. It is accord-
ingly an object of this invention to provide novel methods
for attaining these results as well as for overcoming the
existing disadvantages in prior metallation procedures.
It is among the specific objects of this invention to pro-
vide an improved method enabling one to achieve a
substantially 100% metal ester reaction and utilization in
such metallation process. Other objects and advantages
of the invention will be evident from the ensuing de-
scription.

These and other objects are attained in this invention
which comprises treating a cellulosic material with a
volatile, anhydrous, liquid, organic primary or secondary
amine together with a metallating ester compound, such
as an alkyl metallate of a metal having a valence of
not less than 3 nor more than 4, evaporating said amine
from the wetted, swollen, amine-complexed, tenderized
cellulosic material containing the added metallate and in
which the metal ester exists in residual or partially re-
acted state with the cellulose, and then hydrolyzing this
intermediate by an aqueous medium treatment to re-
generate the cellulose in essentially its original shape
and appearance but possessing such new and improved

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properties as wool-like characteristics and crease, wrinkle
and mildew resistance.

In a more specific and preferred embodiment, the in-
vention comprises soaking a cellulosic textile material
initially in an alkyl amine such as ethylamine, removing
excess amine therefrom and then soaking it in an alkyl
amine solution of an alkyl metal ester mixture such as
ethyl titanate and ethyl antimonite, heating the resulting
product to evaporate amine and by-product ethanol pres-
ent, subjecting the resulting material to heat treatment at
from about 100–180° C. to complete the metallation re-
action, and then regenerating the tendered intermediate
by immersion in aqueous media and recovering the im-
proved product which can be washed, dried, dyed, etc.,
and which possesses desired flame resistance, wrinkle re-
sistance and wool-like properties.

In one practical adaptation of the invention a suitable
textile or other form of cellulosic material such as cot-
ton, rayon, linen, ramie, etc., is initially wetted, at room
or elevated temperature, with a substantially anhydrous
organic amine swelling or complex agent, e.g., ethyl
amine, methyl amine, ethylene diamine, etc., and until
desired conditioning thereof is effected. Excess amine
is then removed from the complexed amine cellulose
product and the latter is then soaked in an organic solu-
tion of an alkyl amine and an alkyl metal ester, such as
ethyl titanate, or a mixture of such titanate with an anti-
monite such as ethyl antimonite. The resulting amine-
metallate-cellulose composition is then subjected to heat-
ing to substantially completely evaporate the amine,
solvent and some by-product alcohol and to further react
the metallate with the cellulose to form the tendered com-
plex intermediate. This intermediate is then treated or
immersed in water or other aqueous media to effect re-
generation of the tenderized cellulose intermediate and
provide a product having substantially the macroscopic
shape, tensile strength, washability, and high melting point
of the original fibrous cellulose material from which it
is derived.

To a clearer understanding of the invention the follow-
ing specific examples are given. These are merely illus-
trative and are not to be construed as in limitation of
the invention.

Example I

A four-ounce per square yard cotton sheeting was
titanated in the following manner: 30 grams of the
fabric was dried in an oven at 105° C. and placed in
a conventional type dyeing machine, comprising a closed
jacketed vessel capable of temperature control and of
flowing liquids through the sample in either direction.
2300 cc. of anhydrous ethylamine containing about 0.1%
of water was circulated through the fabric at 10° C. for
30 minutes. 200 grams of tetra-n-butyl titanate was then
added to the system and the circulation continued, while
the temperature was raised to 40° C. and a pressure of
25 p.s.i.g. prevailed in the system. This temperature con-
dition was maintained for 30 minutes, after which the
system was cooled and the solution drained away from the
fabric. About 90 grams of the solution was held by the
cloth. The drained cloth was then heated in the same
vessel to 110° C. for 1½ hours to evaporate the residual
amine. Some n-butyl alcohol resulting from the titana-
tion reaction between the butyl titanate and the cellulose
was obtained with the amine. The dried cotton at this
point contained 0.4% of nitrogen and 15% of TiO₂. The
titanated fabric was tenderized to about 50% of its
original tensile strength, but on immersing in water, re-
generated to its original strength and appearance.

