

FINISHING COMPOSITION AND PROCESS FOR THE TREATMENT OF FIBROUS MATERIALS

The present invention relates to aqueous finishing agents for a soft hand water and oil repellent treatment for fibrous materials based on perfluoroaliphatic compositions and extenders. Furthermore, a process for providing a soft hand water and oil repellent treatment to fibrous materials is claimed.

Water-, oil- and soil-repellent finishes containing fluorochemical agents or compositions have been known for a long time (see Chwala/Anger "Handbuch der Textilhilfsmittel", 1977, Verlag Chemie, Weinheim, pages 470 ff). A considerable disadvantage of these finishes is their high price. For this reason so-called extenders have been developed, in order to first of all reduce the costs of these finishes and, moreover, to obtain improvements with regard to hand. At first, metal salts containing paraffin emulsions, fatty-modified synthetic resins, waxes and similar products were used for this purpose, but none of them was satisfactory with respect to the overall performance. The addition products of olefins, vinyl- and allyl esters of aliphatic straight chain or branched chain acids and other materials to hydrogen polysiloxanes (U.S. Patent No. 4,004,059) which were later developed, brought an improvement of the water- and oil-repellency, but however, were not sufficiently permanent and did not meet the requirements, above all with regard to the desired soft-hand effect.

Now finishing agents have been found which can be used for the simultaneous, especially smooth and soft hand, water and oil repellent treatment for fibrous materials. These finishing agents contain perfluoroaliphatic group-bearing water and oil repellent agents, selected polyethylene emulsions and fluorine-free soft-hand extender emulsions in

selected proportions. The finishing agents of this invention, i.e., the perfluoroaliphatic group-bearing agent, the polyethylene emulsion, and the fluorine-free polysiloxane soft-hand extender, can be provided as a ready-made formulation or they can be individually added to a finishing bath.

In this way finishing agents result which surprisingly provide very good oil and water repellent properties which have excellent resistance to laundry and dry cleaning. Accordingly, the present invention describes in patent claims 1 to 10 aqueous finishing agents for soft hand water and oil repellent treatment of fibrous materials. A process for soft hand water and oil repellent treatment of the fibrous materials is claimed in patent claims 11 to 13.

Components A) are perfluoroaliphatic group-bearing water and oil repellent agents many of which are commercially available and which contain in the ready-made formulation at least 5% by weight, preferably 5.5 to 15% by weight, more preferably 7 to 12% by weight of fluorine. The perfluoroaliphatic group, R_f , can be straight chain, branched chain, or if sufficiently large, cyclic. Of course, combinations thereof are also conceivable for R_f . The skeletal chain in the perfluoroaliphatic radical can include catenary oxygen and/or trivalent nitrogen hetero atoms bonded only to carbon atoms. These types of fluorochemical agents are well-known to those skilled in the art and they will have no difficulty in using the useful products.

Examples of such perfluoroaliphatic group-bearing water and oil repellent agents include those formed by the reaction of perfluoroaliphatic thioglycols with diisocyanates to provide perfluoroaliphatic group-bearing polyurethanes. These products are normally applied as aqueous dispersions for fiber treatment. Such reaction products are described, for example, in U.S. Patent No. 4,054,592.

Another group of compounds in component A) are perfluoroaliphatic group bearing N-methylol condensation products. These compounds are part of the prior art and are described in the U.S. Patent No. 4,477,498, where the emulsification of such products is dealt with in detail.

Perfluoroaliphatic group- (R_f group-) bearing polycarbodiimides can be obtained by, for example, reaction of perfluoroaliphatic sulfonamide alkanols with polyisocyanates in the presence of suitable catalysts. This class of compounds can be used alone, but often is used with other R_f group-bearing compounds, particularly with (co)polymers. Thus another group of compounds which can be used in dispersions as component A) is mentioned. Among these compounds all known polymers bearing fluoroaliphatic residues can be used, also including condensation polymers, such as polyesters and polyamides which contain the corresponding perfluoroaliphatic groups, but above all, (co)polymers based on, e.g., R_f -acrylates and R_f -methacrylates, which can contain different fluorine-free vinyl compounds as comonomers. In German Patent Publication No. DE-A 2 310 801 (see also British Patent Publication No. GB-A 1.413.051/052) these compounds are discussed in detail by reference to further literature. The manufacture of R_f group- bearing polycarbodiimides as well as the combination of these compounds with each other is described in detail, too.

