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TEXTILE MATERIAL

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1 Claim. (Cl. 117—168)

The present invention relates to a process of producing on textile materials finishes which are fast to wet treatments, especially to washing.

A great number of processes is known in the art for the said purpose. However, none of the hitherto proposed processes was entirely satisfactory. For instance, it is a well known disadvantage of textile fabrics having been rendered water-proof or water-repellent that they lose this property, for instance, when they are repeatedly subjected to the action of rain during wearing, or by washing. Consequently, water-proofed coats and the like could not be washed without having their water-proofness considerably impaired or even completely destroyed, or they had to be freshly impregnated every time they were washed. It may be further mentioned that the known processes give especially unsatisfactory results when applied to textile material from regenerated cellulose such as artificial silk and staple fiber.

It is an object of our invention to furnish a process which will render textile materials permanently water-proof or water-repellent so that the materials may be washed even with hot soap lyes without substantially losing their water-proof or water-repellent character. It is another object of our invention to fix any kind of substances which are difficultly soluble or insoluble in water on textile material so that they are permanently fixed and are not removed therefrom to any substantial degree even by repeatedly washing with hot soap lyes. These and other objects of our invention will be more fully apparent from the following description thereof.

We have found that any kind of textile materials such as wool, silk, cotton, artificial fibers from regenerated cellulose, cellulose derivatives or albuminous substances can be made permanently water-proof or water-repellent in the above sense by a treatment with an aqueous solution of a zirconium compound selected from the group consisting of zirconium oxychloride, zirconium oxy-nitrate and the water-soluble hydrolysates obtainable therefrom. After drying at elevated temperatures which, however, need not be above about 100° C., the textile materials so treated have become permanently water-repellent or water-proof, whereas, for instance, when using other zirconium compounds, they lose this property much more rapidly on washing with soap, especially when the materials consist of regenerated cellulose.

The aqueous solutions of the said zirconium compounds preferably contain alkaline reacting buffer substances, like, for instance, alkali acetates, alkali borates and the like which keep the pH of the solutions at about 2.5–4.5. The textiles may also be treated, after impregnation with the zirconium compounds, in another bath containing such buffer substances.

Impregnating with the said zirconium compounds is preferably carried out by immersing the textile materials for a short time, for instance several minutes, into a hot solution (above about 50° C.) of the zirconium compounds, squeezing or centrifuging and drying at elevated temperatures. The quantities of the zirconium compounds may go up to several per cent (calculated on the weight of the materials), but they need not to be so great as to cause any substantial weightening of the materials.

Soluble salts of organic acids which themselves are insoluble and of hydrophobic character may be used in combination with the zirconium compounds; they may be added to the zirconium treatment bath or the textiles may be pretreated with a solution containing the organic acids. As such acids there come into question the higher fatty acids, acids containing higher aliphatic radicles or other hydrophobic radicles.

Textiles treated in this manner become water-proof or water-repellent and do not lose this property by washing with a warm soap-solution or even by boiling with soap and soda.

We have furthermore found that the excellent properties of the said special zirconium compounds may be made use of in order to permanently fix any kind of textile finishing agents which are water-insoluble or difficultly soluble in water, on textile materials; as such agents there may be mentioned, for instance, paraffins, fatty compounds, waxes, resins and the like which are used for water-proofing, resinous substances used in anti-creasing processes, dulling agents like barium sulfate or titanium dioxide, pigment dyes, stiffening agents like polyvinyl resins etc.

It is a great disadvantage of textile material having been impregnated with such agents that they are more or less rapidly removed therefrom by repeatedly washing.

We have now found that this disadvantage can be overcome to a far-reaching extent by treating the textile material, during or after impregnation with any such finishing agent, with an aqueous solution of a zirconium compound selected from the group of zirconium oxychloride, zirconium oxynitrate and the water-soluble hydrolysates obtainable therefrom, as above mentioned. Also in this respect the said zirconium

compounds have proved to be far superior to other zirconium compounds or compounds of other metals which have been previously proposed, for instance, for water-proofing.

According to our process, for instance, textile fabrics having been water-proofed by impregnating with paraffin or wax, can be so improved that the impregnations become fast to washing and boiling to a far reaching extent. This may be done, for instance, by aftertreating a fabric having been impregnated with an emulsion or solution of paraffin and/or wax with a solution of the said zirconium compounds at room temperature or elevated temperature. It is also possible to add the said zirconium compounds directly to aqueous emulsions of paraffins, waxes and the like, care being taken that the emulsion does not break. The paraffin-, wax- and the like emulsions may contain further substances like glue, olein, soaps, aluminium salts etc.

