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SIZING FABRIC

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This invention relates to the sizing of fabrics and more particularly to the sizing of fabrics with low-substituted cellulose ethers.

The sizing of textiles is a process which is old and well-known, and one which is extensively practiced. The sizing materials at present used, however, suffer from certain disadvantages, one of the most important of which is their relatively low laundering fastness.

A large number of alkyl celluloses of varying properties have been made. These alkyl celluloses vary in their properties, depending both upon the degree of degradation of the cellulose and the extent of alkylation. Thus, there are the following types of alkyl celluloses:

1. Alkyl celluloses soluble only in organic solvents.
2. Alkyl celluloses soluble in water or organic solvents.
3. Alkyl celluloses soluble in water but insoluble in organic solvents.
4. Alkyl celluloses soluble in aqueous alkali at ordinary temperature but insoluble in water.
5. Alkyl celluloses soluble in water at low temperatures but insoluble in water at ordinary temperatures.
6. Alkyl celluloses soluble in aqueous alkali at low temperatures, for example, near the freezing point of the solutions, but insoluble in aqueous alkali at ordinary temperatures, for example, 20° C. or higher and insoluble in water at any temperature.

This invention has as an object the provision of a method of treating fabrics to give them a greatly improved finish as revealed by the appearance and feel.

A further object is the provision of a textile whose finish is substantially fast to laundering. A still further object of the invention is a fabric thus treated. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a fabric, thread, or yarn is impregnated with an aqueous caustic alkali solution of an alkyl cellulose insoluble in aqueous caustic alkali at ordinary temperature but soluble therein at low temperatures, and the impregnated fabric, thread, or yarn thereafter treated with an acid to insolubilize the alkyl cellulose.

In carrying out the process of the present invention textile fabrics, threads, or yarns are treated with a solution of a low-substituted alkyl cellulose which is soluble in aqueous caustic alkali only on cooling. This particular type of alkyl

cellulose, which after once being put into solution at low temperature, may be warmed to room temperature without precipitation, is described in co-pending application of Deane C. Ellsworth and Frederick C. Hahn, Serial No. 681,760, filed July 22, 1934. The preparation of these alkyl celluloses is briefly described below in order to define the material to be used in accordance with the teachings of the present invention.

Cellulose is steeped in caustic alkali solution, the excess solution pressed out to leave a moist alkali cellulose which is then shredded. The alkali cellulose is then aged for longer or shorter time, for example, 7 to 48 hours at 25° C., but preferably not beyond 24 hours at 28° C. or 48 hours at 20° C. The aged alkali cellulose is then etherified at temperatures not above 50° C. and preferably approximately 40°–42° C. with an alkylating agent in amount generally about 1/2 mole to 1 mole per C₆ unit of the cellulose. The etherification reaction is promptly terminated when the desired degree of substitution has been effected. The proper stage of etherification at which to terminate the reaction is readily determined by removing samples of the reaction mixture from time to time, placing them in dilute caustic, and cooling to freezing. If a few drops of the solution, warmed again to room temperature, are then placed between glass plates and the plates pressed or rubbed against each other, a good product will remain clear, while insoluble fibers will readily be noted in an incompletely reacted product. In general, the products contain from 0.25 to 0.60 alkyl groups per C₆ unit of the cellulose. Further details may be found by referring to the above described application.

The reaction products, upon the attainment of the degree of etherification desired, may be washed and dried, or may be washed only and pressed out or may even be used without any purification. In any case, the material is then mixed with sufficient water and caustic to make a solution of desirable concentration, preferably around 6% of the derivative in aqueous caustic alkali, preferably 6% to 8%. This mixture is cooled to a suitable temperature from -5° to -15° C., the mixture being stirred, or the mixture may be frozen. The solution so obtained may be brought back to room temperature, filtered if desired, and used according to the process of the present invention.

