EMULSION FOR HYDROPHOBING TEXTILES

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6 Claims. (Cl. 106--271)

ABSTRACT OF THE DISCLOSURE

A product for hydrophobing textiles and other fibrous materials consists of an aqueous emulsion of paraffin with a quaternary ammonium salt as emulsifier which decomposes and produces water repellency when heated, the emulsion containing 3 to 15 parts by weight of paraffin to 1 part by weight of the quaternary ammonium salt. The salt has one aliphatic residue with at least 12 carbon atoms.

This invention relates to an emulsion for hydrophobing fibrous materials, particularly textiles. It is known in the prior art to treat fibrous materials with quaternary ammonium salts which have at least one higher aliphatic residue and which decompose when heated, so as to produce water repellent effects. The hydrophobing results which are thus obtained are so completely unsatisfactory from the point of view of present day requirements, that the use of a technical charge as hydrophobing products is not even considered any more. The addition of metal salts or synthetic resin precondensates, which has also been suggested, does not provide practically any improvement.

It was also suggested to add emulsions of paraffin to treating baths containing such quaternary salts. This requires a special manufacture of such emulsions.

Furthermore, it was stated that self-emulsifying pastes could be manufactured from quaternary ammonium salts with one half of or at most the same amount by weight of paraffin with the addition of organic solvents, and that these pastes could be used for hydrophobing fibrous materials. These emulsions have often poor stability in concentrated as well as diluted states and the hydrophobing effects produced by them, as well as their resistance against washing, do not satisfy modern requirements. An increase in the concentration of the quaternary ammonium salt does not yield an improvement which would be commensurate with the increased consumption of material.

An object of the present invention is to improve prior art hydrophobing products.

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

During the accomplishment of the objectives of the present invention it was surprisingly found that emulsions having 3 to 15 parts, preferably 5 to 10 parts paraffin to 1 part of a salt of a quaternary nitrogen base which decompose when heated—the base having 1 aliphatic residue with at least 12, preferably at least 16 carbon atoms—are more stable in concentrated, as well as diluted state, than emulsions with a smaller amount of paraffin; it was further discovered that they have hydrophobing effects which are more permanent in washing than those of the known emulsions. Actually, it could have been expected that emulsions with a lower ratio of the emulsifier to the dispersed substance would be less stable and that an increase in the paraffin component which by itself is not wash resistant, would make substantially worse the wash resistance of the produced hydrophobing effects.

The emulsions of the present invention are manufactured in the usual manner preferably in a concentrated state and in use are diluted with water.

As salts of quaternary nitrogen bases are used known compounds having the formulae:

\[ R—NR_2R_3R_4^+X^- \]

or

\[ R—Y—CH_2—NR_2R_3R_4^+X^- \]

wherein \( R \) is an aliphatic, possibly branched off or unsaturated residue with at least 12, preferably at least 16 carbon atoms; \( R_1, R_2 \) and \( R_3 \) are aliphatic, cycloaliphatic or aromatic residues, such as methyl, ethyl, propyl, cyclohexyl or benzyl; however, \( NR_2R_3R_4 \) can also represent a heterocyclic residue, such as pyridine or its homologs, oxyethylmorpholine, N-ethylepiperidine or chinoline. \( X^- \) is an anion used for salt formation, particularly an anion of a strong inorganic preferably volatile acid. \( Y \) is a heteroatom, particularly oxygen, or an atom group containing at least 1 hetero-atom. Carbon amido-groups are, however, less suitable since salts of such quaternary nitrogen bases have in general a worse emulsification capacity—even with respect to small amounts of paraffin—and their aqueous solutions when standing in the heat often produce decompositions of the quaternary salts.

In accordance with the present invention compounds of the following formula are preferred, since they were found to be particularly successful in use:

\[ R—O—CH_2N\text{N(tet.)}^+X^- \]

They include tertiary heterocyclic amines, particularly pyridine. \( X^- \) is the anion of a strong inorganic acid, preferably hydrochloric acid.

The manufacture of the salts of quaternary nitrogen bases takes place in accordance with known processes.

As paraffins are used such having a melting point above 45°C, preferably 30°C—70°C. To avoid difficulties in the manufacture of the emulsion the melting point should not be higher than 90°C.

