

as well as with the detergent. Since some of the detergents, particularly nonionic detergents, are by themselves relatively nonirritating, the described mildness additive is less useful, although the mildness effect of the additive can be established when such detergents, which at normally used concentrations cause little or no skin irritation, are tested at high concentrations and/or longer periods of contact with the skin.

The anti-irritation effect of the mildness additive is exhibited over a wide range of proportions of additive to detergent as indicated above. However, optimum results are generally obtained when the ratio of detergent to mildness additive is in the range of 3:1 to 1:3. This preferred range is applicable regardless of whether the detergent is employed in a dilute or concentrated form.

Anionic detergents which are improved by combination with the described mildness additive include both the soap and the non-soap detergents. Examples of such soaps are the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids (C₁₀ to C₂₆). Non-soap anionic detergents with which the described mildness additives are suitably employed include alkyl sulfates, alkyl sulfonates, alkyl benzene sulfonates, alkyl phenyl polyoxyalkylene sulfonates, alkyl glyceryl ether sulfonates, alkyl monoglyceride sulfates, alkyl monoglyceride sulfonates, alkyl polyoxyethylene ether sulfates, acyl sarcosinates, acyl esters of isethionates, acyl-N-methyl taurides, dialkyl esters of sulfosuccinic acid, and mixtures thereof. In these non-soap detergents, the alkyl or acyl radicals contain from 9 to 20 carbon atoms. As in the soaps, these detergents are employed in the form of sodium, potassium, ammonium, and alkylolammonium salts, as well as similar water-soluble salts. Specific examples include sodium lauryl sulfate, potassium-N-methyl lauroyl tauride, triethanol-ammonium dodecyl sulfonate, potassium polypropylene benzene sulfonate, sodium lauryl sulfonate, dioctyl ester of sodium sulfosuccinic acid, sodium salt of lauryl polyoxyethylene sulfate, and sodium salt of tridecylether polyoxyethylene sulfate.

The cationic detergents which can be reduced in their skin irritation by the addition of the mildness additives of the present invention include, in particular, quaternary ammonium salts which contain at least one alkyl group having from 12 to 20 carbon atoms. Although the halide ions are the preferred anions, other suitable anions include acetate, phosphate, sulfate, nitrite, and the like. Specific cationic detergents include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl trimethyl ammonium chloride, coco dimethyl benzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, stearyl amine salts that are soluble in water such as stearyl amine acetate and stearyl amine hydrochloride, stearyl dimethyl amine hydrochloride, distearyl amine hydrochloride, alkyl phenoxyethoxyethyl dimethyl ammonium chloride, decyl pyridinium bromide, pyridinium chloride derivative of the acetyl amino ethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decyl amine acetate, lauryl dimethyl ethyl ammonium chloride, the lactic acid and citric acid and other acid salts of stearyl-1-amido-imidazoline with methyl chloride, benzyl chloride, chloroacetic acid and similar compounds mixtures of the foregoing, and the like.

Amphoteric, also referred to as ampholytic, detergents which can be improved by the addition of the described mildness additives include alkyl- β -iminodipropionate, alkyl- β -aminopropionate, fatty imidazolines, betaines, and mixtures thereof. Specific examples of such amphoteric detergents are 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline, dodecyl- β -alanine, the inner salt of 2-trimethylamino lauric acid, and N-dodecyl-N,N-dimethyl aminoacetic acid.

As indicated above, the mildness additives of the present invention can also be employed in combination

with nonionic detergents, although the beneficial effects of the addition of the mildness additive are less pronounced since nonionic detergents are inherently not as irritating as the above-described detergents. Nonionic detergents include, in particular, the alkylene oxide ethers of phenols, fatty alcohols, and alkyl mercaptans, the alkylene oxide esters of fatty acids, the alkylene oxide ethers of fatty acid amides, the condensation products of ethylene oxide with partial fatty acid esters, and mixtures thereof. The polyoxyalkylene chain in such agents can contain from 5 to 30 alkylene oxide units in which each alkylene unit has from 2 to 3 carbon atoms. Specific examples of nonionic detergents include nonyl phenol polyoxyethylene ether, tridecyl alcohol polyoxyethylene ether, dodecyl mercaptan polyoxyethylene thioether, the lauric ester of polyethylene glycol, the lauric ester of methoxy polyethylene glycol, the lauric ester of sorbitan polyoxyethylene ether, and mixtures thereof.

The mildness additives of the present invention are particularly effective in reducing the irritation caused by such anionic detergents as the alkyl sulfates and sulfonates and the alkyl benzene sulfates and sulfonates, and by such cationic detergents as the described fatty alkyl-containing quaternary ammonium compounds.

