

ANHYDROUS PERSONAL WASHING AGENT AND USE THEREOF

The present invention relates to a skin cleansing agent, preferably in flowable or pasty state, which comprises water-insoluble but water-swellaable solid particles of organic polymers of natural or synthetic origin.

Flowable or paste-like skin cleansing agents are generally used to clean extremely soiled skin areas, e.g., in the metal-working industry or lacquer and varnish factories. Known skin cleaning formulations, in most cases these are pastes, contain surfactants as detergent surfactant, oleophilic and/or oleophobic solutizer, organic solubilizers, and optionally water. These known products furthermore contain as abrasives sand, wood flour, or plastic powder. These solid substances remove the dirt due to their abrasivity. However, they do not prevent that the dissolved or emulsified soil coagulates when it is subsequently dissolved with water and at least partially deposits on the skin again.

It is accordingly the object of the present invention to improve the known skin cleansing agents with respect to their cleansing action, particularly to prevent coagulation and re-deposition of the dissolved or emulsified soil.

This object is achieved by the addition of water-insoluble organic polymers which merely swell in water to a skin cleansing agent comprising surfactants, organic solvents, water-insoluble abrasives, as well as optionally thickeners, builders, perfumes, preserving agents, dyestuffs, antioxidants and/or keratolytic agents.

Thus the subject matter of the present invention is an anhydrous skin cleansing agent comprising surfactants, organic solvents and water-insoluble abrasives, as well as optionally thickeners, builders, perfumes, preserving agents, dyestuffs, antioxidants, and/or keratolytic agents, which skin cleansing agent is characterized by a content of water-insoluble but water-swellable organic polymers.

The water-insoluble but water-swellable polymers are present as solid particles and have the effect of soil carriers in such a way that the dissolved or emulsified soil, on subsequent dilution with water, does not coagulate and redeposit again but is removed. Furthermore, the water-insoluble, water-swellable polymer in the anhydrous formulation may also act as abrasive, and used either as the sole abrasive or in combination with other abrasives known per se. In the anhydrous formulation, the soil encloses the polymer particles which, on subsequent moistening of the hands, extremely swell under absorption of water and prevent coagulation of the dirt and thus resoiling of the skin. In this connection, the water-insolubility of the particles is an absolute precondition. In addition, the solid particles of the polymer, provided that they are not too finely divided, may also act as abrasive in the anhydrous formulation, in that they mechanically remove the impurities due to their abrasivity.

The effect of the water-swellable polymer particles according to the present invention is both novel and surprising:

In DE-A 35 17 385 a cosmetic skin cleansing agent is described which, however, in an anhydrous fatty phase

comprises an emulsifier and a water-soluble polymer as abrasive. The water-solubility of the polymer is an absolute precondition that the abrasive can completely be removed from the skin by water. The problem of re-deposition of already removed soil, and thus resoiling of the skin is not mentioned in this publication.

Organic polymers of natural or synthetic origin are used as water-insoluble, but merely swellable solid substances. These may be polymers on the basis of modified natural materials, or on the basis of synthetic products. In general, the water-insolubility is achieved by cross-linking. The term polymers comprises homopolymers as well as copolymers and terpolymers.

Suitable organic polymers on the basis of modified natural products are, for example, products on the basis of starch and cellulose which can be modified by grafting preferably with acrylic derivatives. Examples of acrylic derivatives are (meth-)acrylic acid and the salts thereof, (meth-)acrylonitrile, (meth-)acrylamide, and (meth-)acrylic esters, as well as the partial saponification products of these acrylic derivatives.

Suitable synthetic organic polymers are the homo- and copolymers, particularly of the acrylic derivatives mentioned above, whereby particularly the copolymers among one another or with isobutylene and maleic anhydride are to be mentioned. In addition polyurethanes are suitable, too. The polymers may contain as comonomers acrylamidopropane sulfonic acid, vinylphosphonic acid, vinylsulfonic acid, dialkylaminoalkyl(meth-)acrylates, dialkylamino(meth-)acrylamides, as well as the quaternized forms of the two above mentioned basic comonomers.

In addition to the water-swellable solid particles according to the present invention, known, non-swellable abrasives, such as wood flour, plastic powder, or sand may be used.

As detergent surfactant (surfactants) or emulsifiers the skin cleansing agents according to the present invention preferably comprise alkoxylated fatty alcohols, alkoxylated fatty acids, alkoxylated fatty acid glycerides, alkoxylated alkylphenols or alkylsulfates, alkyl-ether sulfates, sorbitan fatty acid esters, fatty acid glycerides; it is understood that the listed products are not meant to be limitative.

Carboxylic acid esters, paraffinic or isoparaffinic hydrocarbons, arylcarboxylic acid esters or terpenes alone or in mixture among one another are used as solvents in the skin cleansing agent according to the present invention.

