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## TREATMENT OF TEXTILE MATERIAL WITH ALKALINE CELLULOSE ZINCATE SOLUTIONS

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This invention relates to the treatment of a textile material. More particularly it relates to treating a textile fabric with a solution of cellulose in alkali metal zincate containing an excess of alkali over the amount required to convert the zinc present to zincate, precipitating the cellulose from the solution upon the fabric and then washing the thus coated fabric preferably to remove most but not all of the zinc present, the zinc left being bonded by the coating to the fabric and giving special desirable properties to the product.

This application is a continuation in part of my copending application Serial No. 423,163, filed December 16, 1941, now abandoned, for Textile material and method of making, which, in turn, contains subject matter derived from my application Serial No. 407,445, issued as Patent 2,322,427, on June 22, 1943.

The invention comprises the herein described product and the method of making it including the incomplete removal of the zinc as stated above. In a preferred embodiment the invention comprises application of the cellulose solution in alkali metal zincate to a fabric to be mercerized, precipitating the cellulose from the solution by means of the mercerizing sodium hydroxide solution, and then washing and drying the product, the precipitation by the mercerizing solution giving a product in which the stiffness or "hand" of the coated textile is not reduced materially by repeated laundering.

The invention comprises also the addition of an acid to cause precipitation of cellulose from alkali metal zincate solution applied to a fabric, washing the fabric and thus formed cellulose coating thereon until most but not all of the zinc present is removed, and then converting the remaining zinc to insoluble form, as by the addition of an alkaline zinc precipitating agent such as sodium carbonate or ammonium hydroxide to establish a pH above 7.

In a preferred embodiment, the invention comprises the use, as textile material to be treated, of cellulosic fabric as, for example, one of cotton or viscose rayon. With such fabrics the alkali metal zincate solution partially dissolves the surface portion of the fabric which, in turn, is reprecipitated along with the cellulose of the cellulose zincate solution. As a result, there is practically integral union of the coating to the inner portions of the cellulosic base material. Also, the partial solution of the base fabric followed by subsequent precipitation causes bonding together of the threads at the positions of crossing. This strengthens the fabrics. It also stabilizes the

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shapes and sizes of the meshes, as in a mosquito netting.

In general, a coating is applied to a textile material, as by passing a fabric through a solution of wood pulp in sodium zincate solution, adding a precipitating agent to precipitate cellulose upon the textile, and then washing and drying the product.

It is necessary that the washing of the fabric with precipitated cellulose thereon be continued until most of the zinc is removed. This is necessary to give a clear, non-hazy film of the cellulose. On the other hand, the washing is not to be continued until the last of the zinc is removed if all of the special results from the cellulose zincate treatment of the fabric are to be obtained.

Washing of the fabric with precipitated cellulose coating adhered thereto is best effected for the present purposes so as to give removal of the zinc compound to about the extent obtained in the following manner: if the precipitation of the cellulose is effected by treatment of the cellulose zincate solution with a concentrated solution of alkali, the alkalinity remaining is partly removed by washing and then neutralized and in fact acidified with an acid such as dilute sulfuric acid. If the precipitation is effected initially by the addition of an acid such as dilute sulfuric, then the additional acidification is of course unnecessary. In either case the acidified treated fabric is washed with water until most of the acid is removed. Then the remaining trace of acid is neutralized as by a dilute solution of sodium carbonate or ammonium hydroxide. That part of the zinc which remains at the conclusion of the washing is precipitated by the carbonate or ammonia treatment. In an alternative method, the final neutralizing with soda or ammonia is omitted and the washing is discontinued when the pH of the washed goods is about 3 to 4.

The treatment of a fabric with the zincate solution, precipitation of the cellulose, and washing out the precipitating agent removes most of the zinc but leaves a substantial proportion of it in the fabric, as, for instance, about 0.02% to 0.4% of the dry weight of the fabric. Larger amounts of zinc than 0.4% may be present in certain goods processed according to this invention but are not necessary. This zinc is itself mostly embedded in the coating of cellulose so that it is anchored thoroughly to the fabric. This zinc left in the coating of the fabric not only retards development of mildew but also increases the retentivity for pigments and fillers as, for example, for iron oxide pigments, thiocyanine or clear filler.