Besides the aforementioned perfluoroaliphatic group-bearing agents further fluorochemical components may be used as component A), for example R_f -group-bearing guanidines (U.S. Patent No. 4,540,479), R_f -group-bearing allophanates (U.S. Patent No. 4,606,737) and R_f -group-bearing biurets (U.S. Patent No. 4,668,406). These classes of components A) are mostly used in combination.

As can be learned from the entire literature, the active compounds of component A) show, in general, one or more perfluoroaliphatic residues with preferably at least 4, especially 6 to 14 carbon atoms each. Component A) is applied in the finishing agents according to the invention in quantities of 25 to 65% by weight based on the weight of the finishing agent. As the components A) preferably contain about 7 to 12% by weight of fluorine, agents which contain 30 to 55% by weight of these components, are particularly suitable.

The emulsifiable polyethylene (polyethylene wax) contained in component B) is well-known and described in, for example, German Patent Publication Nos. DE-A 2 359 966, DE-A 2 824 716 and DE-A 1 925 993. In general, the emulsifiable polyethylenes contain functional groups, preferably COOH-groups, which may partly be esterified. These functional groups are introduced by oxidation of the polyethylene. It is, however, also possible to maintain the functionality by copolymerization of ethylene with e.g., acrylic acid. The emulsifiable polyethylenes contained in component B) have, at 20°C, a density of at least 0.92 g/cm³ and an acid number of at least 5. According to the invention, finishing agents of such emulsifiable polyethylenes are especially preferred which have a density at 20°C of 0.95 to 1.05 g/cm³, an acid number of 10 to 60 and a saponification number of 15 to 80. This material is, in general, commercially available in the form of flakes, pastilles and the like.

Component B), i.e. the dispersion of the emulsifiable polyethylene, is applied in the finishing agents in quantities of 10 to 35% by weight based on the weight of the finishing agent and on a 20 to 35% dispersion (referring to polyethylene wax). The hand of fibrous materials can be made even more pleasant, smoother, and softer by using higher quantities of component B) so that quantities of 20 to 35%

by weight of component B), based on the weight of the entire finishing agent, are particularly preferred.

The polyethylene wax is used as an emulsion. Different emulsifying agents are required. These emulsifying agents may also contribute to the soft-hand effect of the finishing agent.

As component C) modified hydrogen alkyl polysiloxanes are suitable and can be provided in the form of aqueous dispersions. In particular, fluorine-free, soft hand extenders are such compounds which are obtained by modification of hydrogen methyl polysiloxane with a long-chain alkyl residue. This alkyl residue should contain at least 8 C-atoms on average, especially 8 to 18 C-atoms. Low chain alkyl residues may also be present, but the average C-chain length should be at least 8 carbon atoms. Such compounds are described in U.S. Patent No. 4,004,059 mentioned above. Quite particularly, such components C) are preferred which are further modified, i.e., which contain, beside the above-named groups, additional epoxy alkyl groups and which may, in addition, contain aryl, particularly phenyl, groups in the molecule (U.S. Patent No. 4,625,010). Such compounds have a Si-H-content of about 0.02 to 6, especially 0.3 to 1.8% by weight, an epoxide number of about 0.01 to 0.06 and, moreover, per g atom hydrogen of the siloxane at least 0.2 g atom are substituted by an alkyl residue (see above).

The components C) are present on average as 25 to 40% dispersions and, referring to these dispersions, of component C) 25 to 40% by weight, especially 25 to 35% by weight, based on the weight of the finishing agents, are used.

