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WASHING CELLULOSE

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This invention concerns the washing and wet processing of yarns, fibers, fabrics and films which are essentially cellulosic in composition, such as cotton, linen, wood pulp and rayon (hereinafter referred to as "cellulosic fibers").

In the wet processing of cellulosic fibers, the yarn is generally washed with water containing dissolved salts of calcium, magnesium, sodium, etc. These salts are found in natural waters and generally remain in such waters even after the more common processes of water purification. The salt content in clear waters suitable for industrial use may run from the vicinity of 30 parts per million to over 100 parts per million. Calcium and magnesium salts which cause water to be hard may be removed by running the water through a commercial softener which retains the calcium and magnesium and replaces it with a sodium salt, so that the total solids remaining in the water after passing through the softener are only slightly changed.

When cellulosic fibers are washed with salt containing water, the cellulose retains a certain and definite amount of the cations; the water, which remains with the fibers also contains a certain amount of dissolved salts. During the process of drying yarn packages, such as are produced in the manufacture of rayon, these salts creep to the outermost surfaces of the yarn package where the drying is most rapid, and there the salts tend to localize or deposit, so that the final dried yarn package may show small spots or deposits scattered over the package surface. The localization of the salts, particularly under the influence of heat, brings about a change in the cellulose at the point where the salts have localized which, in turn, is followed by a number of undesirable consequences in the subsequent handling of the yarn. "Dye-resist" spots may be a result of the salt deposits. In some cases the yarn is weakened so badly at the points where the salt has localized that breaks follow in a subsequent processing. Sometimes the salt increases the frictional properties of the thread at the spots described so that the threads do not pass at uniform speeds through needles, guides and other textile devices, and jerky thread travel is obtained which may give rise to poor or defective stitch or weave.

It is now well known to chemists familiar with cellulose that cellulose contains carboxyl groups and is slightly acid in nature. Another fact not quite as well realized is the property that cellulose has, through its carboxyl groups, of combining with cations, so that when cellulose is exposed to ordinary wash waters it may pick up, by chemical combination, any cation from the salts which may be in the water. I have discovered that the ability of the cellulosic material to combine with or retain cations, particularly metallic cations, depends upon pH; that at a pH of about 2.75 the metallic cations are entirely displaced from the carboxyl group and replaced by a hydrogen ion, and the metallic cations meanwhile go into solution as salts in the surrounding aqueous medium. Further, I have found that at higher pH, more cations are retainer, and that the carboxyl groups of the cellulose become completely saturated at pH 7 or higher. In this explanation I do not refer to the hydrogen ion of the acids, as a cation, although it is generally so considered. I am referring more particularly to the metallic cations.

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It has been proposed heretofore to remove from hydrolyzed cellulosic esters, salts of the alkaline earth metals by washing the cellulosic esters with acidified distilled water followed by repeated washings with distilled water to remove the salt and acid. The washing of cellulosic material, such as rayon yarn and the like, with acidified distilled water to loosen calcium and magnesium and effect their removal from the yarn is prohibitively costly due to the high cost of distilling water.

I have made the significant discovery that the calcium, magnesium and other cations combined with, or attached to, cellulosic fibers in the form of filaments, threads or fabrics may be displaced and removed by treatment with acidified hard or soft water (salt-bearing water) and that distilled water is not necessary in this operation. My invention, accordingly, provides an improved method of treating the cellulosic fibers with acidified salt-bearing hard or soft water to displace combined cations, followed by washing with distilled or demineralized water to remove the cations displaced by the acidified water.

In order to free the cellulose of calcium and magnesium as well as sodium and other cations, following exposure to hard waters, it is necessary to wash the yarn with water brought to a suitable pH with a little acid, such as sulfuric or hydrochloric acids, until the calcium or magnesium is loosened and freed and this, I have found, may be accomplished with ordinary industrial hard water or with soft water. The cellulose may then be washed with distilled water or its equivalent until the calcium and magnesium salts are substantially removed. The cellulose, following acidification treatment, could

be washed with soft water, and while the calcium and magnesium would be displaced from combination with the cellulose, they would be replaced with sodium. The sodium could, of course, be washed out with distilled or demineralized water, if the cellulose were maintained in an acid condition before the distilled or demineralized water was applied. To free the cellulose completely of cations (other than hydrogen) the demineralized or distilled water wash must follow the acid wash directly. To hasten the cellulose to neutrality in preparation for drying, a bit of aqua ammonia may be added to the distilled or demineralized water in the very last stages of washing, but in so doing, one must be reasonably certain that the undesired cations such as calcium, magnesium and sodium have already been washed out of the cellulose. An amount of aqua ammonia sufficient to bring pH of the water to around 8 or 9 is generally satisfactory. While the use of aqua ammonia brings about the combination of the ammonium cation and cellulose, the ammonium cation will not localize in the form of a salt deposit during subsequent drying as calcium, magnesium, or sodium does. The ammonium cation is largely lost during drying, being volatilized as ammonia.