As carboxylic acids the esters of alcohols having mono- or polybasic carboxylic acids are used; the alcohols used for this purpose are straight-chain or branched-chain and preferably have 1 to 8 carbon atoms, whereby the lower alcohols having 1 to 4 carbon atoms are preferred. Examples are methanol, ethanol, n-propanol, isopropanol, n-butanol, and isobutanol. As an example of a higher alcohol isooctanol is to be mentioned. The carboxylic acid of the carboxylic acid esters preferably has 1 to 10 carbon atoms and may also be straight- or branched-chain. Examples of carboxylic acids are: formic acid, acetic acid, propionic acid as monobasic acids, as well as adipic acid, sebacic acid, or citric acid as polybasic acids. Examples of suitable carboxyl-

ic acid esters are the low carboxylic acid esters known as solvents, such as butylacetate, or higher-boiling derivatives, e.g., methoxy butylacetate.

As thickeners waxes, cellulose derivatives (e.g. cellulose ether), synthetic polymers, fumed silica, and modified bentonites are used.

The cleansing agents according to the present invention may in addition comprise perfumes, preserving agents, grease-restoring agents, dyestuffs, and/or antioxidants.

The quantity ratios of the components may vary within wide ranges. The content of water-insoluble, but water-swellaible polymer particles amounts to 0.3 to 55, preferably 0.1 to 17.6, in particular 1 to 12.5%-wt, relative to the total weight of detergent surfactant (surfactant), solvent and water-swellaible polymer.

Taking the same basis as for the water-swellaible polymer, the content of solvent amounts to 5 to 99, preferably 20 to 98, and in particular 30 to 70%-wt., and that of detergent surfactant (surfactants) amounts to 0.7 to 94.7%-wt, preferably, 1.4 to 79.4, and in particular 29 to 69%-wt.

The amount of further, optionally present components, such as thickeners, grease-restoring agents, perfumes, preserving agents, dyestuffs, antioxidants, and keratolytic agents, which may be present alone or in admixture, amounts to 0 to 90%-wt, relative to the total formulation.

The particle size of the water-swellaible solid par-

ticles is smaller than 1,000 μm , preferably smaller than 500 μm when used as soil carrier and abrasive; e.g., the grain size is in the range of about 50 to 400 μm . If the water-swellable polymer is merely used as soil carrier alone or in combination with other abrasives known per se, the particle size is smaller and is in the order of smaller than 200 μm , preferably in the order of smaller than 150 μm , particularly smaller than 100 μm , e.g., in the range of 10 to 200 μm . Corresponding size fractions are suitably obtained by screening.

The present invention will be illustrated further by the following examples.

Formulation I

15	%-wt	oleic acid neutralized with triethanol-amine (detergent surfactant)
58	%-wt	butylacetate (solvent)
5	%-wt	soy oil (grease-restoring agent)
5.1	%-wt	pyrogenic silicic acid (thickener)
0.4	%-wt	perfume
9	%-wt	polymer component a (according to table I)
7.5	%-wt	polyethyl powder, grain size smaller than 300 μm

Formulation Ia

15	%-wt	nonylphenol 9 EO
30	%-wt	iso-hexadecane
55	%-wt	polymer component a (according to table I) smaller than 100 μm

In order to demonstrate the different cleansing action between water-soluble and merely water-swellable abrasives in the case of polymers, a standard formulation (formulation II) was developed, and equal amounts of polymer components (table I) having the same particle size were incorporated into each of the following formulations.

Formulation used:

Formulation II:

16.2%-wt	fatty alcohol 12/18 5 EO (detergent surfactant)
59.5%-wt	ester mixture (solvent)
5.4%-wt	grease-restoring agent (fatty acid alkyl-ester)
14.2%-wt	thickener (3.4%-wt. pyrogenic silicic acid; 7%-wt. ethyleneglycol distearate; 3.8%-wt. cellulose acetate butyrate)
0.4%-wt	perfume
4.3%-wt	polymer components a to f according to table I

100 %

Table I

As polymer components were used:

Trade name:

a = Favor SAB 922 water-swellable cross-linked polyacrylic acid, partially neutralized

- b = Rhodopol 23 water-soluble xanthan gum, heteropolysaccharide
- c = Aqua-Keep water-swellable see a)
- d = Praestol 2530 water-soluble linear acrylamide-sodium acrylate-copolymer
- e = Natrosol water-soluble hydroxyalkyl cellulose
- f = Sunwet IM 1000 water-swellable acrylic acid-modified starch

Formulations a to f thus obtained were tested with respect to their cleansing action according to the following hand-wash-test:

Description of the method

Hand-wash-test

1. Material and Method

1.1. Test material

- 1.1.1. Lacquer (red); quick-drying lacquer on the basis of fish oil; manufacturer Messrs. Rust Oleum

1.2. Test persons

As test persons a group of six male, dermally healthy persons at the age of 20 to 60 was chosen.