For the purpose of treating textiles, a solution containing from 0.25 to 15% of the alkyl cellulose, and from 4% to 9% alkali may be used. Very

little effect is imparted to fabrics, yarns, etc., by treatment with less than 0.25% solution of the alkyl cellulose. Solutions containing more than about 15% of alkyl cellulose are difficult to make without too much degradation of the cellulose, and, furthermore, such solutions in general render the fabric too stiff for most purposes, altho for some special purposes such stiffness is of advantage, e. g., in making stiff collars for shirts. For most purposes, a solution containing from 1% to 10% alkyl cellulose is satisfactory. In general, it is impossible to dissolve this particular type of alkyl cellulose in less than 4% alkali, and a solution of caustic more concentrated than about 10% may cause gelation of the solution. The optimum concentration of alkali is between approximately 5% and approximately 9%.

The process is generally applicable to alkyl celluloses soluble in dilute aqueous caustic alkali at low temperatures approximating the freezing point, but insoluble therein at higher temperatures approximating room temperature, e. g., 20° to 25° C. Because of the ready preparation of lower alkyl celluloses such as methyl and ethyl cellulose, these lower alkyl celluloses of the above indicated alkali solubility characteristics, are preferred.

Fabrics, threads, and yarns of all kinds may be treated according to the process of the present invention. Thus, cotton, linen, rayon, wool, and silk yarns, threads, or fabrics, or fabrics such as wool and fur felts may be treated with the particular alkyl celluloses above indicated. Cotton fabrics best lend themselves to the processes of the present invention and all types of cotton fabrics ranging from the light voiles and organ-dies, sheeting material and dress goods, to the heavier Indian Head fabrics and men's suiting materials may be satisfactorily treated with the sizing agents of the present invention.

The textile to be treated is passed thru a solution of the alkyl cellulose, then thru squeeze rolls to remove excess solution. The pressure on the rolls may be varied and likewise the concentration of the solution may be varied in order to regulate the amount of alkyl cellulose sized on the fabric. After passing thru the squeeze rolls, the fabric is passed into a bath of dilute acid to coagulate the alkyl cellulose on the fabric. Various acids may be used, acetic, sulfuric, and hydrochloric being satisfactory. The acid bath may be used at elevated or ordinary temperatures, but to avoid tendering the fabric, the temperature of the coagulating bath should not be much above 120° F., and the acid concentration should be so chosen as not to exceed that necessary to secure complete and rapid coagulation of the alkyl cellulose. A 5% solution of sulfuric acid, or a 7.5-10% solution of acetic acid has been found to be quite satisfactory, but the concentrations are not to be limited to these values. More or less concentrated acid than above indicated may be used in certain cases. If acetic acid is used to coagulate the alkyl cellulose, the fabric need merely be rinsed after passing thru the acid bath and thru squeeze rolls, and may then be dried or calendered or given any other desired treatment. Because of the strength of the mineral acids, it is desirable to follow a coagulation thereby with a soap scour of about 20 minutes at 120° F. to remove the last traces of the acid from the cloth before drying lest it be tendered by the remaining traces of the mineral acid on drying.

The scope of the process of the present invention is not necessarily limited to an actual liquid

coagulating bath. The fabric impregnated with the aqueous caustic alkali solution may be passed thru coagulating chambers containing the vapors of weak organic acids, such as formic or acetic. These processes are, however, less convenient than the liquid coagulating bath.

An improved luster may be obtained on textiles, yarns, or threads treated according to the process of the present invention, if these are impregnated under tension or stretched after impregnation or during the coagulation of the alkyl cellulose on the fabric.

From the above description of the process it is evident that a great many factors may be varied. The exact conditions to be used in a particular case will depend upon the fabric to be treated and the effect which it is desired to produce.

The following examples illustrate some of the possibilities of the process of the present invention. These are included for purposes of illustration and not in limitation.

