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METHOD OF RENDERING REGENERATED
CELLULOSE WATER-REPELLENT

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This invention relates to cellulosic fibers, yarns, and fabricated structures which are water-repellent and characterized by modified dyeing capacities, and to a method of simultaneously imparting water-repellency to and modifying the dyeing properties of such cellulosic articles.

It has been proposed previously to render various materials water-repellent by contacting them with organo-silicon halides in vapor form. That method has not proved generally satisfactory. Apart from the obvious inconveniences and difficulties involved in handling substances in the vapor phase in the ordinary textile plant, and the need for specially designed equipment, it has been found practically impossible to apply the organo-silicon halides to the material in the form of a uniform thin film when the vapor form is used. Permeation of the material by the vapors is uneven and spotty, and it has been found that in order to insure uniformity of water-repellency at all portions of the material comparatively prolonged exposure of the material to the vapors, and deposition of a considerable amount of the organo-silicon halide thereon are required.

The method using vapors of the organo-silicon halides is particularly unsatisfactory in the case of cellulosic materials. The organo-silicon halides react with the water normally held by the cellulose when it is in equilibrium with the atmosphere at prevailing ambient temperatures and humidities with evolution of a halogen acid corresponding to the organo-silicon halide used, to form a water-repellent film network. It is possible to render cellulosic material uniformly water-repellent by exposing it to vapors of the organo-silicon halides, but the material shows, after the treatment, a sharp loss in tensile strength and extensibility as the result of the degrading action of the gaseous halogen acid on the cellulose. Since absorption of the organo-silicon halide from the vapor phase is poor, in order to insure any degree of uniform water-repellency to all portions of the cellulose material, it is necessary to expose the cellulose to the vapors, in the presence of the liberated halogen acid, for a comparatively long period of the order of about twenty minutes or more, at a temperature sufficiently high to maintain the halide in the vapor phase. The cellulosic material is seriously degraded, to the point of being without commercial value, under those conditions. For instance, when a fabric comprising regenerated cellulose fibers having the normal regain moisture content of from about 10 to 12% was exposed to vapors of methyl silicon chloride under conditions of

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temperature and time of exposure such that the fabric was uniformly water-repellent, the cellulose was degraded to a marked extent as evidenced by a substantial drop in D. P. (degree of polymerization) of the cellulose and by a serious loss in both tensile strength and extensibility. The drop in D. P. of the treated material, as contrasted to untreated regenerated cellulose, amounted to 18.4%, while the wet tensile strength dropped from 1.63 gms./denier to 1.27 gms./denier, and the wet extensibility dropped from 31% to 18%. Moreover, it was found that the presence of a neutralizing agent in the cellulosic material during treatment with the vapors does not aid in controlling the degrading action of the halogen acid thereon.

I have now discovered that the temperature at which cellulosic material is treated with the organo-silicon halides is controlling as to the extent of degradation of the cellulose by the evolved acid. There is a difference in temperature coefficient as between the reaction involving the organo-silicon halide and water bonded to the cellulose, on the one hand, and the reaction involving the gaseous halogen acid and cellulose, on the other hand. While the reactions are initiated practically simultaneously, the rate at which they proceed to completion is different. Thus, I have found that the reaction between the organo-silicon halide and moisture held by the cellulose proceeds to completion so rapidly that the influence of the temperature is of no practical significance on the rate of film formation, whereas the rate at which the reaction involving the gaseous halogen acid and the cellulose, and thus the extent to which the cellulose is degraded in a given time period, is a direct function of the temperature at which the treatment is carried out. Increased temperatures of treatment cause an increase in the speed of the reaction between the cellulose and the halogen acid, and consequently of the rate and extent of cellulose degradation, especially with increase in the length of the treating period at such temperatures.

The present invention is based upon the discovery of the relationship of temperature to cellulose degradation by the evolved halogen acid and has as a primary object the provision of a method whereby cellulosic materials are rendered uniformly water-repellent by treatment with the organo-silicon halides under conditions such that the treated cellulose is not degraded, or is not degraded to any appreciable extent, as compared with untreated cellulosic material.