These components C) as well as the components A) and B) are obtained in the known manner (see literature as cited). With

regard to the emulsifiers there exist for the dispersing and the dispersion polymerization process no restrictions in principle, i.e., nonionic and usual cationic and anionic emulsifiers can be used. But due to the fact that the finished dispersions, i.e., the components A), B) and C) are mixed during the production of the finishing agent according to the invention and, moreover, are frequently used in combination with other components, it is preferred to use during the manufacture of more or less nonionic or only weakly cationic emulsifiers, in order to keep the hazard of mutual influences as small as possible. The usable emulsifiers are well-known to those skilled in the art and require no further explanation. The emulsifiers are applied in usual quantities. In general, the quantity of emulsifier is 3 to 50, preferably 8 to 40, percent by weight, referring to the solid substance. The manufacture of the finishing agents is easily performed by mixing the components A) to C) in the indicated quantities. These agents have the advantage of being stable one-part finishing agents.

For the process of the soft water/oil-repellent treatment of fiber materials the agents produced in this way are applied directly. The used quantities depend on the desired effects and usually are 40 to 100, especially 50 to 80 g/l, referring to a 25 to 35% by weight finishing agent. The agents according to the invention are preferred, as already mentioned above, because they are one-part finishing agents, but within the scope of the present process it is also possible to prepare, with the corresponding quantities of components A), B) and C,) the usual aqueous finishing baths and those skilled in the art can readily achieve the desired excellent total effects. The finishing process is carried out according to known methods.

In the present process, further auxiliary agents commonly used in the textile industry can, of course, be added to the above-mentioned finishing bath. In this connection,

crease-resistant agents can be added to provide not only the desired crease-resistance, but, in addition, further stabilization of the effects is obtained. Also, filling resins, flameproofing agents, anti-slip agents, and similar products, as well as any catalysts which are also necessary, can be used as additional agents, all in usual quantities.

According to the present invention and according to known methods, fibrous materials of all types can be finished. As fibrous materials, textile materials are useful. Those textiles which consist of cellulose fibers or at least partly contain cellulose fibers are especially useful. As additional fibers, beside cellulose, both synthetic fibers, such as polyester, polyamide or polyacrylonitrile fibers, and wool come into consideration. The process according to the invention can, of course, also be used for the finish of pure synthetic fiber and woolen fiber materials. Oil and water repellent finishes on cotton/polyester-mixed fibers are especially critical and the finishing agents according to the invention particularly show their superiority over the prior art.

The advantages of the present invention over the prior art are less apparent in oil and water repellent properties. But the wash- and dry-cleaning permanencies demonstrate remarkable advantages over the prior art, e.g., U.S. Patent No. 4,004,059.

The significant superiority of the present invention can be seen especially when comparing the hand of fabrics treated according to the present invention. According to the prior art, it was already possible, due to the use of extenders, to obtain a good to very good silicone hand. With this known finish, the smoothness of the surface and, above all, the inner softness is not as good as is desired. With the present invention all requirements are fulfilled so that, on the whole, superior soft-hand effects can be seen.

Surprisingly, by the addition of the selected component B) in the indicated quantities a further, even though small, improvement of the oil and water repellent effects, a remarkable improvement of the permanencies and, above all, a considerable positive influence of the hand can be achieved, since the silicone hand itself has been regarded, in general, as especially soft and smooth on the surface. Furthermore, the effect-stability of the present finishing agents is particularly advantageous. The present invention is described in detail in the following examples, whereby parts mean parts by weight and indications in percent are percent by weight.

Example 1

For obtaining a finishing agent the following components were mixed together (finishing agent I):

Component A 1)

55 parts of a commercially available dispersion (emulsifier: polyethoxylated quaternary ammonium salt) consisting of polymer X (see DE-A 2 310 801) and R_f-polycarbodiimide-emulsion (see Example 1, DE-A 2 310 801) in a weight ratio of 2:1.

Component B 1)

20 parts of a commercially available, non-ionic, finely dispersed, aqueous 20% polyethylene wax dispersion (50% nonylphenol ethoxylated with an average of 15 moles ethylene oxide, referring to polyethylene wax, as emulsifier; polyethylene wax with a density at 20°C of about 1, an acid number of about 13 and a saponification number of about 22).

Component C 1)

35 parts of an aqueous, non-ionic (emulsifier: 3% of a C₁₀-C₁₂ fatty alcohol ethoxylated with 6 moles ethylene oxide) 35% soft-hand extender dispersion (H- and epoxy functional aryl-methyl-C₁₂-alkyl-polysiloxane with the following data: viscosity (25°C) of about 1350 mPa.s, refractive index n_D^{25} 1,460-1,465, Si-H-content of about 1% by weight, epoxide number of about 0.03, ratio of the 2-phenyl-propyl-residues to C₁₂-alkyl residues of about 1:5, no dimethyl-Si-groups).

