3,829,288 PROCESS FOR FINISHING CELLULOSE-CONTAINING TEXTILES
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U.S. Cl. 8—115.6 8 Claims

ABSTRACT OF THE DISCLOSURE
A process for finishing textiles at least partly containing cellulose with aminoplast-resins and organopolysiloxanes from organic solvents, is characterized in that conditions imparting impregnations with baths containing from 5 gr./l. to 60 gr./l. of an organically soluble artificial resin preferably ethephered with lower monovalent alcohols, 5 gr./l. to 50 gr./l. of a hydrogen alkylpolysiloxane, at least 25 ml./l. of a polar solvent and at least 1.5 gr./l. of a dialkylacetamide dissolved in a non-polar solvent. Thereupon the textiles are freed from the surplus bath, dried and condensed.

This invention relates to a process for finishing textiles containing cellulose.

It has been known for a long time to treat cellulose textiles with aqueous emulsions of organopolysiloxanes, whereby in addition to cationic and anionic emulsifiers non-ionic emulsifiers are also used for the making of emulsions, for the hydrophobing of cellulose containing textiles. As catalysts are then used, among others, various types of metal salts. It is also possible to combine the hydrophobing with an artificial resin treatment. These processes have the drawback that they are necessary to emulsify the organopolysiloxanes by a complicated process and that the produced emulsions have only a limited storage period. When combined with an artificial resin care must be taken that it is compatible with emulsifiers and catalysts, so that existing conditions must be examined prior to the starting of the treating baths.

It is also known to make cellulose fabrics hydrophobic by using in the usual manner organohydrogenpolysiloxanes, possibly with diorganopolysiloxanes in the presence of metal holding catalysts, primarily alcohols or acylates in organic water-insoluble solvents. These processes have the drawback that while an adequate hydrophobic effect is produced there is no real improvement of crease strength.

Furthermore, a process for improving the crease strength of cellulose containing textiles is known wherein they are impregnated with clear to opalescent solutions or finely dispersed, permanent water-in-oil emulsions which contain emulsified water soluble methylic compounds of urea or cyclic allylurea, about 2% to 8% water, a hardening catalyst in hydrocarbons or chlorated hydrocarbons with selected emulsifiers. They are then dried and if necessary condensed. This process again requires the use of a comparatively high amount of emulsifiers which considerably disturb the following hydrophobing. Furthermore, the resulting crease resistance is not satisfactory in all cases.

It is also known to finish textiles which at least partly contain cellulose by impregnating them with a solution or dispersion of a resin precondensate which can react under acid conditions either with itself or with the fibrous substance, along with an acid or latent acid catalyst and a halogenized hydrocarbon solvent. Directly thereafter they are subjected to the action of hot water or steam and are then heated. As latent acid catalysts are named, for example, monochloracetic acid and arylsulfonfylholigonides. This process has the drawback that only imperfect crease resistance is produced. Furthermore, the combination with siloxanes without the use of an additional catalyst has no effect upon results. In addition, the introduced catalysts have a corroding effect upon the apparatus being used. Finally, it is absolutely necessary to provide an additional treatment with hot water or steam for hardening the resin.

In addition, agents for making water repellant organic fibrous materials are known which contain, among others, alkylhydrogenpolysiloxanes and aluminumisocarbone as catalysts. This known process discloses the simultaneous use of urea formaldehyde resins and melamine formaldehyde resins. This process has the drawback that due to hydrolysis sensitivity of the aluminum alcohoholets it is necessary to operate entirely without water. When operating without the use of protective gases a quick hydrol-ysis of the catalyst and a decomposition of the baths must be expected. In addition, water repellent effects are produced by this process and possible crease resistance produced after the combination with artificial resins are extremely poor.

An object of the present invention is the provision of a process for refining cellulose containing textiles with aminoplastresins and organopolysiloxanes from organic solvents which does not have the drawbacks of processes known in prior art.

Other objects of the objectives of the present invention will become apparent in the course of the following specification.

In the accomplishment of the objectives of the present invention a process was found wherein conditionally moist textiles are treated with baths containing dissolved 5 gr./l. to 60 gr./l. of an organically soluble artificial resin preferably etherified with lower mono-valent alcohols, 5 gr./l. to 50 gr./l. of a hydrogenalkylpolysiloxane, at least 25 ml./l. of a polar solvent and at least 1.5 gr./l. of a dialkylacetamide in a non-polar water-insoluble solvent. Thereupon the textiles are freed from excessive bath, dried and condensed.