More particularly, the textile material may be first impregnated at room temperature with a bath containing a paraffin emulsion and one of the above zirconium compounds, then squeezed, rapidly passed through an aqueous solution of 1% sodium acetate per liter, again squeezed and dried at from 60–100° C. Or the paraffin-zirconium bath may be made slightly acid to Congo paper by adding soda, buffered at a pH of from 3–4 by adding a suitable amount of sodium acetate or sodium borate or a mixture of acetic acid and sodium acetate, and the material treated therein squeezed and dried at elevated temperatures, for instance, by ironing. The paraffin, zirconium and acetate treatment may also be performed in 3 different baths following each other.

As further examples of our process we may mention the fixing of delustering agents on artificial silk, of animalizing agents on artificial cellulosic fibers or of artificial resins used for rendering textiles stiff or crease-proof. Also dyeings with water-insoluble (pigment) dyestuffs can be more permanently fixed on textile material by a treatment with our zirconium compounds. If, for instance, ice-color dyeings on cotton are aftertreated with one of our zirconium compounds, the shade of the dyeings remains nearly unchanged by subsequently soaping whereas it is considerably lightened when not aftertreated.

Example 1

A fabric which may consist of viscose staple fiber, wool flannel, silk or a mixture of wool and staple fiber (50:50) is treated for 2 to 5 minutes at 90° C. with an aqueous solution containing per liter 2.5 to 10 g. of zirconium oxychloride and 0.5 to 2 g. of crystallized sodium acetate. The fabric is then well centrifuged and dried at 100° C. for 20 minutes. The fabric has become excellently water-repellent and does not lose this property even when washed with soap.

Example 2

A viscose staple fiber fabric is immersed into a 1% hot solution of sodium stearate, centrifuged and dried. Thereupon the fabric is treated as described in the foregoing example. It becomes excellently water-repellent and does not lose this property even by washing with soap or by boiling for 10 minutes with an aqueous solution containing 5 g. Marseilles soap and 3 g. of soda per liter.

Instead of the sodium stearate, any other salt of a hydrophobic acid may be used, as above mentioned. In all cases, the fabrics so treated become excellently water-repellent and do not lose this property by washing with soap or even by boiling.

Example 3

A staple fiber fabric having been impregnated with an aqueous solution of 10 g. of sodium stearate per liter is immersed for some minutes into a bath of 80 to 90° C. containing per liter water, 20 ccm. of a zirconium hydroxide sol (having a zirconium content which corresponds to 9.4% ZrO_2) being obtainable according to Example 4 of the German specification No. 582,682. The fabric is then well centrifuged and quickly passed through an aqueous bath containing 6 g. of crystallized sodium acetate per liter. After having been again centrifuged and dried the fabric has become permanently water-repellent.

Instead of the zirconium hydroxide sol bath there may also be used an aqueous solution containing 5 g. of zirconium oxynitrate and, if desired, 2 g. of crystallized sodium acetate per liter.

Example 4

A viscose staple fiber fabric is immersed in a hot carbon-tetrachloride solution containing 2.5 g. of hard paraffin and 2.5 g. of paraffin oil per liter, centrifuged and the solvent evaporated at 50 to 60° C. Thereupon the fabric is treated for 5 minutes in a bath of 80 to 90° C. containing 5 g. of crystallized zirconium oxychloride (having a zirconium content corresponding to 44% ZrO_2) and 2 g. of crystallized sodium acetate per liter of water. After centrifuging, quickly passing through an aqueous solution of 6 g. of crystallized sodium acetate per liter, again centrifuging and drying at 90 to 100° C. the fabric has become water-repellent and does not lose this property even on washing and boiling.

Instead of the zirconium oxychloride there may also be used with a similar result the same quantity of zirconium oxynitrate or 20 ccm. of the zirconium hydroxide sol mentioned in the foregoing example, in which cases the addition of the sodium acetate to the zirconium bath may be dispensed with.

Example 5

Instead of the paraffins in the foregoing example there may also be used one of the following products:

5 g./l. of a product obtainable by condensing a high molecular fatty acid chloride with a high molecular amine or alcohol as, for instance, stearoyl octadecyl amide or

5 g./l. of a condensation product of a high molecular isocyanate with a high molecular amine or alcohol as, for instance dioctadecylurethane, or

5 g./l. of a condensation product of a high molecular isocyanate or fatty acid chloride with such amines and/or alcohols which contain more than 1 reactive group as, for instance, the condensation product of octadecylisocyanate with ethylenediamine.

By impregnating as described in the foregoing example the fabrics so treated become permanently water-repellent.