This and other objects of the invention are

achieved by treating the cellulosic material containing the moisture normally retained by such material under prevailing ambient temperatures and humidities with a solution of an organo-silicon halide, or mixture of such halides, in a water-immiscible organic volatile solvent for the halides, at a controlled temperature of from 0° C. to about 25° C., preferably at a temperature of from about 5 to 10° C., and most desirably at a temperature of about 7° C.

Cellulosic material treated with the organo-silicon halides in solution, and at the stated temperatures, is found to be effectively and uniformly rendered water-repellent when only relatively small amounts of the organo-silicon halides are applied thereto, as determined by ashing down samples of the treated material and analyzing the ashes for SiO₂ content.

The degree of water-repellency imparted to the cellulosic material ranges from good to excellent, depending upon the amount of the organo-silicon halide applied thereto, and in all cases is uniform at all portions of the material. When lesser amounts of the organo-silicon halides are applied to the material, that is when the ashed down samples analyze from about 0.02% to about 0.09% or from about 0.09% to 0.3% SiO₂, the treated material is characterized by uniform good water-repellency and is serviceable for many purposes, while when larger amounts of the organo-silicon halides are applied, that is when ashed down samples of the treated material analyze from about 0.3% to about 1.0% and generally from about 0.8% to about 1.0% SiO₂, the material is uniformly and completely water-repellent. When the organo-silicon halide is applied from solution as described herein, only a very brief period of contact between the cellulosic material and the solution, of the order of a few minutes, is required to apply the desired amount of the organo-silicon halide to the material. At the controlled temperatures mentioned, and especially at temperatures in the preferred range, the speed of the reaction between the liberated halogen acid and the cellulose is markedly retarded which, coupled with the short treating period required, minimizes the degrading action of the acid on the cellulose, the speed of the reaction being retarded to the extent that degradation of the cellulose is completely avoided under the ideal temperature conditions. The degree of degradation depends upon the temperature, and a slight degradation of the cellulose is observable at the higher temperatures in the stated range, but even at those temperatures the extent of degradation by the liberated acid is considerably less than and cannot be compared with the extent to which cellulosic material is degraded by the liberated acid when it is rendered uniformly water-repellent by exposure to the organo-silicon halides in vapor form.

The organo-silicon halides not only impart water-repellency to the cellulosic material, but also render the same more or less resistant to the water-soluble rayon and cotton dyestuffs which are normally substantive to cellulose, or, in the case of the organic derivatives of cellulose, to dyes of the cellulose acetate dyestuff class. The resistance which the treated materials offer to the dye depends upon the amount of the organo-silicon halide applied thereto, as well as the conditions of dyeing. The amount of halide applied may be effectively controlled when the materials are treated with a solution of the organo-silicon halides at the temperatures specified herein, in

accordance with the invention, by varying somewhat the time of contact of the cellulosic material with the solution. A cellulosic material samples of which, when ashed down, analyze from about 0.8% to 1.0% of SiO₂ and which is obtained by contacting the material with the solution of the organo-silicon halide at a temperature of about 5 to 10° C. for about 10 to 15 minutes, is completely water-repellent and resistant to coloration by the dyes under ordinary dyeing conditions, whereas a material samples of which, when ashed down, analyze from about 0.02 to 0.09%, or from about 0.09% to 0.3% SiO₂, which requires a shorter treating period of about one to three minutes, although characterized by uniform good water-repellency, is less resistant to the dyes, but is dyed to lighter shades than the dyes normally produce on cellulosic materials. The possibility of varying the resistance of the cellulosic material to coloration by the water-soluble rayon or cotton dyes, or the cellulose acetate dyestuffs, by varying the amount of the organo-silicon halide applied to the material, while at the same time imparting from good to excellent water-repellency thereto, permits of combining yarns formed from or comprising treated and untreated cellulosic fibers to obtain, after dyeing, very pleasing and unusual effects. Accordingly, it is possible to produce very interesting and useful effect fabrics by associating together in a fabric yarns composed of or comprising untreated fibers which are not dye-resistant, with yarns composed of or comprising fibers treated in accordance with this invention and which are dye-resistant, under the conditions of dyeing, or which are colored to lighter shades by the dyes. When the treated fibers have applied thereto the lesser amounts of the organo-silicon halides the result is to produce, after dyeing, a fabric in which the untreated fibers are colored to a deeper shade than the treated fibers, whereas, when the treated fibers have applied thereto the larger amounts of the organo-silicon halides, after the dyeing operation, the untreated fibers are colored while the treated fibers are not colored. In this manner, interesting stripe effects, herringbone patterns, etc., can be obtained.