By soft waters is meant water practically free of calcium and magnesium usually obtained by passing the hard waters through a zeolite softener, which retains the calcium and magnesium, exchanging them with sodium. Waters equivalent to, or of the quality of, distilled water may be obtained from steam condensers, or by passing industrial waters through anion-cation exchangers, giving a final water, the solid content of which is generally well below 10 parts per million, none of which is calcium or magnesium and very little of which is cationic.

A suitable degree of acidity for loosening such cations as calcium and magnesium is in the neighborhood of pH 2.5, although a pH varying from around 2 to 5 may be satisfactory for most purposes. In the case of viscose yarns, for example, it is desirable to reduce the pH to a point which is around pH 2.75.

The following is an example of a washing operation carried out in accordance with the invention:

Bobbins of freshly spun viscose yarn, each having about 1 pound of yarn (bone dry) wound thereon, were taken directly after spinning and the regular wash necessary for such bobbins applied. Normally these particular bobbins would have received washes such as follows:

	Minutes
Cold water	50
Hot water	50
Hot water	200
Desulfurizing solution	100
Hot water	20
Hot water	60
Cold water	40

It will be understood that the wash water and desulfurizing material were made up with hard water, and that these liquids were drawn through the yarn by vacuum according to the conventional viscose rayon manufacturing procedure. The cold water in this case would be at a temperature of about 30° C., hot water at about 65° C. The desulfurizing solution is a solution of 0.35% to 0.40% ammonium sulfide at a temperature of about 40° C. The bobbins were washed together until the 20 minutes wash had been completed.

The bobbins were then separated and the control continued washing as shown in the schedule. The test bobbins, having been washed thus far, were now given 110 minutes washing with hard water, acidified with hydrochloric acid—to pH 2, and then finished with 100 minutes of demineralized water.

After drying, the yarns compared as follows in ash content:

	Per cent
Control	0.17
Test	0.025

The ash of the test samples was largely silica, which is inert and harmless.

The dye affinity of the test yarn was noticeably greater than that of the control yarn as shown by the deeper shade of color of the yarn when dyed in the same dye bath with the control.

In the removal of calcium, magnesium, sodium and other cations from yarn, with the object of preventing the localization of their salts on parts of yarn packages during drying, it has been found that in some cases it is not necessary to remove all the undesirable cationic material to prevent localization of salt spots. The salt spots can be reduced to an acceptable minimum in some cases by washing the yarn packages with a demineralized water at a pH of about 5. If the demineralizer is allowed to operate in such a way that the carbonic acid, normally found in the demineralized water, is allowed to remain dissolved in the water, the carbonic acid itself will yield a pH between 4 and 5 and effect a desirable reduction in retained cations. The excess carbonic acid is harmless since it is vaporized in subsequent drying operations. While at the higher range of pH, the removal of cations is not complete, if the washing is prolonged enough, I have found that the ash content can be lowered from the range of from 0.15% to 0.20% to the range of from 0.07% to 0.08%. As I have said, this is satisfactory for certain purposes, but in order to obtain complete removal, a lower pH must be used.

The invention does not deal with the removal from cellulose of those salts which may have been a by-product or impurity from a spinning, dyeing, bleaching or other chemical treatment. The invention relates only to the removal from the cellulose of salts in industrial waters, which the cellulose will adsorb or take up, to a certain extent, depending on pH, and which, under the usual conditions of washing with more or less neutral industrial waters, will stay in the cellulose to an extent where the ash content of an unpigmented, unweighted cellulose will be somewhere in the range of from 0.15% to 0.20% by weight. Pigment, for example, would not be affected; insoluble salts, such as lead sulfide, nickel sulfide and certain forms of iron oxide, would be affected to a small degree. But iron, nickel, lead, etc., as cations combined with the cellulose, would be dislodged by the treatment.

I claim:

1. The improved method of washing cellulosic fibers to remove calcium, magnesium, sodium and other cations normally found in industrial water and adsorbed or taken up by the cellulose from the water which comprises washing the cellulose with ordinary salt-bearing industrial water acidified with an inorganic acid to a pH of from 2 to 5 to loosen and displace said cations, and then washing out the displaced cations and the acid with demineralized water.

2. The improved method of washing cellulosic

fibers to remove calcium, magnesium, sodium and other cations normally found in industrial water and adsorbed or taken up by the cellulose from the water which comprises washing the cellulose with ordinary salt-bearing industrial water acidified with hydrochloric acid to a pH of from 2 to 5 to loosen and displace said cations, and then washing out the displaced cations and the acid with demineralized water.

3. The improved method of washing cellulosic fibers to remove calcium, magnesium, sodium and other cations normally found in industrial water and adsorbed or taken up by the cellulose from the water which comprises washing the cellulose with ordinary salt-bearing industrial water acidified with sulfuric acid to a pH of from 2 to 5 to loosen and displace said cations, and then washing out the displaced cations and the acid with demineralized water.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,802,935	Banigan	Apr. 28, 1931
2,316,379	Wolter	Apr. 13, 1943

OTHER REFERENCES

D. N. Jackman: "Chemistry of Laundry Materials," Longmans, Green and Co., N. Y., 1931, pages 141, 142.

Journal of Phys. Chem., vol. 45, 1941, pages 1152 to 1166.

Matthews: "Bleaching and Related Processes," Chem. Cat. Co., New York, 1921, pages 51, 52.