Example II

An open weave cotton fabric weighing 2.6 ounces

per yard was titanated in the following manner in a resin reaction flask. 10 grams of the dried fabric were immersed for two minutes at 16° C. in 400 grams of ethylamine containing 125 grams of tetraethyl titanate. The solution was then drained from the cloth and the cloth allowed to stand for 30 minutes at temperatures just below the boiling point of the amine. During this aging, the material remained in the flask and was protected from atmospheric moisture. The flask was then heated to 110° C. for 20 minutes to result in excess amine and by-product ethanol being expelled. The residual dry fabric was then soaked in water, washed and dried. The cloth product contained 10% TiO₂ and had a crease recovery of 60% as tested by the method described in Technical Bulletin #T-7, published December 1, 1947, by Monsanto Chemical Co., and in contrast to the product obtained when recourse to solvent evaporation was not effected, was free from visible dust.

Example III

10 grams of the fabric such as that used in Example II was treated in a resin flask with 800 cc. of ethylamine for 30 minutes at reflux temperatures. After draining, 375 grams of ethylamine containing 125 grams of tetraethyl titanate was added to the flask and the sample soaked for one minute and then drained. The fabric retained approximately 20 grams of the solution. The cloth was then held below the boiling point of the amine for 30 minutes and was then heated to 110° C. for 20 minutes to evaporate amine and ethanol present. The fabric was then steamed by blowing steam at 110° C. through the heated flask to result in regeneration of the material to the original strong fabric. The washed and dried fabric was found to be dust-free and to contain 17.7% TiO₂. It had a crease recovery of 72% in accordance with the testing procedure used in Example II.

Example IV

Example III was repeated using a 15% by weight solution of tetraethyl titanate in dimethylamine. The product fabric contained 10% TiO₂, was dust free, and had a crease recovery of about 60.

Example V

A laboratory basket type centrifuge was modified to permit spraying of liquid into the basket and recirculation, during centrifuging, of a liquid treating agent through a fabric in the basket. A sample of 2.6 ounce cotton fabric was placed peripherally in the centrifuge basket. Ethylamine at 10° C. was then passed through the fabric under centrifuging at 500 r.p.m. (radius 2 inches) for 30 minutes to effect preswelling. The amine was then drained from the reservoir and a solution, comprising 960 grams of ethylamine, 240 grams of tetraethyl titanate, and 5 grams of isopropyl antimonite, was passed through the cloth at 10° C. for 15 minutes during centrifuging. The circulation action was then stopped and the centrifuging speed increased to 2400 r.p.m. for 3 minutes to remove the excess of liquid. The temperature of the centrifuge enclosure was raised to 108° C. for 20 minutes during slow rotation to effect evaporation and removal of the residual amine and by-product alcohols. A sample of the treated fabric was then removed, soaked in water, washed and dried. It was found to contain 13% TiO₂, 5% of Sb₂O₃, was dust free, and exhibited a crease recovery rating of 65%.

Example VI

A 56 gram skein of linen yarn of a 100/2 Lea count was dried at 105° C. for one hour and placed in a basket centrifuge vessel such as used in Example V. Ethylamine at 10° C. was circulated through this material for 30 minutes at 500 r.p.m. The amine was then drained off and a solution containing 1080 grams of ethylamine and 240 grams of tetraethyl titanate was introduced into the

vessel and circulated through the skein for 15 minutes at 10° C. The reservoir was then drained and the centrifuge rate increased to 2200 r.p.m. to throw out excess liquid. The swollen titanated skein was then heated to 108° C. to remove residual amine and by-product alcohol and was then water regenerated as in Example IV. The resulting product was dust free, and contained 20% TiO₂, and when woven into a plain, 6 ounce per yard fabric, had a crease resistance value of 80.

Example VII

A one gram swatch of 2.6 ounce cotton cloth was soaked in ethylenediamine for 2 hours at room temperature while protected from moisture. After draining briefly the amine swollen cloth was soaked at 80–90° C. for 30 minutes in 3 grams of tetraisopropyl titanate dissolved in 33 grams of anhydrous ethylenediamine. The solution was then drained off and the amine evaporated from the fabric using radiant heat at temperature of about 110–120° C. After immersing the cloth in water and washing and drying, it was found to contain 20% TiO₂ and had a crease recovery rating of 72.

