

LIQUID SCOURING CLEANSERS

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This invention relates to liquid scouring cleansers. In particular, it relates to viscous, aqueous scouring cleansers containing an abrasive and a binary solvent system. These
10 cleansers are suitable for use as general purpose household cleaning compositions.

General purpose household cleaning compositions for hard surfaces such as metal, glass, ceramic, plastic and linoleum
15 surfaces, are commercially available in both powdered and liquid form. Powdered cleaning compositions consist mainly of builder or buffering salts such as phosphates, carbonates, silicates, etc., and although such compositions may display good inorganic soil removal, they are generally deficient in cleaning ability on
20 organic soils such as the grease/fatty/oily soils typically found in the domestic environment.

Liquid cleaning compositions, on the other hand, have the great advantage that they can be applied to hard surfaces in neat or concentrated form so that a relatively high level of surfactant
25 material is delivered directly to the soil. Moreover, it is a rather more straightforward task to incorporate high concentrations of anionic or nonionic surfactant in a liquid rather than a granular composition. For both these reasons, therefore, liquid cleaning compositions have the potential to provide superior grease and
30 oily soil removal over powdered cleaning compositions.

Nevertheless, liquid cleaning compositions still suffer a number of drawbacks which can limit their consumer acceptability. Thus, they generally contain little or no detergency builder salts and consequently they tend to have poor cleaning performance on
35 particulate soil and also lack "robustness" under varying water

hardness levels. In addition, they can suffer problems of product form, in particular, phase instability, inhomogeneity, lack of clarity, or inadequate viscosity characteristics for consumer use. Moreover, the higher in-product and in-use surfactant concentration necessary for improved grease handling raises problems of extensive suds formation requiring frequent rinsing and wiping on behalf of the consumer. Although oversudsing may be controlled to some extent by incorporating a suds-regulating material such as hydrophobic silica and/or silicone or soap, this in itself can raise problems of poor product stability and homogeneity and also problems associated with deposition of insoluble particulate or soap residues on the items or surfaces being cleaned, leading to filming, streaking and spotting.

Importantly, liquid cleaners suffer from the disadvantage that they do not contain abrasives, which contribute substantially to the cleaning performance of many dry-powder household and industrial cleaning compositions. Liquid cleansers that do contain abrasives can suffer from phase instability including layering and abrasive settling. This phase instability problem is aggravated when solvents are present in the cleanser compositions.

Terpenes are, per se, well-known components of perfume compositions and are often incorporated into detergent compositions at low levels via the perfume. Certain terpenes have also been included in detergent compositions at higher levels; for instance, German Patent Application 21 13 732 discloses the use of aliphatic and alicyclic terpenes as antimicrobial agents in washing compositions; British Pat. No. 1,308,190 teaches the use of dipentenenes in a thixotropic liquid detergent suspension base composition. German Patent Application 29 09 690 teaches the use of pine oil (a mixture mainly of terpene alcohols) in liquid hard surface cleaning compositions.

European Application 81-200540.3 teaches the use of terpenes with solvents such as benzyl alcohol and ethylene glycol dibutyl ether in liquid cleanser compositions. European Application 82-201396.7 teaches the use of terpenes and butyl carbitol (a

trademark for 2-(2-butoxyethoxy)ethanol) in a liquid cleanser, optionally with particulate zeolite builders.

However, the use of the combination of selected terpenes, polar solvents, selected surfactant mixture, abrasive with polymeric acrylic acid thickeners and viscosity enhancers disclosed herein does not appear to have been considered, heretofore.

