# Experiments in the Formulation of Heavy Duty Liquid Detergents from Tallow[1]

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## Abstract

Several tallow-based detergents were investigated in simplified formulations comprising ca. 10–15% active ingredient, 4% foam stabilizer, 10% isopropyl alcohol, 20% $K_4P_2O_7$ and 50–55% water, 1% with respect to carboxymethylcellulose. Disodium 2-sulfoethyl α-sulfostearate or sodium oleate could be used as the only active ingredient or in blends with other tallow-based compounds. The presence of a soluble form of the tallow alcohol sulfates, sodium 9,10-dichlorooctadecyl sulfate, gave maximum detergency in hard water.


## Introduction

LIQUID DETERGENTS, both light and heavy duty, have become increasingly popular in recent years in this country. The total sales of liquid detergents increased from 153 million lb (7% of total detergent sales) in 1955, to 711 million lb (21%) in 1961 (1). If this trend continues it has been estimated that liquid detergents will represent 40% of total detergent sales in 1965 (2).

Many of the detergents, soaps and surface active agents which derive from tallow, are quite water soluble and may be considered in the formulation of liquid detergents. The use of commercially available biodegradable esters of α-sulfo fatty acids, especially the methyl esters, in different types of formulations, has been recently described (4). Heavy duty liquids are among the newest developments and our experiments in formulation primarily concern these. Heavy duty liquid detergents may consist of an active ingredient, usually branched chain alkylbenzene sulfonate, a foam stabilizer and thickening agent, phosphate and silicate alkaline builders, a hydrotropic agent, ethyl or isopropyl alcohols, carboxymethylcellulose, an optical brighter, perfume and water (5,8). Changes in formulation, particularly in the active ingredient, will probably occur when standards of detergent biodegradability are adopted.

Examples of easily soluble biodegradable detergents, surface active agents and soaps which derive from tallow are: triethanolammonium α-sulfostearic acid; salts of a variety of esters of α-sulfo acids such as sodium isopropyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)_2$ or disodium 2-sulfoethyl α-sulfostearate $C_{16}H_{33}CH(SO_3Na)CO_2CH_2CH_2SO_3Na$; tallow alcohol sulfates in the form of sodium oleyl sulfate, sodium 9,10-dichlorooctadecyl sulfate $CH_3(CH_2)_7CHClCHCl(CH_2)_7CH_2OSO_3Na$, or sulfated nonionics $R(OC_2H_4)OSO_3Na$; the *N*-methyltauride or the isethionate ester of oleic acid; and sodium oleate. These have been shown to be biodegradable in the river water die-away test (9).

Our preliminary investigations selected a simplified formulation containing ca. 10–15 % active ingredient, 4% foam stabilizer, 10% isopropyl alcohol, 20% potassium pyrophosphate and 50–55% water, 1% with respect to carboxymethylcellulose. Hydrotropic agents such as sodium or potassium toluene or xylenesulfonate did not appear to be necessary. The foam stabilizer, a commercial alkanolamide (Stepan P-621), was generally useful to increase foam stability in hard water, but may not be essential and could in some cases be replaced by a further amt of the active ingredient.

With compatibility as the first consideration it was found that disodium 2-sulfoethyl α-sulfostearate or sodium oleate could be used either as the only active ingredient, or in blends with sodium isopropyl α-sulfostearate, tallow alcohol sulfates or other fat based surface active agents and detergents.

The liquid detergent formulations are described in terms of their appearance and stability, pH, viscosity and foaming and detergent properties.

## Experimental

*Active Ingredients.* Salts of esters of α-sulfo acids and soluble forms of the tallow alcohol sulfates were prepared as described in previous publications (7,10).

*Formulation.* A stock solution of carboxymethylcellulose, 1% in distilled water, was prepared, 20 ml were placed in a 4-oz jar and the other components were added in amt indicated by the general formula. The mixture was heated to obtain complete solution. If precipitation or separation into two liquid phases occurred on cooling to room temp the formulation was rejected. Stability was further checked over a 90-day shelf life period and by means of a freeze-thaw test.

*Freeze-Thaw Tests.* Formulations stable at room temp were stored in a refrigerator 6 hr at −5C each day and thawed overnight for a 5-day period. Crystallization and other changes in physical appearance were noted.

*Viscosity.* Some of the experimental formulations, and commercial products as well, contain transparent particles too large for the orifice of standard viscosity tubes. Relative viscosity was therefore measured as the drainage time of a 5-ml serological pipet containing the liquid detergent.

