

1

2,693,427

TREATMENT OF TEXTILE AND CELLULOSIC MATERIAL

Carleton L. Kingsford, Malden, Mass., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application July 30, 1947,
Serial No. 764,903

9 Claims. (Cl. 117—56)

The present invention relates to improved methods of applying colloidal silica to textile materials and cellulosic materials other than textile materials whereby the treated materials possess a high coefficient of friction, an excellent slip resistance and a substantially unaltered hand or feel and whereby treated textile materials such as knitted hosiery possess excellent resistance to snagging and running.

In order to impart to textile materials and cellulosic materials other than textile materials a high coefficient of friction and an excellent slip resistance by means of a colloidal silica treatment, relatively high concentrations of colloidal silica have generally been employed heretofore. In accordance with the present invention relatively dilute solutions of colloidal silica are employable in a manner which substantially exhausts the colloidal silica from the solution.

Accordingly, one object of the invention is to provide a method of exhausting colloidal silica from a dilute silica sol unto a textile material and a cellulosic material other than a textile material in sufficient quantities to impart a high coefficient of friction and excellent slip resistance to such materials and to impart to textile materials such as knit fabrics or hosiery excellent resistance to snags and runs and accomplishing these results without substantially altering the feel or hand of the material.

This and other objects of the invention are generally carried out by treating a textile material and a cellulosic material other than a textile material with a solution containing a cationic surface active agent and then further treating the material with a dilute solution of colloidal silica. Another embodiment of the invention is generally carried out by treating textile materials and cellulosic materials other than a textile material with a solution containing a cationic surface active agent and an inorganic salt and then further treating the material with a dilute solution of colloidal silica. Although a preferred method of operation and modifications thereof are hereinafter described, other methods may be used and other modifications will be apparent to those skilled in the art.

In accordance with the invention a textile or other cellulosic material, preferably a size-free woven or knitted fabric is wetted for a suitable length of time by the employ of a liquid bath containing a suitable amount, preferably from 0.1 to 2% based on the bath of a cationic surface active agent as for example cetyl dimethyl benzyl ammonium chloride. The treatment is preferably carried out for a period of from 30 to 60 minutes. The liquid bath is preferably an aqueous long bath having a suitable liquid to fabric ratio as for example, from 50 to 200 parts of liquid to 1 part of fabric being treated which may be expressed, for example, as a ratio of 50:1 to 200:1. The temperature of the bath is preferably maintained between 70 to 100° C., although other temperatures may be used depending upon the length of treating time desired. Although the fabric may be treated with the liquid bath by continuous immersion, alternate dipping and draining, spraying and the like, it is preferred to employ a dye beck, a dye jig or any other suitable equipment of a similar type.

After the fabric has been treated or immersed as given above for the desired period of time, it may be immediately treated with colloidal silica, although it is preferred to rinse the fabric prior to the colloidal silica treatment. In addition, it is preferred to extract excess solution from the fabric at this stage of treatment, al-

2

though this is not essential. Extraction may be accomplished by padding, hydroextraction, wringing and the like, although hydroextraction is preferred particularly when extracting excess solution from knit fabrics or hosiery.

The above conditions may, of course, be varied to some extent. For example, the liquid bath may be a short bath or have other liquid to fabric weight ratios than those hereinbefore specified. Moreover, other proportions of cationic surface active agents may be used and the length of time the fabric is treated may be varied considerably. In addition, when treating delicate knit fabrics, it is generally desirable to enclose such fabrics in an open mesh fabric or cheesecloth bag although this step is not essential. Protective coverings of this type not only serve to prevent a substantial amount of accidental damage, but, in addition, they can be formed together into a chain or continuous strip by sewing one to another. The covered knit fabrics may then be treated in the type equipment hereinbefore described, in a drum compartment tumbler or in other suitable types of equipment or even by hand if desired, although it is preferred to use a drum compartment tumbler for this purpose.

A wide variety of cationic surface active agents may be used, as for example, surface active quaternary ammonium salts, quaternary phosphonium salts and sulfonium salts. Compounds of the above type containing at least one hydrocarbon or suitably substituted hydrocarbon radical having preferably from 10 to 22 carbon atoms are especially suitable for use according to the invention. As examples of such compounds may be mentioned cetyl dimethyl benzyl ammonium chloride, cetyl methyl dibenzyl ammonium chloride, stearyl dimethyl ethyl ammonium bromide, lauryl dimethyl benzyl ammonium iodide, cetyl pyridinium sulfate or chloride, lauryl pyridinium chloride, methyl 6-cetyl quinolinium chloride, cetyl diethyl sulfonium chloride, stearyl trimethyl phosphonium chloride, cetyl dimethyl benzyl phosphonium chloride and the like. Moreover, suitable mixtures of the above cationic surface active agents may be used.