Accordingly, the invention provides an improved phase stable liquid scouring cleanser composition comprising:

- a) from 1% to 10% of synthetic surfactant mixture of paraffin sulfonate (NaPS) and linear alkyl benzene sulfonate (LAS), said mixture of ~~NaPS and LAS~~ ^{NaPS:LAS} having a ratio of from 20:1 to 2:1;
- b) from 0.5% to 5% of a mono- or sesquiterpene or mixtures thereof, the weight ratio of ^{the} surfactant ^{mixture} to terpenes lying between 20:1 to 3:2;
- c) from 0.5 to 3% of a polar solvent having a water solubility at 25°C in the range of from 0.2% to 10%;
- d) from 0.03% to 0.5% of a compound ^(s) selected from alcohols, aldehydes, acetates, ketones and nitriles of the formulas C_nH_mR where $n=10$ or 12 ; $m=14, 16, 17, 18$ or 20 and $R=O, O_2$ or N ;
- e) from 1% to 50% of a water-insoluble abrasive; and
- f) from 0.40% to 1% of a high molecular weight acrylic acid polymeric thickener having a molecular weight range of 0.5 million to 1.5 million; and

wherein the viscosity of said composition is from 1800 to 4000 cps and wherein the pH of said composition is from 8 to 12.

All percentages and ratios mentioned in this specification are by weight, unless otherwise stated.

It has now been discovered, however, that the defects of prior art liquid cleansers can be minimized or overcome through the incorporation therein of a specified mixture of surfactants, acrylic acid polymeric thickeners, and selected terpenes, viscosity enhancers of the alcohol, nitrile, ketone and aldehyde classes as defined herein, in combination with ^{polar solvent e.g.} benzyl alcohol, and with an abrasive.

The present invention provides abrasive-containing liquid cleaning and scouring compositions which have excellent phase stability and suds control across a broad range of usage and water hardness conditions and which provide excellent shine performance together with improved cleaning characteristics both on greasy/oily soils and on inorganic particulate soils, with little tendency to cause filming or streaking on washed surfaces. Importantly, the abrasives used herein are soft, preferably

having a Mohs hardness of 3 or less.

Terpenes - Terpenes, as a solvent class, have limited water-solubility. They can be incorporated into liquid cleaning compositions in homogeneous form, even under "cold" processing conditions, with the ability to provide excellent cleaning characteristics across the range of water hardness on grease/oily soils and inorganic particulate soils, as well as on shoe polish, marker ink, bath tub soil, etc., and excellent shine performance with low soil redeposition and little or no propensity to cause filming, streaking or spotting on surfaces washed therewith. Moreover, the terpenes herein specified, and in particular those of the hydrocarbon class, are valuable in regulating the sudsing behavior of the instant compositions in both hard and soft water and under both diluted and neat or concentrated usage.

Preferred terpenes for odor impact are mono- and bicyclic monoterpenes, especially those of the hydrocarbon class, which include the terpinenes, terpinolenes, limonenes and pinenes, and mixtures thereof. Highly preferred materials of this type are d-limonene, dipentene, alpha-pinene, beta-pinene and the mixture of terpene hydrocarbons obtained from the essence of citrus (e.g., cold-pressed orange terpenes and orange terpene oil phase ex fruit juice). These terpenes are used at concentrations of

0.5%-5%, preferably 1-3%, in the compositions for fragrance and cleaning effects. The weight ratio of surfactant:terpene is between 20:1 and 3:2, preferably 4:1 to 1.5:1.

Viscosity Enhancers - As mentioned hereinbefore, a special problem for thickened liquid scouring cleansers is achieving a stable, high viscosity product. It has been surprisingly discovered that certain alcohol, aldehyde, nitrile, acetate and ketone compounds having VE empirical formulas of C_nH_mR where $n = 10$ or 12 ; $m = 14, 16, 17, 18$ or 20 and $R = O, O_2$ or N , are viscosity enhancers (VE) when used in conjunction with the high molecular weight acrylic acid polymeric thickeners. Some preferred VE compounds are selected from citronellol, geraniol, linalool, nerol, rhodinal, alpha-terpineol, beta-citronellol, rhodinol, citronella nitrile, carvone, fenchone, menthol, isoborneol

and mixtures thereof. These preferred VE compounds are commercially available. These VE compounds are used in the compositions of this invention at concentrations of from ~~about~~ 0.03% to ~~about~~ 0.5%, more preferably from ~~about~~ 0.05% to ~~about~~ 0.25%.

