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(54) Laundry detergent composition, method of manufacture and use thereof.

(57) A laundry product providing grease and oily soil removal benefits on textiles comprises a solid mixture of a primary, secondary or tertiary amine containing not more than 40 carbon atoms or a salt thereof together with a nonionic or anionic surfactant, in water-releasable combination with a flexible sheet-type substrate. The product is made by impregnating the substrate with the mixture in molten state and then cooling the product to solidify the mixture.

Croydon Printing Company Ltd

LAUNDRY DETERGENT COMPOSITION, METHOD OF MANUFACTURE AND USE THEREOF

FIELD OF THE INVENTION

This invention relates to laundry products adapted to provide grease and oil removal benefits and more especially to laundry products in non-particulate solid form that incorporate amine surfactants.

BACKGROUND TO THE INVENTION

Detergent compositions containing alkyl amine surfactants are known in the art, particularly for the purpose of degreasing metals and other hard surfaces. Examples of such compositions in liquid form are disclosed in BP 1438948, USP 3468804 and South African Application No. 6806992, while exemplary particulate detergent compositions are disclosed in DTAS 1034307. A further application of amines as surfactants is in the dry cleaning of textiles, a typical disclosure being that in DTAS 1057275.

Fabric-softening products comprising amines absorbed on non-particulate substrates, designed for addition to drum dryers, have also been suggested in USP 4077891, USP 3895128 and Belgian Patent No. 840402.

Whilst the prior art has disclosed the use of amines as surfactants useful in degreasing applications, it has not recognised the benefits that can be obtained by the combination of certain such amines with nonionic surfactants in a form suitable for use in an aqueous textile laundering process.

Accordingly, the present invention seeks to provide a product in solid non-particulate form adapted to provide enhanced grease and oily soil removal from textiles in an aqueous textile cleaning bath.

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided a laundry detergent product adapted to provide grease and oily soil removal from textiles comprising

(a) a non-particulate flexible substrate in water releasable combination with

(b) a primary, secondary or tertiary amine or salt thereof, containing a total of not more than 40 carbon atoms in the amine radical, at least one, but not more than two groups in the amine radical containing an alkyl or alkenyl group of at least 8 carbon atoms, and

(c) a surfactant selected from water soluble anionic and ethoxylated nonionic surfactants and mixtures thereof,

the amount of (c) present in the mixture being from 0.1 to 10 parts by weight per part of the amine moiety of (b) the mixture being water dispersible or water soluble at 30^{o}C, the total amount of (b) and (c) being from 0.1 to 30 parts by weight per part of (a).

Preferably, the amine is a primary or tertiary amine or amine salt containing not more than 20 atoms in the amine radical and most preferably the amine is a mono C_{12-14} alkyl primary or tertiary amine salt. Mixtures of amines or amine salts can be used.

In accordance with a further aspect of the invention, there is provided a method of making a laundry product adapted to provide grease and oily soil removal comprising the steps of

(a) mixing a primary, secondary or tertiary amine or amine salt containing not more than 40 carbon atoms and at least one but not more than two alkyl or alkenyl groups of at least 8 carbon atoms in the amine radical, with an anionic or ethoxylated nonionic surfactant in an amount of from 0.1 to 10 parts by weight of nonionic or anionic surfactant per part of amine or amine radical, together with from 0 to 10 parts per part of amine or amine radical, of a processing aid selected from C_{12-18} fatty acids, polyethylene glycols of MWt > 4000, inorganic and organic thickening agents as hereinafter defined, and mixtures thereof

(b) forming a fluid mass of the mixture

(c) treating a flexible non-particulate substrate with the fluid mass so as to impregnate and/or coat the substrate and

(d) causing the fluid mass to solidify on the substrate to provide from 0.1 to 30 parts by weight of the mixture per part by weight of the substrate.

DETAILED DESCRIPTION OF THE INVENTION

The amine

The amines suitable for the purposes of the present invention are saturated or unsaturated primary, secondary and tertiary amines or salts thereof, in which the amine portion of the molecule contains not more than 40 carbon atoms and in which at least one and not more than two of the organic groups attached to the nitrogen atom in the amine portion contain an alkyl or alkenyl chain of at least 8 carbon atoms.

The organic group or groups containing more than 8 carbon atoms can be saturated or unsaturated aliphatic in nature, as in material derived from naturally occurring oils and fats such as coconut and palm oil, tallowfat and soya bean oil and marine oils. These aliphatic groups can also be derived from synthetic hydrocarbon materials such as Ziegler olefins and OXO alcohols and can be substantially linear or highly branched in nature. The aliphatic groups may form part of an aralkyl group such as an alkylbenzyl group in which the alkyl portion can have from 8-15 carbon atoms and can be derived from any of the sources given above.

The remaining group or groups in amines useful in the present invention are selected from hydrogen, C_1-C_7 alkyl, C_1-C_4 hydroxy alkyl and benzyl moieties. Preferred groups are hydrogen, methyl and hydroxy ethyl, and no more than one benzyl should be attached directly to the nitrogen atom.