*Foam Height.* Foam height was measured by the Ross-Miles test on 0.25% solutions of the liquid detergent, by wt, at 60C (6), in distilled water and in hard water of 300 ppm (as $CaCO_3$).

*Detergency.* Detergency was measured in the Terg-O-Tometer as the increase in reflectance ΔR after washing 10 swatches of G.D.C. No. 26 (3) standard soiled cotton in 1-liter of solution, 0.25% by wt with respect to the liquid detergent, for 20 min at 60C.

## Discussion

### Syndet-Syndet Formulations

*Solubility.* It is not essential that formulated liquid detergents remain entirely clear liquids; in fact opalescence or pearliness might be considered an attractive feature. For simplicity in our experiments in formulation, however, compatibility was the first consideration, and a number of tallow-based surface active agents and detergents were rejected because

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they were not adequately soluble or were incompatible in the presence of builder and isopropanol.

Sodium and potassium salts of α-sulfopalmitic and α-sulfostearic acid are not soluble enough at room temp and the easily soluble acid triethanolammonium salts apparently formed less soluble mixed salts with the builder. The sodium salts of the methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl esters of α-sulfopalmitic and α-sulfostearic acids are adequately soluble in water but crystallized from solution when used in the general liquid detergent formulation. Esters of secondary alcohols, sodium sec. butyl α-sulfopalmitate and sodium isopropyl α-sulfostearate did not crystallize, but liquid detergent formulations in which they were the only active ingredient separated into two liquid phases. Use of potassium rather than sodium salts of the esters did not cause any change in solubility behavior. Sodium hexadecyl and octadecyl sulfates have limited solubility at room temp. The easily soluble oxyethylated long chain alcohols and fatty acids of tallow were caused to separate as an upper liquid phase by the presence of the builder. The sulfated oxyethylated long chain alcohols $R(OC_2H_4)_n OSO_3Na$ were also incompatible when used as the only active ingredient.

Disodium 2-sulfoethyl α-sulfostearate was the only tallow-based synthetic detergent which could be used as the only active ingredient in the general liquid detergent formulation. This formulation remained a clear liquid for two months and showed only a slight turbidity in the freeze-thaw test, but finally crystallized in 63 days. Disodium 2-sulfoethyl α-sulfostearate, which is both a detergent and lime soap dispersing agent, has the further advantage that blends with otherwise incompatible tallow-based active ingredients give liquid detergents stable for 90 days or more. None of the other four active ingredients can function as the only active ingredient or solubilize other active ingredients in this manner. Blends of disodium 2-sulfoethyl α-sulfostearate with esters of secondary alcohols (sodium sec. butyl α-sulfopalmitate) were compatible but this was not the case with *n*-alkyl esters. Disodium 2-sulfoethyl α-sulfostearate was able also to solubilize commercial samples of the isethionate ester and the *N*-methyltauride of oleic acid.

*Other Properties.* The syndet-syndet formulations (pH 8.0–9.6) are less alkaline than the commercial heavy duty liquids, less viscous (except in the case of

TABLE I

Heavy Duty Liquid Detergent Formulations

[9–15% active ingredient, 4% foam stabilizer, 10% $CH_3CHOHCH_3$, 20% $K_4P_2O_7$, 50–56% $H_2O$ (1% with respect to carboxymethylcellulose)]

