Soaps of Monohydroxystearic Acid in Syndet Compositions

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Abstract

Soaps of monohydroxystearic acid, prepared by sulfation of oleic acid followed by hydrolysis, have been evaluated in syndet compositions. They can be used to replace a substantial proportion of the synthetic surfactant in both liquid and solid detergent compositions without loss of detergent efficiency or foaming properties. In contrast, sodium stearate and sodium oleate adversely affect performance. Compatibility is improved when these hydroxystearate soaps are incorporated in built liquid compositions. Since these materials exhibit the usual response of soaps to pH change and to divalent cations, there is complete assurance that they will be inactivated in ground water as well as in sewage treatment plants.

Introduction

LINEAR ALKYLBENZENE SULFONATE (LAS) is the current answer of the detergent industry to the problem of biodegradability (1). At the same time it is recognized that LAS is a compromise between requirements for a detergent material that can be produced in abundance at low cost and rapid degradability. LAS does not degrade as quickly as the alkylsulfates under aerobic conditions (2), and it is doubtful that it will degrade at an adequate rate in ground water (3).

Soap or some form of soap should be considered as at least a partial replacement for synthetic surfactants. Fats and oils necessary for their manufacture are also available in good volume at reasonable cost. Since soaps are inactivated by water hardness as well as by pH adjustment, they cannot present a problem of carry-over from ground water or sewage treatment. Thus, if half of the synthetics were replaced by soap, the magnitude of the problem would immediately be reduced by half.

Unfortunately, conventional soaps in combination with synthetics do not perform quite as well as the synthetics alone. We have recently found that a monohydroxystearate soap is especially suited for use with synthetic surfactants. Detergency and foaming properties are not impaired and water solubility is enhanced in the presence of this soap.

The hydroxystearate soaps used here were prepared according to a procedure described by Roe et al. (4). The method consists of sulfating oleic acid with H_2SO_4, followed by alkaline hydrolysis. The procedure is said to give predominantly 10-hydroxystearic acid, with lesser amt of the 9-hydroxystearic acid and other isomers. Some polymeric materials may also be present. Repeated recrystallizations resulted in a product melting at 58–59C, as compared with reported melting point values of 80–85C for pure 10-hydroxystearic acid.

TABLE I

Composition of Built Detergents

	Parts by wt	
	A	B
Surfactants (100% active basis)	15	22
Sodium tripolyphosphate	30	30
Tetrasodium pyrophosphate	10	10
Sodium silicate ($Na_2O:3.2\ SiO_2$)	5	5
Sodium carboxymethyl cellulose	1	1
Soduim sulfate	39	32

Experimental

a) Hydroxystearic acid was prepared from a 93% technical oleic acid. The acid, 266.7 g (0.9 moles), was placed in a 2-liter flask and cooled to 10C in an icewater bath. Concd H_2SO_4, 216.0 g (2.2 moles) was added slowly with stirring over a period of 1 hr. The reaction mixture was cooled to 5C and was maintained at this temp for 30 min. Water was then added to bring the total volume to 1.5 liters, and the mixture was boiled for 1 hr. The aqueous layer was withdrawn and the oil layer was washed with additional boiling water. It was then refluxed with 0.5 liters alcoholic potassium hydroxide for 6 hr. The alcohol then was distilled over, the soap was acidified with dilute H_2SO_4 and extracted with warm *n*-hexane. The hexane layer was washed with hot water until sulfate free. The hydroxystearic acid was crystallized from hexane by standing overnight at −25C. Repeated recrystallizations from a high boiling petroleum ether yielded 207 g of a white wax-like product melting at 58–59C, with an acid value of 187.0 and a hydroxy value of 180.6. Sulfur-containing surfactant present was less than 0.005%.

b) Soil removal data were obtained by washing FDS Soiled Cotton in a Launderometer at 55C (5). Each test result reported is the average of a minimum of six swatches from three separate Launderometer runs.

Ross & Miles foam test data (6) are the average of duplicate determinations.

For the dishwashing test, porcelain dinner plates were smeared with 0.5 tsp/plate of a melted soil consisting of 80% hydrogenated fat, 20% flour and enough Oildag for a distinctive dirty coloring. The soiled plates were aged for 24 hr at room temp before use. The detergent was dissolved in 1 liter water at 45C in a dishpan. An additional 3 liters water at 45C were poured into the dishpan through a 2-qt glass funnel from a height of 30 in. directly above the center of the dishpan. The funnel was partially filled with small ground glass stoppers to control the rate of water flow. After 30 sec, the soiled dishes were individually washed with a dishrag until clean. Additional dishes were washed until the foam disappeared. Detergents were compared at 0.10% concn.

c) Materials used in this investigation were as follows, ABS: Ultrawet K, Atlantic Refining Co.; lauric monoisopropanolamide: Ninol AD31, Stepan Chemical Co.; lauric diethanolamide: Ninol AA62 Extra, Stepan Chemical Co.; sodium xylene sulfonate: Ninex 303, Stephan Chemical Co.; octylphenol · 9–10 ETO:

TABLE II

Soil Removal with ABS-Soap Combinations at 55C
(other ingredients in accordance with Table I)