Thus suitable amines include

tallow alkyl amine
tallow methyl amine
tallow dimethyl amine
tallow diethyl amine
coconut alkyl amine
coconut methyl amine
coconut dimethyl amine
myristyl alkyl amine
myristyl methyl amine
myristyl dimethyl amine
lauryl ethyl amine
lauryl diethyl amine
n-decyl benzyl amine
n-dodecyl dihydroxyethyl amine
n-dodecyl dibutyl amine
n-dodecyl amine
cetyl dimethyl amine
di-octyl amine
di-octyl methyl amine
C_{11}-C_{13} alkylbenzyl amine
C_{11}-C_{13} alkylbenzyl dimethyl amine
di-cetyl methyl amine
di-tallow methyl amine
di-tallow hydroxyethyl amine
di-myristyl ethyl amine
di-lauryl hydroxyethyl amine

Mixtures of any of the above may be employed.

Synthesis of the amines can be by any of the methods well-known in the art and which form no part of the present invention.

The amines may be present as such or in the protonated form as salts. For this purpose any of the conventional anions can be used, viz. halides (chlorides, bromides and iodides) sulphates, silicates, methosulphates, borates, phosphates and carboxylates. Suitable carboxylates include formates, acetates, propionates and the C_{12}-C_{18} fatty acid carboxylates derived from naturally occurring triglycerides, especially stearates.

The amine salts may be formed prior to the processing of the product or may in certain instances be formed <u>in situ</u> in a manner to be described.

Preferred amines are the alkyl primary and tertiary amines in which the alkyl group is derived from middle cut coconut alcohol, hardened tallow or synthetic C_{12}-C_{13} alcohol produced by olefin build-up. Although the invention embraces the use of amines containing up to 40 carbon atoms, it has been found that the grease and oily soil removal efficiency declines as the amine molecular weight increases i.e., a larger amount of amine or amine salt is required to achieve the same level of performance Accordingly, preferred amines are those containing not more than 20 carbon atoms in the amine radical and only one group contains more than 8 carbon atoms. In the most preferred embodiments of the invention the amines are primary C_{12}-C_{14} alkyl amines or tertiary C_{12}-C_{14} dimethyl amines.

In the preferred embodiments of the invention, the amines are utilised as salts, the most preferred embodiments being those in which the amine salts, particularly the long chain carboxylates, are formed *in situ* during the processing of the product.

The co-surfactant

An essential component of the present invention is a co-surfactant which may be nonionic or anionic in character. Suitable nonionic detergent materials for the purposes of the present invention can be broadly defined as compounds produced by the condensation of alkylene oxide groups having a hydrophilic nature with an organic hydrophobic compound having a reactive hydrogen atom. The hydrophobic groups may be aliphatic or alkylaromatic in nature and the size of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to provide a water soluble compound having the desired balance between hydrophilic and liphophilic characteristics.

Examples of suitable nonionic detergents include

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol condensed with 20 moles of ethylene oxide per mole of nonylphenol and di-iso-octylphenol condensed with 15 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain

configuration, with from 1 to about 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulphonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodols being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a trade name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactant falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms.

Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 16 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the trade name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

For the purposes of obtaining optimum grease and oily soil removal the nonionic surfactant should have a lower consolute temperature in the range 25-65°C preferably in the range 30-50°C . Preferred nonionic surfactants having this characteristic are the ethoxylated primary or secondary C_9-C_{15} alcohols containing 2-12 ethylene oxide groups per mole of alcohol, more particularly the C_{12}-C_{15} alcohols containing 6-9 ethylene oxide groups per mole of alcohol. Particularly preferred nonionics are those marketed under the trade names Dobanol 45-7 and Dobanol 45-9 by Shell Oil Company.

Synthetic anionic surfactants can also be employed as co-surfactants in the products of the present invention.

A highly preferred class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in USP 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 moles of ethylene oxide.

Other anionic detergent compounds herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from about 8 to 24, expecially 14 to 18 carbon atoms, and β-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactant mixtures can also be employed, for example 5:1 to 1:5 mixtures of an alkyl benzene sulfonate having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an alkali metal preferably sodium; and from about 2% to about 15% by weight of an alkyl ethoxy sulfate having from 10 to 20 carbon atoms in the alkyl radical and from 1 to 30 ethoxy groups and mixtures thereof, having an alkali metal cation, preferably sodium.

As stated earlier, the co-surfactant may comprise a nonionic or anionic surfactant or a mixture of the two, the relative proportions in such a mixture not being of importance for the purpose of the present invention. The total amount of the co-surfactant should be such as to provide from 0.1 to 10 parts by weight of co-surfactant per part of amine, preferably from 1 to 10 parts by weight and most preferably from 1.5 to 5 parts by weight.