An especially important result is obtained when the sodium zincate solution of cellulose is added to a fabric and the fabric then treated with alkali as in the common process for mercerizing cotton. Here the concentrated alkali, say of strength about 20%, precipitates the cellulose. The fabric is then soured in a usual manner, washed and dried. I have discovered that zincate solutions of cellulose so added and then precipitated with alkali are retained on the fabric after repeated launderings better than when the precipitation is effected by acidification. In fact, it has seemed from a number of experiments that the stiffness or "hand" of the fabric containing the coating of cellulose precipitated by strong alkali is either unaltered or actually slightly increased by repeated laundering. The greater retention of the cellulose when precipitated by alkalinity, as compared to precipitation by such agents as sulfuric acid, is considered to be due to the effect of the strong alkali upon the fibers of the cotton or like material at the moment of the precipitation of the cellulose.

As the textile material to be treated, there is selected one that is not rapidly soluble in alkalies at room temperatures. Cotton, flax, and viscose rayon are particularly satisfactory as the textile material. Silk and acetate rayon may also be used if the treatment with my cellulose solution is made rapidly and the treated product is then promptly neutralized with acid. Particular advantages are obtained when glass fibers are used as the textile material, the alkalinity of my solution so modifying the surface portions of the glass fibers, as by incipient or substantial solution, that satisfactory adherence of the cellulose coating is obtained. Glass fibers so coated may be dyed in accordance with technique for viscose rayon or cotton.

The textile material to be treated is preferably in the form of a fabric, although the treatment may be applied less conveniently to the textile material in the form of single strands of yarn or thread.

The cellulose solution in the aqueous sodium zincate solution is prepared as described in my U. S. Patent 2,322,427, issued June 22, 1943, for Cellulose product. Briefly stated, the cellulose-zincate solution is made by dissolving cellulose such as rayon waste, purified cotton linters, or the like in a solution made by dissolving zinc, zinc oxide, or zinc hydroxide in an excess of an alkali metal hydroxide such as sodium or potassium hydroxide at low temperatures and then warming the resulting solution to moderate temperatures, all according to the conditions specifically recited in my said patent.

Zinc oxide is the most convenient to use of the readily available zinc materials. There is no objection to the use of zinc hydroxide except for the unnecessary inconvenience of providing an economical supply of the hydroxide. Also, there is no objection to the use of metallic zinc if one wishes to use zinc and does not object to the relative slowness with which the metal dissolves in the alkali. The three materials give the same product when dissolved in alkali in equivalent proportions and the term "zinc oxide" is used to include all of them.

The sodium hydroxide is used in large excess over the amount theoretically required to convert the zinc compound to zincate and suitably in the proportion of about 8 to 15 parts for 100 parts of water.

The solutions so made are ordinarily practically clear and may be applied to textile materials without further clarification. If desired, however, the solutions so made may be filtered, settled, or centrifuged, to remove any suspended material that may be present in objectionable amount.

The solution is applied to the selected textile material in any suitable or conventional manner. Thus, fabric or thread may be passed through the cellulose solution and then between squeeze rolls to remove excess of solution. Or, the textile material may be passed over a roll which at its lower part only contacts the solution and then between squeeze rolls, a suitable arrangement being a two-roll system in which the lower roll dips into the solution and the overriding roll and lower roll squeeze the textile between them.

After the solution has been placed upon the textile material, the treated material is then subjected to treatment to cause precipitation of the cellulose in situ. This precipitation may be made in various ways.

In a particularly satisfactory method, the treated textile is passed through an acid bath containing, for example, dilute sulfuric, hydrochloric, acetic, or other relatively inexpensive acid in concentration of about 1 to 5 parts for 100 parts of water. A large excess of the acid solution is used, so that acidity remains after precipitation. Particularly good results from the standpoint of toughness of the cellulose film are obtained when the acid used is a strong mineral acid, such as sulfuric or hydrochloric, and its concentration in the bath after the precipitation is approximately 2%, say 1 to 4%. When acetic acid is used, on the other hand, the treated material after drying is inclined to be somewhat softer and suitable for uses in which softness of the textile is required.

