SYNERGISTIC TALLOW-BASED DETERGENT COMPOSITIONS

This application is a continuation of Ser. No. 617,496, filed Feb. 21, 1967, now abandoned.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to detergent compositions based on combinations of saturated or unsaturated tallow alcohol sulfates or saturated or unsaturated tallow alcohol sulfates with an alkyl ester of α-sulfonated saturated tallow acids. The mixture is useful in unbuilt detergent products such as synthetic detergent bars, also as the active ingredient of built detergent products for light or heavy duty washing.

An object of the invention is to provide tallow-based detergents which are biodegradable and which, because of synergism, have improved detergency and other properties.

In general, according to the present invention, detergent products prepared by blending in varying ratios saturated or unsaturated tallow alcohol sulfates with sodium alkyl α-sulfotallowate unexpectedly exhibited marked synergism in detergency. Ternary systems made by the addition of tallow soap flakes to the above blends, and quaternary systems made by the addition of tallow soap flakes and disodium α-sulfotallowate were also synergistic. The saturated (I) and unsaturated tallow alcohol sulfates (II), the disodium α-sulfotallowate (III), the sodium alkyl α-sulfotallowate (IV), and the tallow soap flakes (V) can be represented by the following formulas:

(I) \( \text{RCH}_2\text{CH}_2\text{OSO}_3\text{Na} \)

(II) \( \text{R'CH}_2\text{CH}_2\text{OSO}_3\text{Na}_2 \)

(III) \( \text{RCH(SO}_3\text{Na})\text{CO}_2\text{Na} \)

(IV) \( \text{R'CH(SO}_3\text{Na})\text{CO}_2\text{R''} \)

wherein \( \text{R} = \text{C}_4\text{H}_{9}, \text{C}_8\text{H}_{17} \) or \( \text{R} = \text{C}_6\text{H}_{13}, \text{C}_10\text{H}_{21} \) or derives from the saturated fatty acids of tallow or the fatty acids of hydrogenated tallow, \( \text{R'} = \text{CH}_2(\text{CH}_2)_n\text{CH} = \text{CH} (\text{CH}_2)_m\text{CH} = \text{CH} (\text{CH}_2)_n\), or derives from the fatty acids of tallow, and \( \text{R''} = \text{methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl or secondary butyl}.

The saturated tallow alcohol sulfates, which may analyze as a mixture of about 62% sodium tetradecyl sulfate, 23% sodium hexadecyl sulfate, and 15% sodium octadecyl sulfate, are obtainable from tallow by non-selective catalytic hydrogenolysis followed by sulfation. Either of the principal components, sodium hexadecyl sulfate or sodium octadecyl sulfate or any mixture of the two may be used, instead, in the detergent compositions of our invention.

The unsaturated tallow alcohol sulfates may analyze as a mixture containing 6% sodium tetradecyl sulfate, 28% sodium hexadecyl sulfate, 52% sodium oleyl sulfate and 14% sodium octadecyl sulfate. The unsaturated tallow alcohols are obtainable from tallow by sodium reduction or by selective catalytic hydrogenolysis. Sulfation may require special reaction conditions or a special sulfating reagent to avoid reaction at the double bond. Sodium oleyl sulfate from either an animal or vegetable source may be used instead of the mixture in the detergent compositions of our invention.

The saturated tallow alcohol sulfates are known to be excellent biodegradable detergents but have some restrictions in use because of limited solubility at room temperature. The unsaturated tallow alcohol sulfates are more soluble.

Palmic or stearic acid or the saturated acids of tallow may be sulfonated with sulfur trioxide in the presence of a solvent such as carbon tetrachloride or tetrachloroethylene, and isolated as the α-sulfon acid from which the disodium salt or the sodium salt of the methyl ester may be prepared.

Sodium methyl α-sulfotallowate is principally sodium methyl α-sulfopalmitate and sodium methyl α-sulfostearate. Either of these or a mixture may be used instead.