A requirement of the product of the invention is that the amine-co-surfactant mixture should be water soluble or water-dispersible at 30°C. In the most preferred embodiments of the invention in which the non-particulate substrate is a fibrous non-woven sheet, the composition embodying the amine-cosurfactant mixture should also be solid at this temperature. Mixtures of amines and nonionic and/or anionic surfactants do not have a sharply defined melting point and the requirement that the mixture be solid at 30°C is also intended to mean that the mixture should not soften at 30°C and below.

The non-particulate substrate

The third essential component of the present invention is a flexible non-particulate substrate with which the other components are in water-releasable combination. In the context of the present invention, a water-releasable combination is one that is capable of being separated by water through solution, dispersion, leaching, softening or melting.

The substrate itself may be water-soluble or water insoluble and in the latter case, it should possess sufficient structural integrity under the conditions of the wash to be recovered from a washing machine at the end of the laundry cycle. Structures that are water-disintegratable i.e., that break down in aqueous media to individual fibres or insoluble particles are not considered satisfactory for the purposes of the present invention.

Water soluble materials include certain cellulose ethers, alginates, polyvinyl alcohol and water soluble polyvinyl pyrrolidone polymers, which can be formed into non-woven and woven fibrous structures. Suitable water insoluble materials include, but are not restricted to, natural and synthetic fibres, foams, sponges and films.

The substrate may have any one of a number of physical forms such as sheets, blocks, rings, balls, rods or tubes. Such forms should be amenable to unit usage by the consumer, i.e., they should be capable of addition to the washing liquor in measured amounts, such as individual sheets, blocks or balls and unit lengths of rods or tubes. Certain of these substrate types can also be adapted for single or multiple uses and can accept loadings up to 30 times the substrate weight.

A highly preferred substrate type is a sheet, the form of which is the most advantageous for releasing material rapidly into a wash liquour, particularly under the limited time conditions prevailing in automatic washing machine cycles. Preferably the sheet is water pervious i.e., water can pass from one surface of the sheet to the opposite surface and, for film type substrates, perforation of the sheet is desirable. The most preferred form of the substrate is a sheet of woven or non-woven fabric or a thin sheet of cellular plastic material. Woven fabric sheets can take the form of a plain weave natural or synthetic fibre of low fibre count/unit length, such as is used for surgical dressings, or of the type known as cheese cloth.

Loading limitations on non-woven sheet type substrates limit the amount of material that can be applied to the sheet to a maximum of about ten times the sheet weight. Suitable material which can be used as sheet-type substrates include, among others, sponges, paper and woven and non-woven cloth.

As the name implies, a sponge sheet will be in the form of an absorbent foam-like material. The term "absorbent foam-like material" is intended to encompass three dimensional absorptive materials such as "gas blown foams", natural sponges and composite fibrous based structures such as are disclosed in US Patent Nos. 3311115 and 3430630 specifically incorporated herein by reference. Synthetic organic polymeric plastics material such as polyether, polyurethane, polyester, polystyrene, polyvinylchloride, nylon, polyethylene and polypropylene are most often employed and a particularly preferred material of this type is a hydrophilic polyurethane foam in which the internal cellular walls of the foam have been broken by reticulation. Foams of this type are described in detail in Dulle US

Patent No. 3794029 which is hereby specifically incorporated by reference. A preferred example of this foam type comprises a hyrophilic polyurethane foam of density about 0.038 g/cubic centimetres with a cell count of between 8 and 40 cells per cm. , preferably about 24 to 32 per cm. available from the Scott Paper Company, Eddystone, Pennsylvania, USA, under the Registerd Trade Mark "Hydrofoam".

Paper sheets can also be used in products of the present invention provided that they possess sufficient wet strength to maintain their integrity during use. A paper-based sheet of a type suitable for the purpose of the inventions is disclosed in BP 1370112, the disclosures of which are hereby specifically incorporated by reference.

The preferred non-woven cloth substrates usable in the invention herein can generally be defined as adhesively bonded fibrous or filamentous products, having a web or carded fibre structure (where the fibre strength is suitable to allow carding) or comprising fibrous mats, in which the fibres or filaments are distributed haphazardly or in random array (i.e., an array of fibres in a carded web where a partial orientation of the fibres is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibres of filaments can be natural (e.g. wool, sil, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g. rayon, cellulose, or polyesters).

Methods of making non-woven cloths are not a part of this invention and being well known in the art, are not described in detail herein. Generally, such cloths are made by air or water laying processes in which the fibres or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fibre-laden air or water is passed. The deposited fibres or filaments are then adhesively bonded together, dried, cured and otherwise treated as desired to form the non-woven cloth. Non-woven cloths made of polyesters, polyamides, vinyl resins, and other thermoplastic fibres can be spunbonded, i.e., the fibres are spun out onto a flat-surface and bonded (melted) together by heat or by chemical reactions.

