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(54) Leather treatment

(57) Use of a water-based, air-curable composition which comprises water and a cationic perfluoroalkyl acrylate copolymer having a glass transition temperature of up to 25°C to impart water and/or oil repellency to leather. The composition is particularly useful in the treatment of leather footwear.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a treatment for leather articles so as to provide them with water and/or oil repellency. More particularly, the invention relates to a treatment for leather footwear which is non-damaging to the footwear, and at the same time is environmentally-friendly.

BACKGROUND TO THE INVENTION

[0002] The treatment of clothing, shoes, carpets and a variety of other fibrous articles so as to provide water and/or oil repellence, and thereby stain resistance, is well known. Very often an initial treatment takes place during manufacture of the article, and subsequent treatments may be required to restore the repellent finish lost through use.

[0003] A variety of treatment compositions comprising fluorochemicals have been used to impart water and/or oil repellency. Traditionally, such compositions have been water-based, and their application has involved the use of heat to bond the fluorochemical to the article being treated and to evaporate the water. However, this is far from ideal for the treatment of articles made from leather, especially footwear, as on the application of heat leather tends to dry out, and may even split.

[0004] One example of a water-based treatment composition of this type is disclosed in US-A-5902637. This document discloses a method for restoring the water or oil repellency of clothing, footwear and fabrics which have been previously provided with a water or oil repellent finish. The method involves washing the article to be treated and then, while the article is still wet, spraying the article with a composition comprising a fluoroacrylate copolymer. The article is subsequently dried at a temperature of 55 to 75°C (130 to 170°F), to allow the fluoroacrylate copolymer to bridge with the pre-existing repellent coating on the article, and thus provide a uniform coating. Use of a composition of this type would not be suitable for the treatment of leather articles.

[0005] Treatment compositions not requiring the use of heat have typically included organic solvents, due to their lower boiling points and therefore their relative ease of evaporation as compared to water. However, as the general trend across industry as a whole is to produce environmentally-friendly products, the use of compositions containing organic solvents, even in small amounts, is undesirable.

[0006] US-A-5370919 discloses a composition for the treatment of fibrous articles and which comprises a water-soluble or water-dispersible fluoro-containing polyoxyalkylene compound, a solid water-soluble or water-dispersible anti-soiling agent, and water, and optionally up to 60 weight percent of a water-miscible organic solvent. While the organic solvent is said to be merely optional, the only composition exemplified contains a mixture of water and organic solvent, specifically ethylene glycol. Furthermore, while the composition is said to have general applicability to fibrous articles, including leather, the only test results reported are for textile articles.

[0007] US-A-4668726 discloses another fluorochemical-based composition for imparting water and oil repellency to a variety of fibrous materials, and in particular carpets. The composition comprises a complex mixture of different fluorochemicals in the form of an aqueous emulsion or organic solution. More specifically, the composition comprises a cationic fluorochemical and a nonionic fluorochemical, optionally in combination with a fluoro-containing polyoxyalkylene and/or a hydrocarbon nonionic surfactant.

[0008] US-A-4681790 is yet another disclosure of a fluorochemical-based composition for imparting water and oil repellency to fibrous materials. The composition comprises an allegedly synergistic mixture of an aromatic fluorochemical and a fluoroaliphatic-containing polyoxyalkylene in a liquid vehicle comprising a major portion of water and a minor portion of an organic water-miscible solvent.

SUMMARY OF THE INVENTION

[0009] It has now been found that a relatively simple composition comprising water and a cationic perfluoroalkyl acrylate copolymer having a glass transition temperature of up to 40°C imparts a surprisingly effective water and/or oil repellant finish to leather articles, and in particular leather footwear. The relatively low glass transition temperature of the fluoroacrylate copolymer employed allows air-curing of the composition, i.e. without heating, thereby avoiding damage to the leather being treated. Furthermore, the lack of any substantial amount of organic solvent renders the composition environmentally-friendly.

DESCRIPTION OF THE INVENTION

[0010] In the context of the present Application, when we say that the composition comprises, and preferably consists essentially of, water and the above-described fluoroacrylate copolymer, we mean that these are the only components

essential to achieve the desired effect of water and/or oil repellency in combination with air curing. More specifically, the composition does not require any other water and/or oil repelling components, and more preferably the invention excludes the presence of such components in amounts whereby they would result in a meaningful water and/or oil repellent effect.

