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WATER REPELLENCE FIXATIVE
TREATMENT

Stephen F. Urban, Kenmore, and Warren B. Blumenthal, Niagara Falls, N. Y., assignors to National Lead Company, New York, N. Y., a corporation of New Jersey

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The present invention relates to the treatment of fibrous materials such as textile fabrics and fibrous cellulosic sheet material, for instance, paper and cardboard, in order to render such fibrous material resistant to wetting and to penetration by water. More particularly, the invention relates to a method for inducing water repellence in the fibrous material treated by the employment of a specific water soluble, alkaline zirconium compound, i. e., ammonium dicarbonato zirconylate, and the fixation of the zirconium compound, or a decomposition product thereof, upon the material so treated, whereby the effects of the water repellent treatment will endure through conditions which normally destroy it, either partially or completely. In general, laundering and dry cleaning are examples of processes which destroy water repellence effects.

So-called water repellence processes have little or no effect upon the normal porosity, texture, appearance and other perceptible qualities of the fabric or paper, aside from its resistance to wetting and penetration by water, and in this respect differ from water-proofing processes wherein the fibers of the material are coated and the pores of the material are closed by the water-proofing composition. Fibrous materials having water repellent surfaces, therefore, in general, merely resist wetting of the constituent fibers and the so-called water repellence does not prevent penetration of water into the pores under hydrostatic head. Water-proofing operations are generally more permanent than water repellent operations, since the materials employed in the latter process are relatively more readily removed by ordinary laundering and dry cleaning operations.

It is an object of the present invention to provide a method of treating fibrous materials to obtain water repellence therein and more permanently to fix the water repellence material upon the fibers of the product so treated.

In accordance with the invention, the fibrous material to be treated to produce water repellence therein, whether the same be a textile fabric or a fibrous sheet material, such as paper, is impregnated with a solution containing zirconium, such as the double ammonium zirconium carbonate, wherein the zirconium is present in the anionic form, e. g. in this case, as a dicarbonato zirconylate anion. The impregnation of the fibrous material is performed in any suitable fashion, such as by the use of padding rolls, sprays or immersion in a solution of the water repellence treating material with elimination of the excess solution.

The zirconium compound adheres to the fibrous material being treated and serves to bind to the surface thereof a film of fatty and/or waxy

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material normally incorporated in the solution of the water repellence compound. This film then comprises the hydrophobic exterior of the fibers and is responsible for the water repellent quality. The hydrophobic film thus formed on the material to which water repellent properties are to be imparted is then fixed or anchored on the fibers of that material by a subsequent treatment with a water soluble salt of a polyvalent metal selected from the groups III, IV and VIII of the periodic system, or a mixture of such salts. The anion of the salt of the polyvalent metal appears when used alone to furnish little or no fixative action, this property being induced only when it is used in conjunction with the polyvalent cation. Although the fixative action is a general function of the polyvalent cations of the metals of the stated groups, it will generally be found advantageous to employ salts of such cations which produce colorless aqueous solutions as, for instance, zirconium, tin, aluminum, and others. Immediately, after the action of the fixative salt upon the fibrous material which has been treated with the soluble double ammonium zirconium carbonate, the material may be rinsed without dislodging or destroying the water repellence effect of the hydrophobic film. After rinsing, the fabric or fiber sheet is dried generally at an elevated temperature and will be found to possess very strong and sustained water repellence. For instance, fabrics so treated will exhibit a spray rating of 80 to 100% and paper will shed a spray of water. It will be noted that water dropped upon horizontally placed paper sheets so treated will form rounded globules, whereas on untreated paper, the drops flatten out and wet the paper. Cloth rendered water repellent without the application of the fixative will withstand one to two launderings with Ivory soap, without losing its water repellence, while similar cloth treated with the fixative can withstand four to eight such launderings. Furthermore, a single dry cleaning normally destroys the water repellent quality when no fixative is employed. However, similar cloths made water repellent by including the fixative treatment of the present invention have been found to withstand six dry cleanings.

The following examples are given merely by way of illustration and are not to be deemed as limiting the scope of the invention but as merely illustrative of it as there will obviously be many variations of time, temperature and composition of bath, suitable for employment in order to obtain the results of the invention.

Example I

An aqueous solution of ammonium dicarbonato zirconylate, $(\text{NH}_4)_2\text{ZrO}(\text{CO}_3)_2$, containing one-

tenth mol of this salt (12.3 gm. of ZrO_2) in approximately 100 ml. was mixed with a 5% solution of ammonium oleate, containing a total of 14.8 gm. of the soap. To this mix 30 gm. of a 40% emulsion of paraffin wax was added and the mix stirred well while diluting to 1200 ml. A sample of photographic paper was immersed in this bath for one minute, then removed and rolled free of excess liquid. The so treated paper was then immersed for two minutes in a solution containing 1.9 gm. of basic zirconyl chloride ($Zr_2O_3Cl_2 \cdot 6H_2O$) dissolved in 100 ml. of water. After removal from this solution, the material was rinsed thoroughly in water and dried at 90° C. (194° F.). It was rendered highly water repellent by this process.