Example 1

Twenty g. of methyl cellulose containing an average of one methyl group for every two glucose units of the cellulose molecule (or, in other words, $\frac{1}{2}$ methyl group per glucose unit) prepared according to the above described process, which is more fully described in U. S. patent application 681,760, was well mixed with 180 g. of water and allowed to stand one hour to insure complete wetting. To the slurry thus obtained was added 200 g. of a 10% solution of sodium hydroxide cooled to room temperature. The slurry was thoroughly mixed and then cooled over night to -20° C. The material froze solid and the fibers of methyl cellulose disappeared. It was allowed to warm up to room temperature whereupon a viscous, light-colored solution was obtained.

Example 2

A portion of the solution obtained as in Example 1 above was diluted with an equal weight of 5% solution of sodium hydroxide. A handkerchief lawn was treated with this solution, run thru squeeze rolls to remove excess solution, and immersed for 2.5 seconds in a bath of 10% acetic acid solution heated to 120° F., rinsed in water and dried by ironing. By this treatment the handkerchief lawn had imparted to it a pleasant and fuller feel and appearance, and a greater degree of stiffness. These desirable characteristics of the fabric were not appreciably affected by laundering for one hour at 170° to 180° F. in a solution containing 0.25% neutral soap and 0.1% soda ash in a standard launderometer. Ordinary sizes such as starch are practically completely removed by this launderometer test.

Example 3

A sample handkerchief lawn was treated with a 2.5% methyl cellulose solution as in Example 2 except that it was immersed for three minutes in the acetic acid solution instead of for 2.5 seconds. The treated fabric had a pleasant feel and appearance and was stiffer and fuller than the untreated fabric. The effect was resistant to laundering.

Example 4

A portion of the solution described in Example 1 was diluted to a 3.5% solution of methyl cellulose with 5% caustic solution, and the resulting solution used for treating a piece of hankkerchief lawn according to the procedure in Example

3. It was stiffer and fuller than the fabrics prepared in Examples 2 and 3. The effect was likewise relatively laundry-fast, in comparison with the effect produced by ordinary starch sizes.

Example 5

A sample of men's cotton suiting material (woven to look like linen), was treated with a 2.5% solution of the methyl cellulose described above, according to the procedure in Example 3. A substantially permanent finish, stiff and somewhat linen-like, was obtained.

Example 6

A sample of an Indianhead-type fabric (a coarse harsh cotton fabric), was treated with a 3.5% solution of methyl cellulose according to Example 4. The treated fabric was stiffer and fuller than the treated fabric described in Example 5. The sizing effect was resistant to laundering.

Example 7

Twenty g. of methyl cellulose prepared in accordance with the process disclosed in application Serial No. 681,760 and obtaining $\frac{1}{4}$ of a methyl group per glucose unit was thoroughly mixed with 180 g. of water and allowed to stand one hour. To the slurry thus obtained was added 200 g. of a 10% solution of sodium hydroxide cooled to room temperature. After thorough mixing, the slurry was frozen by cooling overnight at -20°C . On warming up to room temperature, a viscous, light-colored solution was obtained.

Example 8

A portion of the solution of Example 7 was diluted with an equal weight of 5% sodium hydroxide solution to give a solution containing 2.5% methyl cellulose and 5% alkali. A sample of handkerchief lawn was treated with this solution by the same procedure as described under Example 2. The treated fabric was fuller and stiffer than the untreated fabric and had a more pleasant feel and better appearance. The finish was not removed by several repeated launderings.

Example 9

A handkerchief lawn was treated according to Example 3 with the solution described in Example 8. The results were similar to the results obtained in Example 3.

Example 10

A portion of the solution described in Example 7 was diluted to 3.5% methyl cellulose with 5% sodium hydroxide. This solution was used to treat a sample of handkerchief lawn according to the procedure of Example 3. The effects were similar to the effects obtained in Example 3.

Example 11

A sample of Indianhead-type fabric was treated according to Example 9. The effects were similar to the effects obtained in Example 5.

Example 12

An unsized sample of Indianhead-type fabric was treated according to Example 10. The effects were similar to the effects obtained in Example 6.

