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 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

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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 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

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.

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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Continuous Refining of Crude Cottonseed Miscella

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Abstract

A simple, easily controlled process for continuous caustic refining of crude cottonseed miscella in a two-stage system is described. The effect of crude oil quality, oil:hexane ratios, temp, mixing conditions and chemical treatment are noted. The chemical reactions in the process are followed microscopically. The process yields a refined oil of less than: 1.0 bleach oil color, 0.03% free fatty acid and 15 ppm soap, and with 30–40% oil savings over Official Cup Loss. The by-product soap may be used advantageously in the meal from the extractor unit.

Introduction

ALTHOUGH A NUMBER of basic patents (1) for the refining of crude oils in the miscella state have issued in the past two decades, the acceptance of this refining technique as a general practice has been slow due to delay in the development of appropriate equipment and marketing practices. The recent trend toward complete processing of raw materials to finished products at the source area has stimulated an interest in miscella refining of crude solvent extracted and prepressed solvent extracted oils at the seed mill. Thus, the continuous refining of the crude oil-hexane mixture in a completely closed system is a natural development.

The chemical and physical properties of the crude miscella differ considerably from conventional hydraulic, expeller or solvent extracted crudes. The fact that this miscella crude oil may be treated continuously in a relatively simple system to yield quality products makes the De Laval Miscella Refining System a unique process.

This miscella refinery process is shown in Figure 1.

Description of Process

In this process, the crude miscella source may be a) from the pre-evaporator of a direct-solvent extraction plant, b) from a blend of prepressed crude oil and solvent extracted miscella from the press cake, or c) possibly a reconstituted blend of crude oil with hexane.

The crude oil-hexane mixture, 45–65% oil: 35–55% hexane, is pumped through either a heater or cooler to bring to the desired processing temp range, then to a motorized Cuno or similar filter to remove any meal, scale or insoluble impurities that may be present from the extractor, pre-evaporator or storage tank.

The feed next passes through a flow measuring device, such as an indicating rotameter with ratio controller for the reagent treatment system, and enters the pretreatment additive and mixing section. Here a small dosage pump meters an additive in ppm quantities.

The pretreated crude miscella then enters the reaction section, where the refining agent is intimately intermixed and contacted for a given period of time until the impurities in the crude oil are precipitated in the soap phase.

This reaction mixture passes to a heater to assure proper temp for centrifugation in the Hermetic (2) Miscella Separator.

In this specially designed centrifuge, the light colored refined miscella is readily separated from the dark, gummy, fluid soapstock.

The light yellow miscella is pumped to the stripper of the solvent extraction plant for recovery of the hexane. Leaving the stripper at 220F, the refined oil passes to a pressure leaf-type filter, with dosage and precoat system for removal of last traces of soap and any extraneous impurities, before cooling and entering storage as a quality refined or bleached oil product.

The soapstock from the centrifuge may be pumped: to desolventizer-toaster as a meal additive; to a continuous acidulation system for acid oil recovery; or to storage.

Chemistry of Process

Laboratory and actual plant experience have shown that, with direct solvent extracted crude cottonseed oils, the processing conditions in the refinery will

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[1] Presented at the AOCS Meeting in Minneapolis, 1963.