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<p>(21) International Application Number: PCT/NL94/00296 (22) International Filing Date: 22 November 1994 (22.11.94) (71)(72) Applicant and Inventor: BIJSTERVELD, Antonius, Bernardus [NL/NL]; Janseniuslaan 43, NL-4561 Hulst (NL). (74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).</p>	<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: AGENTS FOR CLEANSING SOLID SURFACES</p> <p>(57) Abstract</p> <p>The use of a reaction product of a natural oil, a natural fat, a composition comprising natural or synthetic C₁₀ - C₂₀ fatty acids, or mixtures thereof, and a linear nitrogen compound substituted by one or two alkyl, alkaryl, aralkyl or aryl groups, or a cyclic nitrogen compound containing at least one nitrogen atom wherein each nitrogen atom is substituted by one alkyl, alkaryl, aralkyl or aryl group, or a cyclic nitrogen compound containing at least one nitrogen atom and one adjacent carbonyl group and wherein each nitrogen atom is substituted by one alkyl, alkaryl, aralkyl or aryl group, is disclosed. Compositions comprising the reaction product in amounts of 1 - 30 wt.% are useful as cleansing and washing agents in the printing industry, in particular for the removal of inks, dyes, paints, scales and haze from printing screens and printing devices.</p>		

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AGENTS FOR CLEANSING SOLID SURFACES

Cleaning agents and/or washing agents, processes for their preparation, and a process for the removal of contaminating materials from solid substrates.

5 This invention relates to the use of a reaction product of:
(A) a natural oil, a natural fat, a composition comprising natural
or synthetic C₁₀ - C₂₀ fatty acids, or mixtures thereof, and
(B) a linear nitrogen compound selected from linear nitrogen
10 compounds substituted by one or two alkyl, alkaryl, aralkyl or
aryl groups, or cyclic nitrogen compounds containing at least
one nitrogen atom wherein each nitrogen atom is substituted by
one alkyl, alkaryl, aralkyl or aryl group, or cyclic nitrogen
compounds containing at least one nitrogen atom and one
adjacent carbonyl group and wherein each nitrogen atom is
15 substituted by one alkyl, alkaryl, aralkyl or aryl group,
in cleansing agents and/or in washing agents, or for cleansing and/or
washing purposes.

This invention relates in particular to cleansing agents and/or
washing agents for use in the printing industry, especially in printing
20 processes such as silk-screen printing and offset printing, for the
removal of inks, scale, stains, haze and the like from printing machines.

Usually cleansing of printing machines and parts of printing
machines, in particular rubber parts, is effected by applying mineral oil
products, e.g. white spirit, naphtha, kerosine and thinner, which are
25 optionally mixed with components such as halogenated hydrocarbons,
surfactants, and water. These mineral oil products and their mixtures are
not only harmful to the user and are environmentally unfriendly, but they
appear also to be detrimental to rubber parts of printing machines, e.g.
rollers and the rubber blanket of an offset printing machine. It has
30 therefore been attempted to replace these products and mixtures by other
materials having the desired properties.

EP 435.943 B1 discloses the use of (C₁ - C₅) alkyl esters of
aliphatic (C₈ - C₂₂) monocarboxylic acids for removing inks and the like
from printing machines, in particular from offset printing machines.
35 Preferably a mixture comprising 50 - 100 % wt. of these esters, 0 - 50 %
wt. of vegetable oil and 0 - 10 % wt., preferably 0.5 - 3 % wt. of
surfactant emulsified with up to 50 % wt., preferably 25 - 35 % wt. of
water and 1 - 10 % wt., preferably 3 - 5 % wt of an emulsifier is used.
However, in practical use these esters have been experienced being still

too aggressive towards rubber components, i.e. they cause in particular considerable swelling of the rubber rollers. Moreover, the esters are not capable to degrease the printing machines and their parts to the desired extent.

5 It has surprisingly been found that these drawbacks are obviated by, according to this invention, using a reaction product as described above. It is also according to this invention that said reaction product may be aftertreated with the components (A) or (B) described above.

10 Component (A) comprises a mixture of C_{10} - C_{20} fatty acids having saturated, unsaturated or multiple unsaturated hydrocarbon backbones. This mixture of C_{10} - C_{20} fatty acids comprises particularly lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, palmitoleic acid, oleic acid, linoleic acid and linolenic acid, and is
15 preferably soybean oil.