The concentrated emulsions of the present invention are produced by mechanical emulsification in the usual manner; solvents for paraffin, such as aromatic hydrocarbons, or halogenated aliphatic hydrocarbons can be also included. Despite substantial excess of paraffin with respect to the emulsifyingly acting salt of the quaternary nitrogen base, these emulsions are very stable and can be stored for very lengthy time periods. Diluted emulsions are also stable, so that treating baths during continuous operations leave a much lesser coating upon the foulard rollers than prior art emulsion having less paraffin.

The treated textiles after drying are heated in a known manner to about 120°C—160°C, to complete the decomposition of the salt of the quaternary base and the fixing of the remaining compounds.
The hydrophobic treatment of textiles with the emulsions of the present invention can be further improved in certain cases as far as resistance against hot washing is concerned, by the additional use of salt of (3 or more) valent metals with inorganic or organic acids, particularly salts of zircon with low organic carboxylic acids.

The emulsions of the present invention can be combined with other usual textile finishing products. By way of example, there can be added to the finishing baths crease-proofing products, products preventing swelling, anti-slipping agents, filling agents, softeners, etc.

The following examples are given by way of exemplification only:

**EXAMPLE 1**

30 gr. octadecyl-oxyethyl-pyrindinum chloride were dissolved at 60° C. in 130 gr. water. 195 gr. paraffin—melting point 58/60° C.—were added thereto in a thin spray with the use of a high-speed stirrer. The pre-emulsion was diluted with 295 gr. water containing 6 ccm. acetic acid (60%). Then the final emulsification took place in a high pressure homogenizing machine at a temperature between 60° C. and 70° C. and at 200—300 super-atmospheric pressure. This emulsion contained 4.6% quaternary pyridinium salt and 28.5% paraffin.

200 gr. of the emulsion were diluted with water to 1 liter. A cotton moleskin was impregnated with this bath, squeezed to 70% bath absorption, dried for 30 minutes at 120° C. and thereupon heated for 5 minutes at 150° C.

This fabric in the original untreated condition had a water absorption of 87% (measured upon the Kessmann apparatus with 10 minutes shower duration) and after 5 hot washes with soap and soda according to the norm VTL 8305-125 had a water absorption of 90%. However after the finishing with the emulsion of the present invention the water absorption dropped to only 8.6%. After 5 hot washes the water absorption had risen to 34.8%.

Such good and wash-resistant hydrophobic effects can not be attained with the same finishing of the same cotton moleskin by the use of only the quaternary salt, or by the use of paraffin alone, or by the use of an emulsion having equal parts of paraffin and quaternary salt, as is apparent from the following comparative treatment data:

(a) A bath of 9.2 gr. octadecyl-oxyethyl-pyrindinum chloride per liter water and then squeezing to 70% bath absorption.

(b) A solution of 65 gr. paraffin in 1 liter = 1630 gr. tetrachlorethylene and 100% bath absorption, so that there was the same amount of paraffin upon the fabric as with the previous finishes.

(c) A bath having per liter water 100 gr. of a paste corresponding to Example 1 of British patent specification No. 612,915 (30% stearamido-methyl-pyrindinum chloride and 30% paraffin) with 70% bath absorption.

(d) An aqueous bath of 100 gr. of a paste corresponding to that of paragraph (c), wherein however, stearamido-methyl-pyrindinum chloride is replaced by the same amount of octadecyl-oxyethyl-pyrindinum chloride, with 70% bath absorption.

The results obtained are set forth in the following table:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water absorption (percent)</th>
<th>Immediate</th>
<th>After 5 hot washings</th>
</tr>
</thead>
<tbody>
<tr>
<td>According to present invention</td>
<td></td>
<td>8.6</td>
<td>34.8</td>
</tr>
<tr>
<td>(a) Only pyridinium compound</td>
<td></td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>(b) Only paraffin</td>
<td></td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>(c) Brit. patent No. 612,915</td>
<td></td>
<td>40</td>
<td>63</td>
</tr>
<tr>
<td>(d) Brit. patent No. 612,915, Example 1 with</td>
<td></td>
<td>42</td>
<td>61</td>
</tr>
<tr>
<td>octadecyl compound</td>
<td></td>
<td>87</td>
<td>90</td>
</tr>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

Emulsions were produced in accordance with Example 1 by the use of octadecyl-oxyethyl-morpholine chloride and increasing amounts of paraffin, whereby in each case the total solid content (quaternary salt plus paraffin) amounted to 35%.