- 5 Polar Solvent - The polar solvent of this invention has a water solubility at 25°C in the range of from 0.2% to 10% and is used at a level of from 0.5% to 3%. Benzyl alcohol ($C_6H_5CH_2OH$), the preferred polar solvent, is used in the compositions at concentrations of
- 10 0.5-3%, preferably 1-2%. This polar solvent increases the cleaning power of the compositions.

The weight ratio of terpenes to benzyl alcohol is preferably in the range from 5:1 to 1:5, most preferably 2:1 to 1:2.

- 15 Abrasive - The abrasive is used at a level of 1-50% (preferably 5-40%; most preferably 10-35%).

- It is highly preferred that the abrasives used herein not be undesirably "scratchy." Abrasive materials having a Mohs hardness in the range of about 7, or below, are typically used;
- 20 abrasives having a Mohs hardness of 3, or below, can be used to avoid scratches on aluminum or stainless steel finishes. Suitable abrasives herein include inorganic materials, especially such preferred materials as calcium carbonate and diatomaceous earth, as well as materials such as Fuller's earth, magnesium carbonate,
- 25 China clay, attapulgite, calcium hydroxyapatite, calcium orthophosphate, dolomite and the like. Organic abrasives such as urea-formaldehyde, polyvinyl chloride, methyl methacrylate and melamine-formaldehyde resins can also be used, preferably at a level of 5-15%. The organic abrasives are more compatible with
- 30 detergency builders and sequestrants.

- It is preferred that the abrasives herein have a particle size range in the 100-600 U.S. Sieve Series Mesh, preferably 200-400 U.S. Sieve Series Mesh, size. Diatomaceous earth and calcium carbonate are commercially available in the 5-150 micron particle
- 35 size range, and, as will be seen hereinafter, give excellent cleaning performance. The preferred abrasive is commercially available as Georgia Marble RO-4 Ground Calcium Carbonate.

Surfactants - The selected combination of NaPS and LAS has been found to provide superior phase stability in the cleansers of this invention. The selected ^{used} ~~useful~~ deterative surfactant herein is a mixture of linear alkyl benzene sulfonates (LAS) and paraffin sulfonates (NaPS). Preferably, such deterative surfactants contain an alkyl group in the C_{10} - C_{18} range; the selected surfactants are most commonly used in the form of their sodium, potassium or triethanolammonium salts. The C_{11} - C_{16} alkyl benzene sulfonates and the C_{12} - C_{18} paraffin sulfonates are especially preferred herein.

The compositions herein contain 1% to 10%, preferably 2% to 8%, more preferably 2.5-5%, of the surfactant mixture. The mixture has a ratio of NaPS to LAS of from 20:1 to 2:1, preferably 10:1 to 2:1, and more preferably from 7:1 to 4:1.

Thickeners - The selected thickeners of this invention are high molecular weight acrylic acid polymeric thickeners which have molecular weights of 0.5-1.5 million with preferably some crosslinking of about 1-4%. Examples of suitable thickeners are (1) Sokalan (RTM) PHC-25 ex BASF; (2) Acrysol (RTM) ICS-1 ex Rohm and Haas (works best at high pH 11.9); and (3) Carbopol 941 ex B.F. Goodrich. Carbopol (RTM) 941 works well but leaves a film when rinsed after the product use. The thickeners of this invention are employed at 0.4-1%, preferably 0.45-0.75% by weight of the composition.

The compositions herein must be thickened for dispersion and phase stability at the 1800-4000 cps viscosity range. The compositions of this invention preferably have a viscosity in the 2000-3500 cps range, as measured with a standard Brookfield Viscometer. Thickened compositions tend to cling to vertical surfaces such as walls and windows, which makes them more convenient to use.

pH - The compositions herein are formulated in the range of pH 8-12, preferably about 10-11.5 to avoid hydrolysis of some perfume components. Caus-tics such as sodium hydroxide and sodium carbonate can be used

to adjust and buffer the pH, as desired. An alkaline pH is also essential in obtaining the specified viscosity.