Many of the detergents described hereinabove are employed in their commercial applications in combination with builders or other additives, depending on the intended commercial utility of the detergent. The presence of such additives does not affect the ability of the mildness additive to counteract the skin irritation caused by the detergent. As indicated above, it is believed that the skin irritation is caused by the action of the detergent on the skin in causing the keratin of the skin to break down. Although the detergent itself may not be extremely irritating, it allows other materials employed in combination with the detergent which are highly irritating to come in contact with the living tissue of the skin, even though in the absence of the detergent such materials are non-irritating in not being able to break down the keratin of the skin. The mildness additives of the present invention are, therefore, capable of protecting the skin against skin irritation caused by such additives. Builders employed in commercial detergent formulations are generally alkali salts of weak inorganic acids used alone or in admixtures, such as alkali metal, ammonium or substituted ammonium salts of carbonates, borates, phosphates, polyphosphates, bicarbonates, and silicates. Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, sodium bicarbonate, potassium bicarbonate, sodium mono- and di-orthophosphate, sodium metasilicate, and mixtures thereof.

The built detergent compositions of the present invention can, furthermore, contain other adjuvants normally employed in detergent compositions such as perfumes, anti-tarnishing agents, anti-redeposition agents, bacteriostatic agents, dyes, fluorescers, fabric softeners, oxygen or chlorine bleaches, suds builders, suds depressors, sequestrants, and the like. The inorganic builders or the combination of the builders and the adjuvants described can constitute up to 80% of the built detergent composition, the remainder of the built detergent composition being the detergent and the mildness additive.

The detergent compositions of the present invention include laundry detergents, kitchen detergents, shampoos, industrial detergents, and the like. The use of the mildness additive of the present invention does not affect the effective concentrations of the detergent, and hence concentrations of detergents heretofore employed are also applicable in the modified compositions of the present invention.

The use of the mildness additive is, however, not limited to unbuilt or built detergent compositions. The additive can be employed in any compositions in which a detergent of the type described is employed in aqueous solution in the presence of other materials which may

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cause skin irritation such as, in particular, in aqueous lubricants containing inorganic salts, a particular example of which is aqueous cutting fluids.

In establishing the irritation and the mildness effect of the additive, the skin is contacted by immersion or other means with a solution containing the detergent with and without the mildness additive under standardized conditions more specifically described below. The principal test employed in the data presented below is an animal immersion test using female, albino guinea pigs. The animal, weighing about 300 to 325 g., is immersed up to the thoracic region in the test solution at 40° C. for 4.5 hours per day on three successive days. Each animal is thoroughly rinsed and dried after each immersion. Three days after the last immersion, the skin of each animal is examined for gross changes, and grades are assigned which represent the degree of damage to the skin. In general, three animals are tested simultaneously in the same solution. The grading system is based on a scale of 1 to 10 in which the numbers have the following meanings:

Grade or rating	Gross reaction	Skin damage
1.....	Severe cracking and bleeding, death of skin tissue.	Extremely severe, death in most instances.
2.....	Severe cracking and moderate bleeding.	Do.
3.....	Severe cracking; slight to moderate bleeding.	Severe.
4.....	Moderate cracking.....	Do.
5.....	Slight cracking.....	Moderate.
6.....	Severe scaling.....	Do.
7.....	Edema, slight to moderate scaling.	Do.
8.....	Slight scaling and moderate edema.	Slight.
9.....	Slight redness and edema	Do.
10.....	Normal.....	Normal.

Despite the fact that this exposure test is conducted using extremely dilute solutions, it is an exaggerated test, although it has been established (see Canadian Pat.

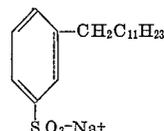
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following additional ingredients were added as indicated: Igepal CA-630, a commercially available nonionic wetting agent of octylphenylxypoly(oxethylene)ethanol; triethanol amine, and capric acid. The triethanol amine is employed to allow salt formation of mildness additives employed in combination with anionic detergents and the capric acid is employed for the same purpose in combination with cationic detergents. In general, the detergent and the mildness additive are each employed in the data illustrated below in a concentration of 15 weight percent based on the described 100 g. concentrate. Where a built detergent is employed, the amount of detergent is accordingly adjusted to take into consideration the lower active detergent concentration.

The following examples illustrate the effect of the mildness additives of the present invention on skin irritation caused by detergents, using the above-described test.

EXAMPLES 1 to 6

The detergent employed in this series of tests was an alkyl benzene sulfonate having the formula



The detergent was employed in 100% active form or in 87% active form, the latter form containing sodium sulfate. The mildness additives employed in this series comprised the dimer of linoleic acid, commercially available as Empol 1022. The dimer acid contained 2-5% of unpolymerized linoleic acid and 19-22% of trimer acid. Table I illustrates the results obtained employing the above-described test. The actual composition of the solution to which the animals were exposed is shown. The remainder of the composition of the test solution not indicated in the table was water.