In carrying out the process of the present invention it was found particularly surprising that the conditional moisture of textiles—contrary to prior art processes—is sufficient to provide for the textiles a very good crease resistance with low amounts of artificial resins. It is noteworthy, that this property is not reached when polysiloxanes results is submitted of the use of the combination of the present invention, so that apparently siloxane has a synergistic effect as far as crease resistance is concerned.

All organically soluble preferably这种aromaticoplastresins are suitable for the process of the present invention. It was found that particularly suitable aminoplastresins are uron-, melamine-, and dihydroxyethyleneurea resins ethephered with lower mono-valent alcohols. In addition ethylene-, propylene-, and acetyleneurea resins ethephered with lower mono-valent alcohols are usable. Furthermore, mono- and dimethyurea ethers with the same alcohols as well as organically soluble carbamate resins and triazine resins can be used as aminoplastresins for the process of the present invention. Acetals and hemiacetals are also usable. In principle according to the present invention it is possible to use all artificial resins which are soluble in organic solvents, including those usable in an aqueous system. The following aminoplastresins can be mentioned individually: dimethoxydimethylolethylene urea, dimethoxydimethyl propylene urea, dimethoxy- and dipropoxy-dimethyl-triazine, dimethoxydimethylolethylene- and dimethoxy-di-methylol-ethoxy-carbamate, tetramethoxy-tetra-methylol-
acetylenediurea, acetal or hemiacetal of diethylene glycol, dimethoxy-dimethyloleourea, highly etherified penta- or hexamethyloxime, dimethoxy- and di-n-butoxy- dimethyloleourea and tetramethoxy-dimethyloletheroxy- ethylene urea. The amount of etherified aminoplastresins is 5 gr. to 60 gr., preferably 10 gr. to 40 gr. per liter of the treating bath, whereby the amount also depends upon the textile substance being treated.

The treating baths used in accordance with the process of the present invention contain organopolysiloxanes with hydrogen atoms bound to silicon, as for example, alkylhydrosiloxanes, particularly methylhydrogen or ethylhydrogenpolysiloxanes. These organopolysiloxanes can be also mixed with small amounts of diorganopolysiloxyxanes which do not contain any hydrogen atoms bound to silicon, as particularly dimethylpolysiloxane or diethyl- polysiloxane. Obviously it is also possible to use instead of these mixtures suitable polyhydrosilanes, namely, to jointly hydrotize for the making of organopolysiloxanes which do not contain hydrogen atoms bound to silicon with small amounts of such silanes which do not have any hydrogen atoms bound to silicon. The amount of organohydrosiloxanes is 5 to 50 gr., preferably 10 to 30 gr. per liter of the treating bath.

As catalysts for the process of the present invention are suitable dialkyldimethylacetales, whereby their commercial availability can be used. Alkyl resin can is then more than 2, particularly 4 to 12 carbon atoms. As acids those are used which have more than 1, particularly 4 to 18 carbon atoms. Obviously it is also possible to use saturated or unsaturated dicarboxic acids with 4 and more carbon atoms. The following catalysts can be individually named: dibutylindiaurate, dibutylindiacetate, dibutylinmaleate, diocytlinmaleate, diocytlindioctoate, dilaurylindiasuccinate, dihexylindadiate, diocytlindistearate and dibutylin-2-ethylhexoate. Particularly preferred are dibutylinindiaurate, dibutylinindiacetate and dibutylinmaleate. The amount of the catalysts is then at least 1.5 gr., preferably 2 gr. to 10 gr. per liter of the treating bath.

To carry out the process of the present invention it is absolutely necessary to add a polar solvent to the treating bath. As polar solvents are suitable dimethylformamide, dimethacetales and specially lower alcohols, particularly mixtures of lower alcohols. As particularly preferred was found a mixture of methanol and isopropanol in the volume ratio of 3:1. The amount of the polar solvent is at least 25 ml., preferably 50 ml. to 200 ml. per liter of the treating bath.

Hydrocarbons, particularly halogenated hydrocarbons of technical quality were found to be suitable as organic, non-polar water-insoluble solvents used for the making of treating baths. As such solvents can be named: trichloroethylene, tetrachloroethylene, methylene chloride, chloroform, tetrachlorcarbon, 1,1,2-trifluortrichloroethane and 1,1,1-trichloroethane. Toluol, xylol, benzol and test-bein are their combustible.