In accordance with another embodiment of the invention, an appropriate amount preferably from 0.02 to 0.1% of a suitable inorganic salt may be used along with the cationic surface active agent in the liquid bath. Although the above concentrations of inorganic salts are preferred, other concentrations may be used. Moreover, as suitable inorganic salts may be mentioned water-soluble salts of mono, di and tri-valent metals which are generally usable as dyeing assistants for direct cotton dyes, as for example, NaCl, BaCl₂, Na₂SO₄, Al(CHO₂)₃, Al(CH₃CO₂)₃ and the like. In general, the employ of salts of the above type results in a higher degree of colloidal silica exhaustion or a higher degree of fixation of the colloidal silica to the fabric. Moreover, woven fabrics or knit fabrics treated according to this embodiment of the invention and then further treated with colloidal silica possess a high coefficient of friction and excellent slip resistance and, furthermore, retain these characteristics to a high degree after a substantial number of home launderings. When this embodiment of the invention is employed, the other conditions of operation are preferably the same as have already been described hereinbefore, although other methods and modifications may be used.

After the fabric has been treated in accordance with the above methods or embodiments, it is further treated whether extracted or not, but preferably while still wet for an appropriate length of time, as for example, from 30 to 60 minutes with a liquid bath containing a suitable amount, preferably, from 0.01 to 0.2% of colloidal silica calculated as SiO₂. The liquid bath is preferably an aqueous long bath having, as for example, a liquid to fabric weight ratio of from 50 to 200 parts of liquid to 1 part of fabric being treated which may be expressed, for example, as a ratio of 50:1 to 200:1. The fabric is preferably prevented from becoming dry after treatment with the cationic agent and prior to the treatment in this bath either by treating it immediately or by temporarily storing it in clear water for a suitable period of time, that is, for a period of preferably not more

than 6 hours. During the treatment the liquid bath is maintained at a suitable temperature and pH, as for example, a temperature of about 75 to 100° C. and a pH of about 6 to 7, although the temperature may be lower than 75° C. and the pH may be above or below the values indicated above depending upon the duration of treating time desired and the type material being treated. The same types of equipment as hereinbefore described or other types of equipment and even hand manipulation may be used.

The above conditions may, of course, be varied to some extent if desired. For example, the bath may have higher or lower liquid to fabric weight ratios than those specified and the duration of treating time may be less than 30 minutes or greater than 60 minutes. Moreover, the bath may contain more and even less colloidal silica depending upon the degree of slip resistance, or in the case of knit fabrics, the degree of resistance to snags and runs desired. However, it is preferred to avoid relatively high concentrations as in that case the colloidal silica tends to dust off after the fabric has been dried and, in addition, excessive quantities of colloidal silica would be lost when the treating bath is discharged to the sewer.

A preferred source of colloidal silica is a silica sol containing from 0.1% to 20% or more of SiO₂. A portion of the sol may be added to the liquid bath until the desired concentration of SiO₂ is attained and the pH may then be adjusted to the desired value or the pH of the silica sol may be adjusted to the desired value and the sol may then be diluted until the desired SiO₂ concentration is attained. In the latter case, the diluted sol may be used as the liquid bath. In general, the liquid bath containing colloidal silica is prepared just prior to the fabric treatment.

For purposes of the invention a silica sol capable of being diluted and stable for a period of time in an aqueous solution is preferred. Such a sol may be prepared, as described in Example I, in accordance with U. S. Patent to John F. White, Number 2,375,738. Sols of this type generally have a pH of from about 9 to 10 as initially prepared and may be adjusted by acid addition to a lower pH if desired, depending upon the type fabric or material being treated. Moreover, dilute, acidified sols of the above type are generally stable for a suitable period of time.

Other types of silica sols may also be used as for example the sols prepared by reacting water-soluble silicates with an acid and subjecting the acidified silicate to treatment with alcohol and/or cooling to remove the electrolyte as described in U. S. Patent to Morris D. Marshall, No. 2,285,449, and U. S. Patent to John F. White, No. 2,285,477. It is also possible to use sols prepared by treatment of an alkali silicate with ion-exchange material, as described in U. S. Patent to Paul G. Bird, No. 2,244,325.

After the fabric has been immersed in the colloidal silica solution for the desired length of time, it is generally finished by rinsing in clear water followed by drying at a suitable temperature preferably from 200 to 225° F., although other drying temperatures and even room temperature may be used.