TABLE I

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
1.....	0.15	100	-----	-----	Igepal.....	0.05	4	-----	-----
2.....	0.15	100	Acid.....	0.15	{ Igepal..... Igepal..... TEA.....	{ 0.016 0.016 0.034 }	9	5	1:1
3.....	0.15	-----	-----	-----	-----	-----	(¹)	-----	-----
4.....	0.15	100	Acid.....	0.15	TEA.....	0.10	7+	7+	1:1
5.....	0.176	87	-----	-----	-----	-----	(¹)	-----	-----
6.....	0.176	87	Acid.....	0.15	TEA.....	0.10	8	8	1:1

¹ Death.

639,398) that the test correlates extremely well with the skin irritation effect observed on human skin.

In preparing the test solution, a 100 g. concentrate is first prepared which is then employed in the test solution in 1% by volume concentration. In order to prepare a homogeneous concentrate which is readily dilutable, the

EXAMPLES 7 to 15

The tests and determination of results illustrated in Examples 1-6 were repeated using sodium lauryl sulphate instead of the alkyl benzene sulfonate. The results are illustrated in Table II.

TABLE II

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
7.....	0.15	100	-----	-----	Igepal.....	0.05	3	-----	-----
8.....	0.15	100	Acid.....	0.15	{ Igepal..... Igepal..... TEA.....	{ 0.016 0.016 0.034 }	7	4	1:1
9.....	0.15	100	do.....	0.10	{ Igepal..... Igepal..... TEA.....	{ 0.016 0.016 0.034 }	6+	3+	3:2
10.....	0.15	100	do.....	0.20	{ Igepal..... Igepal..... TEA.....	{ 0.016 0.016 0.044 }	7	4	3:4
11.....	0.1305	100	-----	-----	Igepal.....	0.05	4+	-----	-----
12.....	0.1305	100	Acid.....	0.15	{ Igepal..... Igepal..... TEA.....	{ 0.016 0.016 0.034 }	7	3	7:3
13.....	0.15	100	-----	-----	-----	-----	(¹)	-----	-----
14.....	0.15	100	Acid.....	0.15	TEA.....	0.10	7-	7-	1:1
15.....	0.15	100	do.....	0.05	TEA.....	0.033	5+	5+	3:1

¹ Death.

EXAMPLES 16 TO 19

The tests and determination of results illustrated in Examples 1-6 were repeated using a soap detergent, i.e., the triethanol amine salt of lauric acid. Although the detergent is relatively mild at a 1% of concentrate level, i.e., 0.15% in test solution, the mildness effect of the additive is particularly shown when the detergent is employed in higher concentrations. The results are illustrated in Table III.

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TABLE III

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
16	0.15	100	-----	-----	TEA	0.06	7+	-----	-----
17	0.15	100	Acid	0.15	TEA	0.15	8+	1	1:1
18	0.45	100	-----	-----	TEA	0.18	(1)	-----	-----
19	0.45	100	Acid	0.45	TEA	0.45	7+	7+	1:1

¹ Death.

EXAMPLES 20 AND 21

The tests and determination of results illustrated in Examples 1-6 were repeated using a commercially avail-

taining 40% of a linear alkane sulfonate, 43% of sodium sulfate, and 15% of sodium chloride. The following results were obtained (Table IV).

TABLE IV

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
24	0.375	40	-----	-----	-----	-----	(1)	-----	-----
25	0.375	40	Acid	0.15	TEA	0.10	7	7	1:1

¹ Death.

able amphoteric detergent "Deriphat" 151 C containing N-coco- β -aminopropionic acid. The active component of the detergent was 70%; it was employed in the concentrate in a concentration of 23.2%. A 2% (containing 0.464% of the "Deriphat" 151 C) test solution caused the deaths of the animals in the described test. When dimer acid (0.15% of test solution) and triethanol amine (0.10% of test solution) was added, the rating of skin irritation decreased to an average of 9.

EXAMPLES 22 AND 23

The tests and determination of results illustrated in Examples 1-6 were repeated using a commercially available amphoteric phenolic detergent commercially avail-

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EXAMPLES 26 AND 27

The tests and determination of results illustrated in Examples 1-6 were repeated using "Orvus" K, a commercially available modified ammonium lauryl sulfate detergent containing an amide builder having the following composition:

	Percent
Alkyl sulfate	37.5
Alkanol amide	9.2
Unsulfated alcohol	1.2
Ammonium sulfate	0.9
Ammonium chloride	1.0
Denatured ethyl alcohol	20.0

The following results were obtained (Table V).

