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**DETERGENT COMPOSITIONS**

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**ABSTRACT OF THE DISCLOSURE**

Detergent compositions are based on mixed nonionic and amine oxide detergent active compounds with an alkali metal carbonate as the detergency builder. Preferably the detergent active compounds are present within the ratios of from 3:1 to 1:3 parts by weight in a combined amount of from about 5 to 25% by weight. The use of the mixed detergent active compounds tends to mitigate the adverse effects of the carbonate detergency builder, especially to diminish inorganic deposition on washed fabrics and consequently improve fabric softness, and to improve detergency.

The invention relates to detergent compositions, and in particular to detergent compositions adapted for fabric washing.

Detergent compositions, particularly those adapted for fabric washing, commonly incorporate as major ingredients detergency builders together with detergent active compounds. Conventional detergency builders are commonly inorganic materials, particularly the condensed phosphates, for example sodium tripolyphosphate. It has, however, been suggested that the use of phosphate detergency builders can contribute to eutrophication problems. Alternative detergency builders which have been proposed, for example sodium nitrilotriacetate (NTA) and synthetic polyelectrolyte materials, tend to be more expensive or less efficient than the phosphate detergency builders, or otherwise unsatisfactory for one reason or another.

It is known that sodium carbonate can function as a detergency builder by removing the calcium from hard water in the form of precipitated calcium carbonate. But this precipitation takes some time, during which the unprecipitated calcium can interact with fatty soil and with the detergent active compounds in detergent compositions, leading to inferior detergency when compared with compositions based on sodium tripolyphosphate as the detergency builder, and the precipitated calcium carbonate tends to accumulate on washed fabrics, which can lead to fabric harshness.

We have now found that a detergent composition with an alkali metal carbonate detergency builder is improved by incorporating mixed amine oxide and nonionic detergent active compounds. Such compositions tend to give decreased inorganic deposits on washed fabrics and the fabrics feel softer after washing, compared with commercially available carbonate-based detergent compositions.

According to the present invention, a detergent composition comprises from about 5 to 25% by weight of mixed amine oxide and nonionic detergent active compounds with from about 25 to 90% by weight of an alkali metal carbonate detergency builder.

The alkali metal carbonate used may be any water-soluble carbonate or mixtures thereof, although the alkali metal carbonates, particularly the sodium salt, are preferred for reasons of cost and efficiency. The carbonate salt may be wholly or partially neutralised, for example a sequi-carbonate may be used in partial replacement for the carbonate salt. The amount of the alkali metal car-

bonate in a detergent composition can be varied widely, but should be within the range of from about 25 to 90% by weight, whilst the practical range varies according to the conditions under which the detergent composition is intended to be used. Thus, in a detergent composition intended for use under typical North American washing conditions, that is at low product concentrations, the amount of alkali metal carbonate in a detergent composition would preferably be from about 25 to 75%, particularly from about 45 to 70%, by weight. Lower proportions of carbonate within the useful range tend to be more suitable under conditions of higher product concentrations in use.

The amine oxide and the nonionic detergent active compounds used should normally be within the range of from about 1:3 to 3:1, preferably from about 2:1 to 1:2 parts by weight, and at a ratio of about 1:1 for optimum detergency. However, for economic reasons it is normally desirable to use less of the amine oxide than the nonionic detergent active compound, that is to operate within the range of about 1:3 to 1:1 parts by weight, respectively, as the amine oxide is usually considerably more expensive than the nonionic compound. The minimum amount of amine oxide for any significant benefits in accordance with the invention is about 1 part to 10 parts of the nonionic compound. The total concentration of the amine oxide and nonionic detergent active compounds is generally within the range of from about 5 to 25%, preferably from about 10 to 14% by weight. If any more than about 20% by weight of the mixed detergent active compounds are used, this can give rise to processing difficulties with very little increased detergency for the extra cost involved, both for the extra amounts of the active ingredients and for overcoming any processing difficulties.

Any detergent active nonionic compound can be used in the composition of the invention, many such materials being known in the art and being commercially available. They are generally condensation products of organic compounds having a hydrophobic group and a reactive hydrogen atom with an alkylene oxide, usually ethylene oxide. Examples of suitable nonionic compounds include condensation products of alkyl phenols, preferably with about 6-16 carbon atoms in the alkyl groups, with ethylene oxide, generally 5 to 25 EO, (i.e. 5 to 25 units of ethylene oxide per molecule); condensation products of aliphatic (preferably C<sub>8</sub>-C<sub>18</sub>) natural or synthetic alcohols with ethylene oxide, generally 5 to 15 EO, and condensation products of polypropylene glycol with ethylene oxide. Other nonionic compounds which can be used are the condensation products of diols with alkylene oxides, especially ethylene oxide, for example alkane (C<sub>10</sub>-C<sub>20</sub>) diol-5-12 EO condensates. Mixed nonionic compounds may be used if desired. Many other suitable nonionic detergent active compounds are described in the literature, for example in "Surface Active Agents and Detergents," Vols I and II by Schwartz, Perry and Berch.