In place of the precipitation by acid, the cellulose may be precipitated in any manner described in my said patent, or by (1) heating the textile and adhering cellulose solution by steam heat, air, or quick immersion in hot water; (2) drying the coated textile in air at atmospheric temperatures, the cellulose precipitating as the water is evaporated; (3) addition of electrolytes such as soluble salts or additional alkali such as sodium, potassium, or lithium hydroxide; or (4) by admixing alcohol, acetone, glycerine, glycol, or like water-soluble dehydrating materials into the water solution to cause precipitation of cellulose.

When non-volatile strong acid such as sulfuric has been used for precipitating the cellulose, then the textile set with adhering cellulose must be neutralized with ammonium hydroxide, sodium carbonate, or the like or washed to remove the acid. When there has been used, in making the precipitation, no agent that is harmful to the textile, even though the agent is not removed by drying, then the washing may be omitted and the textile and precipitated cellulose film dried directly. Washing is not harmful in any case.

Drying is required to remove water from the treated product, this drying being effected in any usual manner such as passing the treated textile material over steam heated drying rolls, through hot air driers, or over heated calenders.

The invention will be illustrated in further detail by description in connection with the following specific examples:

*Example 1*

The anti-mildew effect of my treatment is illustrated by this example.

A cotton fabric was treated with a cellulose ether solution containing 5% of the ether and also treated with 5% cellulose in aqueous sodium zincate solution. These fabrics were washed with sulfuric acid, rinsed thoroughly to remove about as much zinc as possible. Fabrics were then dried and treated with various commercial anti-mildew agents and were subjected to culture tests with *Chaetonium globosum*.

In all cases the fabrics originally were increased 15 to 20% in strength by the cellulose treatment. In all cases, however, the samples subjected to the mildew test showed 15 to 20% less strength when they had been treated with the cellulose ether than when treated with the solution of cellulose in zincate.

To samples without any commercial anti-mildew agent, one coated with the cellulose ether and one with the cellulose zincate, were also subjected to the mildew test. After three weeks, the ether treated sample showed complete loss of textile structure and could not be removed whole from the cultur medium. The cellulose-zincate treated sample retained its structural form and could be lifted from the medium. Although the cotton itself had been attacked, the cellulose film containing zinc was not attacked.

A third plain fabric with no cellulosic coating and no added anti-mildew agent, when subjected to the cultur test, showed complete loss of textile structure.

*Example 2*

The following example shows in detail the effect of applying the zincate solution of cellulose before mercerizing, upon the "hand" of the stock, both before and after laundering.

A cotton fabric is padded through full strength solution of cellulose (about 5% on the dry basis) dissolved in sodium zincate solution of the kind described. The treated fabric is divided into two parts. One part is soured in dilute sulfuric acid, rinsed and dried. The other part is passed through mercerizing caustic solution (about 20%), then washed thoroughly with warm water on a mercerizing frame, and then either dried or soured in dilute sulfuric acid, rinsed and dried. On examination of the two fabrics it is found that the one coagulated by the mercerizing process is sheerer and slightly stiffer than the one treated by the acid coagulation.

Upon washing the two samples in a laundry wheel for 1 hour, it is found that the fabric coagulated by mercerizing has lost very little hand and also shows considerably less shrinkage than the same fabric coagulated by the acid method.

It is to be noted that in the mercerizing method of coagulation, there is no substantial loss of cellulose from the treating solution and the cellulose is bonded better to the cotton.

When, on the other hand, a cellulose ether solution is applied and later precipitated in the mercerizing liquid, there is removal of a substantial part of the ether during the processing described. Although the ether is precipitated by the strong caustic present initially in the mercerizing pad, there comes a stage, in the washing of the fabric carrying the precipitated ether, at which the ether is in contact with alkali of the most favorable concentration for dissolving the ether. In washing the cellulose precipitated from the zincate, on the other hand, the zinc compound becomes excessively diluted before the alkalinity reaches what would otherwise be a favorable concentration for solution of the cellulose.