Example VIII

10 grams of triethyl aluminate, Al(OEt)₃, were dissolved in 100 grams of anhydrous ethylamine. A one gram swatch of 2.6 ounce cotton cloth was immersed in this solution for one hour in a reaction flask at reflux temperature. Excess liquid was then drained from the flask, the cloth being protected from atmospheric moisture by means of passage of a current of dry nitrogen thereover. The flow of nitrogen was continued to evaporate the amine leaving the aluminum compound in the fabric. After vaporization of the amine, the flask was warmed to about 108° C. in an oven with the nitrogen still flowing over the fabric to remove any ethanol resulting from the reaction between the cellulose and metallate. The cloth was then removed and immersed in water, washed and dried. It had an ash content of about 8% indicating the introduction of considerable aluminum into the cloth. No dust appeared in the dried cloth. Its crease recovery rating was about 55.

Example IX

A solution of n-butyl ferrate was prepared by reacting ferric chloride with n-butanol in the presence of ammonia. The reaction product was mixed with an equal volume of benzene and the solid ammonium chloride filtered off. The benzene was distilled off leaving a solution of butyl ferrate in butanol analyzing 28 grams of Fe per liter. Ten grams of this liquid was mixed with 100 grams of ethylenediamine. A one gram swatch of 2.6 oz. cotton cloth was soaked for one hour at room temperature in pure ethylenediamine. It was then drained and immersed in the butyl ferrate-amine mixture, warmed to 50° C. and held for one hour in a closed flask. The cloth was then removed and placed in a flask through which a stream of dry air was passed. The air was preheated to about 110° C. to hasten evaporation of the butanol and residual amine present. Steam at 110° C. was then passed through the hot flask for 5 minutes, and was washed and dried. It had a reddish brown color and on ignition left a 5% ash residue. Its iron content was retained even after repeated launderings.

Example X

Using the procedure of Example V a portion of the 2.6 ounce cotton fabric was first treated with ethylamine and then with a solution consisting primarily of 500 grams of tetraethyl titanate, 10 grams of triisopropyl antimonite, 50 grams of triisopropyl aluminate and 2000 grams of ethylamine. The washed, dried product fabric contained 10% TiO₂, 5% Sb₂O₃, and 2.8% Al₂O₃. It was flame resistant, substantially free of afterglow, mildew resistant, resistant to loss of tensile strength on exposure to sunlight, and suffered substantially no yellowing on heating to 140°

C. for 2 hours. The product of Example V, containing no aluminum, yellowed markedly at this temperature.

Example XI

11 grams of 2.6 oz. cotton fabric was placed in the centrifuge apparatus used in Example V. Ethylamine was circulated through the sample for 30 minutes at 10° C. and the sample drained at 50 r.p.m. for 1 min. Using precautions against contacting the sample with atmospheric moisture, 1600 cc. of dry isopropanol and 425 g. of tetra-isopropyl titanate were placed in the machine, warmed to reflux temperature, circulated through the fabric for 30 min. and drained at 2000 r.p.m. for 3 min. The temperature of the vessel, still closed against atmospheric moisture, was raised to 108° C. in 40 min. and held at temperature for 20 min. The resulting dry, rather brittle tender fabric was immersed in water and a strong fabric resulted containing approximately 20% TiO₂ and showed a crease recovery rating of about 75.

The significance of the crease recovery figures for the products of the above examples, will be apparent from the following control figures:

| Untreated Cotton Cloth | Untreated Linen Cloth | Wool |
|------------------------|-----------------------|-------|
| CR=40 | CR=30 | CR=85 |

Although described as applied to certain specific and preferred embodiments the invention is obviously not restricted to such embodiments. Hence, many variations can be undertaken without departing from the underlying principles and scope of the invention.

Thus, in the first step of swelling a cellulosic material with the amine, the cellulose can be immersed in the pure amine or in the solution of the amine in a suitable organic solvent (alcohol, benzene, toluene, xylene, etc.). The material can then be drained and immersed in the amine solution of the alkyl metallate which may also contain a volatile organic solvent. After these swelling and treating steps the amine together with any volatile solvent present is evaporated from the cloth and in the presence of the alkyl metallate. The product at this point comprises an anhydrous metallated cellulosic intermediate adapted to be recovered as a special intermediate product or treated with an aqueous medium to hydrolyze and stabilize the metallated cellulosic material to final form. In using ancillary volatile organic solvents it is preferable that the organic solvent be more volatile than the amine used, but this is not essential. For simplification of operating procedures organic solvents use is preferably omitted, the cellulose material being swollen in the pure amine and then treated with the amine solution of the alkyl metallate. If desired, the metallation process can be effected as a one-step operation by immersing the original dried cellulosic material in a solution of the metal ester in the amine.