Any detergent active amine oxides may be used, the more conventional compounds having the general formula:



where R<sub>1</sub> is a C<sub>10</sub>-C<sub>22</sub> alkyl or alkenyl group and R<sub>2</sub> and R<sub>3</sub> are C<sub>1</sub>-C<sub>4</sub> alkyl groups or C<sub>2-3</sub> hydroxyalkyl groups. R<sub>1</sub> is preferably a linear alkyl group and R<sub>2</sub> and R<sub>3</sub> are preferably the same group, for example methyl groups. Specific amine oxides which may be mentioned are dimethyl hardened-tallow amine oxide and dimethyl cocoamine oxide. Alternative amine oxides include compounds containing a benzene ring in the group R<sub>1</sub>, with R<sub>2</sub> and

$R_3$ , being as before, for example dimethyl ( $C_8-C_{18}$ ) alkyl benzyl amine oxide. Other suitable amine oxides are compounds in which the nitrogen atom is contained in a heterocyclic ring, for example N-alkyl morpholine-N-oxides. Other types of amine oxides are described in the literature, for example in the book "Surface Active Agents and Detergents" mentioned above, and many specific amine oxides, some being novel compounds, are listed in the following Examples. It will be appreciated that amine oxides have a dative or semi-polar bond and as such are not "nonionic detergent active compounds" for the purposes of this specification, although amine oxides are for convenience sometimes included within that term in the art.

It has been proposed hitherto to use at least the more common types of amine oxides in detergent compositions, especially the amine oxides with high alkyl groups ( $C_{18}$  and above) which have useful fabric softening properties. However, the benefit of using amine oxides in the present compositions is rather to alleviate the deficiencies of sodium carbonate as a detergency builder, and amine oxides which do not otherwise have any useful fabric softening properties are effective for this purpose. The use of the amine oxides gives other valuable benefits, as more particularly described in the Examples.

In addition to the essential ingredients in the detergent compositions, it is generally desirable to add a proportion of an alkali metal silicate, particularly a sodium silicate, for example sodium alkaline or meta-silicate. A low level of silicate, for example from about 5 to 15% by weight, is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines. The presence of silicate can also contribute to decreased inorganic deposition and at higher levels may give an improvement in detergency. However, the amount of silicate should not normally exceed about 30% by weight of the composition. The amount and type of the silicate also has an effect on the pH of the composition, which is preferably within the range of from about pH 10 to 11, for a 0.1% by weight aqueous solution of the composition.

The detergent compositions of the invention may include any of the usual optional ingredients, for example, perfumes, colourants, fabric softening agents, fungicides, germicides, enzymes, fluorescent agents, anti-redeposition agents such as SMC, hydrotropes and in the case of liquid compositions opacifiers and organic solvents such as lower aliphatic alcohols. Other ingredients such as chemical bleaches, for example sodium perborate with or without the presence of per-acid precursors, chlorine-liberating bleach compounds and inorganic salts such as sodium sulphate and sodium chloride may also be present if desired. The compositions also usually contain amounts of water, for example in the range of from about 5 to 15% by weight in the case of powdered detergent compositions.

Minor amounts of detergent active compounds other than the nonionic and amine oxide compounds may be included in the compositions, but it is preferable to exclude from the compositions any anionic detergent active compounds, as the presence of any significant amounts of these compounds, for example more than about 5% by weight, tends to give decreased detergency, possibly due to some interaction with the amine oxide detergent active compounds.

Detergency builders other than sodium carbonate may be included in the compositions if desired though they will normally be in small amounts of, say, up to about 10 percent by weight of the composition. Examples of such detergency builders include, for example sodium triphosphate, sodium nitrilotriacetate, sodium citrate, sodium salts of oxidised polysaccharides, sodium carboxymethylsuccinate, sodium oxydisuccinate, sodium hydrofuran tetracarboxylate, sodium mellitate and polyelectrolyte builders such as sodium copolyethylene-maleate, and other precipitant builders such as sodium orthophos-

phate, sodium  $\alpha$ -sulphonated fatty acids and sodium ( $C_{10}-C_{20}$ ) alkenyl succinates. It should be noted that some of these detergency builders, especially the sequestrant builders, can have a tendency to inhibit inorganic deposition on washed fabrics. Polyphosphates such as sodium triphosphate are particularly efficient in this respect. Weaker sequestrant builders such as sodium citrate, tetrasodium cyclopentane dicarboxylate, sodium mellitate and sodium carboxymethylsuccinate can also have an inorganic deposition inhibiting effect but they need to be used in higher amounts, of, say, from about 20% to 40% by weight for an appreciable effect, unless they are used in conjunction with other anti-deposition agents.