Example 6

A viscose staple fiber fabric is impregnated with a paraffin- or wax-emulsion containing per liter of water 7 g. of oleic acid, 1.2 g. of triethanolamine, 0.45 g. of potassium hydroxide and 3 g. of paraffin or wax. The fabric so im-

pregnated is passed through an aqueous solution containing per liter 50 to 60 g. of crystallized zirconium oxychloride (44% ZrO_2), and thereupon through squeezing rollers into a rinsing bath containing per liter of water 10 g. of crystallized sodium acetate. Finally, the fabric is again squeezed and dried at 90 to 100° C. It has become excellently and permanently water-repellent.

Example 7

A staple fibre fabric is introduced for a short time into a bath which has been prepared by adding to a solution of 12.4 parts of crystallized zirconium oxychloride (44% ZrO_2) in 500 parts of water an aqueous emulsion containing 7 parts oleic acid, 1.2 parts of triethanolamine, 0.45 part of potassium hydroxide, 3 parts of paraffin or wax and 88 parts of water. Thereupon the fabric is squeezed, rinsed in a bath containing 10 g. of crystallized sodium acetate per liter of water, again squeezed and dried. By adding the ingredients to the impregnation bath as they are removed therefrom by the fabric, it is possible to impregnate fabrics continually in this manner. After drying the fabrics so treated have become excellently water-repellent and do not lose this property by washing and boiling.

Example 8

A fabric having been impregnated in the usual manner with a paraffin-glue-emulsion is immersed in an aqueous solution of 10 g. per liter of crystallized zirconium oxychloride (44% ZrO_2) to which up to 4 g. per liter crystallized sodium acetate may have been added or 20 ccm. per liter of the above mentioned zirconium hydroxide sol. The fabric is then squeezed or centrifuged, passed through a rinsing bath containing 6 g. of crystallized sodium acetate per liter of water, again squeezed or centrifuged and dried. The fabric has become water-repellent and does not lose this property by washing, boiling, fulling or treatment with acids.

Example 9

A viscose artificial silk fabric is passed through a bath containing per liter of water 17 g. of the emulsion described in the following paragraph and 12 g. of zirconium oxychloride (46% ZrO_2), squeezed, rinsed in a bath containing 10 g. per liter of crystallized sodium acetate, again squeezed and dried.

The above mentioned emulsion is prepared in the following manner: 8.8 parts of technical n-dodecyl salicyclic acid are made slightly alkaline by adding triethanolamine, diluted with 20 parts of water, the whole added to a warm mixture of 7.5 parts of oleic acid, 4 parts of triethanolamine, 4.5 parts of ceresin and 3 parts of paraffin (melting point 52° C.), preferably in a kneading machine.

The fabric treated in this manner is excellently water-repellent, permeable to air and has a full soft feel. Its water-repellent character is not destroyed by washing with soap or even by boiling with soap and soda.

Example 10

A mixed fabric from cotton and viscose staple fiber is impregnated with an aqueous emulsion containing per liter 20 g. of a weakly acid paraffin emulsion (containing about 18% paraffin, 8% glue, 6% aluminium hydroxide, 6% formic acid, 1% colophony), 24 g. of zirconium oxychloride and 4 g. of sodium acetate. After squeezing the fabric is shortly passed through a 0.5% aqueous sodium acetate bath, squeezed and dried at about 100° C. It has become permanently water-repellent.

Instead of the above emulsion, other paraffin emulsions containing aluminium compounds may be used with a similar result, for instance such as contain resin acid salts.

Example 11

A fabric used in the foregoing example is impregnated with an emulsion containing per liter of water: 5 g. of sodium oleate, 3.2 g. of paraffin, 3.2 g. of ceresin, 2.8 g. of a montanic acid ester and 24 g. of zirconium oxychloride (46% ZrO_2) which has been buffered at a pH of 4.0 to 4.5 by adding sodium acetate or sodium tetraborate or a mixture of soda and sodium acetate. After squeezing and drying at temperatures above 80° C., the fabric is excellently water-repellent and does not lose this property by repeatedly washing with soap.

Similar results are obtained if the paraffin or ceresin are partly or wholly replaced by the ketones and/or alcohols which are obtainable from stearic acid, train oil fatty acids and similar high molecular acids by distillation of their calcium salts and, if desired, subsequent reduction. Also these hydrophobic compounds are permanently fixed on the fabrics by the zirconium treatment.