It is also within the scope of the invention to combine cellulosic fibers treated in accordance therewith with fibers of other types, such as wool, silk, etc. Also, fibers, yarns, or fabrics which have been dyed in a previous operation may be treated with the organo-silicon halides in accordance with this invention and rendered water-repellent without degradation of the cellulose, provided the dye carried thereby is not affected by the solvent in which the organo-silicon halide is dissolved, and in this case the water-repellent film will assist in fixing the dye on the material.

Fibers, yarns, or fabrics may be satisfactorily rendered water-repellent at temperatures between about 0° C. to 25° C., with a medium comprising the water-immiscible solvent containing about 1% of the organo-silicon halide, or mixture of halides, the treated material having affixed thereto a well-imbedded firmly anchored uniform thin film comprising the product of reaction between the moisture held by the cellulose and the organo-silicon halide, which film does not impair the natural flexibility or pliability of the material, and which is completely resistant to laundering or scouring with aqueous media.

The process of the invention is adaptable for the treatment of all cellulosic material, including fibers, yarns and fabrics comprising regenerated

celluloses, natural cellulosic fibers, such as cotton, jute, ramie, linen, etc., yarns or fabricated structures comprising or consisting of such natural cellulosic fibers, as well as fibers or the like comprising organic lower fatty acid esters of cellulose such as cellulose acetate.

The cellulosic material to be treated should contain the amount of moisture which it retains when it is in equilibrium with the atmosphere at prevailing ambient temperatures and humidities. The moisture held by regenerated cellulose for example may be its normal regain moisture which may vary from about 8 to 16% by weight, while that held by the natural cellulosic material may vary from 6 to about 9%. If, as may be the case with cellulose acetate, the moisture retained by the material is too low, it may be adjusted by reconditioning the material at a higher relative humidity, while if the material retains an excessive amount of moisture it may be desirable to pre-treat it by soaking it in an organic solvent at a low temperature of about 10° C. or thereabout prior to treating it with the solution of the organo-silicon halide. In any event, it is essential to avoid the presence of water in bulk.

Cellulosic materials which are rendered water-repellent and more or less dye-resistant by the described process are suitable for use for many important purposes due to the fact that the inherent tensile strength, extensibility, and flexibility of the material are substantially preserved, which is in contrast to cellulosic materials which, after exposure to vapors of the organo-silicon halides, are unsuitable for most uses, due to lack of strength and extensibility.

Organo-silicon halides which may be used in accordance with the invention include alkyl silicon halides, such as ethyl, propyl, butyl, etc., aryl silicon halides, such as phenyl silicon halides, etc., aralkyl silicon halides, for example phenyl methyl silicon halides, and alkaryl silicon halides, such as tolyl silicon halides.

Water-immiscible organic volatile solvents may be used are, for example, the hydrocarbon solvents of the paraffinic, naphthenic or aromatic series, including such solvents of the dry cleaning type derived from natural sources, as Stoddard's solvent, the naphthenes, or cyclo paraffins, aromatic hydrocarbons such as benzene, toluene, solvent naphtha, the xylenes or similar solvents, synthetic dry-cleaning solvents of the chlorinated hydrocarbon type such as carbon tetrachloride, etc.

The treated material may be after-treated by washing it in alkaline solution, such as an aqueous solution of ammonium, sodium or potassium hydroxide or sodium carbonate, for example, to remove any halogen acid present.