The absorbent properties desired herein are particularly easy to obtain with non-woven cloths and are provided merely by building up the thickness of the cloth, i.e., by superimposing a plurality of carded webs or mats to a thickness adequate to obtain the necessary absorbent properties, or by allowing a sufficient thickness of the fibres to deposit on the screen. Any diameter or denier of the fibre (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fibre that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which further makes the non-woven cloth especially suitable for impregnation by means of intersectional or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

The choice of binder-resins used in the manufacture of non-woven cloths can provide substrates possessing a variety of desirable traits. For example, the absorbent capacity of the cloth can be increased, decreased, or regulated by respectively using a hydrophilic binder-resin, a hydrophobic binder-resin or a mixture thereof in the fibre bonding step. Moreover, the hydrophobic binder-resin, when used singly or as the predominant compound of a hydrophobic-hydrophilic mixture, provides non-woven cloths which are especially useful as substrates when the surfactant-substrate combinations disclosed herein are used in an automatic washer.

When the substrate herein is a non-woven cloth made from fibres, deposited haphazardly or in rando array on the screen, the compositions exhibit excellent strength in all directions and are not prone to tear or separate when used in the washer. Apertured non-woven substrates are also useful for the purposes of the present invention. The apertures, which extend between opposite surfaces of the substrate are normally in a pattern and are formed during laydown of the fibres to produce the substrate. Exemplary apertured non-woven substrates are disclosed in US Patent Nos. 3,741,724, 3,930,086 and 3,750,237, the disclosures of which are specifically incorporated herein by reference.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant. Preferably, the fibres are from 45 to 50 mm in length and are from 1.5 to 5 denier (Denier is an internationally recognised unit in yarn measure, corresponding to the weight in grams of a 9,000 meter length of yarn). Preferably, the fibres are at least partially orientated haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. Conveniently, the cloth comprises about 70% fibre and 30% binder-resin polymer by weight and has a basis weight of from 10 to about 100, preferably 20 to 60 grammes per square yard.

A particularly preferred example is an air-laid non-woven cloth comprising 70% regenerated cellulose (American Viscose Corporation) and 30% hydrophobic binder-resins (Rhoplex HA-8 on one side of the cloth, Rhoplex HA-16 on the other; Rohm & Haas, Inc.). The cloth has a thickness of 4 to 5 mils., a basis weight of about 28 g. per square metre, and an absorbent capacity of 6. A 30 cm length of the cloth 21 cm. wide, weighs about 1.78 grams. The fibres are 1/4 in length, 1.5 denier and are orientated substantially haphazardly. The fibres are lubricated with sodium oleate.

A further preferred substrate is a water-laid, non-woven cloth commercially available from C.H. Dexter Co. Inc. The fibres are regenerated cellulose, about 0.95 cm. in length, about 1.5 denier, and are lubricated with a similar standard textile lubricant. The fibres comprise about 70% of the non-woven cloth by weight and are orientated substantially haphazardly; the binder-resin (HA-8) comprise about 30% by weight of the cloth. The substrate is about 4 mils. thick, and it has a basis weight of about 28 g. per square metre and an absorbent capacity of 5.7. One foot length of the cloth, 21 cm. wide, weighs about 1.66 grams.

The total loading of water releasable components on the substrate should be such as not to exceed 30 times the substrate weight and in the case of sheet-type substrates should be limited to 10 times the substrate weight, preferably from 2-7 times the substrate weight. The size and shape of the substrate is a matter of choice and is determined principally by factors associated with the convenience of its use. Thus a sheet-type substrate should not be so small as become trapped in the crevices of the machine or the clothes being washed or so large as to be awkward to package and dispense from the container in which it is sold. For the purposes of the present invention sheets ranging in plan area from 185 sq. cm. to 1850 sq. cm. are acceptable, the preferred area lying the range of from 740 to 1480 sq. cm for foamed sheets. Such a size has the additional advantage of being too large to be swallowed by e.g., small children, thereby minimising the risk of internal damage from ingestion of the materials absorbed on the substrate.

Optional components

A wide range of optional components can be applied to the substrate, subject only to loading limitations, compatibility with the other components and feasibility of incorporation. Thus organic surfactants other than those identified as essential components can also be applied provided that their presence does not detract from the grease and oily soil removal capability of the combination of the present invention. Other materials, such as organic chelating agents, anti-redeposition agents, suds modifying agents, fluorescers, perfumes, pigments and dyes can also be incorporated. The invention is particularly adapted to be used in conjunction with the product disclosed in German Patent Application DTOS, 2744642 published April 13th 1978, the disclosures of which are specifically incorporated herein by reference. DTOS 2744642 teaches the incorporation of an organic peroxy bleach precursor on a flexible non-particulate substrate, for the purpose of providing enhanced removal of oxidisable stains from textiles when added to a laundry wash liquor containing an inorganic persalt.

A preferred optional ingredient in the product of the present invention is a processing aid which serves as a plasticiser for the other materials during their application onto or into the substrate and also enhances the tactile aesthetics of the product. Suitable materials for this function include C_{12}-C_{18} fatty acids and polyethylene glycols of MWt > 4000 more preferably MWt $\geqslant 6000$.