The baths can be made in any desired manner. Preferably the aminoplastresin and the hydrogenpolysiloxane, as well as the polar solvent are stirred jointly and diluted with the non-polar solvent. Finally the catalyst is added. However, it is also possible to mix together in advance the four component parts of the bath and then to produce the treating bath by the addition of the non-polar solvent. Before the baths can be used for treatment it is necessary to allow them to stand for a certain time in order to produce a reaction ready system. It was found that for room temperature a waiting time of 3 to 8 hours is sufficient. The treating bath is ready for use and the best possible results are then obtained. Only if the standing time is too long is there a drop, particularly in the crease angle. If the bath prior to preparation is activated at a higher temperature at about 30° C. to 55° C., then it can be made ready after 1 to 60 minutes, depending upon the reactivity of the artificial resin. Then it can be assumed that the same results will take place up to 8 hours at the activating temperature, while after that time period a drop will take place again particularly as far as crease resistance is concerned. Obviously it is also possible to cool the bath after activation to normal temperature, whereby the bath is then again usable up to 3 days.

The process of the present invention can be used for treating fabrics of cellulose fibers as well as those of regenerated cellulose fibers. Obviously it is also possible to treat mixed fabrics of cellulose fibers and synthetic fibers, particularly polyester, -polyamide- and polycrylonitrile fibers to make them crease proof and hydrophobic in accordance with the process of the present invention.

To carry out the process of the present invention it is absolutely necessary that the above-mentioned fabrics should be treated with the bath not when they are absolutely dry but when they are in a conditionly moist state. It was found that already the action of the normal relative air moisture upon the moisture in the fabrics is sufficient to provide very good results. The term "conditionally moist textiles" means the amount of moisture in percentage of the weight of the textiles received at the room temperature under certain relative moisture after the balance is set (see German book Handbuch der Werkstoffprüfung, 2 ed., vol. 5, pages 278 to 382 and 379 to 382). If for some reason the moisture is less moisture then prior to the treatment it can be conditioned for a short time, for example, by treatment with steam.

In carrying out the treatment the conditionally moist fabric is immersed into the bath, pressed in the usual manner to bath reception of 90 to 130%, then dried at 80 to 110° C. and finally condensed for a few minutes at 120 to about 160° C. The fabric thus treated has an exceptionally good crease resistance and water repellency determined according to the spray test (AATCC 22-1952) is also good.

The advantages of the process of the present invention are apparent. The making of the baths is extremely simple, since they are produced without an emulsifier by simple joint stirring. Furthermore, according to the process of the present invention all organically soluble artificial resins can be used, including those usable in an aqueous system, but in considerably lesser concentrations. The small usable amounts of in the average 25 to 35 gr./l. artificial resin are particularly surprising if it is taken into consideration that the resulting crease resisting angles (according to DIN 53890) in case of an aqueous treatment correspond to considerably greater used amounts of artificial resin. Thus the process as compared to all prior processes with aqueous and organic media by using comparable amounts of artificial resin results in a considerably better crease resistance of the fabric. Since the baths of the present invention do not have an emulsifier they provide a much greater possibility of combination with other textile auxiliary agents. It should be particularly stressed that for cotton and cotton mixed fabrics the process of the present invention in addition to an exceptionally good crease resistance also produces a good hydrophobic action.

It is also possible to apply the baths of the present invention silicic acid esters, polyethylene, optical brightening agents, hydrophilizing agents, anistatic and other agents, whereby crease resistance does not suffer while the good properties of the added substance come completely into effect.

It is most surprising and could not be foreseen that the process of the present invention which uses treating baths which are practically devoid of water, produces excellent crease resistance solely by the condensation action of the fabric. Up to now there was an erroneous opinion in the industry that cellulose containing fabrics can be made sufficient crease resistant only when at least small amounts of water along with the artificial resin are applied upon the fabric in the treating bath or when the fabric treated
with artificial resin is treated with water or steam prior to condensing. It is also most surprising that in the process of the present invention only alkyl-Sn-acrylates suffice to fix wash resistance upon the fibers by the hydrogen polysiloxane as well as the aminoplast resin. In this connection it was particularly surprising that the process of the present invention will produce the described combination of excellent effects.