[0011] The composition may, however, include as additional components materials conventionally used in the treatment of leather, or which aid application of the composition to leather. For example, when the composition is to be applied as a spray, the composition may include a propellant of any of the types conventionally used in the field. Suitable examples include butane, propane and carbon dioxide gas, or simply compressed air.

[0012] Most preferably, however, other than a propellent, if desired, the composition will contain no other added components, i.e. components not present in the polymer as supplied.

[0013] It is critical to the present invention that the fluoroacrylate copolymer has a glass transition temperature (Tg) of no greater than around 40°C. Preferred fluoroacrylate copolymers have Tg values of no greater than around 30°C, for instance up to around 25°C, with the most preferred Tg range being from 15 to 22°C. Mixtures of fluoroacrylate copolymers may be used if desired.

[0014] Fluoroacrylate copolymers suitable for use in the present invention are typically formed by copolymerising a fluoro-containing acrylate monomer with a fluorine-free polyoxyalkylene monomer, although fluorine-containing polyoxyalkylene monomers may also be used. Preferably, the fluoroacrylate copolymers are prepared by reaction of at least one fluorine-containing monomer or oligomer capable of being prepared by telomerisation, with another monomer or oligomer. Such preferred copolymers exclude, for instance, copolymers prepared from perfluoroalkyl sulphonate oligomers, which may give rise to harmful byproducts.

[0015] The fluoroacrylate copolymer may be linear, but preferably it is branched, as branched polymer structures have been found to improve the film-forming property at low temperature. Particularly preferred are branched copolymers having active cure sites in the branch positions. Aliphatic, rather than aromatic, copolymers are also preferred.

[0016] Particularly preferred examples of commercially available fluoroacrylate copolymer materials suitable for use in the present invention are Nuva ACFP Liquid and Nuva ACFPM Liquid (trade marks), both supplied by Clariant. Other fluoroacrylate copolymers of the same general class as these materials are particularly suitable for use in the present invention. Nuva ACFP Liquid and Nuva ACFPM Liquid are supplied as aqueous fluoroacrylate copolymer emulsions, and comprise mixtures of different fluoroacrylate copolymers. Generally, they comprise a solids content of around 20 weight % fluoroacrylate copolymer, and may either be used as supplied, or further diluted, according to the type of finish required on the leather to be treated. Higher amounts of the polymer may, however, be used.

[0017] Nuva ACFP Liquid contains a very small amount, for example up to 1 weight %, of acetone. Such a small amount of organic solvent, and slightly higher amounts, can be tolerated as any effect on the environment is negligible, particularly once further diluted with water. Nuva ACFPM Liquid is the solvent-free version of Nuva ACFP Liquid, and therefore contains the same polymer species as Nuva ACFP Liquid. Both materials typically contain an emulsifier, to aid dispersion of the fluoroacrylate copolymers into water. Typical amounts of emulsifier are up to 7 weight %, although slightly higher amounts, for instance up to 10 weight %, may be tolerated.

[0018] The fluoroacrylate copolymer is typically included in the treatment composition in an amount of 0.5 to 20 weight %, preferably 1 to 15 weight %, more preferably 2 to 10 weight %, and most preferably 2 to 6 weight %, based on the total weight of the treatment composition, depending upon the application and the level of repellency required.

[0019] Additional organic solvent is not purposefully added to the treatment composition. Furthermore, it is preferred that any organic solvent is present in an amount of less than 1 weight %, more preferably less than 0.5 weight %, based on the total weight of the treatment composition.

[0020] The treatment composition of the present invention may be used to protect a variety of leathers, including suede and nubuck. The composition may also be used to protect a variety of leather articles, but preferably it is used to protect leather footwear, for instance shoes, boots and sandals.

[0021] The composition may be applied to the leather to be treated by spraying or coating. As mentioned above, if the composition is to be applied by spraying it may include a propellant. However, preferably, for environmental reasons, a propellant is not used, and the composition is applied by means of a pump spray device. After treatment, the leather is left to dry at ambient temperature, typically up to around 25°C. Drying may take up to 24 hours, but typically takes around 12 to 16 hours, or is complete within 12 hours.