Bath I

With this finishing agent I an aqueous finishing bath is prepared as follows:

60 g/l finishing agent I,

40 g/l of an about 60% solution of aminoplast resin (contains dimethylol-dihydroxy-ethylene urea and pentamethylol melamine both etherified with methanol in a ratio of 12:1 and about 5% neutral salt),

6 g/l of a 30% zinc nitrate solution (pH-value of about 1.0) and 2 g/l of 60% acetic acid.

Bath II

Like bath I, instead of the finishing agent I the components A 1) to C 1) being added to the bath separately, but in equivalent quantities.

Bath III

Like bath II, but with twice the amount of component B 1).

Bath IV (comparison)

Like bath II, but without component B 1).

Bath V (comparison)

Like bath II, but instead of component C 1) the same amount of an α,ω -dihydroxy-polydimethylsiloxane (viscosity 20°C): ca. 5000 mPa.s) in aqueous dispersion is used.

Finish

With baths I to V a polyester/cotton coat poplin 67/33 (about 210 g/cm²) was padded (pick up of about 65%), then dried at 110°C for 10 minutes and cured at 150°C for 5 minutes.

The result of the finishes are shown in the following table. The washes are usual 40°C household machine washes and the dry cleanings (DC) were performed in the presence of 2 g/l of a usual detergent and 2 g/l water (bath proportion 1:10). Measurements were taken after washing and dry cleaning after a 5-day exposure to normal climate. The oil repellency test was made according to AATCC 118-1972, the water-repellency test according to DIN 53888 (a= water absorption in percent; b= water-repellent effect) and according to the Spray test procedure corresponding to AATCC 22-1974.

The finishes according to the invention are, with regard to the effects, but above all with regard to the soft hand, significantly superior to the comparative finishes.

	<u>Original</u>				<u>5x40°C-washing</u>				<u>1 x DC</u>				<u>Hand</u>
	a	b	Spray Oil		a	b	Spray Oil		a	b	Spray Oil		
Bath I	8	4 4 4	100	4-5	6	5 5 5	100	4	25	5 3 2	100	4	internally particularly soft and rich with a pleasant surface smoothness (very good soft-hand effect)
Bath II	7	5 5 5	100	4-5	7	5 5 5	100	4	28	4 2 2	100	4	approximately like above
Bath III	9	5 5 5	100	4-5	10	5 5 5	100	4	26	4 3 2	100	4	internally outstandingly soft with a pleasant richness and surface smoothness (excellent soft-hand effect)
Bath IV (comparison)	14	4 4 3	100	4-5	13	4 3 3	100	3	28	4 2 2	90	3	soft and smooth on surface
Bath V (comparison)	9	4 4 3	100	1	11	4 3 2	100	0	26	4 2 2	90	0	particularly soft hand with good surface smoothness
Untreated	85	1	0	0	-				-				-

Example 2

For obtaining finishing agents II and IIa, the following components were mixed together:

Component A 2)

40 parts of a formulation corresponding to Example 1 of the PCT Application WO 86/02115 (about 6% fluorine).

Component B 2)

10 and 20 parts (II and IIa, resp.) of a commercially available, non-ionic, finely dispersed 21% polyethylene wax dispersion (25% tallow fatty amine ethoxylated with 8 moles ethylene oxide, referring to polyethylene wax, as emulsifier; polyethylene wax with density of about 0.96 g/cm³ at 20°C, acid number of 27 and saponification number of about 52).

Component C 2)

40 parts of a 15%, aqueous soft-hand extender emulsion of an addition product of n-hexadecene (α -olefin with 16 C-atoms on average) to methyl hydrogen polysiloxane (mole ratio 1:2) manufactured according to U.S. Patent No. 4,004,059 (reaction in butyl acetate during a total of 1.5 hours; stabilizer: tertiary hexadecylmercaptan; emulsification as described).