If a dyed fabric or material is desired as the finished product, it is generally desirable to dye the fabric or material a shade which is about 50% heavier than is normally desired prior to the treatment. By dyeing prior to treatment, it is possible to obtain a more uniform and consistent control of shade and depth of color in the finished goods. However, the fabric or material may be dyed after treatment in which case dyeing may be accomplished after the fabric has been rinsed or after it is dried. In general, when dyeing is accomplished after the two-bath treatment, it is usually necessary to readjust the dye formula since the natural dyeing characteristics of the fabric or material are generally altered as a result of the treatment.

A further understanding of the invention will be obtained from the following examples, which are illustrative but not limitative of the present invention.

EXAMPLE I

Preparation of a silica sol

Seventy-three pounds of 66° Bé. H₂SO₄ are diluted with 358 pounds of water and charged to a mixing tank.

Four hundred and seventy-two pounds of a sodium silicate solution analyzing 8.9% Na₂O and 29% SiO₂ are diluted with 337 pounds of water and added with stirring to the acid solution. The mixture sets to a gel a few minutes after the mixing is completed. After 16 hours ageing, the syneresis liquor is siphoned off and the gel crushed to one-inch lumps. These lumps are washed with a continuous flow of water for 16 hours and the washed gel is then covered with 750 pounds of water containing 0.9 pound of NaOH. After standing 6 hours the excess solution is drained off and a portion of the gel is charged to an autoclave. The gel is heated for 3 hours, using steam at 215 pounds per square inch absolute pressure in the jacket of the autoclave. The contents of the autoclave are then blown out and the small amount of residual, undispersed gel is removed by filtration. The solution so produced contains about 12.5% SiO₂ and can be diluted to concentrations as low as 0.1% if desired.

EXAMPLE II

A sample of white wool flannel is treated by the employ of a dye jig for 45 minutes in an aqueous long bath having a liquid to fabric weight ratio of 200:1 and containing 0.5% cetyl dimethyl benzyl ammonium chloride based on the bath, and this concentration of cationic surface active agent is maintained substantially constant. The bath is maintained at a temperature of 80° C. during the treating period. Excess solution is removed by the employ of squeeze rolls and the fabric after washing in plain water is then further treated while still wet for a period of 45 minutes in an aqueous long bath (150:1) containing 1% of the silica sol as prepared in Example I, that is the bath contains about 0.125% SiO₂. The bath is maintained at a temperature of approximately 90° C. and at a pH of about 7 during the treating period. The fabric is then rinsed with clear water and dried at a temperature of 225° F.

A sample of heavy cotton sheeting is treated in the same manner as described above.

Both fabrics have a high coefficient of friction and a high degree of slip resistance and are substantially unaltered in hand or feel. Moreover, they retain these characteristics after a substantial number of home launderings.

An analysis of each of the above aqueous solutions of colloidal silica before and after the fabric treatment shows the following results:

	Percent SiO ₂ Prior to Treatment	Percent SiO ₂ After Treatment	Percent Exhaustion
Wool flannel	0.125	0.085	32
Cotton sheeting	0.125	0.104	17

The per cent exhaustion is calculated according to the following formula:

$$\frac{\text{Percent SiO}_2 \text{ prior to treatment} - \text{percent SiO}_2 \text{ after treatment}}{\text{percent SiO}_2 \text{ prior to treatment}} = \text{percent exhaustion}$$

EXAMPLE III

A size-free miracle cloth (spun regenerated cellulose or rayon) is treated in a dye beck for a period of about 60 minutes with an aqueous long bath having a liquid to fabric weight ratio of 50:1, said bath containing 0.3% of cetyl dimethyl benzyl ammonium chloride and 0.03% of BaCl₂ both based on the bath and the concentrations of these ingredients are maintained substantially constant during the treating period. The bath is maintained at a temperature of about 70° C. during the immersion period. The fabric is given a short wash in clear water, is hydroextracted and then further treated, while still wet, in another aqueous long bath having a liquid to fabric weight ratio of 50:1 for a period of 60 minutes, said bath contains 0.2% by weight of the silica sol as prepared in Example I, that is, the bath contains 0.025% SiO₂. This bath is maintained at a temperature of about 80° C. and at a pH of about 6 during the treating period. The fabric is then rinsed in clear water and dried at a temperature of 225° F.

A size-free cellulose acetate fabric is treated in the same manner as described above.

5

A size-free nylon flare chute is treated in the same manner as described above except that the first and second long baths have a liquid to fabric weight ratio of 150:1.