Further, although the methyl ester is generally preferred, other alkyl esters may be used, specifically the ethyl, n-propyl, isopropyl, n-butyl, isobutyl or secondary butyl esters.

Disodium α-sulfotallowate is principally disodium α-sulfopalmitate and disodium α-sulfostearate. Either of these or any mixture of them may be used instead.

Commercial tallow soap flakes is principally sodium oleate, sodium palmitate and sodium stearate. Any of these or any mixture of them may be used instead.

Comparison of saturated (I) and unsaturated tallow alcohol sulfates (II), disodium α-sulfotallowate (III), sodium methyl α-sulfotallowate (IV), and tallow soap flakes (V) led to the discovery that the solubility of the saturated tallow alcohol sulfates could be markedly improved by blending with sodium methyl α-sulfotallowate.

The favorable solubility and wetting properties of blends of sodium methyl α-sulfotallowate with saturated or unsaturated tallow alcohol sulfates are shown in Table I.

The Krafft point, shown in Table I, is the temperature at which a 1% dispersion changes sharply to a clear solution on gradual heating, and is a convenient measure of solubility. The Krafft point of saturated tallow alcohol sulfate, 46° C., was lowered to values from 33° to 43° in I–IV combinations and from 31° to 38° in I–III–IV–V combinations. It was lowest at high ratios of IV, 33° in the I–IV combination and 31° in the I–III–IV–V combination, showing the importance of the α-sulfo ester...
component. Similarly, the Kraft point of II was lowered from 34° to values of 26° and 29° in II-IV combinations and II-III-IV-V combinations, respectively, at high ratios of IV, the α-sulflo ester.

Wetting properties, partly a function of solubility, are also shown in Table I. The wetting properties of I in distilled water were improved from a value of greater than 5 minutes to values of 27 seconds (I-IV combination at 1:1 ratio) and 29 seconds (I-III-IV-V combination at 1:1:1:1:1 ratio). The wetting time of II, which is fairly soluble and has a low wetting time (27 seconds), was not greatly improved by blending; the lowest value obtained by blending was 20 seconds (II-III-IV-V combination at 1:1:1:2:1 ratio). II-IV combinations contain compounds easily soluble in hard water and at 1:1; 3:2 and 2:3 ratios have good wetting properties in hard water. The II-III-IV-V combinations also have good wetting properties in hard water.

Built and unbuilt solutions of the 5 components and their combinations in soft and hard water, prepared as hot clear solutions, become turbid or partially precipitated on standing for 24 hours. Built II-IV combinations in hard water (300 p.p.m.) containing 0.01% II+0.04% IV+0.20% builder, and 0.02% II+0.03% IV+0.20% builder, remained clear after standing for more than a year. All solutions containing soap were turbid or opalescent. The builder was representative of the usual type and had the following composition: 55% Na₂P₂O₇, 24% Na₂SO₄, 10% Na₃P₂O₇, 10% Na metasilicate, 1% carboxymethylcellulose.

Because of the unusual solubility and stability characteristics, built systems containing unsaturated tallow alcohol sulfates and sodium methyl α-sulfolatomate as the essential active ingredients have very desirable properties as heavy duty liquid detergents. For this purpose the two components should be present in the ratio of 20–40% II to 80–60% IV.

Further comparison of I, II, III, IV, and V led to the unexpected discovery of marked synergism in detergency, in blends of I or II in varying ratios with IV; with or without the presence also of V in ternary systems, or III and V in quaternary systems.

Detergency was measured as the increase in reflectance after washing standard soiled cotton, 10 swatches per liter, in 0.25% built detergent solutions in hard water of 300 p.p.m., using the Terg-O-Tometer, for 20 minutes at 60° C., and 110 cycles per minute. The results are shown in Table II. By analysis of variance a difference in ΔR of 1.1 was significant at the 95% confidence level.

In the form of built solutions containing a single active ingredient, I, II and IV are good detergents (ΔR values of 30.5, 30.7 and 31.7, respectively), and III and V are poor detergents (ΔR values of 7.6 and 3.0 respectively).