The linear or cyclic nitrogen compounds are linear, primary or secondary monoamines, secondary cyclic mono- or diamines or secondary cyclic mono- or diamides. The nitrogen atom of the linear, primary or secondary amines may bear one or two substituents selected from alkyl,
20 alkaryl, aralkyl or aryl groups. Examples for these groups are methyl, 2-tolyl, benzyl and phenyl, but also cyclohexyl. Dimethylamine is the preferred compound.

The nitrogen atom of secondary cyclic mono- or diamines can bear only one substituent on each nitrogen atom, which is selected from
25 the groups mentioned above. Examples for such compounds are 1-methylpyrimidine, 1,4-dimethylpiperazine, 1,3-dimethylimidazolidine, 1-methylpyrrolidine, 1,2-dimethylpyrazolidine, 1-methylpiperidine and 1-methylindoline. Preferably 1-methylpyrrolidine is used.

The nitrogen atom of the secondary cyclic mono- or diamides can also bear only one substituent on each nitrogen atom, which is selected
30 from the groups mentioned above. Examples for such compounds are 1-methyl-2-pyrrolidone, 1-methyl-2-piperidone and 1,4-dimethyl-2,5-piperazinedione. Preferably 1-methyl-2-pyrrolidone is used.

The reaction product is prepared in a medium pressure reaction
35 vessel, optionally equipped with a jet nozzle, by contacting component (A) with (B) in a ratio of 10:1 to 1:2, preferably in a ratio of 5:1 to 1:1.

The reaction temperature is usually 140° - 270°C , but it is preferred to conduct the reaction at a temperature of 215° - 240°C when

component (B) is dimethylamine and at a temperature of 160° - 180°C when component (B) is 1-methyl-2-pyrrolidone. Higher temperatures than those mentioned here result in the formation of darkly coloured products, which is undesired for aesthetic and cosmetic reasons, as will be more apparent in the following parts of the description of this invention. On the other hand, lower temperatures than those mentioned above decrease the conversion of the reaction to commercially unacceptable levels.

The reaction time is a half to three hours, preferably one and a half hour. Prolonged reaction times result in the formation of darkly coloured products, which are undesired for reasons mentioned above.

When the reaction is performed in the presence of dimethylamine, it is preferred to use dimethylamine in the gaseous state. In that case the gaseous dimethylamine is added to the reaction mixture by way of the jet nozzle. It is, however, possible to perform the reaction with a 60 % wt. solution of dimethylamine in water, although this procedure has the disadvantage that the reaction must take place in a essentially two-phase system. Moreover, from a process-technological point of view, it is unfavourable that more energy is required to heat the reaction mixture to the desired temperature.

The cleansing agents or washing agents or compositions thereof comprise the reaction product as described above in amounts of 1 - 30 % wt, preferably 5 - 15 % wt., emulsion-stabilizing compounds in amounts of 0 - 5 % wt., preferably 0.5 - 1 % wt., and water in amounts of 65 - 99 % wt, preferably 84 - 95 % wt., with the proviso that the total of the three components is 100 % wt.

As emulsion-stabilizing compounds surfactants, emulsifiers, detergents and the like can be used. It is, however, preferred to use a surfactant, in particular a non-ionic surfactant, as otherwise the pH of the cleansing agent has to be adjusted to the desired value, i.e. about 7. Non-ionic surfactants, which are preferably used, are those obtained by condensation of alkylphenols or long-chain alcohols with ethylene oxide or propylene oxide. It is preferred to use nonylphenol or dodecylphenol.

Hand soaps suitable for removing greasy dirt from the human skin, in particular hands, contain very often organic solvents, abrasives and alkaline and chlorine-containing organic compounds. Most of these constituents, and therefore also the corresponding hand soaps, are detrimental to the physical condition of the human skin as they dehydrate and roughen the skin by removing naturally occurring fats. According this

invention it has been found that excellent hand soaps having none of these disadvantages can be composed using the reaction product described above. They preferably comprise 25 - 60 % wt. of the reaction product, 0 - 5 % wt., in particular 0.5 - 1 % wt., of emulsion-stabilizing compounds and 0.5 - 2 % wt. of water. These hand soaps appear to be very effective to remove greasy industrial dirt from hands. Additionally, it has been demonstrated that these hand soaps according to this invention have dermatological properties. When the hand soaps of this invention were applied to the human skin, which was irritated by the frequent use of aggressive hand soaps, e.g. those which contain petroleum distillates, or human skin, which was dehydrated by solvents, in particular organic solvents, the physical condition of the skin was observed to improve substantially within short periods of time.