Thickening agents are also useful ingredients in products of the present invention and are defined as materials that increase the viscosity or reduce the fluidity of the mixture such as silica, talc, kaolinite and montmorillonite as well as High MWt organic materials such as carboxymethyl cellulose derivatives, alginates, polyacrylates and starch.

Levels of incorporation of the optional ingredients can be as low as 0.001 parts by weight per part of substrate as in the case of ingredients such as dyes, fluorescers and perfumes and can be as high as 10 parts per part of substrate for surfactants. More commonly however, for one-time-use products, the level of incorporation for individual optional ingredients such as chelating agents, surfactants and bleach precursors is in the range 0.1-3.0 parts by weight per part of substrate.

The product of the present invention can be made in a variety of ways and is not critically dependent on any particular manufacturing route. Thus aqueous or non-aqueous solutions and dispersions and molten mixtures of the components can be formed and applied to the flexible non-particulate substrate. One technique of application is by immersion of the substrate in the component solution or dispersion followed by removal of the excess liquor by squeeze rolls.

In this method, the mixture of amine, surfactants etc., in liquid form, is placed into a pan or trough which can be heated, if necessary, to maintain the contents in liquid form. To the liquid mixture is then added any further additive. A roll of absorbent substrate is then set up on an apparatus so that it can unroll freely. As the substrate unrolls, it travels downwardly and, submersed, passes through the pan or trough containing the liquid mixture at a slow enough speed to allow sufficient impregnation. The treated substrate then travels, at the same speed, upwardly and through a pair of rollers which squeeze off excess bath liquid. The impregnated substrate is then cooled to room temperature, after which it can be folded, cut or perforated to uniform lengths, and subsequently packaged and/or used.

The rollers used resemble "squeeze rolls" used by those in the paper and paper-making art; they can be made of hard rubber or steel. Preferably, the rollers are adjustable, so that the orifice between their respective surfaces can be regulated to control the amount of the liquid on the substrate.

In another method of application, the amine and other ingredients in liquid form is sprayed onto an absorbent substrate as it unrolls. The unrolled substrate web is arranged to slide over the spray nozzle which comprises a horizontally disposed tube formed with a slit extending along its top surface. The molten slurry of amine co-surfactant mixture and any additives mixed therewith is forced through the slit into the substrate and the excess liquid is then squeezed off by the use of squeeze rollers. A melt temperature in the range of 40°-80°C preferably 45°-75°C is used and the molten material should have a viscosity of less than 5000 centipoises at 50°C, preferably no more than 500 centipoises.

Other variations include the use of metal "nip" rollers onto the leading or entering surfaces of which the impregnating mixture is sprayed, which variation allows the absorbent paper to be treated, usually on one side only, just prior to passing between the rollers wherein excess liquid is squeezed off. This variation additionally involves the use of metal rollers which can be heated to maintain the impregnating mixture as a liquid. A further method involves separately treating a desired number of the individual plies of a multi-ply paper and subsequently adhesively joining the plies with a known adhesive-joiner compound; this provides a composition which can be treated on one of its outer sides, yet contains several other plies, each of which is treated on both sides.

For the preferred sheet-type substrates of the present invention any of the above techniques can be employed but the most convenient process has been found to be that employing a molten mixture of the components at a temperature in the range 40-100°C. For systems of this type that contain suspended solids, some refinements are desirable in order to prevent segregation of the suspended solids and also to prevent build-up of solidified molten material over long periods of operation.

In the modified process for handling a suspension of solids in a melt the suspension in the form of a uniform dispersion is fed into a v-shaped trough formed by the generally upright portion of the face of a heated, rotating horizontal roll and a plate inclined thereto so as to leave a small clearance between the bottom of the plate and the roll face. A thin coating of suspension is carried downwards through the clearance and is transferred to a second horizontal roll in contact with the first but rotating in the opposite direction. This second roll is in contact with a continuously advancing web of substrate material and its direction of rotation is such as to make its direction of movement opposite to that of the substrate at the point of contact. Under these conditions the coating on the roll transfers to the substrate and impregnates it without any build-up of the suspended solids occurring on the roll. In order to ensure uniform distribution of the molten suspension the impregnated substrate is preferably passed over one or more further counter rotating rolls that serve to spread the suspension evenly over the substrate before it is cooled in an air stream to solidify the impregnating material.

In order to provide a mixture having suitable characteristics i.e., solidification over a range of temperature to give a waxy rather than a crystalline solid, certain of the amine-co-surfactant mixtures suitable for the purposes of the invention need to be blended with a plasticising or thickening agent.

For amine-co-surfactant mixtures melting in the optimum range i.e., 50°-80°C, a processing aid is not essential in the preferred method of manufacture of products in accordance with the invention. Such mixtures inherently possess the correct viscosity characteristics for satisfactory application to the substrate and indeed may themselves be used as carriers for other, optional, ingredients, such as chelating agents, high melting point bleach precursors and soil suspending agents. Nevertheless, additives of a waxy character may still be employed in order to provided robustness to the process, for example, by reducing dust or by modifying the range of temperatures over which the application process can be carried out. The additives may also servea funtional purpose in the productby enhancing the rate of release and dissolution of the amine-co-surfactant mixture in aqueous media and by modifying the tactile impression created by the product.