Soaps - As mentioned hereinabove, one special problem associated with the use of liquid cleansers is their tendency to over-suds in use. It has been discovered that soaps, especially the alkali, ammonium and alkanolammonium salts of C_{12} - C_{24} fatty acids, are especially useful as suds suppressors when conjointly present with terpenes and benzyl alcohol in the instant compositions. Soap concentrations of at least about 0.005%, preferably 0.05% to 0.4%, provide this important suds control function. Soap prepared from coconut oil fatty acids is preferred.

Other Ingredients - The compositions herein can contain other ingredients which aid in their cleaning performance. Conventional additives such as detergency builders, water softeners, carrier liquids (especially water), perfumes, and the like can be used. For example, it is highly preferred that the compositions with organic abrasives contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water-soluble phosphates such as triphosphate and sodium ortho- and pyrophosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polymphosphonates and phosphates (DEQUEST^(RIM)) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail herein. See U.S. Pat. No. 3,579,454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 1% to about 25% of the composition. Colorants and perfumes can be used with all abrasives.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include perfumes, dyes, optical brighteners, soil suspending agents, deterative enzymes, gel-control agents, freeze-thaw stabilizers,

bactericides, preservatives, and the like. Nonionic surfactants at a level of 0.2-0.5% are excellent freeze-thaw stabilizers.

The compositions herein typically contain up to about 90% water as a carrier. Water-alcohol (e.g., ethanol, isopropanol, butanol, etc.) mixtures can also be used.

Since the compositions herein are in liquid form, they can be prepared by simply blending the essential and optional ingredients in the aqueous carrier.

The following examples are given by way of illustrating the compositions herein.

EXAMPLE 1

<u>Component</u>	<u>Concentration in Cleanser</u>
<u>Thickener</u>	
Sokalan PHC-25	0.67%
<u>Surfactants</u>	
NaPS	3.0%
LAS	0.6%
Neodol 45-7	0.30%
<u>Solvent</u>	
Benzyl Alcohol	1.30%
<u>Perfume Mix #1</u>	
Citrus Terpenes	1.85%
Citrus Phase Oil	0.15%
Other Components	0.15%
<u>Abrasive</u>	
CaCO ₃ (Avg. 50-60 microns)	30.0%
<u>Other</u>	
Na ₂ CO ₃	3.0%
Dye	0.005%
NaOH	0.5%
Coconut/Lauric Fatty Acid	0.2%
Water	To Balance

Definitions

NaPS : Sodium C₁₃-C₁₆ paraffin sulfonate

LAS : Sodium salt of linear C_{11.8} alkyl benzene sulfonate

Perfume Mix #1: The "Other Components" of the perfume mix #1

5 contain 50-60% viscosity enhancing compounds of alcohol, nitrile and aldehyde of the C₁₀H₂₀O, C₁₀H₁₇N and C₁₀H₁₈O formulas.

Neodol 45-7 : A condensate of one mole of C₁₄-C₁₅ fatty alcohol with 7 moles of ethylene oxide.

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EXAMPLES 2 and 3Impact of Terpenes on Product Viscosity

Examples 2 and 3 were made in 2000 gram batches using a Lightening mixer. The ingredients were added in the order in
15 which they appear. A viscosity reading was recorded 5 minutes after each ingredient was added.