All three of the above fabrics possess a high coefficient of friction, a high degree of slip resistance and are substantially unaltered in hand or feel. Moreover, they retain these characteristics after a substantial number of home launderings.

An analysis of each of the above employed aqueous solutions of colloidal silica before and after the fabric treatment shows the following results:

	Percent SiO ₂ Prior to Treat- ment	Percent SiO ₂ After Treatment	Percent Exhaus- tion
Miracle cloth.....	0.025	0.0025	90
Cellulose acetate fabric.....	0.025	0.020	20
Nylon flare chute.....	0.025	0.0175	30

EXAMPLE IV

Dyed and size-free nylon stockings are enclosed in a cheesecloth bag and are then immersed with agitation for a period of 60 minutes in an aqueous long bath (150:1), said bath containing about 0.1% cetyl dimethyl benzyl ammonium chloride and about 0.02% BaCl₂ both based on the bath. The concentrations of the above ingredients are maintained substantially constant during the treating period and the temperature of the bath is maintained at approximately 70° C. after a short wash in clear water. Excess liquid is removed by hydroextraction. The protected stockings are then immersed, while still wet for a period of 60 minutes in an aqueous long bath (150:1) comprising 0.11% by weight of the silica sol as prepared in Example I, that is, the bath contains about 0.014% of SiO₂. The bath is maintained at a temperature of approximately 85° C. and at a pH of about 7 during the treating period. The stockings are then rinsed in clear water and dried at a temperature of 200° F.

Dyed, size-free rayon (regenerated cellulose) stockings are enclosed in a cheesecloth bag and treated in the same manner as described above.

An analysis of each of the above aqueous solutions of colloidal silica before and after the immersion period shows the following results:

	Percent SiO ₂ Prior to Immer- sion	Percent SiO ₂ After Immersion	Percent Exhaus- tion
Nylon stockings.....	0.014	0.0025	82
Rayon stockings.....	0.014	0.0056	60

In both instances the stockings possess a high degree of resistance to snags, runs and holes and retain these characteristics after a substantial number of home launderings. Moreover, the stockings are substantially unaltered in feel or hand as a result of the treatment.

Colloidal silica can be successfully applied to a variety of textile and/or cellulosic fibers, yarns and fabrics such as wools, cottons, native celluloses, papers, re-

6

generated celluloses, cellulose esters, nylon and the like in accordance with the methods hereinbefore described or by suitable modifications thereof. Moreover, if desired, equipment of the type herein described or other suitable equipment may be used depending upon whether the material to be treated is in the form of fibers, yarns or fabrics.

What is claimed is:

1. The method of finishing a textile material which comprises treating said textile material with an aqueous solution comprising a cationic surface active agent and an inorganic salt and then further treating said material while it is still wet with an aqueous solution containing from 0.01 to 0.2% colloidal silica at a temperature of 75 to 100° C., the weight ratio of said aqueous solution to textile material being between 50:1 and 200:1.
2. The method according to claim 1, but further characterized in that the textile material is a cellulose textile material.
3. The method of finishing a textile material which comprises immersing said textile material in an aqueous solution containing a surface active quaternary ammonium salt and an inorganic salt, immersing the textile material while it is still wet in an aqueous solution containing from 0.01 to 0.2% of colloidal silica at a temperature of 75 to 100° C., the weight ratio of said aqueous solution to textile material being between 50:1 and 200:1 and thereafter drying said material.
4. The method according to claim 3, but further characterized in that the inorganic salt is barium chloride.
5. The method according to claim 3, but further characterized in that the inorganic salt is sodium chloride.
6. The method according to claim 3, but further characterized in that the inorganic salt is sodium sulfate.
7. The method according to claim 3, but further characterized in that the quaternary ammonium salt is cetyl dimethyl benzyl ammonium chloride and the inorganic salt is barium chloride.
8. The method according to claim 3, but further characterized in that the quaternary ammonium salt is cetyl methyl dibenzyl ammonium chloride and the inorganic salt is barium chloride.
9. The method according to claim 3, but further characterized in that the quaternary ammonium salt is stearyl dimethyl benzyl ammonium chloride and the inorganic salt is barium chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,343,095	Smith	Feb. 29, 1944
2,408,654	Kirk	Oct. 1, 1946
2,416,892	Barnard et al.	Mar. 4, 1947
2,421,363	Young	May 27, 1947
2,443,512	Powers et al.	June 15, 1948
2,526,684	Powers	Oct. 24, 1950
2,527,329	Powers	Oct. 24, 1950

FOREIGN PATENTS

Number	Country	Date
483,496	Great Britain	Apr. 21, 1938