The following examples are given by way of exemplification only:

**EXAMPLE 1**

To produce the treating bath 30 gr. dimethoxydimethylolethyleneurea, 15 gr. methylhydrogenpolysiloxane (viscosity at 20° C. 30 cp.) and 100 ml. of a mixture of methanol and isopropanol in volume ratio 3:1 are stirred jointly, filled with tetrachloroethylene to 1 L, whereupon 6 gr. technical dibutyltindilaurate (active substance 99.78%, residue HCl) are stirred in. The bath thus produced is held for 15 minutes at 40° C. and then a cotton poplin (q.m. weight 122 gr.) is saturated therewith, is pressed to 100% bath reception and is then condensed for 4 minutes at 140° C.

In order to show the effect of the relative moisture of the finishing chamber, the fabric was stored at different relative moisture and then treated, whereby the following results were produced.

**TABLE 1**

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Crease Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>127</td>
</tr>
<tr>
<td>10%</td>
<td>122</td>
</tr>
<tr>
<td>15%</td>
<td>111</td>
</tr>
<tr>
<td>20%</td>
<td>132</td>
</tr>
<tr>
<td>25%</td>
<td>145</td>
</tr>
</tbody>
</table>

The spray test according to AATCC produced for all samples the value 100.

**EXAMPLE 3**

28 gr. of an hereinafter described aminoplast resin is stirred with 15 gr. ethylhydrogenpolysiloxane (viscosity at 20° C. about 38 cp.), 100 ml. dimethylformamide and 8 gr. technical dibutyltindilaurate (acid number 170) and filled with tetrachloroethylene to 1 L. The resins were:

(a) dimethoxy-dimethylolethyleneurea
(b) dimethoxy-dimethylopropylenurea
(c) dimethoxy-dimethyloctadecanoate
(d) acetol of diethylene glycol
(e) dimethoxy-dimethyloctadecanoate
(f) tetra-methoxy-tetraethyl-aceylene-diurea
(g) hexamethyloctalamine highly etherified with methanol

A cotton poplin (q.m. weight 122 gr.) conditioned at 100% relative moisture was immersed in the above described baths (previously activated at 40° C. for 30 minutes), was pressed to 100% bath reception, dried at 110° C. for 15 minutes and finally condensed for 3 minutes at 150° C. For comparison purposes, the same amounts were treated in (A) etherified resins and (B) non-etherified resins in H2O with the use of the usual catalysts. The treating conditions were the same as indicated above. The following table shows particularly clearly the advantageous crease resistant effects of the process of the present invention:

**TABLE 2**

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Crease Angle (°)</th>
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<tbody>
<tr>
<td>5%</td>
<td>127</td>
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<tr>
<td>10%</td>
<td>122</td>
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<td>20%</td>
<td>132</td>
</tr>
<tr>
<td>25%</td>
<td>145</td>
</tr>
</tbody>
</table>

The spray test according to AATCC produced for all samples the value 100.

**EXAMPLE 4**

To 150 ml. of a mixture of methanol and isopropanol (3:1) were added 40 gr. of hexamethyloctalamine highly etherified with methanol, 20 gr. hydrogenmethylpolysiloxane (viscosity at 20° C. 40 cp.) and 10 gr. dipropyltindilaurate and the resulting mixture was filled with tetrachloroethylene to 1 L. Into the bath thus produced was immersed after an activating time period of 30 minutes at 50° C. a conditioned polyester-cotton fabric (65:35, 133 gr./m2), it was squeezed to 120% bath reception, dried for 10 minutes at 120° C. and condensed for 3 minutes at 150° C. The produced effects are clearly superior over those which are produced under the same treating conditions by the application of water.

**EXAMPLE 5**

To the bath produced as described in Example 4 were added 0.2% (based on weight of fabric) of an optical brightener having the formula

\[
\text{Na}_{2} \text{O}_{5} \quad \text{OH} \quad \text{CH} \quad \text{CH} \quad \text{N} \quad \text{Na}_{2} \text{O}_{5}
\]

and cotton poplin was treated therewith. The treatment shows a clear brightening without any diminution of mechanical-technical examined values.