Other specific additives which can be used to advantage in detergent compositions according to the invention include aromatic solvents containing one or more substituted aromatic rings, which in the latter case may be fused or linked. Dibutyl phthalate and analogous solvents are particularly efficient. When appreciable levels of the solvents are used, it may be desirable to include in the composition a porous substance to absorb the solvent, for example a micro-porous silica or aluminosilicate. The amount of solvent should be from about 4% by weight of the composition up to a maximum level of 1 part solvent to 1 part of total detergent active compounds.

Additives to accelerate the rate of precipitation of calcium carbonate may also be used advantageously, for example nucleating agents such as finely ground calcite or aragonite. For maximum effect as much additive should be used as possible, for example from about 10% to about 50% by weight. However, it should be noted that some such additives may tend to increase inorganic deposition on washed fabrics. Conversely, additives to inhibit inorganic deposition may tend to decrease detergency, so it is necessary to balance the two effects for optimum properties in the compositions.

The compositions of the invention may be solid compositions, for example in powdered, granular or tablet form, semi-solid paste or gel compositions, or they may be liquids. The compositions can be made by conventional processes, for example by spray-drying aqueous slurries to produce detergent powders, but the nature of the amine oxide and nonionic detergent active compounds used may require that the aqueous slurries so formed have increased moisture levels to provide adequate flow properties for pumping and spray-drying.

In some cases the amine oxide in particular can cause slurry thickening, even when used at low levels and in this case alternative processing techniques may be adopted, for example the amine oxide and nonionic compound may be together or separately added to the slurry immediately prior to spray-drying or sprayed onto the particulate sodium carbonate in a suitable mixing vessel. In this event it may also be helpful to admix with the amine oxide or amine oxide/nonionic mixture a small amount of a solvent, such as isopropyl alcohol, but this compound is volatile and its excessive use should be avoided.

When normal slurry making is used for the production of compositions containing higher levels of nonionic detergent active compounds, it may be beneficial to add materials to decrease the tendency for the nonionic compounds to separate out during slurry-making. Examples of suitable nonionic slurry separation inhibitors are ethylene-maleic anhydride copolymers and vinylmethylether-maleic anhydride copolymers the use of which is described in more detail in our Canadian Pat. No. 704,074. If the resultant powders are sticky, whether or not the slurry separation inhibitors are used, it may be desirable to add to the resultant powders flow aids, which are commercially available materials, such as "Alusil AN," a sodium aluminosilicate.

Whilst the compositions are of particular utility in the field of fabric washing they can also be used for other general or specific cleaning purposes. It should be noted for fabric washing purposes that the action of sodium

carbonate in removing the calcium from the hard water in the form of calcium carbonate can take a short time, and it may be desirable to delay the addition of clothes to the wash solution until the free calcium level is decreased to an acceptable level, which may take say, from ½ to, say, 5 minutes or more in adverse conditions. This tends to improve the detergency of the compositions and contribute to decreased inorganic deposition.

The detergent compositions according to the invention are illustrated by the following Examples in all of which parts are by weight except where otherwise indicated.

#### EXAMPLE 1

A detergent powder was prepared by conventional slurry-making and spray-drying techniques to the following formulation:

Ingredient:	Percentage
Dimethyl hardened tallow amine oxide (obtained as "Aromox" DMHTD) -----	8
Sec-alcohol (C <sub>11</sub> -C <sub>15</sub> )-7EO (obtained as "Tergitol" 15-S-7) -----	10
Sodium carbonate -----	65
Sodium metasilicate -----	10
Sodium carboxymethylcellulose -----	1
Fluorescent agent -----	1
Water to 100	

This composition was compared for detergency, fabric feel, inorganic deposition and soil anti-redeposition properties against a commercially available sodium carbonate-built detergent powder with a comparable formulation except for the absence of the amine oxide, using identical washing conditions in each case. For these tests 6 soiled tea towels, 6 soiled pillow cases and 6 soiled hand towels were washed in a domestic washing machine at 0.15% product concentration, in water of 18° French hardness (Ca:Mg at 2:1) at 50° C. The washed fabrics were compared firstly for appearance by a panel of assessors who decided that overall there was a very slight preference for the articles washed in the composition according to the invention.

On repeated washing of the same articles the levels of inorganic deposits on the fabrics were measured and found to increase to maxima of about 0.85% at 10-15 wash cycles, for the composition according to the invention, whereas the deposit on fabrics washed in the comparative carbonate-based product increased progressively well beyond that figure as the number of wash cycles was increased to 25. Evaluation of the feel of the same washed fabrics was undertaken by a panel of 24 assessors who decided by a majority of on average over 22 to 2 that after 1, 5 and 10 wash cycles the articles washed by the composition according to the invention were softer.