| No. | Active ingredient | Total active ingredient % | pH | Relative viscosity, drainage time, 5 ml pipet, seconds | Foam height[a] 0.25%, 60C (6) mm | | Detergency 0.25%, 60C ΔR | | Freeze-thaw test |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Distd. water | 300 ppm | Distd. water | 300 ppm | |
| 1 | 11% Disodium 2-sulfoethyl α-sulfostearate[b] | 11 | 8.8 | 7 | 175 | 215 | 18 | 16 | Slight turbidity |
| 2 | 4% Disodium 2-sulfoethyl α-sulfostearate, 7% sodium isopropyl α-sulfostearate[c] | 11 | 8.2 | 47 | 190 | 190 | 17 | 16 | Clear |
| 3 | 3% Disodium 2-sulfoethyl α-sulfostearate, 6% sodium oleyl sulfate[d] | 9 | 8.0 | 8 | 220 | 220 | 24 | 18 | Clear |
| 4 | 3% Disodium 2-sulfoethyl α-sulfostearate, 6% sodium 9,10-dichlorooctadecyl sulfate[e] | 9 | 8.6 | 26 | 210 | 215 | 24 | 22 | Slight turbidity |
| 5 | 3% Disodium 2-sulfoethyl α-sulfostearate, 7% sulfated nonionic[f] | 10 | 9.6 | 27 | 210 | 215 | 16 | 14 | Slight turbidity |
| 6 | 6% Sodium oleate,[g] 3% disodium 2-sulfoethyl α-sulfostearate, 6% sodium oleyl sulfate | 15 | 9.3 | 24 | 230 | 180 | 22 | 16 | Clear |
| 7 | 6% Sodium oleate, 3% disodium 2-sulfoethyl α-sulfostearate, 6% sodium 9,10-dichlorooctadecyl sulfate | 15 | 9.5 | 28 | 220 | 160 | 21 | 20 | Clear |
| 8 | 6% Sodium oleate, 3% disodium 2-sulfoethyl α-sulfostearate | 9 | 9.3 | 33 | 225 | 155 | 20 | 17 | Clear |
| 9 | 6% Tallow soap,[h] 3% disodium 2-sulfoethyl α-sulfostearate | 9 | 9.7 | 48 | 230 | 105 | 22 | 16 | Slight turbidity |
| 10 | 6% Sodium oleate, 3% sodium isopropyl α-sulfostearate | 9 | 10.0 | 18 | 220 | 135 | 21 | 17 | Clear |
| 11 | 6% Sodium oleate, 6% sodium oleyl sulfate | 12 | 8.8 | 17 | 230 | 180 | 25 | 17 | Clear |
| 12 | 6% Sodium oleate, 6% sodium 9,10-dichlorooctadecyl sulfate | 12 | 9.7 | 29 | 225 | 175 | 27 | 24 | Slight haze |
| 13 | 5% Sodium oleate, 5% sulfated nonionic | 10 | 9.8 | 33 | 230 | 200 | 20 | 15 | Clear |
| 14 | 9% Sodium oleate, 1% disodium 2-sulfoethyl α-sulfostearate | 10 | 10.4 | 22 | 230 | 155 | 26 | 14 | Clear |
| 15 | 9% Sodium oleate, 1% sodium isopropyl α-sulfostearate | 10 | 10.5 | 20 | 230 | 115 | 25 | 15 | Clear |
| 16 | 10% Sodium oleate | 10 | 10.2 | 66 | 240 | 160 | 25 | 15 | Clear |
| Commercial heavy duty liquid detergents | | | | | | | | | |
| I | | | 11.8 | 40 | 235 | 235 | 16 | 15 | |
| II | | | 11.3 | 52 | 230 | 235 | 15 | 14 | |
| III | | | 10.0 | 48 | 240 | 240 | 14 | 14 | |

[a] Stable 5 min or more.
[b] $C_{16}H_{33}CH(SO_3Na)CO_2CH_2CH_2SO_3Na$.
[c] $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)_2$.
[d] $CH_3(CH_2)_7CH{=}CH(CH_2)_8OSO_3Na$.
[e] $CH_3(CH_2)_7CHClCHCl(CH_2)_8OSO_3Na$.
[f] $C_{16}H_{33}(OC_2H_4)_2OSO_3Na$.
[g] By neutralization of technical oleic acid wtih sodium hydroxide.
[h] By neutralization of tallow fatty acids with sodium hydroxide.

No. 2), and the foaming properties are not so pronounced.

The detergent properties of commercial heavy duty liquid detergents are equalled or exceeded; this is particularly true in the case of No. 4, which shows excellent foaming and detergent properties for a blend of disodium 2-sulfoethyl α-sulfostearate with sodium 9,10-dichlorooctadecyl sulfate. The syndet-syndet formulations give perfectly clear solutions in hard water.

**Soap-Syndet Formulations**

Soap in the form of sodium oleate or a tallow soap could be used as the only active ingredient in the general formulation but opaque, milky dispersions resulted when used in washing experiments in hard water. Other effects are shown in Table I. All systems listed were stable for 90 days or more.

The pH of the soap-syndet systems ranged from 9.3–10.5; viscosity was decreased by the presence of synthetic detergent. Soap can be used with esters of α-sulfo acids or with soluble forms of the tallow alcohol sulfates. Formulations with the isethionate ester or the *N*-methyl tauride of oleic acid in place of the α-sulfo esters (formations No. 8 and 10) gave slightly lower values for detergency in hard water ($\Delta R = 12$, 15, respectively). Combinations of sodium oleate with a sulfated nonionic (No. 8) gave the best foaming properties in hard water. Combinations in which sodium 9,10-dichlorooctadecyl sulfate was one of the active ingredients (No. 7, No. 12) had superior detergency in hard water.

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