	<u>Ingredient</u>	<u>Example 2</u>		<u>Example 3</u>	
		<u>Formula</u>	<u>Viscosity</u>	<u>Formula</u>	<u>Viscosity</u>
	Soft water	59.00%	-	58.00%	-
20	Sokalan PHC-25	0.65%	100 cps	-	-
	Acrysol ICS-1	-	-	0.98%	25 cps
	Anionic surfactant*	2.8%	-	2.8%	-
	Neodol 45-7	0.5%	400 cps	0.5%	50 cps
	Benzyl alcohol	1.5%	-	1.5%	-
25	Lauric fatty acid	0.10%	-	0.10%	-
	Coconut fatty acid	0.10%	25 cps	0.10%	25 cps
	NaOH	0.25%	550 cps	0.25%	225 cps
	Na ₂ CO ₃	3.00%	250 cps	3.00%	150 cps
	CaCO ₃	30.00%	1250 cps	30.00%	1500 cps
30	Perfume mix #1**	2.15%	2750 cps	2.15%	2700 cps

*NaPS/LAS ratio 5:1.

**The perfume mix #1 comprises organic compounds which contain about 3-4 parts citronellol, citronella nitrile and
35 dihydro mercinol. This amount provides about 0.06-0.09% of viscosity enhancers by weight of the total composition.

Note in Examples 2 and 3 that the addition of the viscosity enhancing perfume mix had a profound impact on product viscosity. Without the perfume mix, the formulations would experience abrasive settling and layering and have viscosities of only 1250 and 1500 cps vs. 2750 and 2700 cps, respectively.

EXAMPLES 4 - 14

Impact of Selected Compounds on Product Viscosity

Base Formula I

	<u>Ingredient</u>	<u>Wt. %</u>
10	Soft water	Balance
	Sokalan PHC-25	0.65
	Anionic surfactant*	3.6
	Neodol 45-7	0.50
	Benzyl alcohol	1.3
15	Lauric fatty acid	0.1
	Coconut fatty acid	0.1
	NaOH	0.2
	Na ₂ CO ₃	3.0
	CaCO ₃	30.00
20	Colorant	0.01
	Citrus terpenes	2.00

*NaPS/LAS ratio 5:1.

Selected Compounds

	<u>Example</u>		
25	4	0.15% Citronellol	5350 cps
	5	0.15% Dihydro Mercinol	4900 cps
	6	0.15% Citronellal	3500 cps
	7	0.15% Citronella Nitrile	3000 cps
30	8	0.15% Fenchyl Acetate	2300 cps
	9	0.15% Linalyl Acetate	2250 cps
	10	0.15% Camphene	1750 cps
	11	0.15% Alpha-Pinene	1650 cps
	12	0.15% Eucalyptol	2050 cps
35	13	0.15% Para Cymene	1700 cps
	14	0.15% Terpinolene	1800 cps

The base Formula I has a viscosity of 1900 cps. The selected compounds of Examples 4-14 were added separately to the base Formula I and the viscosity measured. The compounds of Examples 4-7 show profound impact on viscosity enhancement.

The compounds of Examples 8, 9 and 12 show marginal improvement. The compounds of Examples 10, 11, 13 and 14 show reduced viscosity impact. Examples ^{4,5}10, 11, 13 and 14 are included for comparative purposes only.

Other VE compounds of the empirical formulas, e.g., menthol, isoborneol, carvone and fenchone, were found to produce a profound impact on viscosity of Base Formula I.

EXAMPLES 15 - 20

Impact of LAS on Viscosity

Base Formula II

<u>Ingredient</u>	<u>Wt. %</u>
Soft water	Balance
Acrysol ICS-1	0.49
Surfactant:	
NaPS	Variable)
LAS	Variable) see below
Benzyl alcohol	1.5
NaOH (50%)	0.25
Na ₂ CO ₃	3.00
CaCO ₃ (same as above)	30.00
Perfume mix #1	2.15

<u>Examples:</u>		<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>
NaPS concentration		2.8%	2.8%	2.8%	2.8%	2.8%	3.5%
LAS concentration		0.3	0.4	0.5	0.6	0.7	-
5 Viscosity (cps)		1400	1900	2100	2500	3150	1500
Stability:		Top Layer	OK at room temp. only	OK	OK	OK	Abrasive settles
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The above data show that combinations of NaPS and LAS have synergistic benefits for viscosity enhancement, as well as phase stability. ^{15 and 16 are} Examples ^{15 and 16 are} 20 is included for comparative purposes only.