[0022] It is believed that, on drying and concomitant crosslinking of the fluoroacrylate polymer, a substantially continuous film is formed on the leather, thereby providing good water and/or oil repellant properties.

[0023] The composition may be used to provide an initial protective coating to leather, and/or it may be used to rejuvenate a protective coating which has been damaged through wear.

[0024] The present invention is now further illustrated by the following examples.

EXAMPLES

[0025] The water repellency properties of treatment compositions according to the present invention were evaluated using the following tests.

(1) Water Repellency Rating Test

[0026] Various isopropanol (IPA)/water mixtures are dropped on to a test material using a pipette. Each drop is removed from the test material after 30 seconds using a tissue. The water repellency rating corresponds to that mixture having the highest IPA content which does not mark or wet the test material. The water repellency rating values and the corresponding IPA/water mixtures are shown in Table 1, below.

Table 1

Rating	Mixture	
	IPA %	Water %
1	2	98
2	5	95
3	10	90
4	20	80
5	30	70
6	40	60
7	50	50
8	60	40
9	70	30
10	80	20
11	90	10
12	100	0

(2) Oil Repellency Rating Test

[0027] This test is used to determine the oil repellency of a fabric, and is carried out in accordance with the industry standard test AATCC 118. Various standard test liquids, shown in Table 2 below, are dropped on to a test material using a pipette. Each drop is removed from the test material after 30 seconds. The oil repellency rating corresponds to the highest-numbered test liquid which does not mark or wet the test material. The oil repellency ratings corresponding to the standard test liquids are also shown in Table 2 below.

Table 2

Oil Repellency Rating	Test Liquid
1	"Nujol" or Liquid Paraffin B.P. Grade 1
2	65:35 "Nujol": n-hexadecane by volume @ 70°F (21°C)
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane
7	n-octane
8	n-heptane

(3) Spray Rating Test

[0028] This test is used to determine the repellency of a fabric to surface wetting by water, and is carried out in accordance with the acknowledged, worldwide standard BS EN 24920 1992, ISO 4920 AATCC 22. A specific volume

(250 ml) of distilled water is sprayed on to a test material which has been mounted on to a ring and inclined at 45° to the vertical, such that the centre of the test material is 150-152mm below the spray nozzle. Immediately after the spray ceases, the holder together with the test material is removed and tapped twice.

[0029] A spray rating is then assigned by comparing the appearance of the test material with both descriptive and pictorial standards taken from the AATCC Spray Test Rating Chart. The spray ratings are shown in Table 3, below.

Table 3

Rating	Description
0 ISO 0	Complete wetting of whole of upper and lower surfaces
50 ISO 1	Complete wetting of whole of upper surface
70 ISO 2	Partial wetting of whole of upper surface
80 ISO 3	Wetting of upper surface at spray points
90 ISO 4	Slight random sticking or wetting of upper surface
100 ISO 5	No sticking or wetting of upper surface

EXAMPLE 1

[0030] The water and oil repellency rating tests were carried out on test materials as shown in Table 4, below, which had been pre-treated with 5 weight %, 10 weight % and 15 weight % aqueous solutions of Nuva ACFP Liquid (corresponding to approximate active polymer amounts of 1 weight %, 2 weight % and 3 weight %, respectively), and air-cured for 24 hours.

Table 4

Material	Rating	Untreated	NUVA ACFP Content / wt.%		
			5	10	15
Nubuck	Water Oil	4 3	7 3	10 3	11 4
Leather	Water Oil	3 0	9/10 4	11/12 4	12 4
Nylon	Water Oil	0 0	12 7	12 7	12 7
Polyester	Water Oil	4 2	12 7	12 7	12 7
Carpet	Water Oil	2/3 0	3 0	3 0	3/4 1

[0031] The results reported in Table 4 show that, while the water and oil repellency ratings for the carpet samples were consistently poor, the water repellency ratings for the leather samples were comparable to those for the synthetic fibres, polyester and nylon. Furthermore, while the oil repellency ratings for the leathers were lower than those for the synthetic fibres, they were significant, and much improved over the oil repellency ratings for the carpet samples.

[0032] Further investigation of the water and oil repellency properties of the composition of the present invention has demonstrated it to be superior to a commercially-available solvent-based fluorochemical footwear protector, sold as Footwear Proofer by the present Applicant, on a majority of leather and nubuck samples tested. Furthermore, the composition of the present invention has been shown to have consistently superior water and oil repellency properties over a variety of other commercially-available footwear protectors based on waxes or silicones.