With finishing agents II and IIa the following baths were prepared:

90 and 100 g/l of finishing agents II and IIa, respectively, 30 g/l of a 60% aqueous solution of pentamethylol melamine trimethylether, 6 g/l of the catalyst solution of Example 1 and 2 g/l of 60% acetic acid (baths I and II, respectively).

The textile material described in Example 1 was finished using the two baths as described in Example 1, thereby yielding the following effects and additionally incorporating a comparison in accordance with the prior art (bath III with 80 g/l, of an agent prepared from A 2) and C 2), i.e., without the polyethylene base dispersion).

		Original				5x40°C-washing				1 x DC				Hand
		a	b	Spray	Oil	a	b	Spray	Oil	a	b	Spray	Oil	
Bath I	6	5	5	100	4-5	5	5	100	4	26	4	100	4	particularly soft, rich hand with excellent surface smoothness
		5				5				3				
Bath II	4	5	5	100	4-5	4	5	100	4	24	4	100	4	like bath I, with increased internal softness
		5				5				4				
Bath III (comparison)	7	5	5	100	4-5	10	4	100	3	29	3	90	3	soft and smooth on surface
		4				4				2				

Example 3

A cotton fabric (170 g/m²) was dipped into an aqueous bath containing the following components, squeezed to a pick up of about 70%, dried shortly at 105°C, and cured for 5 minutes at 155°C:

40 g/l Asahi Guard AG 310 (dispersion based on perfluoroalkyl acrylate polymer with approximately 9% fluorine), 15 g/l of the polyethylene wax dispersion described in Example 1 (polyethylene wax with $d(20^{\circ}\text{C}) = 0.93$, acid/saponification number = 16), 20 g/l of a 25%, nonionic dispersion of a soft-hand extender (H-functional methyl-C₁₀₋₁₂-alkylpolysiloxane with 11 mole percent Me-Si-H-groups and 89 mole percent Me-Si-alkyl-groups, a viscosity at 25°C of 930 mPa.s and $n_D^{25} = 1.453$), 20 g/l of an aqueous, about 50% solution of pentamethylol-melaminemethylether, 20 g/l of a 45% aqueous solution of dimethylol-dihydroxy-ethylene urea, 2 g/l 60% acetic acid and 8 g/l magnesium chloride hexahydrate (bath I).

The finish according to the invention provides a fabric with a very good permanent oil and water repellency and a very pronounced soft-hand effect. The prior art finish provides somewhat less oil and water repellency and, above all, the soft hand effect is less pronounced. Details can be taken from the following table.

	<u>Original</u>			<u>5x40°C-washing</u>			<u>1 x DC</u>			<u>Hand</u>
	a	b	Oil	a	b	Oil	a	b	Oil	
Bath I	6	5 5 4	5	7	5 5 4	4-5	23	4 3 3	4	pronounced soft- hand effect
Bath II (prior art)	7	5 4 4	5	9	5 4 4	3-4	27	4 2 2	3	moderate to good soft hand
Untreated	82	1	0	-			-			-

If instead of the aminoplast/catalyst system a usual antislip agent based on polysilicic acid/basic aluminum chloride (active substance about 16%) is added to this bath I in quantities of 15 g/l, the resistance to slippage is improved at the same time, if, e.g., a polyester knitwear is finished.

Example 4

In the same way as described in Example 1, the following two silicones can be used for making component C):

n_D^{25}	viscosity (25°C) (mPa.s)	Si-H-content (% by weight)	epoxide number
1.453	1150	about 0.04	0.02
1.451	1050	about 0.08	0.05

The effect level of corresponding finishes is in accordance with the results indicated in Example 1.

Example 5

The fabric described in Example 1 was dipped into a bath containing the following components, squeezed up to a pick up of 55%, is dried and cured for 3 minutes at 160°C:

32 g/l R_f-acrylate copolymer (cationic dispersion based on the acrylate of C₆-C₁₀-perfluoroaliphaticN-ethyl-N-β-hydroxy-ethyl-sulfonamide with a fluorine content of about 10%),

15 g/l of a 27% polyethylene wax dispersion (polyethylene wax with $d = 0.98$ (20°C), acid number 25, saponification number 50; 50%, referring to the polyethylene wax, of an emulsifier mixture from C_{16/18} fatty alcohol ethoxylated with an average of 40 moles ethylene oxide per one mole

alcohol and an emulsifier according to Example 1 of U.S. Patent No. 3,904,661, in a ratio of 1:9) and 20 g/l of component C 1) from Example 1 of this patent application containing the modified hydrogen alkyl polysiloxane of Example 1 of U.S. Patent No. 4,625,010, as soft hand extender (bath I).