Amines useful as swelling agents herein comprise any primary or secondary alkyl or aryl amine or mixtures thereof, more volatile than the alkyl metallates employed, and which, preferably, boil at not greater than 180° C. Examples thereof include methylamine, ethylamine, propylamine, isopropylamine, dimethylamine, diethylamine, dimethylethylamine, diisopropylamine, methylethylamine, butylamine, ethylenediamine, propylenediamine, morpholine, and the like. The degree of metallation appears promoted to the maximum ranges by the use of the lower molecular weight, preferably straight chain primary alkyl amines. In some instances, a combination of a small primary amine molecule such as methylamine, ethylamine or ethylenediamine can be used with a more bulky molecule such as isobutylamine, tetraarybutylamine, diethylamine, diisopropylamine or morpholine, etc. While preferably the process is carried out without the use of solvents other than the amines, more volatile

solvents such as cyclohexane, isopropyl alcohol, heptane and the like can be used in conjunction therewith. However, it will be found preferable that they be removed as by draining or evaporation, prior to undertaking the final critical step of evaporating the amine from the cellulosic material in the presence of the alkyl metallate.

Metal esters utilizable herein comprise compounds, especially alkyl metallates, corresponding to the formula Me(OR)_x wherein Me includes titanium, zirconium, hafnium, thorium, aluminum, iron (ferric), e.g., metals which form water insoluble oxides and have a coordination number at least one greater than the valence of the metal in the oxide form (which number is usually 6), with R being a monovalent hydrocarbon or chlorinated hydrocarbon radical such as an alkyl (methyl, ethyl, butyl, amyl, isopropyl, isobutyl, isoamyl, beta-chloroethyl, etc.), cycloalkyl (cyclobutane, cyclopropyl, cyclopentane, cyclohexane, etc.), aryl (phenyl, benzyl, naphthyl, etc.), alkaryl (tolyl, xylyl, ethyl phenyl, etc.), aralkyl (benzyl, phenylethyl, phenylpropyl, etc.), and x is 3 and 4, the valence of the metal in its highest state of oxidation. Also utilizable are the hydrolyzable esters of antimony, such as the various antimonates and antimonites. They correspond to the formula (RO)₃Sb, wherein R is a monovalent hydrocarbon radical, such as the various alkyls, aryls, aralkyls, cycloalkyls mentioned above, e.g., methyl, ethyl, propyl, butyl, cyclopropyl, phenyl, naphthyl, tolyl, anthranyl, benzyl, xylyl, ethyl phenyl, phenyl propyl, etc., as well as the monochloro and dichloro derivatives of these compounds. Especially useful are trialkyl antimonites in which the hydrocarbon radical contains from 1-12 and preferably from 1-6 carbon atoms. Examples thereof include trimethyl, ethyl, isopropyl, butyl, hexyl, octyl, benzyl, phenyl antimonites and their various mixtures. These esters are applied under substantially anhydrous conditions, although the presence of small amounts of water, as indicated in connection with the titanium esters, can be tolerated. The antimony ester is preferably used in combination, that is, simultaneously with the titanium or zirconium esters, or they may be applied sequentially, e.g., before or after the titanating step, but prior to the water-washing step. Especially useful are metal ester compounds containing an alkyl hydrocarbon radical of an alcohol having from, say, 1-12 and preferably from 1-6 carbon atoms in its chain. In addition to the simple ortho esters of the metals which are preferred for use, the partially hydrolyzed or condensed polymetallates can be used, particularly those having a degree of polymerization not greater than 10. The alkyl metallates can be used either alone or in admixture with each other and the metallates of the group IV-A metals, e.g., titanium, zirconium, hafnium, thorium, in combination with an alkyl antimonite are especially useful when production of a product resistant to photodegradation is desired. An especially useful combination comprises an alkyl titanate and an alkyl antimonite. When such preferred combination is used from about 15-25% of the combined oxides of the metals is introduced into the cellulose. Preferably, the weight ratio of titanium oxide to antimony is substantially equal. Useful ranges for the other contemplated metals comprise the molecular equivalent ranges. In general, the final product can contain from about 2% up to 40% or more of the metal or mixtures, calculated as the oxide, and usually contains from about 5-35% of metal oxide or oxides and preferably from about 10-30%. Specific examples of alkyl metallates utilizable herein include tetraethyl titanate, hexaethyl dititanate, tetrapropyl titanate, tetrakispropyl titanate, octapropyl trititanate, tetramethyl titanate, tetraoctyl titanate, triethyl aluminate, triisopropyl aluminate, tributyl aluminate, triethyl ferrate, triisopropyl ferrate, tetrapropyl zirconate, tetraethyl zirconate, tetrapropyl zirconate, and the like, including the various polyaluminates, polyferrates, and polyzirconates having D.P.'s up to 10 and containing organic radicals of from one to 8 carbon atoms. The ester can be used with the amine either as a pure