A sample of cotton drill treated in the same fashion withstood eight launderings, while another sample withstood six dry cleaning operations before losing its water repellence characteristics.

Example II

Same as Example I except that 3.0 gm. of stannous chloride was used in place of the basic zirconyl chloride.

Example III

Same as Example I except that 2.5 gm. of ferrous sulfate was used in place of the basic zirconyl chloride.

Example IV

A strip of paper of the type used for application thereto of sensitized photographic gelatin, and in which it is desired to produce hydrophobic characteristics, was immersed in an aqueous solution of the double ammonium zirconium carbonate, i. e. ammonium dicarbonato zirconylate, containing about 12.3 gm. ZrO_2 , 13 gm. ammonium palmitate, and 12.3 gm. dispersed wax. After immersion for one minute at 40° C., the paper was removed, dipped in water and then passed through rollers to remove excess of liquid.

The water repellence ingredients of the bath were then fixed upon the paper by immersing the so treated paper in an aqueous bath containing 3% stannous chloride. After the paper had soaked in the bath for a few minutes, the paper was removed and dried. After drying, the paper shed a water spray and was found to be an excellent carrier sheet for the preparation of sensitized photographic paper.

The first stage of the treatment described herein constitutes the subject matter of an application for patent filed by Henry L. Van Mater, September 20, 1944, under Serial No. 555,044, now Patent No. 2,457,853, granted January 4, 1949. It will be understood that the usual fatty substances forming soap can be employed herein, i. e., the soluble salts of oleic acid, palmitic acid, stearic acid and the like, and that if waxes be added to the bath, other waxes may be used in lieu of the paraffin wax employed in the illustrated examples.

The procedures of the present invention have particular application to improve water repellence treatments of fibrous fabrics and to successful water repellence treatments of fibrous cellulosic sheets as, for instance, paper sheets to be employed in the manufacture of sensitized photographic and print paper.

What is claimed is:

1. A process for inducing water repellance in cellulosic fibrous materials which comprises immersing the fibrous material in an aqueous bath containing ammonium dicarbonato zirconylate

and a water soluble soap, and thereafter immersing said so treated material in an aqueous solution containing a salt which yields a cation of a metal selected from the group of metals of groups three, four and eight of Mendeleeff's periodic arrangement of the elements, then rinsing and drying the material.

2. A process for inducing water repellance in cellulosic fibrous materials which comprises immersing the fibrous material in an aqueous bath containing ammonium dicarbonato zirconylate and a water soluble soap, and thereafter immersing said material in an aqueous solution containing a soluble zirconium salt wherein zirconium is a cation, then rinsing and drying the material.

3. A process for inducing water repellance in cellulosic fibrous materials which comprises immersing the fibrous material in an aqueous bath containing ammonium dicarbonato zirconylate and a water soluble soap, and thereafter immersing said material in an aqueous solution containing a soluble aluminum salt wherein aluminum is a cation, then rinsing and drying the material.

4. A process for inducing water repellance in cellulosic fibrous materials which comprises immersing the fibrous material in an aqueous bath containing ammonium dicarbonato zirconylate and a water soluble soap, and thereafter immersing said material in an aqueous solution containing a soluble tin salt wherein tin is a cation, then rinsing and drying the material.

5. A process for inducing water repellance in paper which comprises immersing the paper in an aqueous water repellance bath containing a water soluble soap and a water soluble alkaline double ammonium zirconium carbonate for a time sufficient to saturate the paper with the solution, thereafter immersing the so saturated paper in an aqueous solution of zirconyl chloride to fix the water repellance materials upon the fibers of the paper, then rinsing and drying the paper.

6. A fibrous material having water repellance properties comprising a base of cellulosic fibrous material, a hydrophobic coating thereon of the reaction product of an aqueous solution of ammonium dicarbonato zirconylate and a water soluble soap and a fixative for said coating comprising a polyvalent metal cation selected from the group of metals consisting of groups three, four and eight of Mendeleeff's periodic arrangement of the elements.

7. A paper sheet having water repellance properties and having on the surface thereof a hydrophobic coating of the reaction product of an aqueous solution of ammonium dicarbonato zirconylate and a water soluble soap and a fixative for said coating comprising a polyvalent metal cation selected from the group of metals consisting of groups three, four and eight of Mendeleeff's periodic arrangement of the elements.

STEPHEN F. URBAN.

WARREN B. BLUMENTHAL.

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