As previously mentioned the amine can be incorporated as such or in the form of an amine salt. The latter form is preferred and a highly preferred salt is a long chain fatty acid salt of the amine. This salt can be formed prior to the mixture of the components and their application to the substrate but more preferably the salt is formed in situ in the molten co-surfactant-amine mixture by reaction of the free amine with the chosen fatty acid. A slight excess of fatty acid is added relative to that required for stoichiometric reaction with the amine and this acts as a processing aid in the manner described above.

Products made in accordance with the present invention are adapted to provide grease and oily soil benefits when used as the sole source of detergent for a standard 3.5 kg load of soiled fabrics in a conventional washing machine holding 20 litres of water.

However, these benefits are also observed when the product is employed as an additive to commercially available, heavy-duty laundry detergents containing from 5-15% anionic and or nonionic surfactants and from 10-80% inorganic builder salts. Such commercially available detergents are normally used at a product concentration in the range 0.1%-1.0% by weight. For both types of use the product should be added with the soiled fabrics at the beginning of the wash cycle. The invention is illustrated in the following examples in which parts and percentages are on a weight basis unless otherwise stated.

EXAMPLE 1

150 g. of powdered n-dodecylamine hydrochloride are added to 500 g. of C_{14}-C_{15} primary alcohol (a substantially linear alcohol with < 25% 2-methyl branching) condensed with an average of seven moles of ethylene oxide per mole of alcohol[1] and the mixture heated to 70°C with agitation to give a homogeneous dispersion. The dispersion is transferred to a hold tank before being pumped to the applicator which comprises a head formed with a rectangular slot orifice having a length of 25 cms. The applicator head extends laterally of, and is in contact with the surface of, a continuous web of 0.5 cm thick Hydrofoam[2] polyurethane foam substrate which is drawn from a reel past the orifice by a system of rolls. After impregnation by the mixture, the treated substrate is cooled and rewound on to a product reel before being cut into pieces approximately 25 cms square.

Each sheet contains 5.0 g. of alcohol ethoxylate and 1.5 g. of amine hydrochloride and provides grease and oily-soil removal when added to a 3.5 kg load of soiled fabrics in 20 litres of water at 30°C. A similar benefit is also seen when the sheet is added together with 3.5 kg of soiled fabrics to 20 litres of a wash liquor containing any one of the following detergent compositions at 0.625% product concentration.

	A	B	C	D
Sodium C_{12} alkyl benzene sulphonate	8.0	6.0	1.0	8.0
Ethoxylated nonionic surfactant	2.0	4.0	15.0	2.0
Sodium Tripolyphosphate	35.0	20.0	45.0	60.0
Sodium silicate	5.0	5.0	5.0	-
Sodium Perborate	25.0	30.0	15.0	-
Tetrasodium EDTA	0.5	0.4	0.2	-
Minors	4.0	4.0	4.0	4.0
Water Sodium Sulphate and Miscellaneous		TO	100	

[1] Available commercially from Shell Chemical Co. under the trade name Dobanol 45-7.

[2] Hydrophilic polyurethane foam of density 0.038 grs/ml^3 and cell count of 24-32 per linear cm. supplied by Scott Paper Co. of Eddystone, Pennsylvania U.S.A.

In the above formulation the amine can be replaced by any one of dodecyl dimethyl amine, lauryl dihydroxyethylamine, myristyl amine, decyl diethylamine, dioctyl amine and tallow dimethyl amine.

Also in the above formulation the nonionic co-surfactant can be replaced by: Tallow alcohol condensed with respectively 11 and 25 moles of ethylene oxide per mole of alcohol, Dobanol 45-9, a C_{14}-C_{15} primary alcohol condensed with an average of nine moles of ethylene oxide per mole of alcohol, Dobanol 45-11, a C_{14}-C_{15} primary alcohol condensed with an average of eleven moles of ethylene oxide per mole of alcohol, Neodol 23-6 a C_{12}-C_{13} primary alcohol condensed with an average of six moles of ethylene oxide per mole of alcohol, marketed by the Shell Oil Co., Synperonic (RTM) A7, A9, A11, A14 and A20, a range of primary C_{13}-C_{15} alcohols with about 50% 2-methyl branching condensed with an average of respectively 7, 9, 11, 14 and 20 moles of ethylene oxide per mole of alcohol supplied by Imperial Chemical Industries Ltd., Lial 125E4,a highly branched C_{12}-C_{15} primary alcohol condensed with four moles of ethylene oxide per mole of alcohol and Lial 169E11, a C_{16}-C_{19} highly branched primary alcohol condensed with an average of eleven moles of ethylene oxide per mole of alcohol supplied by Liquichimica SA, Tergitol (RTM) 15S6, 15S9 and 15S11,C_{11}-C_{15} secondary alcohols condensed with an average of 6, 9 and 11 moles ethylene oxide respectively per mole of alcohol supplied by Union Carbide Corporation and sucrose ester ethoxylates.