The cleansing agents or washing agents or compositions derived hereof are very useful in various cleaning and wash processes in the printing industry. For example, print screens of silk-screen printing machines are cleaned very effectively with these agents, which has the additional advantage that harmful and environmentally unfriendly solvents such as thinner and the like can be abandoned. It has also been demonstrated that these agents are very effective washing agents during offset printing, but also that for cleaning the offset printing machine they can be applied to remove inks, stains, scale and haze from rubber rollers, metal cylinders and rubber blankets. Additionally, they protect in particular the rubber components against dehydration and wear, which results in prolonged times of operation. Another advantage is that only one product can be used where usually different organic solvents and agents were required for a smoothly running printing process. Yet another advantage is that the cleansing and washing agents have been shown to be non-toxic, biodegradable, non-corrosive, non-irritating and non-volatile, which improves the working environment with respect to safety and health.

The cleansing agents or the compositions derived hereof have been demonstrated to strongly penetrate substances like paints, coatings, dyes and the like. A process has been developed to remove these contaminating materials from various solid substrates, in particular paint stripping, i.e. the removal of paints and coatings from solid substrates such as painted or coated surfaces. Examples for painted or coated surfaces are painted or coated fuselage and wing parts, painted or coated body parts of car etc. The process comprises the degradation of

paints or coatings to particles having a diameter of 3 - 5 μm , which are dispersed into the cleansing agents yielding a contaminated mixture. The contaminated mixture is then collected, whereafter the particles originating from the paints or coatings are separated from this mixture yielding a purified cleansing agent. The separated particles are transported as chemical waste and the cleansing agent is reused in the paint stripping process.

The cleansing agents of the present invention are useful for cleaning smooth, washable surfaces, which may be of natural or synthetic origin or a combination thereof. Such surfaces may be or may be part of domestic devices, e.g. tables, doors, chairs, televisions, sanitary goods, of exteriors and interiors of cars, boats, caravans etc. They do not only remove all kinds of dirt from these surfaces, but also re-establish their natural shine and provide a protective film without leaving streaks.

The cleansing agents of the present invention are also very useful to clean all kinds of rims, which may be varnished and/or which may contain aluminum and/or alloys. The cleansing agent removes effectively tarry contaminations in particular and provides a protective film to the rim.

The cleansing agents of the present invention are powerful aids for the removal of graffiti from stone, concrete, steel and the like. The cleansing agent is applied on the surface by means of a brush and is allowed to absorb for about 5 minutes. The graffiti are then easily removed by using a high pressure sprayer.

Other applications of the cleansing agents of the present invention comprise car wash cleaning products, paint brush cleaning products, paint removing products and the like, where the absence of organic solvents and/or substances in particular, such as halogenated hydrocarbons, alcohols, caustic mixtures, silicones etc, and the cleaning power of the agents are the main advantages over the normally encountered products.

The invention is further illustrated by the following examples.

Example 1

Soybean oil fatty acids with the following properties

5

Density (g/ml)	0.847
Moisture and volatile matter ^a (% wt.)	0.03
Acid value ^b (mg KOH/g)	190 - 205
Free acid content ^c (ml 0.25 n NaOH)	18 - 25
Solidification point (°C)	15

10

^a according A.O.C.S. Official Method Ca 2c-25.

^b according A.O.C.S. Official Method Da 14-48

^c according A.O.C.S. Official Method Ac 5-41

15

were reacted with 30 % wt. gaseous dimethylamine at a temperature of 215°C and at a pressure of 8 bar in a medium pressure reactor vessel equipped with a jet nozzle during 1.5 h. The light brown reaction product was then cooled to room temperature.

Example 2

20

The procedure of example 1 was repeated at atmospheric conditions, except that 45 % wt. of a solution of 60 % wt. dimethylamine in water is used.

Example 3

25

The reaction product of example 1 or 2 was aftertreated with 25 % wt. of a vegetable oil at a temperature of 50°C and at atmospheric pressure in a reaction vessel during 0.5 h. The light brown reaction product was then cooled to room temperature.

Example 4

30

This example demonstrates the multifunctional application of the product of example 3 in offset printing.

35

A washing agent was prepared by dispersing 15 % wt. of the product of example 3 followed by diluting the dispersion with water in a ratio of 1:2. The washing agent was used in an offset printing machine for removing the present ink, paper fibers and dust from the rubber blankets.

Example 5

The reaction product of example 1 or 2 was aftertreated with 25 % wt. 1-methyl-2-pyrrolidone at a temperature of 140°C and at a pressure of 1 bar in a medium pressure reaction vessel during 25 h. The light brown reaction product is then cooled to room temperature.