TABLE V

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
26	0.40	37.5	-----	-----	-----	-----	6	-----	-----
27	0.40	37.5	Acid	0.15	TEA	0.10	9-	-3	1:1

able as "Amphicide" 50 containing in 75% concentration the following active components:

- 1 part of the sodium salt of 2-[(2-hydroxy-5-nonylbenzene)methylamino]ethane sulfonic acid, and
- 3 parts of the sodium salt of 2-[(3-dimethylaminomethyl-2-hydroxy-5-nonylbenzyl)methylamino]ethane sulfonic acid.

The concentrate contained 22.5% of the "Amphicide" and was employed as a 2% test solution containing

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EXAMPLES 28 AND 29

The tests and determination of results illustrated in Examples 1-6 were repeated using "Standpol" ES-2, a commercially available 26% active detergent containing the sodium salt of lauryl C₁₂ through C₁₄ diether sulfate. The following results were obtained (Table VI).

TABLE VI

Example No.	Detergent		Dimer Additive		Other additive		Average rating	Improvement in rating	Ratio of detergent to mildness additive
	Percent concentration	Percent active	Type	Percent concentration	Type	Percent concentration			
28	0.5718	26	-----	-----	-----	-----	5	-----	-----
29	0.5718	26	Acid	0.15	TEA	0.10	8+	3+	1:1

EXAMPLE 30

To a 1% solution of a shampoo commercially available as "Prell" was added 2% by weight of the solution of the triethanol amine salt of the dimer acid of Examples 1-6. Using the above-described exposure test, a rating of 7 was obtained. In the absence of the mildness additive the animals exposed died.

The foregoing examples have illustrated the mildness-inducing effect of the mildness additives when employed in combination with skin irritating detergents. In many detergent-containing compositions the skin irritation caused by the detergent is compounded by detergent builders or other components present in the composition. The foregoing examples clearly demonstrate that the mildness agents employed in combination with the detergents are particularly effective in reducing skin irritation where the skin irritation is compounded by the presence of other agents, organic or inorganic. In view of the fact that the overall chemical structure of the mildness additives of the present invention is similar to that of a detergent, it will be apparent that the mildness additives of the present invention can be employed in combination with a skin irritating detergent in any environment, i.e., in the presence of any component in which the detergent can exist. The foregoing examples further illustrate that the greatest benefit of the described invention is realized when the mildness additives are combined with detergents or with detergent-containing compositions which cause skin irritation.

In view of the extreme diversity of detergent compositions available today, it will be apparent that a demonstration of reduced skin irritation of all detergent compositions with the described mildness additives is not possible. However, such is not deemed necessary and the foregoing examples are deemed sufficient to illustrate the scope of the invention but are not intended to limit the scope of the invention to such.

What is claimed is:

1. In the method of utilizing an aqueous detergent composition involving contact with the skin, said detergent composition containing a skin irritating detergent selected from the group consisting of anionic, cationic, non-ionic, and amphoteric organic detergents, the improvement comprising reducing the skin irritation of said composition by incorporating therein a mildness additive in an amount of .005 to 10 parts by weight based on said skin irritating detergent, said mildness additive comprising the polymerized product of 2 to 4 molecules of a monomeric C_{12} to C_{26} fatty acid, said product containing 2 to 4 carboxyl or carboxyl salt groups, said mildness additive

being soluble or colloiddally dispersible in aqueous media, the mildness additive and detergent compositions being stable and compatible in aqueous media.

2. The method of claim 1 wherein the mildness additive is the dimer and contains two carboxyl groups or carboxyl salt groups.

3. The method of claim 2 wherein the mildness additive is the dimer of linoleic acid.

4. The method of claim 1 wherein the detergent is an anionic detergent.

5. The method of claim 4 wherein the anionic detergent is alkyl benzene sulfonate, alkyl sulfate, alkyl benzene sulfates, or alkyl sulfonate.

6. The method of claim 1 wherein the detergent is a cationic detergent.

7. The method of claim 1 wherein the cationic detergent is a quaternary ammonium compound.

8. The method of claim 1 wherein the detergent composition contains from 10 to 80% by weight of the composition of water soluble inorganic detergent builders.

9. The method of claim 1 wherein the detergent is an amphoteric detergent.

10. The method of claim 9 wherein the amphoteric detergent is an alkyl- β -imino propionate.

11. The method of claim 5 wherein the detergent composition contains from 10 to 80% by weight of the composition of water soluble inorganic detergent builders.

12. The process of claim 1 wherein the weight ratio of mildness additive to detergent is from 0.33 to 3.

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