EXAMPLE II

150 g. of powdered n-dodecylamine hydrochloride are added to 500 g. of Dobanol 45-7 nonionic surfactant and 450 g. of technical grade stearic acid and the mixture is heated with agitation to 70°C to provide a uniform dispersion. This is then pumped to an applicator assembly comprising two heated horizontally disposed, steel-faced rolls. The first roll is provided with an inwardly inclined plate extending the length of the roll so as to form a v-shaped trough therebetween, the bottom of the trough being constituted by the nip between the roll and the bottom edge of the plate, the direction of rotation of the roll being downward at the nip so as to provide a bead of material on the roll surface. The other roll has a faster speed of rotation in the same direction as the first so that a thin coating of the dispersion is transferred from one roll to the other, at the nip between the rolls, and is carried around the second roll. The second roll is in contact with a continuous web of substrate material and at the point of contact the direction of movement of the roll surface is opposed to the direction of movement of the web so that the dispersion is wiped off the roll on to the substrate. The substrate is a 25 cm wide web of apertured non-woven fibre formed of regenerated cellulose fibres bonded with an ethyl acrylate binder (70% fibre 30% binder solids) having a basis weight of 40 g. per sq. metre and 17 apertures/ sq. cm., available from Chicopee Manufacturing Co., Milltown, New Jersey U.S.A. under the Code No. AK 30ML1379.

After impregnation, the substrate web passes over two further counter rotating heated rolls that provide further spreading of the dispersion on the substrate before being cooled in a cooled air stream and wound onto a product reel. The roll of impregnated substrate is subsequently cut and folded to give sheets of size approximately 25cm x 25cm (weight 25 gr.) each bearing a total weight of

1.5g	n-dodecyl amine hydrochloride
5.0g	Dobanal 45-7
4.5g	Stearic acid

The sheets have a smooth slightly sandy feel.

EXAMPLE III

Example II is repeated with the addition to the molten dispersion of 150g of Tallow alcohol and 120g of Polyethylene glycol 6000. The sheets so formed have a waxy feel and each contains

1.5g	n-dodecyl amine hydrochloride
5.0g	Dobanol 45-7
4.5g	Stearic acid
1.5g	Tallow alcohol
1.2g	Polyethylene glycol 6000

In the above example, the Dobanol 45-7 can be replaced by sodium C_{12} alkyl benzene sulphonate or by sodium C_{12} alkyl sulphate. In the above example, the n-dodecyl amine hydrochloride can be replaced by coco dimethyl amine hydrochloride or by primary tallow amine hydrochloride to give a similar product.

EXAMPLE IV

Example III is repeated except that 300 g of primary coco amine stearate are added to the molten mixture in place of the dodecylamine hydrochloride. The resulting mxiture is a homogeneous melt, as the stearate salt melts at approximately 50°C and is [illegible] with the remaining ingredients. The sheet produced has a smooth non-gritty feel.

An identical product is obtained if the amine stearate is formed <u>in situ</u> in the melt by addition of 170 g amine and 130 g stearic acid separately to the mixture of the other ingredients at 70°C.

EXAMPLE V

Example III is repeated replacing the n-dodecyl amine hydrochloride in the dispersion by 75 g of ditallow methyl amine hydrochloride to give a sheet product comprising

7.5g	ditallow methyl amine hydrochloride
5.0g	Dobanol 45-7
4.5g	Stearic acid
1.5g	Tallow alcohol
1.2g	Polyethylene glycol 6000

The sheet so formed has a waxy, slightly sandy feel and provides similar grease and oil-removal benefits to those provided by the products of Examples I-IV. A sheet used with a heavy duty laundry detergent product at a concentration of 125 grs. product in 20 litres of water also gave some fabric softening benefits. In the above example the 75g of ditallow methyl amine hydrochloride is replaced by 100g of a 3:1 mixture of ditallowmethyl amine hydrochloride and C_{12-14} alkyl dimethyl amine stearate and satisfactory cleaning together with some fabric softening is obtained.

EXAMPLE VI

The following compositions is made up

170g	coco dimethylamine
450g	technical stearic acid
150g	tallow alcohol
120g	polyethylene glycol 6000
500g	Tetracetyl ethylene diamine
500g	Dobanol 45-7
50g	Ethylene diamine tetramethylene phosphonic acid
15g	Optical brightener

The tallow alcohol, polyethylene glycol, Dobanol 45-7 and stearic acid are mixed and heated with agitation to a temperature of 70°C. The coco dimethylamine is then added and the mixture held for 15 minutes to ensure complete conversion of the amine to the salt. The remaining ingredients are then added as finely powdered solids and mixed well to form a homogeneous dispersion which is then applied to a cellulosic substrate following the procedure in Example II to give a smooth sheet product that contains (per sheet)

5.0g	TAED
5.0g	Dobanol 45-7
3.0g	Cocodimethylamine stearate
0.5g	EDTMP
1.5g	Tallow alcohol
1.2g	Polyethylene glycol 6000
0.15g	Optical brightener.