5 The product showed the following properties:

Density (g/ml)	0.96
Melting point (°C)	12
pH (1 % wt. in H ₂ O)	7.7
Flash point (°C, ASTM D-93)	> 100
10 Dispersable in H ₂ O (% wt.)	15
Corrosivity	none

Example 6

15 Soybean oil fatty acids were reacted with 25 % wt. 1-methyl-2-pyrrolidone at a temperature of 140°C and at a pressure of 1 bar in a medium pressure reactor vessel during 2.5 h. The light brown reaction product was then cooled to room temperature.

The product showed the following properties:

Density (g/ml)	0.935
20 Melting point (°C)	-15
pH (1 % wt. in H ₂ O)	7.6
Flash point (°C, ASTM D-93)	> 110
Dispersable in H ₂ O (% wt.)	1

25 Example 7

A cleansing agent was prepared by dispersing 15 % wt. of the product from example 5 and 0.5 % wt. of an emulsifier in water.

The product showed the following properties:

Density (g/ml)	0.962
30 Viscosity (cP, 25°C)	10 - 25
pH (1 % wt. in H ₂ O)	6.5
Flash point (°C, ASTM D-93)	> 100

Example 8

The biodegradability of the product of example 5 was tested by O.E.C.D. screening tests (Methods: NEN 6633 and 6634). The product was for more than 90 % biodegradable.

5

Example 9

The product of example 5 was tested for toxicological properties.

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Oral	LD 50	5,000 - 15,000 mg/kg on rat
Dermal	LD 50	8,000 - 24,000 mg/kg on rabbit
	LC 50	1,670 - 5,000 mg/l on lepomis machrochirus
	LC 50	2,040 - 3,216 mg/l on pimephalis promelas
	LC 50	7,096 - 21,300 mg/l on salmo gairdner

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Example 10

A cleansing agent for domestic use was prepared by dispersing 10 % wt. of the product from example 5 and 0.5 % wt. of the non-ionic surfactant nonylphenol in water. A smooth, washable, dirty glass surface was cleansed by applying a cloth lightly moistened with the cleansing agent resulting in a clean and shiny glass surface.

20

Example 11

The cleansing agent of example 5 or 6 was applied to a water-resistant printing screen by means of a brush in an amount of 75 ml/m². When the screen was contaminated with dry ink the product was allowed to be absorbed for a period of 5 minutes. Hereafter the screen was rinsed with water and a clean screen was obtained.

25

Example 12

The cleansing agent of example 5 or 6 was applied to a non-water-resistant printing screen by means of a brush in an amount of 75 ml/m². When the screen was contaminated with dry ink the product was allowed to be absorbed for a period of 5 minutes. Hereafter the screen was cleansed by using a cloth lightly moistened with the product of example 7.

30

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Example 13

The cleansing agent of example 5 was used during 5 months of

operation in an automatic silk-screen cleaning machine. When an identical amount of a common agent such as thinner was used, the cleaning machine could be operated for only three weeks.

5 Example 14

The cleansing agent of example 5 was used for removing coatings from coated fuselage parts. The heterogeneous liquid waste containing the cleansing agent and the small particles originating from the coating were separated by filtering the waste, whereafter the cleansing agent was recovered and reused for the removal-process. In this way only an amount of cleansing agent equal to 1/5 of the usually required amount of dichloromethane sufficed.

15 Example 15

A hand soap was prepared by dispersing 30 % wt. of the product of example 3 and 1.5 % wt. of an emulsifier in water. The hand soap was applied on dry hands and after rubbing the hands for 20 to 30 seconds and rinsing the hands with cold or hot water, all greasy dirt was removed.

20 Example 16

A cleansing agent for cleansing synthetic parts of cars and furniture was prepared by dispersing 10 % wt. of the product of example 3, 5 % wt. of soybean oil, 2% wt. dodecylphenol and 0,5 % wt. of an emulsifier in water. The cleansing agent is a useful substitute for silicone-based cleansing agents containing organic solvents.

25 Example 17

A cleansing agent for car wash purposes was prepared by dispersing 30 % wt. of the product of example 6, 5 % wt. dodecylphenol and 1 % wt. of an emulsifier in water.

30 Example 18

A cleansing agent for household use was prepared by dispersing 10 % wt. of the product of example 6, 5 % wt. of a surfactant and 1 % wt. of an emulsifier in water.

35 Example 19

The cleansing agent of example 6 was used for cleaning paint brushes. The product showed the following advantages over the usual

organic solvents as thinner:

-
- the paint brush did not need to be washed out with water
-
- 5 the paint brush remained soft
-
- paint rests precipitated from the aqueous mixture
-
- 10 more paint brushes than usually possible with an equal amount of organic solvent were cleaned with only 100 ml of the cleansing agent.