In assessing the soil anti-redeposition properties of the compositions, clean test cloths of a variety of different types were washed together with the soiled fabrics mentioned above, when it was found that the amount of soil deposited on the test cloths made of nylon and polyester fibres were significantly lower on using the composition of the invention.

The detergent composition of this Example was further evaluated in machine washing trials against a commercially-available sodium tripolyphosphate-built detergent powder containing 40% sodium tripolyphosphate, 16% sodium linear sec-alkyl benzene sulphonate, 5% alkaline silicate and the usual fluorescent agent and anti-redeposition additives. The results showed an improvement in detergency for the amine oxide-nonionic active based composition according to the invention, whilst the fabric feel and antiredeposition properties of both compositions were very satisfactory.

#### EXAMPLE 2

In order to compare the detergencies of detergent compositions containing mixed amine oxide and nonionic de-

tergent active compounds with compositions containing the same compounds alone, and with comparative commercially-available products, a series of compositions were prepared and the detergencies determined using a variety of different standard soiled test cloths under standard conditions at 0.15% product concentration in water of 18° French hardness (Ca:Mg at 2:1) at 50° C. The results were as follows in Table I.

TABLE I

Formulation	Percent detergency with different test cloths		
	VCD <sup>1</sup>	AS9 <sup>2</sup>	ERTC 41A <sup>3</sup>
A—[Sodium carbonate, 60%; alkaline silicate, 10%; amine oxide <sup>4</sup> , 6%; non-ionic compound <sup>5</sup> , 6%; water to 100%]	44.4	77.6	85.7
B—[Sodium carbonate, 60%; alkaline silicate, 10%; amine oxide <sup>4</sup> , 12%; water to 100%]	39.6	73.6	82.3
C—[Sodium carbonate, 60%; alkaline silicate, 10%; nonionic compound <sup>5</sup> , 12%; water to 100%]	28.8	67.2	79.7
D—[Commercially available sodium tripolyphosphate-based product as described in Example 1]	45.4	68.5	86.0
E—[Commercially available sodium carbonate-based product, as described in Example 1]	27.2	78.7	86.1

<sup>1</sup> 65% "Daeron" polyester/35% cotton test cloth soiled with vacuum cleaner dust.

<sup>2</sup> A cotton test cloth soiled with a mixed fatty soil (90%) and particulate soil (10%) of indian ink and ferric oxide.

<sup>3</sup> A cotton poplin test cloth soiled with 4 parts of fatty soil and egg albumin and 1 part of particulate soil.

<sup>4</sup> "Aromox" DMCDW (dimethylcocoamine oxide).

<sup>5</sup> "Tergitol" 15-S-9 (sec-alcohol) (C<sub>11</sub>-C<sub>15</sub>)-9EO).

These results show that the amine oxide/nonionic mixture in formulation A is better than either of the formulations with the amine oxide or the nonionic detergent active compound alone and over the full range of test cloths the composition of the invention is better than either of the commercially-available detergent compositions.

#### EXAMPLES 3 TO 7

A series of detergent compositions were prepared in order to determine the optimum content of the amine oxide and nonionic detergent active compounds. The compositions had the formulation:

Ingredient:	Percentage
Dimethyl cocoamine oxide -----	<sup>1</sup> x
Sec-alkyl (C <sub>11</sub> -C <sub>15</sub> )-9EO ("Tergitol" 15-S-9) --	<sup>1</sup> x
Sodium carbonate -----	60
Alkaline silicate -----	10
Water to 100	

<sup>1</sup> 4, 5, 6, 7 or 8% in Examples 3 to 7, respectively, as shown in Table 2 below.

The detergencies of the compositions were determined using standard procedures and the same variety of test cloths as described in Example 2 with the following results in Table 2, which includes the results for a comparative product A built with sodium tripolyphosphate (as described in Example 1).

TABLE 2

Example:	x, percent	Percent detergency with different test cloths		
		VCD	AS9	ERTC 41A
3-----	4	37	76	77
4-----	5	39	76	77
5-----	6	44	78	84
6-----	7	45	77	85
7-----	8	43	78	85
Comparative product A-----		47	72	84

These results show increasing detergency up to a total concentration of the amine oxide and nonionic compound of 12% in Example 5, after which there is little benefit from any additional detergent active compounds.