[illegible]

1. A laundry detergent product adapted to provide grease and oily soil removal for textiles characterised in that it contains

(a) a non-particulate flexible substrate in water-releasable combination with

(b) a primary, secondary or tertiary amine or salt thereof containing a total of not more than 40 carbon atoms in the amine radical and at least one but not more than two groups in the amine radical containing an alkyl or alkenyl group of at least 8 carbon atoms, or a mixture of such amines or amine salts and

(c) a surfactant selected from water soluble anionic and ethoxylated nonionic surfactants and mixtures thereof

the amount of (c) present being from 0.1 to 10 part per part of the amine moiety of (b), the mixture of (b) and (c) being water dispersible or water soluble at 30°C, the total amount of (b) and (c) being from 0.1 to 30 parts by weight per part of (a).

2. A laundry detergent product according to Claim 1 characterised in that (b) comprises a primary or tertiary amine salt containing not more than 20 carbon atoms in the amine moiety preferably a mono C_{12}-C_{14} alkyl amine C_{12}-C_{18} fatty acid salt.

3. A laundry product according to either of Claims 1 or 2 characterised in that the amount of anionic and/or nonionic surfactant (c) is from 1 to 10 preferably from 1.5 to 5 parts by weight per part of the amine moiety.

4. A laundry detergent product according to any one of Claims 1 to 3 <u>characterised in that</u> the surfactant (c) is substantially linear C_{12}-C_{15} primary alcohol condensed with an average of from 6-9 ethylene oxide groups.

5. A laundry product according to any one of Claims 1 to 4 <u>characterised in that</u> the total amount of (b) and (c) is in the range from 1 to 10, preferably from 2 to 7 parts by weight per part of substrate.

6. A laundry product according to any one of Claims 1 to 5 <u>characterised in that</u> the non particulate flexible substrate is a sheet, preferably an apertured non woven fibrous sheet and in that the composition incorporating the amine and co-surfactant is a solid at 30°C.

7. A method of making a laundry product adapted to provide grease and oily soil removal <u>characterised in that</u> it comprises the steps of

(a) mixing a primary, secondary or tertiary amine or amine salt containing not more than 40 carbon atoms and at least one but not more than two alkyl or alkenyl groups of at least 8 carbon atoms in the amine radicals, with an anionic or ethoxylated nonionic surfactant in an amount of from 0.1 to 10 parts by weight of nonionic and/or anionic surfactant per part of amine or amine salt, together with from 0 to 10 parts per part of amine or amine salt of a processing aid selected from C_{12}-C_{18} fatty acids, polyethylene glycols of MWt > 4000 and mixtures thereof and organic and inorganic thickening agents.

forming a fluid mass of the mixtures

treating a flexible non-particulate substrate with the fluid mass so as to impregnate and/or coat the substrate and

(d) causing the fluid mass to solidify on the substrate to provide from 0.1 to 30 parts by weight of the mixture per part by weight of the substrate.

8. A method of making a laundry product according to Claim 7 characterised in that the mixture is heated to a temperature in the range of 40 to 100°C so as to form a molten mass thereof and in that the impregnated and/or coated substrate is cooled to a temperature $< 30^{\circ}C$ to solidify the mixture.

9. A method of making a laundry product according to Claim 8 characterised in that an amine salt is formed in the molten mass by reaction of the amine and a C_{12}-C_{18} fatty acid which is added in stoichiometric excess of that required to react with the amine.

10. A method of removing grease and oily soil stains from textiles in an aqueous wash liquor containing from 50-1500 ppm anionic or nonionic surfactant and from 100-80,000 ppm of inorganic builder salts characterised in that it comprises the addition to the liquor of a product comprising

(a) a non-particulate flexible substrate in water-releasable combination with

(b) a primary, secondary or tertiary amine or salt thereof containing a total of not more than 40 carbon atoms in the amine radical and at least one but not more than two groups in the amine radical containing an alkyl or alkenyl group of at least 8 carbon atoms, and

(c) a surfactant selected from water soluble anionic and ethoxylated nonionic surfactants and mixtures thereof.

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EUROPEAN SEARCH REPORT

Application number
EP 79 20 0782

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 4 080 162 (COLGATE-PALMOLIVE) * claim 4; column 4, lines 3 to 14; column 9, example 11 * --	1,4
X	DE - A1 - 2 708 516 (HENKEL & CIE) * page 18, table 1; pages 18 and 19; example 1 * --	1,4
	US - A - 4 129 515 (PROCTER & GAMBLE) * claims 1, 4 to 6 * --	1,4
A	DE - A1 - 2 539 270 (HOECHST) * complete document * --	
A	DE - A1 - 2 512 616 (PROCTER & GAMBLE) * complete document * ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 11 D 3/30
C 11 D 1/83

TECHNICAL FIELDS SEARCHED (Int.Cl.3)

C 11 D 1/00
C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	21-03-1980	SCHULTZE

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