Example 13

Twenty g. of methyl cellulose prepared according to the process disclosed in application Serial

No. 681,760 and containing $\frac{1}{4}$ of a methyl group per glucose unit were thoroughly mixed with 180 g. of water and allowed to stand one hour to insure complete wetting. To the slurry thus obtained was added 200 g. of a 10% solution of sodium hydroxide cooled to room temperature. The mixture was then frozen by cooling overnight at -20°C . On warming to room temperature, a light-colored solution was obtained.

Example 14

A portion of the solution prepared in Example 13 was diluted with an equal weight of 5% sodium hydroxide to give a solution containing 2.5% methyl cellulose and 5% alkali. This solution was used for treating a piece of handkerchief lawn according to Example 2. The effect was similar to the effect obtained in Example 2 and Example 8.

Example 15

A sample of handkerchief lawn was treated with the solution of Example 14 according to the procedure in Example 3. The effects obtained were similar to the effects obtained in Example 3 and Example 9.

Example 16

The solution used in Example 13 was diluted to 3.5% methyl cellulose with a 5% solution of sodium hydroxide. The resulting solution was used for treating a sample of handkerchief lawn according to the procedure of Example 6. The treated fabric was similar to the fabrics obtained in Example 4 and Example 10.

Example 17

An Indianhead-type cotton fabric was treated according to Example 16. A substantially permanent sizing and stiffening effect was obtained similar to that obtained in Examples 6 and 12.

Example 18

A 5% solution was made, by the procedure of Example 1, of a methyl cellulose prepared according to the process disclosed in application Serial No. 681,760 and containing $\frac{1}{4}$ methyl group per glucose unit. A sample of 48/48 cotton fabric was impregnated with this solution, run thru squeeze rolls to remove excess solution, and then immersed for 2 minutes in 10% sulfuric acid to coagulate the methyl cellulose on the fabric. The fabric was then rinsed thoroughly with water and dried by ironing. A good sizing effect was obtained and was not removed by boiling one hour in 0.5% neutral soap solution.

Example 19

A portion of the methyl cellulose solution described in Example 18 was diluted to 2.5% methyl cellulose with sodium hydroxide and used to treat a piece of 48/48 cotton fabric according to the procedure of Example 18. A good sizing effect was obtained but less pronounced than in the preceding example. The finish imparted rather linen-like properties to the fabric and was not removed by laundering one hour at the boil in 0.5% neutral soap solution.

Example 20

A sample of unfinished cotton voile was treated with the methyl cellulose solution described in Example 18, then immersed for 2 minutes in 5%

acetic acid to coagulate the methyl cellulose on the fabric. The fabric was then rinsed and dried by ironing. An organdy effect was obtained which was not lost on laundering.

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Example 21

The solution described in Example 18 was diluted to 2.5% methyl cellulose with 5% sodium hydroxide and the resulting solution used for treating a 48/48 unfinished cotton fabric. The fabric was then immersed for 3 minutes in 10% sulfuric acid at 120° F. to coagulate the methyl cellulose, rinsed thoroughly, and dried by ironing. A substantially laundry-fast finish was obtained.

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Example 22

A 48/48 unfinished cotton fabric was sized as in Example 21 except that 25% acetic acid was used instead of 10% sulfuric acid for coagulation of the methyl cellulose. The results were substantially the same as those obtained in Example 21.

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Example 23

A sample of 48/48 fabric was treated as in Example 21 except that 10% acetic acid was used instead of 10% sulfuric acid to coagulate the methyl cellulose. The results obtained were comparable with those obtained in Example 21.

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Example 24

A sample of 80/60 cotton fabric was treated according to the procedure of Example 21 except that 10% acetic acid was used instead of 10% sulfuric acid to coagulate the methyl cellulose. A substantially permanent, rather linen-like finish, was obtained.

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Example 25

A sample of 80/60 cotton fabric was treated with a 10% solution of methyl cellulose in 6% sodium hydroxide, the methyl cellulose containing approximately one-half methyl group per glucose unit. A substantially permanent finish was obtained.