#### EXAMPLE 8

A further batch of the detergent composition of Example 5 was tested for detergency with a variety of test

cloths under standard conditions as described in Example 2, except for varying total product concentrations. For comparative purposes the same tests were undertaken with a commercially-available sodium tripolyphosphate-built detergent powder A, as described in Example 1. The results were as follows in Table 3, the detergency for the comparative powder A being shown in parenthesis following each result for the composition according to the invention:

TABLE 3

Product concentration, percent:	Percent detergency for different test cloths				
	VCD	AS9	ERTC 41A		
0.75.....	29 (17)	72 (59)	52 (24)		
0.1.....	36 (31)	73 (62)	62 (45)		
0.125.....	38 (38)	78 (65)	82 (63)		
0.15.....	44 (47)	78 (72)	84 (84)		
0.2.....	47 (49)	81 (77)	88 (94)		
0.4.....	48 (52)	85 (78)	88 (95)		

These results show that, overall, the detergency of the composition according to the invention is significantly better than the comparative composition at lower product concentrations, and is generally comparable at higher product concentrations when the detergency would otherwise be expected to be much worse than the sodium tripolyphosphate-based product.

## EXAMPLE 9

A detergent composition was prepared by conventional spray-drying techniques with the following formulation:

Ingredient:	Percentage
Dimethylcocoamine oxide ("Aromox" DMCDW) .....	6
Sec-alkyl (C <sub>11</sub> -C <sub>15</sub> )-9EO ("Tergitol" 15-S-9) ..	6
Sodium carbonate .....	60
SCMC .....	1
Fluorescent agent .....	1
Water to 100	

This composition was assessed for detergency, fabric feel and for inorganic deposition against the commercially available sodium carbonate and sodium tripolyphosphate-based products as described in Example 1. Using the detergency test described in Example 1 to compare the composition of the invention with the commercially-available sodium tripolyphosphate-based detergent powder, there was distinct preference for the appearance of the halved articles washed using the former composition.

The halved articles were assessed for fabric feel by a panel of experienced assessors who showed only a slight preference for the conventional sodium tripolyphosphate-based composition, whereas conventional sodium carbonate based products normally cause much inferior fabric feel properties.

On repeated washing of the same halved articles in the composition of the invention the levels of inorganic deposition were found to increase as follows, the much worse ash levels for the comparative sodium carbonate-based product being also given for purposes of comparison.

Product	Inorganic deposit, percent at No. of wash cycles				
	5	10	15	20	25
Example 9.....	0.56	0.73	0.82	1.03	1.06
Comparative product.....	0.80	2.10		6.4	

These results show a very marked improvement for the composition of the invention.

## EXAMPLES 10 TO 21

A series of detergent compositions were prepared with the following formulation:

Ingredient:	Percentage
Sec-alkyl (C <sub>11</sub> -C <sub>15</sub> )-9 EO ("Tergitol"-15-S-9) .....	6
Amine oxide <sup>1</sup> .....	6
Sodium carbonate .....	60
Sodium alkaline silicate .....	10
Water to 100.	

<sup>1</sup>The amine oxide was varied in each example as shown in Table 4 below; and in a control product the 6% of amine oxide was replaced by a further 6% of the same nonionic compound.

The levels of inorganic deposits formed on washing terry towelling with these compositions were determined, using water of 18° French hardness (Ca<sup>2+</sup>:Mg<sup>2+</sup>, 2:1) at 50° C. and a product concentration of 0.15%, the washing load being added 30 seconds after the composition in each case, as in all washing tests in the Examples. The results after 10 and 20 wash cycles were as follows:

TABLE 4

Amine oxide	Percent inorganic deposit	
	10 wash cycles	20 wash cycles
Example:		
10..... Pyridine-N-oxide.....	2.8	6.1
11..... Dimethylcocoamine oxide.....	1.6	2.1
12..... Dimethyl dihardened tallow amine oxide.....	1.5	2.0
13..... Dimethyl-N-(heptylamido) propylamine oxide.....	1.9	2.1
14..... Dimethyl-N-(undecylamido) propylamine oxide.....	1.6	1.9
15..... Dimethyl-N-(tridecylamido) propylamine oxide.....	1.3	1.6
16..... Dimethyl-N-(heptadecylamido) propylamine oxide.....	1.4	1.4
17..... Dimethyl-N-(tridecoylethyl) amine oxide.....	1.7	1.8
18..... Amine oxide of acetylated polyethyleneimine.....	1.3	1.7
19..... N-dodecyl morpholine N-oxide.....	1.4	
20..... Dimethyl secondary alkyl (C <sub>10</sub> -C <sub>14</sub> ) amine oxide.....	3.0	6.0
21..... 1,3-diaminopropane-N-stearoyl-N'-dimethyl-N'-oxide.....	1.4	1.7
Control.....	4.0	8.0

These results show very considerable reductions in inorganic deposits for several of the amine oxides, though two of them, when used alone, namely in Examples 10 and 20, do not give as great a reduction as would be desired.