In binary systems the presence of III or V lowers the detergency (ΔR values) of I, II or IV, whereas the presence of IV markedly enhances the detergency of I or II in all the ratios in which they are combined. High ΔR values of 32.9 to 34.9 for the I-IV and II-IV combinations are shown in Table II. These values are significantly greater than the values for I, II or IV alone. Blends of 20–80% I (or II) with 80–20% IV are therefore synergistic.

In ternary systems some combinations of III with I or II have good detergent properties, with ΔR values of 30.1 or 32.5, but synergism is established only in blends of minor amounts of V with I (or II) and IV. Blends of 20% V with 20–40% I (or II) and 40–60% IV are synergistic.

In quaternary systems, minor amounts of soap should be present. Blends of 20% V with 20–40% I (or II) plus 20–40% III plus 20–40% IV are synergistic with high ΔR values ranging from 33.2 to 36.3.

Table III lists the synergistic detergent compositions of our invention and their detergent and foaming properties in comparison to those containing only the active ingredient. The foam height of binary systems is nearly independent of variation in the ratio of the components and ranges from 180 to 195 mm. The presence of soap in ternary and quaternary systems lowers foam height to values which range from 135 to 160 mm.

The detergent combinations of our invention permit selection depending upon the particular use and the advantages to be sought. All are excellent detergents.

The binary systems containing I and IV have the advantage of simplicity, low-cost, ready availability and relatively high foaming properties, the II-IV combinations.

### Table I—Kraft Point and Wetting Time

<table>
<thead>
<tr>
<th>Active Ingredient component:</th>
<th>Wetting time, seconds, 25°C., Draves Test a</th>
<th>0.20% unbuilt solution in distilled water, C.</th>
<th>0.05% total active ingredient+0.20% builder, 300 p.p.m.</th>
<th>402</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>69</td>
<td>&gt;500</td>
<td>&gt;502</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>54</td>
<td>&gt;500</td>
<td>&gt;502</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>68</td>
<td>25</td>
<td>29</td>
<td>20</td>
</tr>
<tr>
<td>IV</td>
<td>29</td>
<td>21</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>V</td>
<td>28</td>
<td>14</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>I-IV combinations:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4:1</td>
<td>43</td>
<td>72</td>
<td>&gt;505</td>
<td>00</td>
</tr>
<tr>
<td>3:2</td>
<td>41</td>
<td>45</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>2:3</td>
<td>37</td>
<td>22</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>1:4</td>
<td>33</td>
<td>22</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>II-III-IV-V combinations:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1:1</td>
<td>33</td>
<td>22</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>1:2:1</td>
<td>31</td>
<td>20</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>2:2:1</td>
<td>31</td>
<td>20</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>3:2:1</td>
<td>31</td>
<td>20</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>1:1:1:2:1</td>
<td>29</td>
<td>20</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>II-III-IV-V combinations:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1:1:1</td>
<td>29</td>
<td>20</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>1:1:1:1:1</td>
<td>29</td>
<td>20</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>1:2:1:1:1</td>
<td>29</td>
<td>20</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>1:1:1:1:2</td>
<td>29</td>
<td>20</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

* I, saturated tallow alcohol sulfates; II, unsaturated tallow alcohol sulfates; III, di-tallow-α-sulfatolates; IV, sodium methyl α-sulfatolates; V, soap.
* A temperature at which a 75% turbid suspension becomes clear on gradual heating.
* Not soluble enough for test.
have somewhat similar properties but are more soluble and could have somewhat different applications. Specific II–IV combinations, those in which the ratio of active ingredients are 20–40% II to 80–60% IV, because of solubility and stability characteristics, have very desirable properties as liquid detergents.

Ternary systems of I with IV and V are inexpensive and have only moderate forming properties, desirable in certain types of washing machines and washing operations. II–IV–V systems are similar, but are more easily soluble.