The following examples will illustrate specific embodiments of this invention:

Example I

A fabric woven from yarns formed from fibers of regenerated cellulose and which weighed about 300 grams and contained about 11% moisture was soaked in carbon tetrachloride at 10° C. for about 60 seconds. The pre-treated material was given a one-minute immersion in a bath consisting of 15 cc. of methyl silicon chloride in 1500 cc. carbon tetrachloride at 7° C. The treated sample was then immersed in a dilute aqueous solution of ammonium hydroxide maintained at 10° C. for about 20 minutes, after which it was washed with running water at room temperature until neu-

tral. The treated material was then dried. The D. P. of the cellulose was the same as that of an untreated sample, and the fabric had a bursting strength in pounds of 102.00 which was only slightly less than the bursting strength of 104.5 pounds of the untreated material. The treated fabric showed good uniform water-repellency. The treated material was immersed in water containing 6.7 gms. of Brilliant benzo blue 6 BA per liter, and a small amount of sulfonated oil. The ratio of dyeing solution to cellulose material was 1.5 cc. to 1 gm. After boiling the material and solution together for about 10 minutes and rinsing the material, it was found to be dyed to a lighter shade of blue than the dyestuff normally produces on untreated regenerated cellulose under similar dyeing conditions. Ashed down samples of the treated material analyzed from about 0.02% to about 0.3% SiO₂.

Example II

A fabric manufactured from yarns formed of fibers of regenerated cellulose, and which weighed about 300 grams and contained about 11% moisture was immersed for ten minutes in a bath consisting of 15 cc. methyl silicon chloride dissolved in 1500 cc. of Stoddard's solvent at between 5 and 10° C. The treated fabric was immersed in a dilute aqueous solution of ammonium hydroxide at 10° C. for about 10 minutes, and was then washed with running water at room temperature until it was neutral. The D. P. of the cellulose and bursting strength of the fabric were substantially the same as the D. P. of the cellulose and bursting strength of an untreated regenerated cellulose fabric. The treated fabric was uniformly and completely water-repellent. The treated material was immersed in water containing 6.7 gms. of Brilliant benzo blue 6 BA per liter, and a small amount of sulfonated oil. The ratio of dyeing solution to cellulose material was 1.5 cc. to 1 gm. After boiling the material and solution together for about 10 minutes and rinsing the material, it was found to have completely resisted coloration by the dyestuff. Ashed down samples of the material analyzed from about 0.8% to about 1% SiO₂.

The ashing down procedure was carried out as follows: About 150 gms. of the treated material were dried at 105° C. for about 10 hours, cooled, and weighed. The sample, which was free from moisture was heated slowly with a Mekker (Fischer) burner until the cellulose was charred, precautions being taken to prevent loss by too rapid charring of the cellulose. The charred residue was then heated to about 1400° C. for about 6 hours, and weighed to constant value. The residue was calculated as % SiO₂.

I claim:

1. The method of rendering fibers, yarns and fabrics comprising regenerated cellulose containing the moisture normally held by cellulose in equilibrium with the atmosphere at prevailing ambient temperatures and humidities completely water-repellent and resistant to coloration by dyestuffs which normally dye regenerated cellulose, without substantial degradation of the cellulose, which comprises treating the fibers, yarns, and fabrics with a solution of an organo-silicon halide selected from the group consisting of alkyl, aryl, and aralkyl silicon halides in a water-immiscible organic solvent therefor for from ten to fifteen minutes at a controlled temperature between 0 and 10° C., washing the treated material, prior to drying thereof, with a dilute aque-

ous alkaline solution at 10° C. for about ten minutes, then washing the material with water at room temperature until it is neutral, and then drying the article.

2. The method of rendering fibers, yarns and fabrics comprising regenerated cellulose containing the moisture normally held by cellulose in equilibrium with the atmosphere at prevailing ambient temperatures and humidities completely water-repellent and resistant to coloration by dyestuffs which normally dye regenerated cellulose, without substantial degradation of the cellulose, which comprises treating the fibers, yarns, and fabrics with a solution of an organo-silicon halide selected from the group consisting of alkyl, aryl, and aralkyl silicon halides in a water-immiscible organic solvent therefor for from ten to fifteen minutes at a controlled temperature of about 7° C., washing the treated material, prior to drying thereof, with a dilute aqueous alkaline solution at 10° C. for about ten minutes, then washing the material

with water at room temperature until it is neutral, and then drying the article.

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