Example 12

A fabric of fibers of animal or vegetable origin is impregnated with the following emulsion:

40 g. of a paraffin wax emulsion containing 18% of a triethanolamine soap, 8% hard paraffin, 8% of ceresin, 7% of a wax-like montanic acid ester and 2% of triethanolamine are diluted with warm water to 800 ccm. and then added to a solution of 24 g. of zirconium oxychloride (46% ZrO_2) in 200 ccm. of warm water. After cooling to 30° C., there are added 3 g. of calcined soda, thereupon 2 ccm. of glacial acetic acid, and, after some time, 6 to 9 g. of crystallized sodium acetate.

After impregnation the fabric is squeezed or centrifuged and dried at temperatures above 50° C. It has become permanently water-repellent.

Example 13

Cotton cloth is impregnated with an emulsion containing per liter of water 40 g. of polyvinylacetate, 2 g. of polyvinylalcohol, 24 g. of zirconium oxychloride (46%) and 10 to 15 g. of crystallized sodium acetate. The fabric is squeezed and dried. It has acquired a permanent stiff finish which is not destroyed by repeatedly boiling the fabric for 20 minutes with an aqueous solution of 5 g. of soap and 3 g. of soda per liter. Whereas the weight of the fabric is 7.77 g. before impregnation and 8.54 g. after impregnation and drying, it is 8.50 g. after the fourth washing.

Example 14

A viscose artificial silk fabric is impregnated, after desizing, dyeing and drying, on the foulard with a solution containing in 100 liters of water, 14 kg. of dimethylol urea and 3.5 liters of a zirconium oxychloride solution having a zirconium content which corresponds to about 10% ZrO_2 and buffered with sodium acetate. The fabric is then squeezed, dried as usual and subjected to a temperature of 120° C. for 10 minutes. The fabric has become excellently crease-proof and water-repellent and does not lose these properties, for instance, on being washed three times.

Example 15

A mixed fabric of mercerized cotton and staple fiber is impregnated with an aqueous solution containing per liter 80 g. of urea, 190 g. of formaldehyde and 30 ccm. of the zirconium hydroxide sol mentioned in Example 3. If desired, suitable softening agents may also be added. Thereupon the fabric is dried on a cylinder drying machine and subjected for 5 to 8 minutes to a temperature of 140° C. The fabric has become crease-proof, water-repellent and unshrinkable to a far-reaching extent and does not appreciably lose these properties by washing.

Example 16

50 kg. of a mixed wool staple fiber yarn are treated after drying with an aqueous solution containing in 100 liters, 50 kg. of dimethylol urea, 4 liters of an aqueous zirconium oxychloride solution containing about 80 g. of ZrO_2 per liter and buffered with sodium acetate, and 1.8 kg. of a 28% emulsion of paraffin. The yarn is centrifuged until its weight is 85% higher than it was originally, and dried at 65° C. The yarn is worked up into carpets or tapestry which are aftertreated for 10 minutes at 120° C. The fabrics are excellently water-repellent and their surface is very fast against crushing.

Example 17

A mixed worsted fabric (45% wool and 55% staple fiber from cuprammonium cellulose solution) is treated similarly as described in Example 14 with a solution containing 15 kg. of dimethylol urea and 3.8 liters of zirconium hydroxide sol in 100 liters of water. Suitable softening and finishing agents may be added. The fabric is then dried as usual, treated for 10 minutes at 125° C., steamed and finished as usual. The fabric has an extraordinarily full feel, is crease-proof and does not take up water. These properties are not lost during washing.

Example 18

A viscose artificial silk fabric having been delustered in known manner by aftertreating with a titanium dioxide suspension is treated for 5 minutes in an aqueous bath of 80 to 90° C. containing 20 ccm. of the zirconium hydroxide sol mentioned in Example 3, squeezed, shortly rinsed in a solution of 6 g. of crystallized sodium acetate per liter of water, again squeezed and dried at 80 to 100° C. The pigment has been permanently fixed thereby on the fibers and is not removed therefrom by soaping or even by boiling for 10 minutes with a solution containing 5 g. of Marseilles soap and 3 g. of soda in 1 liter of water.

Example 19

A dyed cellulose acetate artificial silk satin is impregnated with an emulsion containing per liter water 8 g. of paraffin and wax, 4 g. of soap and 24 g. of zirconium oxychloride (46% ZrO_2), and buffered with sodium acetate at a pH of 4.2. After drying at 90° C., the fabric is permanently water-repellent.

This application is a continuation in part of our co-pending application Ser. No. 221,452, filed July 26, 1938.

We claim:

In the process of producing finishes on textile material the improvement which comprises impregnating the material with an aqueous paraffin emulsion containing a zirconium compound selected from the group consisting of zirconium oxychloride, zirconium oxynitrate and the water-soluble hydrolysates obtainable therefrom, rapidly passing the so-treated material through a dilute aqueous sodium acetate solution and finally drying the material at an elevated temperature.

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