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Example 26

An unfinished cotton fabric was impregnated with a 5% solution of an ethyl cellulose containing $\frac{1}{4}$ of an ethyl group per glucose (C₆) unit. The solution was prepared by treating the ethyl cellulose with a 7% sodium hydroxide solution and cooling to -20° C. After impregnation the fabric was immersed for 1 minute in 5% sulfuric acid, rinsed in water, then soaped for 10 minutes at 60° C. It was dried by ironing. The fabric was made stiffer and fuller by the treatment and the effect was substantially laundry-fast as compared to the ordinary sizes containing starch.

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Example 27

A light unfinished cotton fabric suitable for an organdy finish was treated with a 15% solution of a methyl cellulose in 6% caustic, the methyl cellulose containing one-half methyl group per glucose unit. After impregnation, the fabric was treated in a bath of 0.5 molar sulfuric acid and 0.5 molar sodium sulfate. A stiff, organdy effect was obtained on the fabric.

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Instead of the coagulation bath used in Example 27, any of the following baths will give satisfactory results:

1. Acetic acid (2.0 molar, or approximately 12%).

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2. Sulfuric acid (0.5 molar) plus sodium chloride (1.0 molar).

3. Sulfuric acid (0.5 molar) plus ammonium sulfate (0.5 molar).

4. Sulfuric acid (0.5 molar) plus magnesium sulfate (0.1 molar).

5. Sulfuric acid (0.5 molar) plus potassium chromium sulfate (0.1 molar).

6. Sulfuric acid (0.5 molar) plus stannic ammonium chloride (0.1 molar).

7. Acetic acid (2.0 molar) plus sodium acetate (0.5 molar).

8. (a) Sodium sulfate (2.0 molar) followed by (b) sulfuric acid (0.5 molar).

9. Ammonium sulfate (18%) plus ammonium hydroxide (0.2%) followed by (10), (11), or (12).

10. Sulfuric acid (11%).

11. Sulfuric acid (8%) plus sodium sulfate (26%), plus dextrose (4%).

12. Sulfuric acid (13%) plus sodium sulfate (18%).

As compared with treatment of fabrics with alkyl celluloses from organic solvent solutions, the process of the present invention has certain advantages. One class of these advantages deals with the procedural convenience involved in using aqueous solutions. Thus, sizing with organic solvent solutions increases fire and explosion hazards and is distinctly a hazard to the health of the worker. In addition, because of these hazards special equipment other than that ordinarily in use must be employed. The sizing process of the present invention has further advantages resulting from the different effect produced with a given concentration of size upon the fabric. Sizing by the present process results in a less harsh effect and a more linen-like finish. This is probably connected with the greater penetration of the sizes of the present invention.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. Process of sizing fabrics with water insoluble methyl cellulose which is dissolved by aqueous caustic soda at low temperatures approximating the freezing point but not dissolved by the same at ordinary temperature, which comprises impregnating a cotton fabric with a solution containing approximately 2.5% of said methyl cellulose containing approximately $\frac{1}{2}$ methyl group per glucose unit, said solution also containing approximately 5% caustic soda, removing excess solution from the fabric and coagulating the methyl cellulose on the fabric by treatment with 10% acetic acid, and thereafter drying.

2. The process of producing adherent water insoluble laundry-fast sizing on fabrics with water insoluble methyl cellulose which is dissolved by dilute aqueous caustic soda at low temperatures approximating the freezing point but not dissolved by the same at ordinary temperature, which comprises impregnating a cotton fabric with a dilute aqueous caustic alkali solution of said methyl cellulose, and thereafter coagulating the methyl cellulose on the fabric by exposure to a weak acid.

3. The process of producing adherent water insoluble laundry-fast sizing on fabrics with water insoluble ethyl cellulose which is dissolved by dilute aqueous caustic soda at low temperatures near the freezing point thereof but not dissolved

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by the same at ordinary temperature, which comprises impregnating a cotton fabric with a dilute aqueous caustic alkali solution of said ethyl cellulose, and thereafter coagulating the ethyl cellulose on the fabric by exposure to a weak acid.