**EXAMPLE 6**

A mixture of 40 gr. dimethoxydimethylolethyleneurea, 15 gr. hydrogenmethylpolysiloxane (ratio of hydrogen atoms bound to silicon to methyl groups 4:1, viscosity at 20° C. 30 cp.), 150 ml. dimethylacetamide and 10 gr. technical dibutyltindilaurate (acid number 280) is added to a solution containing 1000 ml. perchloroethylene and after activating for 15 minutes at 50° C. is applied to different
textile samples in the manner described in Example 3. The following results are produced

| Crease angle according to | Spray test DIN 58890 | according to AATCC22-
<table>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Warp</td>
<td>Wett</td>
<td>1002</td>
</tr>
<tr>
<td>(a)</td>
<td>Viscose staple fibre (q.m. 153 g.)</td>
<td>110</td>
</tr>
<tr>
<td>(b)</td>
<td>Viscose filament (q.m. 87 g.)</td>
<td>128</td>
</tr>
<tr>
<td>(c) Cotton-polyester 50:50 (q.m. 101 g.)</td>
<td>140</td>
<td>140</td>
</tr>
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</table>

EXAMPLE 7

To the bath produced in accordance with Example 6 were added additionally 5 gr./l. hydrophilizing agent (di-n-octyl-sodium-sulfosuccinate) and then the above-described treatment was carried out. While the spray value dropped to 0, no diminution of the crease angle could be ascertained.

EXAMPLE 8

A cotton-polyamide mixed fabric 80:20 (q.m. weight about 112 g.) was treated at 80% relative air moisture with a bath containing 30 gr./l. ethoxydimethylolurorn, 12 gr. methylhydrogenpolysiloxane (see Example 1 for details), 3 gr. dimethyolphosiloxane (viscosity 750 cp.), 150 ml. ethanol and 8 gr. technical diocyltindilaurate per 1 l. (solvent tetrachlorethylene). The fabric was heated for 10 minutes to 50° C., then cooled to 20° C., impregnated, pressed to a bath reception of 110% and fixed in the usual manner by drying and condensing. The fabric thus treated has an excellent crease resistance (measured according to DIN 53890) and a good water repellent effect (measured according to AATCC 22-1952).

What is claimed is:

1. A process for finishing at least partly cellulose containing textiles, comprising preparing and activating a bath containing
   (a) 5 gr./l. to 60 gr./l. of an organic soluble artificial resin selected from the group consisting of methylolated ureas, methylated carbamate, methylolated melamine, acetals and hemiacetals of diethyleneoglycol, and their etherified derivatives, etherified with alkyl alcohols with 1 to 4 C-atoms,
   (b) 5 gr./l. to 50 gr./l. alkylpolysiloxanes containing hydrogen atoms bound to silicon with a viscosity of from 30 to 50 cp.
   (c) at least 25 ml./l. of a polar solvent selected from the group consisting of alkyl alcohols containing 1 to 3 C-atoms, dimethylformamide, dimethylacetamide and their mixtures and
   (d) at least 1.5 gr./l. of dialkyltlicacylate, the alkyl groups containing 3 to 12 C-atoms and the acyl groups containing 2 to 18 C-atoms, the substances (a) to (d) being dissolved in a non polar water-insoluble organic solvent, the activating being effected before using the bath by remaining it at room temperature to 55° C. for 8 hours to 1 minute, whereby the remaining time is inversely proportional to the temperature, impregnating the textile having at least a humidity content corresponding to the humidity obtained by storing the textile at a relative humidity of at least 30% till equilibrium is reached, in said bath, then removing excessive bath from said textile, drying at 80° C. to 110° C. and condensing it at 120° C. to about 160° C.

2. A process in accordance with claim 1, wherein the organic soluble artificial resins are selected from the group consisting of methylolated ureas, methylolated carbamates, and methylolated melamine, etherified with alkyl alcohols containing 1 to 4 C-atoms.

3. A process in accordance with claim 2, wherein the organic soluble artificial resins are selected from the group consisting of methylolated dihydroxyethylene urea, methylolated uron, and methylolated melamine, etherified with alkyl alcohols with 1 to 4 C-atoms.

4. A process in accordance with claim 1, wherein the alkylpolysiloxanes containing hydrogen atoms bound to silicon are selected from the group consisting of hydrogenmethylpolysiloxanes and hydrogenmethylpolysiloxanes.

5. A process in accordance with claim 1, wherein the said dialkyltlicacylate is selected from the group consisting of dibutyltindilaurate, dibutyltindicate and dibutyltlnmaleate.

6. A process in accordance with claim 1, wherein the said dialkyltlicacylate selected from the group consisting of a mixture of methanol and isopropanol.

7. A process in accordance with claim 1, wherein the non-polar solvent is selected from the group consisting of chlorinated and fluorinated hydrocarbons.

8. A process in accordance with claim 1, comprising adding to the bath dialkylpolysiloxanes.

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