EXAMPLE 2

[0033] The spray rating test was carried out on leathers of varying degrees of surface roughness and on polyester, each of which had been pre-treated with a 20 weight % aqueous solution of Nuva ACFP Liquid (approximately 4 weight % polymer) and cured for 24 hours prior to testing.

[0034] The results achieved are presented in Figure 1. In Figure 1, test materials 1 and 4 were different nubuck leathers; test materials 2 and 3 were different smooth leathers; and test material 5 was polyester.

[0035] The results show that the treatment composition under test imparts a far superior spray rating, i.e. water repellency, to leather than to polyester. This is somewhat surprising bearing in mind the results of the water repellency test which shows that, at lower concentrations of Nuva ACFP Liquid, the results on the different leathers and the different synthetics were essentially comparable.

Claims

1. Use of a water-based, air-curable composition for the treatment of leather to impart water and/or oil repellency thereto, wherein the composition comprises water and a cationic perfluoroalkyl acrylate copolymer having a glass transition temperature (Tg) of up to 40°C.

2. Use according to claim 1, wherein the composition consists essentially of water and the copolymer.

3. Use according to claim 1 or claim 2, wherein the copolymer has a Tg of up to 25°C.

4. Use according to any preceding claim, wherein the copolymer is a branched copolymer.

5. Use according to any preceding claim, wherein the composition comprises 0.5 to 30 wt.% of the copolymer.

6. Use according to any preceding claim, for the treatment of leather footwear.

7. Use according to any preceding claim, wherein the composition is applied to the leather by spraying.

8. Use of a composition according to claims 1 to 6, wherein the composition is applied to the leather by coating.

9. Leather footwear which has been treated with a composition as defined in any of claims 1 to 5.

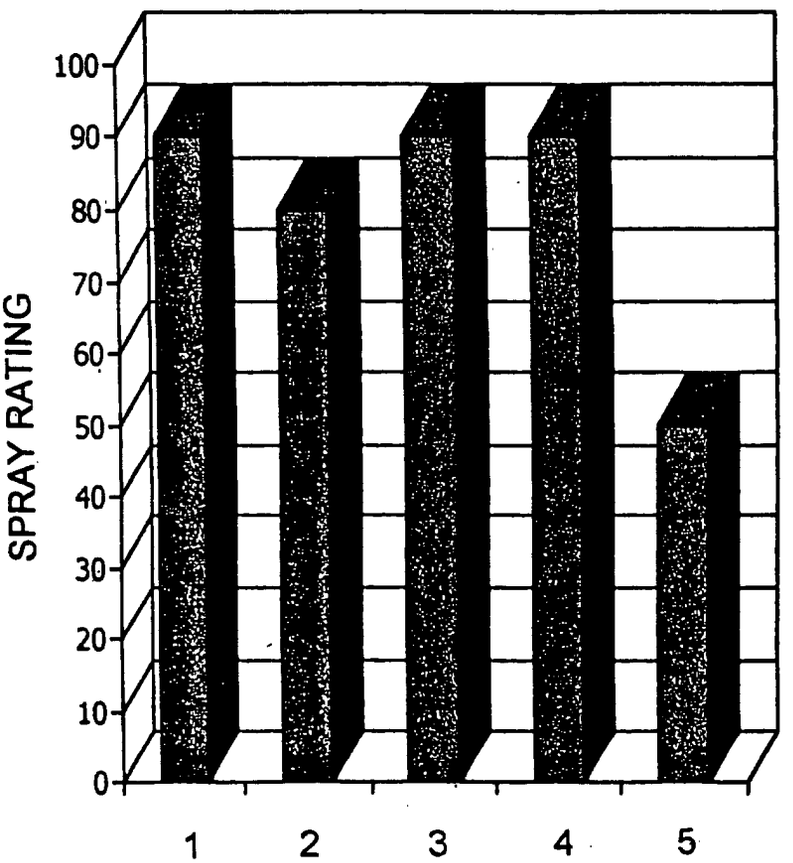
SPRAY RATING
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
MATERIALS TESTED

FIGURE 1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 2519

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 July 2001	Neugebauer, U

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 30 2519

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82