*Example 3*

A cotton sheeting is singed in usual manner and then treated with an aqueous solution containing 3% cellulose, 8.5% of sodium hydroxide, and 2.9% of zinc oxide. The treated fabric is then allowed to dry if a continuous machine is used. Otherwise it is allowed to stand for several minutes and is then passed through sulfuric acid, washed thoroughly and then either kiered or handled in any manner usual at this stage.

When the fabric is finally finished it will be noted that the surface hairs which were not completely removed by the singeing but which were at least partly changed chemically by the singeing have dissolved in the zincate solution and have given results which normally would have required a coating solution containing about 4 or 5% of cellulose, in a non-zincate solution, for obscuring the hairs, as contrasted with 3% of cellulose in the zincate solution used to accomplish the result of dissolving off the hairs and thus giving the fabric a clean, non-fuzzy appearance. This would not happen with viscose or other alkaline (non-zinc) solutions of cellulose because of the lack of solvent power in such solutions as applied to the fabric.

*Example 4*

In this treatment, the singeing may be omitted when its degrading effect and the increased rate of solubility of the fuzz is not desired.

In many cases it is desirable to apply a cellulose solution to a fabric and set the cellulose with high heat leaving the cellulose dissolving agent in the fabric for substantial periods of time, as for example, in sizing. With zincate solutions of cellulose, it is possible to pass the yarn or goods through the solution and dry to a moisture content as low as 1% and then allow the goods to stand in this form for hours or weeks without any deterioration in strength or without any objectionable swelling or changing of the textile fibers themselves. In the case of other alkali solutions of cellulosic materials, such as ethers or viscose, the fabric or yarn would lose its strength immediately upon drying, and become still weaker on standing. When certain organic solvents for cellulose are used, the fabric would actually dissolve on the long contact.

It is also to be noted that the cellulose-zincate treated goods, containing all the alkali in dried form, actually increases in strength on standing and becomes stronger than fabric obtained with any of the previously used finishing treatments.

*Example 5*

Sodium zincate solution is prepared as follows: 100 parts of zinc oxide are stirred into 280 parts of water. 280 parts of caustic soda are then introduced and stirred in the zinc oxide and water mixture until the sodium hydroxide is dissolved. Then 100 parts of water are admixed. This gives a solution of sodium zincate.

To dissolve the cellulose in the zincate solution, 27 parts of powdered viscose rayon are stirred into a mixture of 218 parts of water and 175 parts of chopped ice. Then 120 parts of the zincate solution prepared as above are added and thoroughly stirred into the mixture.

As soon as the temperature of the whole mixture is lowered by the melting ice to −3° C., warming is started at once and the temperature raised to approximately 15° C.

This solution of cellulose in sodium zincate may

be used directly on fabric. When, however, it is desired that the treated fabric be not too stiff, as in the case of treated cotton sheeting, the solution is diluted, as, for example, to about one-half of its usual concentration before application to the fabric.

The solution, either at the original concentration or after dilution, is applied to the selected fabric by one of the machines described previously. The thus impregnated and coated fabric is passed through a sulfuric acid bath of concentration 2 to 5 parts of the acid for 100 parts of the solution.

The sulfuric acid causes precipitation of cellulose not only upon the surface of the fabric but also within the fabric at positions to which the cellulose solution has penetrated. The fabric is then thoroughly washed and dried.

*Example 6*

The cellulose-zincate solution described under Example 5 is applied to marquisette mosquito netting.

The mosquito netting is first thoroughly singed and mercerized and then can dried. The dried goods are then padded through the cellulose-zincate solution and passed immediately to a tentering frame where the goods are held out to width and then dried while tentered. The dry goods are then soured in dilute sulfuric acid, washed, can dried, padded through a solution of direct dye, and finally frame dried to width.

*Example 7*

The cellulose-zincate solution of Example 5 is applied to spun rayon.

The spun rayon fabric is padded through a solution of the cellulose-zincate solution which has been diluted down to one-third of the original cellulose content with a 4% caustic solution and is allowed to fall immediately into a large box containing 2% sulfuric acid in water. After passage through the sulfuric acid bath, the goods are washed thoroughly with water and are then dyed to shade in a dye tub or on a dye gig and are finally frame dried.