liquid or as a solution of in an organic solvent (alcohol, benzene, toluene, xylene, cyclohexane, etc.).

The important step of evaporating in accordance with this invention the amine from the metallate wetted cellulose advantageously effects an improved penetration and complete reaction of the metallating agent. This is evident from the lack of production herein of an undesired dusty form of product. Advantageously also, recourse to this step eliminates the necessity of resorting to an expensive organic solvent washing treatment before the regeneration step and recovery of unreacted metal esters which induces dustiness. In carrying out the evaporation step the amine is evaporated from the cellulose while the later is in intimate association with the metallate and preferably only the amount retained by the cellulosic material after the amine-metallate composition treatment is allowed to drain off. The amount of metal penetrating and remaining in the cellulosic material depends somewhat upon the concentration of the solution with which the cloth is treated. It also depends upon the characteristics of the fabric with respect to the amount of liquid it can hold. With a relatively high concentration and a high liquid holdup one obtains on evaporation the higher amounts of metal oxide firmly affixed in the product. When the amount of metal take-up is small, either due to low concentrations of the treating solution or to low hold-up in the cloth, recourse can be had, if desired, to several treatments in succession. In such successive treatments, it is preferable that the process be carried through the step of evaporating the amine and then the swelling and alkyl metallate treatment is repeated. It is also possible to make successive treatments by carrying each through the hydrolysis step.

The use of a fluid aqueous medium for the hydrolysis step is also variable. Simple immersion in water is satisfactory. However, by steaming the material, especially in the case of textile fabrics, the advantage of removing small traces of volatile residues, especially the amines, is realized. Similarly, the cellulosic material can be immersed for preswelling in the pure volatile liquid amine composition after which it can be immersed in a liquid medium containing both the alkyl metallate and amine. If desired preswelling operation can be carried out in a solution of the amine in a suitable organic solvent after which the excess is drained away and the metallation step carried out as previously described. Preferably, the swelling and metallating solutions are substantially anhydrous. However, it is feasible that small amounts of water can be present in the amine solution employed in the preswelling operation inasmuch as it becomes drained away prior to the metallation step. Alternatively, the amine swollen and metal complexed cellulose can be regenerated by contact with a fluid aqueous medium such as water, steam or water vapor in a gaseous carrier. When combining alkyl metallates of aluminum and titanium together with an alkyl antimonite, it will be found advantageous to place the esters in one amine solution. However, recourse to successive treatments and evaporation steps for each agent can be effected should this be desired.

The process is admirably suited to the treatment of long or continuous lengths of cotton textile materials. The fabric may be fed from a roll into a range which consists for example of an initial chamber in which the fabric is immersed in a pure amine. The time of holding the cloth in this liquid may be increased considerably by employment of the J box, well known in the textile industry. The next unit of the range would be a second chamber similar to the first and carrying a J box in which the material is penetrated with an amine solution of the alkyl metallate. Upon leaving this chamber, the excess solution can be pressed out as with rollers and the liquid bearing cloth can be subjected to temperatures up to 180° C. to cause evaporation of the amines and by-product alcohols. The fabric can then pass to a final chamber in

which the steam atmosphere of approximately 110° C. is maintained. Following this the material can be washed and dried by normal procedures.

The manner in which the alkyl metallates affect the cellulosic materials is not well known. It has been observed that this metallation tends to increase resistance to inflammability and to improve crease recovery of fabrics and to prevent mildew. It is thought that the metal compound reacts and becomes chemically bonded to the cellulose to effect these results. It is possible that some cross-linking mechanism will serve to explain the new wool-like properties obtained. Combinations of various reagents have certain effects. While titanium and zirconium seem best for flame retardance and crease recovery there is a considerable afterglow present when a titanated material has been ignited and the flame expired. Additional aluminum treatment reduces this afterglow. The antimony serves to impart resistance to photodegradation of tensile strength and dye color retention of titanated fabrics.