For comparison with the prior art, the same finish was prepared as in bath I without the polyethylene wax dispersion (bath II).

	<u>Original</u>			<u>Hand</u>
	a	b	Oil	
Bath I (according to the invention)	8	5 5 4	5	excellent soft-hand- effect with very good internal softness
Bath II (prior art)	9	5 4 4	4	moderate soft hand

The durability after laundering and dry-cleaning is the same as that observed in the other examples of the invention.

Claims

1. Aqueous treatment composition for conferring a soft water/oil-repellent finish on fibre materials, based on perfluoroaliphatic compositions and extenders and characterised by the following composition (sum 100%):
- 5 A) 25 to 65% by weight, relative to the treatment composition, of a water/oil-repellent containing perfluoroaliphatic groups and at least 5% by weight of fluorine in dispersion,
- 10 B) 10 to 35% by weight, relative to the treatment composition, of a 20 to 35% strength dispersion of an emulsifiable polyethylene having a density (at 20°C) of at least 0.92 g/cm³ and an acid number of at least 5 and
- 15 C) 25 to 40% by weight, relative to the treatment composition, of a 25 to 40% strength fluorine-free dispersion of a soft-handle extender based on a modified hydrogenalkylpolysiloxane.
2. Treatment composition according to Claim 1, characterised in that mixtures of water/oil-repellents containing perfluoroaliphatic groups are used as component A).
- 20 3. Treatment composition according to Claims 1 and 2, characterised in that
- 25 - polyurethanes containing perfluoroaliphatic groups,
- N-methylol condensation products containing perfluoroaliphatic groups,
- polycarbodiimides containing perfluoroaliphatic groups and/or



- polymers or copolymers containing perfluoroaliphatic groups are used in the form of a dispersion individually or in a mixture as component A).

4. Treatment composition according to Claims 1 to 3, characterised in that the agents containing perfluoroaliphatic groups in component A) contain 5.5 to 15% by weight of fluorine, relative to the dispersion.

5. Treatment composition according to Claims 1 to 4, characterised in that the emulsifiable polyethylene in component B) has a density of 0.95 to 1.05 g/cm³, an acid number of 10 to 60 and a saponification number of 15 to 80.

6. Treatment composition according to Claims 1 to 5, characterised in that the emulsifier content in component B) is at least 3% by weight, in particular 8 to 40% by weight, relative to the polyethylene wax.

7. Treatment composition according to Claims 1 to 6, characterised in that 20 to 35% by weight of component B) is contained therein.

8. Treatment composition according to Claims 1 to 7, characterised in that mixtures of silicone-based soft-handle extenders are used as component C).

9. Treatment composition according to Claims 1 to 8, characterised in that

- an H-functional C₈₋₁₈-alkylmethylpolysiloxane and/or
- H- and epoxy-functional C₈₋₁₈-alkylmethylpolysiloxane, each of which, if desired, may contain aryl groups, are used in the form of a dispersion as component C).

10. Treatment composition according to Claims 1 to 9, characterised in that 25 to 35% by weight of component C) is contained therein.

11. Process for conferring a soft water/oil-repellent finish on fibre materials, in particular on textiles, characterised in that an aqueous liquor containing 40 to 100, in particular 50 to 80, g/l of the about 25 to 35% strength by weight treatment composition according to Claims 1 to 10 or the corresponding amounts of components A), B) and C) is applied to the material and said



material is finished in the usual manner.

12. Process according to Claim 11, characterised in that additionally 10 to 45 g/l of a commercially available, 40 to 60% strength by weight amino resin are used.

13. Process according to Claims 11 and 12, characterised in that furthermore customary textile auxiliaries are used in a known manner.