## EXAMPLES 22 TO 34

A series of laboratory tests were undertaken using both an amine oxide and sodium tripolyphosphate to inhibit inorganic deposition. The general formulation used was the same as described in Examples 10 to 21 except for the addition of 0.3% of sodium tripolyphosphate. The following amine oxides were found to give no noticeable inorganic deposit after 5 wash cycles using the same conditions as described for Examples 10 to 21.

Ex.	Amine oxide
22.....	N,N-dimethyl-2-hydroxy hexadecylamine oxide.
23.....	N,N-dimethyl-2-hydroxy dodecylamine oxide.
24.....	Bis-(N-2-hydroxyethyl)-2-hydroxy hexadecylamine oxide.
25.....	Bis-(N-2-hydroxyethyl)-2-hydroxy dodecylamine oxide.
26.....	Dimethyl-N-(heptylamidopropyl)amine oxide.
27.....	Dimethyl-N-(undecylamidopropyl)amine oxide.
28.....	Dimethyl-N-(heptadecylamidopropyl)amine oxide.
29.....	Do.
30.....	Amine oxide of methylated tetra-ethylene pentamine.
31.....	Amine oxide of polyethylene imine.
32.....	N-dodecyl morpholine-N-oxide.
33.....	1,3-diamino propane-N,N',N'-trimethyl-N-stearyl-N,N'-diamine oxide.
34.....	Dimethyl-N-(tridecoylethyl)amine oxide.

## EXAMPLES 35 TO 38

The procedure of Examples 22 to 34 was repeated with four amine oxides which under the conditions of

Examples 22 to 34 did give appreciable inorganic deposits, except that the amount of sodium tripolyphosphate was increased to 0.4% in Examples 35 and 36 and to 0.8% in Examples 37 and 38, whereupon no inorganic deposits were found.

Ex.	Amine oxide
35	Dimethyl-N-(p-octylbenzyl sulphonamido-propyl)amine oxide.
36	1,2-diaminoethane-N,N',N'-trimethyl-N-(heptadecylamidoethyl) diamine oxide.
37	Pyridine-N-oxide.
38	Tri(2-hydroxyethyl)amine oxide.

## EXAMPLE 39

A detergent composition according to the invention, which was difficult to process into a powder by conventional slurry-making techniques, was made by firstly preparing an aqueous slurry of all the ingredients except for the amine oxide and nonionic detergent active compounds and spray-drying the slurry to give a powder of low moisture content (3%). A mixture of 8 parts of "Tergitol" 20

## EXAMPLES 40-54

A series of detergent solutions were prepared with varying proportions of an amine oxide (Aromox DWCDW) and different nonionic detergent active compounds totaling in each example 12%, or with 12% of either of the detergent active compounds alone for comparative purposes, with either 30% (in Examples 40-42 and comparative products (a) and (b)) or 40% (in Examples 43-54 and comparatives (c) to (j)) of sodium carbonate and with 10% of sodium alkaline silicate. The compositions were compared for their fabric washing detergency using a Terg-O-Tometer at a product concentration of 0.15% in water of 18° French Hardness (Ca<sup>2+</sup>:Mg<sup>2+</sup>, 2:1) at 50° C. Test cloths as described in Example 2 were used and added after the composition in each case, and washing was carried out for 10 minutes followed by a 1 minute rinse. The percentage detergency was determined by calculation from the light reflectances of the test cloths before and after washing: the results are shown in Table 5 below.

TABLE 5

Example	Nonionic compound	Amine oxide	Percent		
			Nonionic	Detergency	
			VCD	ERTC 41A	
40	Tergitol 15-S-9 <sup>1</sup>	3	9	29	77
41	do	6	6	32	70
42	do	9	3	34	70
Comparative:					
(a)	do	0	12	30	65
(b)	do	12	0	32	68
43	do	3	9	37	71
44	do	6	6	38	74
45	do	9	3	37	71
Comparative:					
(c)	do	0	12	33	68
(d)	do	12	0	33	68
46	Dobanol 45-9EO <sup>2</sup>	3	9	33	72
47	do	6	6	38	75
48	do	9	3	37	73
Comparative:					
(e)	do	0	12	33	70
(f)	do	12	0	34	69
49	Alfol 1412-8EO <sup>3</sup>	3	9	38	73
50	do	6	6	39	76
51	do	9	3	39	72
Comparative:					
(g)	do	0	12	34	70
(h)	do	12	0	33	70
52	TEA-11 EO <sup>4</sup>	3	9	36	72
53	TEA-11 EO <sup>4</sup>	6	6	35	77
54	TEA-11 EO <sup>4</sup>	9	3	35	74
Comparative:					
(i)	TEA-11 EO <sup>4</sup>	0	12	32	67
(j)	TEA-11 EO <sup>4</sup>	12	0	33	69

<sup>1</sup> Secondary linear alcohol (C<sub>11</sub>-C<sub>15</sub>)-9EO.