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CLAIMS

1. An improved phase stable liquid scouring cleanser composition comprising:

- 5 (a) from 1% to 10% of synthetic surfactant mixture of paraffin sulfonate (NaPS) and linear alkyl benzene sulfonate (LAS), said mixture of ~~NaPS and LAS~~ ^{NaPS : LAS} having a ratio of from 20:1 to 2:1;
- (b) from 0.5% to 5% of a mono- or sesquiterpene or mixtures thereof, the weight ratio of ^{the} ~~surfactant:terpene~~ ^(s) lying between 20:1 to 3:2;
- 10 (c) from 0.5 to 3% of a polar solvent having a water solubility at 25°C in the range of from 0.2% to 10%;
- (d) from 0.03% to 0.5% of ^(s) a compound selected from alcohols, aldehydes, acetates, ketones and nitriles of the formulas C_nH_mR where $n = 10$ or 12 ; $m = 14, 16, 17, 18$ or 20 and $R = O, O_2$ or N ;
- 15 (e) from 1% to 50% of a water-insoluble abrasive; and
- 20 (f) from 0.40% to 1% of a high molecular weight acrylic acid polymeric thickener having a molecular weight range of 0.5 million to 1.5 million; and

25 wherein the viscosity of said composition is from 1800 to 4000 cps and wherein the pH of said composition is from 8 to 12.

2. The composition of Claim 1 wherein the ratio of said mixture of NaPS and LAS is from 10:1 to 2:1 and is present in said composition at a level of from 2% to 8%.

3. The composition of Claim 1 wherein the ratio of said mixture of NaPS and LAS is from 7:1 to 4:1 and is present at a level of 2.5% to 5%.



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4. The composition in accordance with Claim 1 wherein the terpene is selected from d-limonene, dipentene, alpha-pinene and beta-pinene, and mixtures thereof, and is present at a concentration of 1% to 3% and wherein the weight ratio of surfactant mixture to terpene is 4:1 to 1.5:1.
- 5 5. The composition in accordance with Claim 1 wherein said (d) is present at a concentration of 0.05 to 0.5%.
6. The composition in accordance with Claim 1 wherein said polar solvent is benzyl alcohol present at a concentration of from 0.5 to 3%.
7. The composition in accordance with Claim 1 wherein the weight ratio of terpene to benzyl alcohol is in the range of from 5:1 to 1:5.
8. The composition in accordance with Claim 1 which ~~in addition~~ contains from 1% to 2% by weight of benzyl alcohol and wherein the ratio of terpene^(s) to benzyl alcohol is from 2:1 to 1:2.
9. A composition in accordance with Claim 1 wherein (d) is selected from citronellol, geraniol, dihydro mercinol, linalool, nerol, rhodinal, alpha-terpineol, beta-citronellol, rhodinol, citronella nitrile, carvone, fenchone, menthol, isoborneol and mixtures thereof.
- 5 10. A composition in accordance with Claim 1 wherein (d) is selected from citronellol, dihydro mercinol, citronellal and citronella nitrile and mixtures thereof and is present at a level of 0.05% to 0.25% of said composition.
11. A composition in accordance with Claim 1 which comprises from 5% to 40% of an abrasive having a particle size range of 5-150 microns, said abrasive having a Mohs hardness of 7 and below.



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12. A composition in accordance with Claim 11 wherein said abrasive is present at a level of 10% to 35%.

13. A composition in accordance with Claim 1 which comprises from 0.45% to 0.75% of said acrylic acid polymeric thickener and wherein said viscosity is from 2000 to 3500^{cps} and wherein said pH is 10 to 11.5.

14. A composition in accordance with Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 which comprises from 0.2% to 0.5% of a nonionic surfactant.