Quaternary systems containing I–III–IV–V have the advantage of wide application to a variety of soil removal problems because they contain different detergency types. They are the least expensive since I and IV are partially substituted for by the lower priced III and V. These quaternary systems have only moderate foaming properties which is sometimes advantageous. Although the II–III–IV–V quaternary systems are more soluble, they are more expensive than the I–III–IV–V systems.

All of the components of the detergent combinations of our invention are easily biodegradable. This has been shown by river water tests and studies in a laboratory scale activated sludge unit (J. K. Weil and A. J. Storton, J. Am. Oil Chemists’ Soc., 41, 355–358 (1964); T. C. Cordon, E. W. Maurer, J. K. Weil, and A. J. Storton, Development in Industrial Microbiology, 6, 3–15 (1964)). The alcohol sulfates (I and II) are even degradable under anaerobic conditions. Under these conditions both linear and branched chain alkylbenzenesulfonates did not degrade and disrupted the normal digestion process. The \( \alpha \)-sulfro esters (IV) did not degrade but did not interfere with the normal digestive processes (E. W. Maurer, T. C. Cordon, J. K. Weil, M. V. Nuti-Zaponza, W. C. Ault, and A. J. Storton, J. Am. Oil Chemists’ Soc., 42, 189–192 (1965)).

Combinations of tallow alcohol sulfates and \( \alpha \)-sulfro esters also have desirable properties in the absence of builder. This is shown in Table IV. At 0.25% concentration in the absence of builder or inorganic salts I or II is the best single component detergent in soft (distilled) water (AR values 35.4 and 35.1, respectively), and IV is the best in hard (300 p.p.m.) water (AR value 31.2).

In distilled or soft water synergism is shown by I–IV combinations of 40–60% I with 60–40% IV (AR values 36.6). In water of intermediate hardness (100 p.p.m.) synergism is shown by combinations of 60–80% I (or II), with 40–20% IV (AR values 36.9, 37.3, and 35.8) and 36.2).

Table IV also shows that foam is excellent for I (II and II) and IV combinations except in hard water where the ratio of I is high (foam height of 90 mm. for the 80% I–20% IV combination). I–IV combinations are also more soluble than I alone.

<table>
<thead>
<tr>
<th>Table II—Detergency and Foaming Height of 0.25% Built Solutions in Hard Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergency, AR^a</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Detergent, AR^b</td>
</tr>
<tr>
<td>0.25 I</td>
</tr>
<tr>
<td>0.25 II</td>
</tr>
<tr>
<td>0.25 IV</td>
</tr>
<tr>
<td>0.05 I+0.20 IV</td>
</tr>
<tr>
<td>0.10 I+0.15 IV</td>
</tr>
<tr>
<td>0.35 I+0.05 IV</td>
</tr>
<tr>
<td>0.10 I+0.20 IV</td>
</tr>
<tr>
<td>0.15 I+0.10 IV</td>
</tr>
</tbody>
</table>

^1, saturated tallow alcohol sulfonates; II, unsaturated tallow alcohol sulfonates; III, disodium \( \alpha \)-naphthalene sulfonate, IV, sodium methyl \( \alpha \)-naphthalene sulfonate, V, soap. |
We claim:

1. A biodegradable detergent composition consisting of
   (a) 4% by weight of a sulfate selected from the group consisting of a saturated tallow alcohol sulfate of the formula 
   \[ R'\text{CH}_2\text{CH}_2\text{OSO}_4\text{Na} \]
   and individual and mixed alkyl radicals derived from the saturated fatty acids of tallow, and R' is selected from the group consisting of 
   \[ \text{CH}_3(\text{CH}_2)_3\text{CH}==\text{CH}(\text{CH}_2)_6 \]
   and individual and mixed alkyl radicals derived from the fatty acids of tallow;
   (b) 4% by weight of a disodium \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{Na} \]
   wherein R is the same as above;
   (c) 8% by weight of a sodium alkyl \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{R}' \]
   wherein R is the same as above and R' is methyl; 
   (d) 4% by weight of tallow soap flakes of the formula 
   \[ R'\text{CH}_2\text{CO}_2\text{Na} \]
   wherein R' is the same as above; and
   (e) 80% by weight of a builder having the composition, 55% \( \text{Na}_2\text{P}_2\text{O}_{10} \)
   24% \( \text{Na}_2\text{SO}_4 \)
   10% \( \text{Na}_2\text{P}_2\text{O}_7 \)
   10% Na metasilicate and 1% carboxymethyl cellulose.