<sup>2</sup> Alcohol (C<sub>11</sub>-C<sub>15</sub>)-9EO (80% linear alcohol, 20% α-methyl branched-chain alcohol).

<sup>3</sup> Primary linear alcohol (C<sub>11</sub>-C<sub>14</sub>)-8EO.

<sup>4</sup> Tallow ethanolamide-11EO.

15-S-7 (secondary alcohol (C<sub>11</sub>-C<sub>15</sub>)-7EO), 6 parts of "Aromox" DMCDW (dimethyldicoamine oxide) and 3 parts of isopropyl alcohol of 70° C. was sprayed onto the spray dried powder in a mixing vessel and thoroughly mixed in, during which procedure the isopropyl alcohol evaporated. This gave a powder of rather high bulk density (34 lbs./cu.ft.) which was slightly sticky and had the following formulation:

Ingredient:	Percentage
Sodium carbonate	65
Sodium silicate	10
"Tergitol" 15-S-7	8
"Aromox" DMCDW	6
Fluorescent agents	1
Sodium carboxymethyl cellulose	0.5
Water to 100.	

The addition of 2% of "Alusil" AN flow aid gave a considerable reduction in stickiness and consequent improvement in flow properties.

In a further processing trial, it was found that the addition of 2% of tallow soap gave a product of lower bulk density (23 lbs./cu. ft.) without any deterioration in other properties.

Comparison of the results shows that the better detergencies are generally obtained with the Examples according to the invention, especially Examples 41, 44, 47, 50 and 53, where the amounts of amine oxide and nonionic detergent active compounds are equal and a synergistic effect is demonstrated.

Further compositions according to the Examples 41, 44, 47, 50 and 53 were tested for inorganic deposition after 10 and 20 wash cycles on cotton terry towelling fabric using the same washing procedure in a Terg-O-Tometer. The results were as follows:

Example:	Percent inorganic deposit	
	10 washes	20 washes
41	1.1	1.4
44	1.0	1.4
47	1.2	1.6
50	1.3	1.3
53	0.9	1.0

When no amine oxide was present in the compositions, i.e. as in comparative products (a), (c), (e), (g) and (i) the levels of inorganic deposits were all about 4% after 10 washes and 8% after 20 washes.

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## EXAMPLES 54 TO 57

Four detergent compositions were prepared with mixed detergency builders and their inorganic deposition properties were determined by the procedure described for Examples 41, 44, 47, 50 and 53 with the results shown in Table 6 below. All the compositions had the formulation:

Ingredient:	Percentage
Nonionic detergent (Alfol 1412-8EO) -----	6
Amine oxide (Aromox DMCDW) -----	6
Sodium carbonate -----	40
Additional detergency builder (as shown in Table 6) -----	10
Sodium alkaline silicate -----	10
Water to 100	

TABLE 6

Ex.	Additional builder	Percent inorganic deposit	
		10 washes	20 washes
54	Sodium nitrilotriacetate.....	0.5	0.7
55	Sodium triphosphosphate.....	0.1	0.1
56	Sodium citrate.....	0.5	0.6
57	Sodium carboxymethylsulfonate..	0.7	0.9

The figures demonstrate much lower inorganic deposits with the addition of a small amount of an additional sequestrant builder. Sodium triphosphosphate is particularly efficient in this respect.

## EXAMPLES 58 TO 61

Four detergent compositions were prepared of which two included a solvent, dibutyl phthalate, to improve the detergency in respect of fatty soil on synthetic fabrics. The compositions were evaluated in a Terg-O-Tometer to determine the percentage detergency with a 65% "Dacron" polyester/35% cotton test cloth soiled with used motor vehicle crankcase oil, using a procedure in which the test cloth was firstly rubbed with a stiff (70%) paste of the product, rinsed and then washed and rinsed normally using water of 18° French Hardness (Ca<sup>2+</sup>:Mg<sup>2+</sup>, 2:1) at 50° C. using a product concentration of 0.2%. The formulations and their detergencies were as follows:

Ingredient:	Percent in each Example			
	58	59	60	61
Nonionic compound (Tergitol 15-S-7)...	10	10	10	10
Dimethyl di-hardened tallow amine oxide (Aromox DMHTD/W).....	6	6	8	8
Sodium carbonate.....	60	60	60	60
Sodium alkaline silicate.....	8	8	8	8
Dibutyl phthalate.....	5	5	5	5
Water.....	100	100	100	100
Percent detergency.....	73.6	63.7	74.6	61.0

These results were very good for a difficultly removable soil, and a significant benefit is shown for the addition of the solvent. In further tests it was found that the solvent benefit was not achieved with some other amine oxides in admixture with nonionic compounds or with the use of dimethyl hardened tallow amine oxides alone as the detergent active compound. For a significant improvement in detergency it appeared that a minimum amount of about 4% of the dibutyl phthalate was needed and that there should be an excess of the nonionic detergent compound over the amine oxide, but not more than about 7 parts of the nonionic compound to two parts of the amine oxide.