Various advantages of this treatment, namely, the introduction of flame resistance, crease recovery and resistance to mildew, into cellulosic materials has been known. The particular advantage of this invention lies in a more economical and simple process which gives a 100% use of the ester remaining on the material under treatment and without causing undesirable dustiness in the final product. Another advantage resides in the fact that when pure amines and metallates are used the physical strength of the anhydrous amine-metallate tenderized intermediate is considerably greater than when prepared in alcohol or hydrocarbon solutions. This increase in strength of the in process material renders possible the continuous range application described above. While this process is particularly well adapted to the improvement of textile materials, such as cotton, linen, ramie, and the like, it can also be applied to other forms of cellulosic, such as wood pulp, wood, paper, cellulose sponges, cellulosic wall board and insulating materials, etc.

While elevated or boiling temperatures can be used in the reaction of the metal ester with the cellulose being treated, these are not essential. The reaction can be accomplished at lower temperatures through the employment of longer contact time and may be considered to be at the discretion of the operator. The temperature used in removal of solvents after completion of the reactions is likewise flexible and one can employ any suitable vaporization conditions. The variable reaction times, temperature, pressure of the system when swelling and complexing as well as when reacting and tenderizing the swollen and complexed product by ester treatment, are dependent upon the character of the initial cellulose material, the physical attributes of the swelling agent and the degree of subsequent metallization or degree of change of physical and chemical properties desired. Hence, such conditions cannot be specifically set out for all individual cases. Where relatively low-boiling liquids are used, such as methylamine, either low temperature operation at atmospheric pressure, or higher temperature operation at a pressure sufficient to maintain the major portion of ammonia derivative in the liquid state, is required. Short times of contact in both complexing steps, particularly at sub-zero temperatures, are advantageous and effective. A minimum of about 30 minutes of contact is preferred in the first step, that is, swelling and complexing the cellulose with the ammonia derivative; while a minimum of about 15 minutes is preferred in the second complexing, or tenderizing step, during which addition and reaction is effected of the ester with the complexed cellulose. The reaction of the ester-ammonia-derivative-complexed cellulose intermediate with water depends on penetration, a period of about 15 minutes to an hour at room temperature being preferred for use in this step.

As already stated, the invention provides a novel modified cellulose textile having a novel combination of properties, including the single fiber and fabric characteristics

of wool, increased liveliness, greater bulk, mildew resistance, crease and handle resistance, abrasion resistance, flame resistance, greater warmth and insulating characteristics, washability and high melting point. Having the crease resistance and resilience approaching that of wool, upon release after pressing, the fibers and textile will readily spring apart, a characteristic known as recovery. These attributes assure production of a material having desired loft (high bulk or volume for a given weight) properties which afford ready production of wool-like, open, porous fabrics of high covering power and thick, warm fabrics with a minimum of weight, qualities demanded in all apparel fabrics. Additionally, my modified product exhibits other improved characteristics, e.g., mildew resistance, abrasion resistance, extensibility, elasticity and flame resistance, to afford a unique combination of properties which assure essential texture, warmth, fit, and durability characteristics and thereby enhance its value for acceptance by textile manufacturers and the garment industry.

During the treatments, the strength of the cellulose material undergoing modification becomes poor and fabrics such as used in the above examples lose strength to such an extent that they are easily damaged by punctures and tears. It is believed that the cellulose is degenerated under the conditions of the process by a breaking of the cross-linkage of cellulose. The titanium, or other metal, enters into combination with the cellulose and the anhydrous product has poor strength due to this lack of cross-linkage between molecular units of the cellulose fiber. Upon treatment with water, however, there is strong evidence that cross-linkage again takes place and the fabric resumes its original strength. The cross-linkage at this time is believed to be somewhat different and a new chemical bonding takes place through the titanium or other metal which has entered into the complex structure. The improved properties are believed to be due in large measure to this new cross-linkage or bonding both units of the cellulose structure. When the product has received normal washing, it is substantially nitrogen-free indicating a relatively pure metal-modified cellulosic material.