*Example 8*

Fabricated glass wool fibers are padded through a solution of the cellulose-zincate solution which has been diluted 50% with water. After that the fabric is immediately neutralized in dilute sulfuric acid.

In the above examples additional ingredients may be incorporated in the cellulose-zincate solution to give special effects.

Thus, there may be used a pigment or a dye. In such case the coloring material is precipitated and dried. Any kind of dye or pigment may be used so long as it is not decomposed or objectionably discolored by alkalinity of the cellulose solution. Even direct dyes may be used in this process as their inclusion in the cellulose film on the finished product makes them at least moderately fast.

Also, I may incorporate starch into the cellulose solution. Thus I may use potato, corn, or any usual laundry starch in the proportion of about 20 to 100 parts for 100 parts of dissolved cellulose. With the starch, there may be included any usual textile filler, so that the application of the solution and suspended material produces a backfilling of the textile.

There may be used agents to modify the film in the direction of greater plasticity such as oils, waxes, and flexibilizing resins such as alkyd resins, soft urea-formaldehyde resins, methacrylate resin, and the like. These agents if water-soluble may be applied in solution or if not soluble emulsified in the solution before application to the textile material.

My cellulose-zincate solution, being of relatively low viscosity for a given content of cellulose, penetrates well into the surface portions of penetrable textile material being treated and thus gives excellent anchorage of the cellulose after regeneration in the textile material.

For some purposes, however, I may include in the solution a wetting or penetrating agent. For this purpose I have found particularly suitable a minor proportion of one of the conventional sulfated higher alcohol wetting agents, a water-soluble protein condensation product, and sulfonated hydrocarbon wetting agents. The wetting agents selected should be not decomposable rapidly by 10% sodium hydroxide and should not cause precipitation of the cellulose from the cellulose solutions I have described. To avoid possible decomposition of certain wetting agents by the sodium hydroxide and premature precipitation of cellulose, I prefer to introduce the wetting agent, if used at all, into the cellulose solution immediately before the use of the solution so that only a very short time of contact of the wetting agent with the alkali cellulose solution is allowed before the solution is applied to the textile.

While cellulose-zincate solutions made as described above give outstanding results, less satisfactory solutions may be used if the high quality of the treated fabric is not to be maintained. Thus, there may be used solutions made by dissolving cellulose at ordinary temperatures in my zincate solution or at my low temperatures with different ratios of zinc to sodium hydroxide and different concentrations of the zincate solution from those described above. When, however, the cellulose is dissolved in the sodium zincate at ordinary room temperatures, there is produced a finished solution that is objectionably high in viscosity for a given concentration of dissolved cellulose, that does not penetrate well into the fabric being treated, that does not give the desired resistance to shrinkage of a treated fabric on being washed with water, and that does not carry pigments into the fabric so as to give the desired uniformity and depth of coloring when pigments are used. When zinc in ratios substantially above those shown are used, there is uneconomical use of the zinc and unnecessarily increased cost of the solution and the stability of the solution at low temperatures is adversely affected. When the ratio of zinc oxide to sodium hydroxide is much less than that shown above, then there is required for making the solution of cellulose even lower temperatures than those that are preferred with the optimum ratio of zinc oxide and there is produced, even with the use of abnormally low temperatures, a solution of the cellulose that is unstable at room temperatures. If one is prepared to accept these serious disadvantages, then any solution of cellulose in sodium zincate may be used.

It will be understood that certain details given are for the purpose of illustration, not restriction of the invention, and that variations within the spirit of the invention are intended to be included within the scope of the appended claims.

What I claim is:

1. In treating a textile material to provide a firmly adhering coating thereupon, the method

which comprises applying to the textile material a solution of unsubstituted cellulose dissolved in an aqueous alkali metal zincate solution containing an excess of alkali over the zinc present, contacting the textile material and applied solution with an agent causing precipitation of cellulose from the said solution upon the fabric, and washing the thus coated fabric to remove most but not all of the precipitating agent, the incomplete washing thus effected serving to remove most but not all of the zinc compound from the product.