It is a precondition that all test persons

have a palm skin structure which is caused by manual work.

1.3. Test quantities

A defined amount of typical dirt (or lacquer) and the amount of test substance is determined before the test starts.

1.4. Assessment scheme

Assessment is carried out after washing according to a 0-5 points-scale. The degree of residual impurities on the palm of the hand is assessed.

- 0 = clean
- 1 = slight residual soil
- 2 = medium residual soil
- 3 = considerable residual soil
- 4 = extreme residual soil
- 5 = no cleansing effect

1.5. Performance

In the morning and in the afternoon the following washing is carried out using one product each:

- 0.5 ml test soil (cf. 1.1.1.) is applied to the palm and shortly rubbed into the skin
- allowed to dry for 3 minutes
- 0.5 ml of the test product is applied and shortly rubbed into the skin
- approximately 1 ml water is added; washing for 20 seconds
- rinsing under running, cold water
- assessment of the cleansing effect accord-

ing to the 5-points-scale

The results thus obtained are shown in table II:

Table II

Product/ test person	a	b	a	c	a	d	a	e	a	f
1	2.5	4.5	2	3	2	3.5	1	1.5	1.5	2
2	3	4	3	4	2.5	4	2	2.5	2	2
3	2.5	4.5	3	2.5	3.5	4	2.5	2	2.5	2.5
4	3	4.5	3.5	2.5	2.5	4	2	2.0	5	2.5
5	3	3.5	2	3	2	3	2	3	1.5	2
6	3	4.5	3	3.5	4	3.5	1.5	2	1.5	1
Ø	2.8	4.3	2.8	3.1	2.8	3.7	1.8	2.2	1.6	2

Test II

In this test it was tested whether the increased cleansing effect was maintained with additional incorporation of a common insoluble and non-swellable abrasive (polyethylene powder was chosen). For this purpose, a certain amount of water-soluble or water-swellable polymer having the same particle distribution was incorporated into a standard formulation comprising 7.5% polyethylene powder, the cleansing effect was then tested.

Formulation III

15 %-wt. fatty alcohol C₁₂-C₁₈ 5 EO (detergent surfactant)

9.3%-wt. dimethyl adipate
 36.3%-wt. dimethyl glutarate
 9.4%-wt. dimethyl succinate } (solvent)
 5 %-wt. isooctyl stearate (grease-restoring agent)

2.3%-wt. fumed silica
 7 %-wt. ethyleneglycol distearate } (thickener)
 3.8%-wt. cellulose acetate butyrate

0.4%-wt. perfume

4.0%-wt. polymer components a, c, d, or f
 (according to table I smaller than 45 μ m)

7.5%-wt. polyethylene powder smaller than 300 μ m

The results obtained are shown in table III

Table III

Product/ Test person	f	a	c	a	d	a
1	2	1	0.5	1	3	0.5
2	1	1	1	1	3	1.5
3	1.5	1.5	1	1.5	2.5	1.5
4	1.5	1	1.5	2	3	1
5	1.5	1	1	1	2.5	2
6	0.5	1	1.5	2	2	1.5
$\emptyset$	1.3	1.1	1.1	1.4	2.7	1.3

Test III

Test III shows that a considerable amount of cleaning product can be saved, if the polymer according to the

present invention is used, i.e., the soil carrying capacity is superior.

Formulation as in test II; 0.5 ml of the product according to the present invention with polymer component a compared to 1 ml of the product not claimed by the present invention with polymer component d was used for washing.

The results obtained are shown in table IV

Table IV:

Product/ Test person	a (0.5 ml)	d (1.0 ml)
1	1	1.5
2	1	1.5
3	1	2
4	0.5	1
5	1	1.5
6	1	2
Ø	0.9	1.6

Formulation IV

	Formu- lation A	Formu- lation B	Formu- lation C	Formu- lation D	Formu- lation E
Fatty alcohol					
C ₁₂ -C ₁₈ 5 EO	15 g	15 g	15 g	15 g	15 g
Dimethyl adipate	9.3 g	9.3 g	9.3 g	9.3 g	9.3 g
Dimethyl glutarate	36.3 g	36.3 g	36.3 g	36.3 g	36.3 g
Dimethyl succinate	9.4 g	9.4 g	9.4 g	9.4 g	9.4 g
Aerosil	5.0 g	5.0 g	5.0 g	5.0 g	5.0 g
Polyethylene powder smaller 315 µm	7.5 g	-	-	-	7.5 g
Favor smaller 315µm	-	7.5 g	-	-	-
Favor smaller 45µm	-	-	-	4.0 g	4.0 g