A cotton satin was finished with these emulsions in baths which always contained 200 gr. of the emulsion, 10 gr. crystalline oxochloride and 8 gr. sodium acetate. The drying and the heating of the fabrics took place in accordance with the procedure of Example 1.

The spraying examination prior to and after hot washings produced the following results:

<table>
<thead>
<tr>
<th>Ratio of quaternary salt to paraffin</th>
<th>Water absorption (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediate</td>
</tr>
<tr>
<td>1:1</td>
<td>47</td>
</tr>
<tr>
<td>1:2</td>
<td>59</td>
</tr>
<tr>
<td>1:5</td>
<td>7.0</td>
</tr>
<tr>
<td>1:10</td>
<td>8.7</td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

60 gr. of hexadecyl-oxyethyl-pyrindinum chloride were dissolved in 100 ml. water at 65° C. 180 gr. molten paraffin (melting point 58/60° C.) were added by a high-speed stirrer, then 220 ml. water were added and this pre-emulsion was homogenized.

To facilitate the emulsification, specifically in the case of higher melting paraffins, it is possible to also use a solvent for them in amounts of 3%—10% with reference to the weight of the emulsion.

The amount ratio between the salt of the quaternary base and paraffin can be also increased, up to a ratio of 1:15.

**EXAMPLE 4**

As described in Example 1, an emulsion of 160 gr. of a 19% aqueous solution of octadecyl-oxyethyl-dimethyl ammonium chloride and 120 gr. paraffin (melting point 50/52° C.) was produced with the addition of water and acetic acid by stirring and homogenization.

A cotton fabric which was treated with a bath containing 400 gr. of this emulsion, 40 gr. of a 50% dimethyloxoyethylene urea, 10 gr. crystalline oxochloride and 8 gr. crystalline sodium acetate, dried and subsequently heated, receives a water absorption of 10%, which after 5 hot washings is increased to only 19%.

**EXAMPLE 5**

A cotton moleskin was saturated with a bath containing per liter 200 gr. of the emulsion indicated in Example 1, 40 gr. of a 50% aqueous pre-condensation solution (35% of dimethylyurethene urea and 15% of a methyl-ether of hexamethyloxymelamine), 15 gr. crystalline oxochloride as well as 8 gr. crystalline sodium acetate; it was dried and cured for 6 minutes at 150° C. As the result of a spray test the fabric was found to have a water absorption of 7.9% which was increased after 5 hot washings to only 23.2%.

It is apparent that the examples described above have been given solely by way of illustration and not by way of limitation and that they are capable of many variations and modifications within the scope of the present invention. All such variations and modifications are to be included within the scope of the present invention.

What is claimed:

1. Product for hydrophobing fibrous materials, said product consisting of an aqueous emulsion of paraffin with a quaternary ammonium salt which decomposes when heated as emulsifier having the formula

\[ R-O-CH_2-N.(tetr.)+X^- \]

wherein R is an alkyl with at least 12 carbon atoms, \( N.(tetr.) \) is a tertiary heterocyclic nitrogen base and X is the anion of a volatile inorganic acid, wherein the emul-
sion contains 3 to 15 parts by weight paraffin to 1 part by weight of the quaternary ammonium salt, said paraffin having a melting point between 45° C. and 90° C.

2. Product in accordance with claim 1, wherein the alkyl R has at least 16 carbon atoms.

3. Product in accordance with claim 1, wherein the tertiary heterocyclic nitrogen base is pyridine.

4. Product in accordance with claim 1, wherein the inorganic acid is hydrochloric acid.

5. Product in accordance with claim 1, wherein the emulsion contains 5 to 10 parts by weight paraffin to 1 part by weight of the quaternary ammonium salt.

6. A fibrous material treated by the product described in claim 1.

References Cited

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<table>
<thead>
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<th>Inventor</th>
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ALLAN LIEBERMAN, Primary Examiner.