2. In treating a textile fabric to provide a firmly adhering cellulose coating thereupon, the method which comprises applying to a cellulosic fabric a solution of unsubstituted cellulose in an aqueous solution of an alkali metal zincate containing an excess of alkali over the zinc present, precipitating cellulose from the said solution upon the fabric by the addition of an acid precipitating agent, washing with water to remove the precipitating agent until the pH becomes about 3 to 4, and then discontinuing the washing, the incomplete washing thus effected leaving a substantial proportion of zinc compound in the washed product.

3. The method described in claim 2, the said cellulosic fabric being viscose rayon.

4. In treating a textile material to provide a firmly adhering coating thereupon, the method which comprises applying to the textile a solution of unsubstituted cellulose in an aqueous alkali metal zincate solution containing an excess of alkali over the zinc present, precipitating the cellulose in the applied solution by treatment with an aqueous caustic alkali solution of concentration adequate to cause mercerization of cellulosic textiles, washing the resulting product to remove alkalinity therefrom, and then drying the washed material, the precipitation of the cellulose by the said caustic alkali solution and the subsequent washing and drying causing such firm bonding of the precipitated cellulose to the base fabric that there is no substantial loss of stiffness of the fabric on repeated laundering.

5. The method described in claim 1, the fabric used being composed of glass fibers, the precipitation being effected by the addition of acid and the alkali metal zincate solution causing a roughening of the surface of the glass fibers so that the cellulose when precipitated adheres to the surfaces and the cellulose coating which results from the treatment giving to the glass fabric dyeing properties characteristic of cellulose fabrics.

6. The method described in claim 2 which includes adding an alkaline zinc precipitating material after the said washing with water, so as to neutralize acid and convert to insoluble form zinc remaining at that stage.

7. The method of making a clean cellulosic fabric which comprises singeing an originally somewhat fuzzy fabric to degrade the cellulose fuzz and increase its solubility in sodium zincate solution, applying to the singed fabric a solution of unsubstituted cellulose in sodium zincate solution, then applying a precipitating agent to precipitate cellulose from the said solution as a coating upon the fabric, and washing and drying the product, the treatment described causing a part of the singed fuzz to dissolve in the sodium zincate solution and the rest of the fuzz to be obscured by the cellulose coating.



8. In treating a textile fabric to provide a firmly adhering cellulose coating thereupon, the method which comprises applying to the fabric a solution of unsubstituted cellulose in an aqueous solution of an alkali metal zincate containing an excess of alkali over the zinc present, precipitating cellulose from the said solution upon the fabric by adding an acid precipitating agent, then washing the treated textile with water to remove most but not all of the precipitating agent and zinc compound present, adding to the material so washed an alkaline zinc precipitating agent and then drying the product.

9. The method of treating cellulose textile material which comprises applying to the material an alkaline solution of unsubstituted cellulose in an aqueous sodium zincate solution, subjecting the material to treatment with an aqueous caustic alkali solution of mercerizing strength whereby said unsubstituted cellulose is precipitated on the material, and washing the material to remove alkalinity therefrom.

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## REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,085,783 | Aylsworth | Feb. 3, 1914 |
| 1,269,340 | Vanderkleed et al. | June 11, 1918 |
| 2,009,015 | Powers | July 23, 1935 |
| 2,072,770 | Reid | Mar. 2, 1937 |
| 2,129,708 | Schreiber | Sept. 13, 1938 |
| 2,204,859 | Hyatt et al. | June 18, 1940 |
| 2,322,427 | Edelstein | June 22, 1943 |
| 2,289,085 | Halewijn | July 7, 1942 |
| 2,299,612 | Clayton et al. | Oct. 20, 1942 |

FOREIGN PATENTS

| Number | Country | Date |
|---|---|---|
| 320,062 | Great Britain | Oct. 2, 1929 |

OTHER REFERENCES

Trotman, Bleaching, Dyeing and Chem. Tech. of Textile Fibres, 1925, Griffin & Co. Ltd., London, page 336. (Copy in Div. 43.)

Salvin, Influence of Zinc Oxide on Paint Molds, Ind. & Eng. Chem., vol. 36, No. 4, April 1944. pages 336–340.