Table VHand-wash-test:

Amount of product: 0.5 ml

Test person	0.5ml A	lacquer B	0.3ml C	lacquer D	0.7ml A	lacquer E
1	1.0	0.5	3.0	2.5	1.5	1.0
2	1.0	0.5	2.0	2.0	1.0	0.5
3	0.5	0	3.0	1.0	1.0	0.5
4	0	0.5	1.5	1.0	1.0	0.5
5	0.5	0.5	2.5	2.0	1.5	1.0
X	0.6	0.4	2.4	1.7	1.2	0.7

Test A compared to B: abrasive PE compared to abrasive FAVOR

=> no considerable difference; in case of this particle size the soil carrying capacity does scarcely take effect.

Test C compared to D: without abravise (FAVOR used as soil carrier)

=> soil carrying capacity can clearly be recognized.

Test A compared to E: abrasive PE compared to abrasive PE and soil carrier FAVOR

=> soil carrying capacity becomes evident even in abrasive-containing formulations.

Summary:

The washing tests carried out clearly show the superiority of water-insoluble, but water-swellaable polymers (Favor SAB, Sunwet IM 1000, Aqua-Keep) compared to water-soluble polymers (test I). Test II shows that the superiority of these polymers is maintained, even if a common abrasive is incorporated. The degree of improvement achieved by a polymer according to the present invention used in combination with a common abrasive becomes evident in test III. Although half of the cleaning product was used, an improved cleaning effect was achieved, compared to the full amount of product which comprises a water-soluble polymer.



P A T E N T C L A I M S

1. Anhydrous skin cleansing agent comprising surfactants, organic solvents, and water-insoluble abrasives as active components, as well as optionally thickeners, builders, grease-restoring agents, perfumes, preserving agents, dyestuffs, antioxidants, and/or keratolytic agents, characterized by a content of water-insoluble, but water-swellaable organic polymers as soil carrier, and optionally as the sole abrasive or in combination with other water-insoluble abrasives which are known per se.

2. Skin cleansing agent according to claim 1, characterized by a content of natural, optionally modified or synthetic organic polymers.

3. Skin cleansing agent according to claims 1 or 2, characterized by a content of water-swellaable organic polymers of 0.3 to 55, preferably 0.1 to 17.6, particularly 1 to 12.5%-wt, relative to the total weight of detergent surfactant (surfactant), solvent, and water-swellaable polymer.

4. Skin cleansing agent according to any one of claims 1 to 3, characterized by a content of water-swellaable polymers on the basis of poly(meth-)acrylic acid and the salts thereof, graft copolymers of acrylic derivatives with starch and cellulose and their derivatives, saponification products of poly(meth-)acrylonitrile, (meth-)acrylamides, acrylic esters and/or polyurethanes.

5. Skin cleansing agent according to claim 4, charac-



terized by a content of water-swellaable polymers which comprise as comonomers acrylamidopropane sulfonic acid, vinylphosphonic acid, vinylsulfonic acid, dialkyl aminoalkyl(meth-)acrylates, dialkyl aminoalkyl(meth-) acrylamides, or the quaternization forms thereof.

6. Skin cleansing agent according to any one of claims 1 to 5, characterized by a content of alkoxyated fatty alcohols, alkoxyated fatty acids, alkoxyated fatty acid glycerides, alkoxyated alkylphenols, alkyl sulfates, alkyl ether sulfates, sorbitan fatty acid esters, and fatty acid glycerides as detergent surfactant.

7. Skin cleansing agent according to any one of claims 1 to 6, characterized by a content of carboxylic acid alkyl esters, preferably esters of mono- or polybasic carboxylic acids having 1 to 10 carbon atoms with alcohols having 1 to 8, particularly 1 to 4 carbon atoms, paraffinic or isoparaffinic hydrocarbons, aryl carboxylic acid esters or terpenes alone or in admixture among one another as solvent.

8. Skin cleansing agent according to any one of claims 1 to 7, characterized by a content of cellulose derivatives, fumed silica, modified bentonites, and/or waxes as thickeners and builders.

9. Skin cleansing agent according to any one of claims 1 to 8, characterized by a particle size of the water-swellaable polymers of smaller than 200 μm , preferably smaller than 150 μm , particularly smaller than 100 μm , if exclusively used as soil carrier, as well as of smaller than 1,000 μm , preferably smaller than 500 μm , if used as soil carrier and abrasive.



10. The use of the agent as claimed in claims 1 to 9 for cleaning the skin, characterized in that a sufficient amount of the agent is applied to the skin, distributed thereon and removed with water.