2. The composition of claim 1 wherein the sulfate is a saturated tallow alcohol sulfate.

3. The composition of claim 1 wherein the sulfate is an unsaturated tallow alcohol sulfate.

4. A biodegradable detergent composition consisting of
   (a) 8% by weight of a sulfate selected from the group consisting of a saturated tallow alcohol sulfate of the formula 
   \[ R'\text{CH}_2\text{CH}_2\text{OSO}_4\text{Na} \]
   and individual and mixed alkyl radicals derived from the fatty acids of tallow, and R' is selected from the group consisting of 
   \[ \text{CH}_3(\text{CH}_2)_3\text{CH}==\text{CH}(\text{CH}_2)_6 \]
   and individual and mixed alkyl radicals derived from the fatty acids of tallow;
   (b) 4% by weight of a disodium \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{Na} \]
   wherein R is the same as above;
   (c) 4% by weight of a sodium alkyl \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{R}' \]
   wherein R is the same as above and R' is methyl; 
   (d) 4% by weight of tallow soap flakes of the formula 
   \[ R'\text{CH}_2\text{CO}_2\text{Na} \]
   wherein R' is the same as above; and
   (e) 80% by weight of a builder having the composition, 55% \( \text{Na}_2\text{P}_2\text{O}_{10} \)
   24% \( \text{Na}_2\text{SO}_4 \)
   10% \( \text{Na}_2\text{P}_2\text{O}_7 \)
   10% Na metasilicate and 1% carboxymethyl cellulose.

5. The composition of claim 4 wherein the sulfate is a saturated tallow alcohol sulfate.

6. The composition of claim 4 wherein the sulfate is an unsaturated tallow alcohol sulfate.

7. A biodegradable detergent composition consisting of
   (a) 4% by weight of a sulfate selected from the group consisting of a saturated tallow alcohol sulfate of the formula 
   \[ R'\text{CH}_2\text{CH}_2\text{OSO}_4\text{Na} \]
   and individual and mixed alkyl radicals derived from the fatty acids of tallow, and R' is selected from the group consisting of 
   \[ \text{CH}_3(\text{CH}_2)_3\text{CH}==\text{CH}(\text{CH}_2)_6 \]
   and individual and mixed alkyl radicals derived from the fatty acids of tallow;
   (b) 4% by weight of a disodium \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{Na} \]
   wherein R is the same as above;
   (c) 4% by weight of a sodium alkyl \( \alpha \)-sulfotallowate of the formula 
   \[ \text{RCH}(\text{SO}_2\text{Na})\text{CO}_2\text{R}' \]
   wherein R is the same as above and R' is methyl; 
   (d) 4% by weight of tallow soap flakes of the formula 
   \[ R'\text{CH}_2\text{CO}_2\text{Na} \]
   wherein R' is the same as above; and
   (e) 80% by weight of a builder having the composition, 55% \( \text{Na}_2\text{P}_2\text{O}_{10} \)
   24% \( \text{Na}_2\text{SO}_4 \)
   10% \( \text{Na}_2\text{P}_2\text{O}_7 \)
   10% Na metasilicate and 1% carboxymethyl cellulose.

8. The composition of claim 7 wherein the sulfate is a saturated tallow alcohol sulfate.

9. The composition of claim 7 wherein the sulfate is an unsaturated tallow alcohol sulfate.

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U.S. Cl. X.R. 252—121, 138, 161