## EXAMPLES 62 TO 65

Four detergent compositions were prepared to a similar formulation except for one optional ingredient which was either calcium carbonate (in the form of finely ground aragonite or calcite), additional sodium carbonate or sodium sulphate. The base formulation was as follows:

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Ingredient:	Percentage
Nonionic detergent (Alfol 1412-8EO) -----	6
Amine oxide (Aromox DMCDW) -----	6
Sodium carbonate -----	40
Sodium alkaline silicate -----	8
Additive (see Table 7) -----	30
Water to 100	

The compositions were tested for their detergencies in a Terg-O-Tometer using standard test cloths as described in Example 2, with water of 18° French hardness (Ca<sup>2+</sup>:Mg<sup>2+</sup>, 2:1) at 50° C. and with a product concentration of 0.15%. The results are shown in Table 7.

TABLE 7

Additive	Percent detergency	
	VCD	ERTC 41A
Example:		
62..... Calcite.....	45	79
63..... Aragonite.....	44	81
64..... Sodium carbonate.....	44	82
65..... Sodium sulphate.....	40	75

These results show the benefit of having either calcite or aragonite or additional sodium carbonate present, at least under the low product concentration test conditions. It should be noted that the compositions of Examples 62 and 63 have a lower pH than the composition of Example 64 and is correspondingly safer for domestic use.

What is claimed is:

1. A solid detergent composition consisting essentially of from about 5 to 25% by weight of a mixture of (a) an amine oxide detergent active compound having the formula  $R_1R_2R_3N \rightarrow O$  where  $R_1$  is a  $C_{10}$ - $C_{22}$  alkyl or alkenyl group or a  $C_8$ - $C_{18}$  alkyl benzyl group or a  $C_8$ - $C_{18}$  alkyl amido group and  $R_2$  and  $R_3$  are  $C_1$ - $C_4$  alkyl groups or  $C_2$ - $C_3$  hydroxyalkyl groups or where  $R_2$  and  $R_3$  are conjoined to form a heterocyclic ring with the nitrogen atom, and (B) a nonionic detergent active compound which is a condensation product of an aliphatic alcohol or an alkyl phenol with ethylene oxide, the ratio of the amine oxide to the nonionic detergent active compound being from about 3:1 to 1:10 parts by weight, from about 25% to 75% by weight of an alkali metal carbonate detergent builder, and from about 10% to about 50% by weight of finely ground calcium carbonate.

2. A composition according to claim 1, wherein the alkali metal carbonate detergent builder is sodium carbonate.

3. A composition according to claim 1, wherein the amount of the alkali metal carbonate is from about 45% to 70% by weight of the composition.

4. A composition according to claim 1, wherein the ratio of the amine oxide to the nonionic detergent active compound is from about 3:1 to 1:3 parts by weight.

5. A composition according to claim 1, wherein the ratio of the amine oxide to the nonionic detergent active compound is about 1:1 parts by weight.

6. A composition according to claim 1, wherein the amine oxide detergent active compound has the general formula:



wherein  $R_1$  is a  $C_{10}$ - $C_{22}$  alkyl or alkenyl group and  $R_2$  and  $R_3$  are the same or different  $C_1$ - $C_4$  alkyl groups or  $C_2$ - $C_3$  hydroxy alkyl groups.

7. A composition according to claim 11, wherein the group  $R_1$  is a linear alkyl group and the groups  $R_2$  and  $R_3$  are methyl groups.

8. A composition according to claim 1, wherein the amount of the mixed amine oxide and nonionic detergent active compounds is from about 10% to 14% by weight.

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9. A composition according to claim 1, additionally comprising an aromatic solvent in an amount of from about 4% by weight to a level not greater than that of the total detergent active compounds.

10. A composition according to claim 9, wherein the solvent is dibutyl phthalate.

11. A composition according to claim 1, additionally comprising not more than about 10% by weight of sodium tripolyphosphate.

12. A composition according to claim 1, additionally comprising from about 5 to 15% by weight of sodium silicate.

13. A detergent composition according to claim 1, in particulate form.

## References Cited

## UNITED STATES PATENTS

3,537,993 11/1970 Coward et al. ----- 252—135

## 14

3,590,001 6/1971 Taylor et al. ----- 252—547  
3,574,125 4/1971 Paassen ----- 252—551

## OTHER REFERENCES

5 Uses and Applications of Chemicals and Related Materials; Gregory, Volume II, 1944, p. 60.  
"DeSoto's New Syndet," *Detergents and Specialties*, pp. 40, 41, 1970.

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15 252—139, Dig. 1, 528