4. The process of producing adherent water insoluble laundry-fast sizing on fabrics with water insoluble lower alkyl cellulose which is dissolved by dilute aqueous caustic soda at low temperatures approximating the freezing point but not dissolved by the same at ordinary temperature, which comprises impregnating a cotton fabric with a dilute aqueous caustic soda solution of said lower alkyl cellulose, and thereafter coagulating the lower alkyl cellulose on the fabric by exposure to a dilute acid.

5. The process of producing adherent water insoluble laundry-fast sizing on fibrous materials with water insoluble lower alkyl cellulose which is dissolved by dilute aqueous caustic alkali at low temperatures approximating the freezing point but not dissolved by the same at ordinary temperature, which comprises impregnating a fibrous material with a dilute aqueous caustic soda solution of said lower alkyl cellulose, and thereafter coagulating the lower alkyl cellulose on the fibrous material by exposure to a dilute acid.

6. The process of producing adherent water insoluble laundry-fast sizing on fibrous material which comprises impregnating a fibrous material with a low substituted water insoluble lower alkyl cellulose dissolved in aqueous caustic soda of 4-10% strength, said alkyl cellulose being water insoluble and undissolved by dilute aqueous caustic soda at room temperature but dissolved therein at temperatures approximating the freezing point and thereafter coagulating the said alkyl cellulose on the fibrous material by treatment with an acidic coagulant.

7. A fabric having an adherent water insoluble laundry-fast sizing of a low substituted water insoluble lower alkyl cellulose, said alkyl cellulose being water insoluble and undissolved by dilute aqueous caustic soda at room temperature but dissolved therein at temperatures approximating the freezing point.

8. A fabric having an adherent water insoluble laundry-fast sizing of a low substituted water insoluble lower alkyl cellulose, said lower alkyl cellulose being water insoluble and undissolved by 6% aqueous caustic soda at room tem-

perature but dissolved therein at temperatures approximating the freezing point.

9. A fabric having an adherent water insoluble laundry-fast sizing of a low substituted water insoluble ethyl cellulose, said ethyl cellulose being water insoluble and undissolved by 6% aqueous caustic soda at room temperature but dissolved therein at temperatures approximating the freezing point.

10. A fabric having an adherent water insoluble laundry-fast sizing of a low substituted water insoluble methyl cellulose, said methyl cellulose being water insoluble and undissolved by 4% aqueous caustic soda at room temperature but dissolved therein at temperatures approximating the freezing point.

11. A fibrous material having an adherent coating of a low substituted water insoluble lower alkyl cellulose, said alkyl cellulose being of such degree of substitution and degradation that it is undissolved by 6% aqueous caustic soda at ordinary room temperatures but is dissolved by 6% aqueous caustic soda at temperatures above and near the freezing point thereof, the said coating constituting a laundry-fast water insoluble sizing.

12. The process of producing adherent water insoluble laundry-fast sizing on fibrous materials which comprises impregnating a fibrous material with a dilute aqueous caustic alkali solution of a water insoluble lower alkyl cellulose and thereafter coagulating the lower alkyl cellulose on the fibrous material, the said alkyl cellulose being water insoluble and undissolved by dilute aqueous caustic soda at ordinary room temperatures but dissolved by aqueous caustic soda at temperatures above and near the freezing point thereof.

13. The process of producing adherent laundry-fast sizing on textiles without deleteriously affecting the water absorptivity of the textile which comprises impregnating the textile with a dilute aqueous caustic soda solution of a water insoluble alkyl cellulose whose alkyl substituents belong to the group consisting of ethyl and methyl, and thereafter coagulating the alkyl cellulose on the textile by treating the impregnated material with a dilute acid, the said alkyl cellulose being of such degree of substitution and degradation that it is not dissolved by 6% aqueous caustic soda at ordinary room temperatures but is dissolved by 6% aqueous caustic soda at temperatures approximating the freezing point.

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