Other evidence of the existence of a chemical combination of treating metal with the cellulose resides in the excellent mildew resistance which the metallated, especially the titanated, cellulose exhibits. This result does not occur when recourse is had to precipitation of TiO_2 in a cellulosic fabric from an aqueous solution.

I claim:

1. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool, comprising reacting a cellulose textile material under anhydrous conditions in the presence of a volatile, liquid nitrogenous chemical swelling agent for cellulose selected from the group consisting of primary and secondary amine compounds which swell the cellulose and form nitrogenous complexes with the cellulose and containing a radical selected from the group consisting of $-NH_2$ and $>NH$, with a water hydrolyzable organic compound selected from the group consisting of

(1) an ester corresponding to the formula $Me(OR)_x$ wherein Me is a metal selected from the group consisting of titanium, zirconium, hafnium, thorium, aluminum, iron and antimony, which forms a water-insoluble oxide and has a valence selected from the group consisting of 3 and 4 and a coordination number in the oxide state at least one greater than the valence, R is selected from the group consisting of hydrocarbon and chlorinated hydrocarbon radicals, and x corresponds to the valence of the metal, and

(2) a condensed ester of said hydrolyzable ester resulting from the reaction of said ester with water, continuing said reaction until a highly tendered metal ester-amine cellulose complex intermediate

product is formed of substantially reduced tensile and tear strength over that of the swollen cellulose textile obtained from said chemical swelling agent treatment, substantially completely evaporating said nitrogenous chemical swelling agent from said metal ester-amine cellulose complex intermediate product, contacting the resulting product with aqueous media consisting essentially of water which regenerates and restores said product to substantially the tensile strength of the original untreated cellulose textile material, and recovering the resulting chemically modified cellulose product.

2. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool comprising reacting a cellulose textile material under anhydrous conditions in the presence of a volatile, liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose, with a water hydrolyzable organic antimony ester corresponding to the formula $Sb(OR)_3$ in which R is selected from the group consisting of hydrocarbon and chlorinated hydrocarbon radicals, continuing said reaction until a highly tenderized antimony ester-amine cellulose complex intermediate is obtained having a substantially reduced tensile and tear strength compared to the swollen cellulose textile obtained from said chemical swelling agent treatment, substantially completely evaporating said alkyl amine swelling agent from the said ester-amine cellulose complex intermediate, subjecting the resulting product to contact with aqueous media consisting essentially of water which generates and restores said cellulose intermediate to substantially the tensile strength of the original untreated textile material, and recovering the resulting modified product containing in chemical combination with cellulose from about 2% up to 40% of said metal, calculated as the oxide.

3. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool comprising reacting a cellulose textile material under anhydrous conditions in the presence of a volatile, liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose, with a water hydrolyzable organic titanium ester corresponding to the formula $Ti(OR)_4$ in which R is selected from the group consisting of hydrocarbon and chlorinated hydrocarbon radicals, continuing said reaction until a highly tenderized titanium ester-amine cellulose complex intermediate is obtained having a substantially reduced tensile and tear strength compared to the swollen cellulose textile obtained from said chemical swelling agent treatment, substantially completely evaporating said alkyl amine swelling agent from the said ester-amine cellulose complex intermediate, subjecting the resulting product to contact with aqueous media consisting essentially of water which regenerates and restores said cellulose intermediate to substantially the tensile strength of the original untreated textile material, and recovering the resulting modified product containing in chemical combination with cellulose from about 2% up to 40% of said metal, calculated as the oxide.

4. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool, comprising immersing a cellulose textile material under anhydrous conditions in a volatile, liquid alkyl amine chemical swelling agent for cellulose which forms nitrogenous complexes with cellulose until a swollen nitrogenous complexed cellulose product is obtained, removing under anhydrous conditions excess amine reactant from the swollen cellulose product and reacting said product under anhydrous conditions in a solution of a water hydrolyzable organic ester corresponding to the formula $Me(OR)_x$ wherein Me is a metal selected from the group consisting

of titanium, zirconium, hafnium, thorium, aluminum, iron and antimony, which forms a water-insoluble oxide and has a valence selected from the group consisting of 3 and 4 and a coordination number in the oxide state at least one greater than the valence, R is an alkyl radical, and x corresponds to the valence of the metal, continuing said reaction until an anhydrous, highly tendered metal ester-amine cellulose complex intermediate results having a tensile and tear strength substantially reduced over that of the amine-swollen cellulose textile obtained from said alkyl amine swelling agent treatment, removing under anhydrous conditions excess ester reactant from said tenderized complex intermediate and substantially completely volatilizing said alkyl amine swelling agent therefrom, immersing the resulting complex intermediate in aqueous media consisting essentially of water which regenerates and restores the intermediate to substantially the tensile strength of the original untreated cellulose textile and recovering the resulting modified cellulose product containing, in chemical combination with the cellulose, from about 5% to 35% of said metal, calculated as the oxide.

5. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool, comprising immersing a cellulose textile material under anhydrous conditions in a volatile, liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose until a swollen nitrogenous complexed cellulose product is obtained, removing under anhydrous conditions excess amine reactant from said product and reacting the latter at the boil under anhydrous conditions with a solution of water hydrolyzable titanium tetraisopropylate until a highly tendered metal ester-amine cellulose complex intermediate is obtained having a tensile and tear strength substantially reduced over that of the swollen cellulose textile obtained from said alkyl amine treatment, removing under anhydrous conditions excess unreacted titanate reactant from said cellulose complex intermediate and substantially completely volatilizing said alkyl amine swelling agent therefrom, subjecting the resulting product to contact with water which regenerates and restores said intermediate to substantially the tensile strength of the original untreated cellulose textile material, and thereafter recovering the resulting chemically modified cellulose product.

6. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool, comprising immersing a cellulose textile material under anhydrous conditions in a volatile, liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose until a swollen nitrogenous complexed cellulose product is obtained, removing under anhydrous conditions excess amine reactant from said product and reacting the resulting product at the boil and under anhydrous conditions with a solution of alkyl ortho esters of antimony and titanium until a highly tenderized metal ester-amine cellulose complex intermediate is obtained having a tensile and tear strength substantially reduced over that of the swollen cellulose textile obtained from said alkyl amine treatment, substantially completely evaporating the alkyl amine swelling agent from said cellulose complex intermediate, subjecting the resulting product to contact with water which regenerates and restores said intermediate to substantially the tensile strength of the original untreated cellulose textile material, and thereafter recovering the resulting chemically modified cellulose product.

7. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease

resistance and bulk characteristics of wool, comprising immersing a cellulose textile material under anhydrous conditions in a volatile liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose until a swollen nitrogenous complexed cellulose product is obtained, removing under anhydrous conditions excess amine reactant from said product and reacting the resulting product at the boil under anhydrous conditions with a solution of water hydrolyzable tetraisopropyl antimonite and tetraisopropyl titanate until a highly tendered metal ester-amine cellulose complex intermediate is obtained having a tensile and tear strength substantially reduced over that of the swollen cellulose textile obtained from said alkyl amine treatment, removing under anhydrous conditions excess unreacted antimonite and titanate from said cellulose complex intermediate and heating the product to substantially completely volatilize and remove said alkyl amine swelling agent, subjecting the resulting product to contact with water which regenerates and restores said intermediate to substantially the tensile strength of the original untreated cellulose textile material, and thereafter recovering the resulting chemically modified cellulose product.

8. A method for preparing a cellulose textile material possessing substantially the single fiber, liveliness, crease resistance and bulk characteristics of wool, comprising immersing a cellulose textile material under anhydrous conditions in a volatile, liquid alkyl amine chemical swelling agent for cellulose which swells the cellulose and forms nitrogenous complexes with cellulose until a swollen nitrogenous complexed cellulose product is obtained, removing under anhydrous conditions excess amine reactant from said product and reacting the resulting product at the boil under anhydrous conditions with a solution of ethyl ortho titanate and ethyl ortho antimonite until a highly tendered metal ester-amine cellulose complex intermediate is obtained having a tensile and tear strength substantially reduced over that of the swollen cellulose textile obtained from said amine swelling agent treatment, removing under anhydrous conditions excess unreacted titanate and antimonite reactants from said cellulose complex intermediate and heating the resulting product to evaporate and substantially completely remove alkyl amine swelling agent remaining therein, subjecting the resulting product to contact with water which regenerates and restores said intermediate to substantially the tensile strength of the original untreated cellulose textile material, and thereafter recovering the resulting chemically modified cellulose product.

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