Example 20

15 A cleansing agent for removing paint was prepared by dispersing 50 % wt. of the product of example 6, 2 % wt. of dodecylphenol and 48 % wt. of an aqueous solution containing 25 % wt. NaOH.

Example 21

20 A cleansing agent for removing graffiti was prepared by dispersing 98 % wt. of the product of example 6 and 2 % wt. of a non-ionic surfactant. The cleansing agent was applied on the graffiti using a brush and was allowed to be absorbed for 5 minutes. Hereafter the graffiti were easily removed using a high pressure sprayer.

25

Claims

1. Use of a reaction product of:
- (A) a natural oil, a natural fat, a composition comprising natural or synthetic C₁₀ - C₂₀ fatty acids, or mixtures thereof, and
- (B) a linear nitrogen compound selected from linear nitrogen compounds substituted by one or two alkyl, alkaryl, aralkyl or aryl groups, or cyclic nitrogen compounds containing at least one nitrogen atom wherein each nitrogen atom is substituted by one alkyl, alkaryl, aralkyl or aryl group, or cyclic nitrogen compounds containing at least one nitrogen atom and one adjacent carbonyl group and wherein each nitrogen atom is substituted by one alkyl, alkaryl, aralkyl or aryl group,
- in cleansing agents and/or in washing agents, or for cleansing and/or washing purposes.
2. Use according to claim 1, wherein said reaction product is aftertreated with (A) and/or (B).
3. Use according to claims 1 and 2, wherein (A) comprises one or more from lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, palmitoleic acid, oleic acid, linoleic acid and linolenic acid.
4. Use according to claims 1 - 3, wherein
- (A) is soybean oil, and
- (B) is dimethylamine or 1-methyl-2-pyrrolidone.
5. A process for preparing the reaction product as described in the preceding claims, wherein (A) is contacted with (B) in a ratio of 10 : 1 to 1 : 2 at a temperature of 140° - 270°C.
6. Process according to claim 5, wherein (A) is contacted with (B) in a ratio of 5 : 1 to 1 : 1 at a temperature of 215° - 240°C when (B) is dimethylamine and 160° - 180°C when (B) is 1-methyl-2-pyrrolidone, during a half to three hours, preferably one and a half hour, and wherein said dimethylamine is in the gaseous state and said 1-methyl-2-pyrrolidone is in the liquid state.
7. Cleansing agent composition comprising
- (i) the reaction product as described in the preceding claims in an amount of 1 - 30 % by weight, preferably of 5 - 15 % by weight,
- (ii) emulsion-stabilizing compounds in amounts of 0 - 5 % by

- weight, preferably of 0.5 - 1 % by weight, and
- (iii) water in an amount of 65 - 99 % by weight, preferably of 84 - 95 % by weight, with the sum of (i) - (iii) being 100 % by weight.
- 5 8. Hand soaps comprising
- (i) the reaction product as described in the preceding claims in an amount of 25 - 60 % by weight,
- (ii) emulsion-stabilizing compounds of 0 - 5 % by weight, preferably 0.5 - 1 % by weight, and
- 10 (iii) water of 0.5 - 2 % by weight.
9. Use of the reaction product as described in the preceding claims as a cleansing agent or as a washing agent in the printing industry.
10. Use of the reaction product according claim 9 for the removal of
15 inks, dyes, paints, scale, stains and haze from printing screens and printing devices.
11. A process for the removal of contaminating materials from solid substrates, comprising the following steps:
- (1) applying the cleansing agent according to the preceding claims
20 on the contaminated substrates to degrade and disperse said contaminating materials into said cleansing agent yielding a contaminated mixture,
- (2) collection of the contaminated mixture from step (A) and separation of said contaminating materials from said mixture
25 yielding a purified cleansing agent.
12. Reaction product of soybean oil and 1-methyl-2-pyrrolidone prepared as described in the preceding claims.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/NL 94/00296

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D9/00 C11D7/40 B41N3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C11D B41N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US-A-5 011 621 (C. J. SULLIVAN) 30 April 1991 see column 5, line 60 - line 64 see column 3, line 4 - line 18 see column 2, line 17 - line 20 ---	1,3-5
X	EP-A-0 213 519 (HENKEL) 11 March 1987 see page 2, line 31 - page 3, line 19; claim 9 ---	1,3
A	FR-A-2 269 572 (BUNKER RAMO) 28 November 1975 see examples 1-3 ---	1,3,10
A	US-A-5 310 496 (A. B. TAYLOR) 10 May 1994 see column 4, line 33 - line 57 -----	1,3,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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