Surfactant composition, %					Reflectance units gained			
ABS	Lauryl mono-isopropanol-amide	Sodium hydroxy-stearate	Sodium stearate	Sodium oleate	2-gr water		15-gr water	
					0.20%	0.35%	0.20%	0.35%
13	2	...	....	....	8.8	16.1	6.6	15.7
8	2	5	....	....	9.8	20.0	5.9	16.6
8	2	....	5	.	7.8	16.0	5.7	12.2
8	2	. .	. . .	5	10.8	17.1	4.9	13.6
3	2	10		....	8.8	20.3	5.4	14.4
3	2	....	10		6.1	13.5	4.6	6.8
3	2	....	....	10	9.6	14.0	3.3	11.2
20	2		....	. . .	12.8	18.9	8.5	17.1
10	2	10		....	14.3	21.5	5.9	19.3
10	2	....	10		9.4	16.9	5.4	13.9
10	2			10	12.4	18.4	5.1	13.8

TABLE III

Soil Removal Using Combinations of Hydroxystearate Soap with Oleyl Isethionate and with Tallow Sulfate at 55C
(other ingredients in accordance with Table I)

Surfactant composition, %				Reflectance units gained			
Oleyl ester of sodium isethionate	Sodium tallow sulfate	Lauryl monoisopropanolamide	Sodium hydroxystearate	2-gr water		15-gr water	
				0.20%	0.35%	0.20%	0.35%
20	....	2	....	13.7	19.3	11.5	16.6
10	....	2	10	15.8	20.0	10.2	17.7
5	....	2	15	14.1	17.7	6.4	16.8
....	20	2	...	12.9	17.7	9.6	13.6
....	10	2	10	13.4	19.7	9.6	16.6
	5	2	15	13.8	20.2	8.9	18.5

Triton X100, Rohm & Haas Co.; oleyl ester of sodium isethionate: Igepon AP-78, General Aniline & Film Corp.; sodium tallow sulfate: Sipex TS, American Alcolac Corp.; sodium lauryl sulfate: Duponol WA, E. I. duPont deNemours; LAS: Calsoft F, Pilot Chemical Co.

Discussion of Results

The built detergent compositions used in this program are shown in Table I. They are representative of commercial practice. Soil removal data using both 15 and 22% active are shown in Table II. All compositions in this series contained 2% lauryl isopropanolamide and either ABS or a mixture of ABS and soap. Except for the lowest test concn in hard water, combinations containing hydroxystearate soap outperformed ABS. In contrast, combinations of sodium stearate or sodium oleate with ABS were generally less effective than ABS without soap.

Soil removal results in Table III were obtained with built compositions containing 22% active, using either the oleyl ester of sodium isethionate or sodium tallow sulfate as the major active. With one-half of the isethionate ester replaced by the hydroxystearate soap, performance was as good as the product without soap. With three-fourths of the isethionate ester replaced, there was some decrease in effectiveness, particularly at the lower concn in 15 g water. In the case of sodium tallow sulfate—sodium hydroxystearate blends, detergency was excellent even with three-fourths of the tallow sulfate replaced by the soap.

Ross and Miles foam test data are shown in Table IV for ABS-soap combinations. The hydroxystearate soap did not depress the foam volume or stability, even in hard water. Oleate soap depressed the foaming action to a moderate extent, while stearate soap substantially lowered foaming action. Similar results were obtained when these soaps were used in combination with other anionic surfactants in built compositions.

TABLE IV

Ross & Miles Foam Test
0.20% Built Compositions at 43C
Sample a–k in 2-Gr Water, l-n in 15-Gr Water
(all compositions contained 2% of lauryl monoisopropanolamide and other ingredients in accordance with Table I)

Sample	ABS, %	Sodium soap, %	Soap type	Foam height (cm)			
				0 min	1 min	5 min	10 min
a	13	....	....	16.5	14.5	13.5	13.0
b	8	5	hydroxystearate	18.0	15.0	15.0	14.0
c	8	5	stearate	5.0	4.5	4.2	4.0
d	8	5	oleate	15.0	13.0	12.5	12.0
e	3	10	hydroxystearate	17.0	15.5	15.0	14.5
f	3	10	stearate	2.5	2.0	2.0	1.5
g	3	10	oleate	10.0	9.0	9.0	8.5
h	20	.	......	17.5	15.5	15.5	15.0
i	10	10	hydroxystearate	18.0	16.0	16.0	15.0
j	10	10	stearate	7.5	6.5	6.5	6.0
k	10	10	oleate	14.5	13.0	13.0	12.0
l	13	..	....	18.5	16.0	15.5	15.0
m	8	5	hydroxystearate	18.0	15.0	15.0	14.5
n	8	5	stearate	4.0	3.5	3.5	3.0

TABLE V

Dishwashing Test, 0.10% Concn
Water Initially at 45C

	Parts by wt							
	a	b	c	d	e	f	g	h
LAS	30	30	25	25	....	....	....	....
Sodium lauryl sulfate	....	....	....	....	30	30	25	25
Lauryl diethanolamide	5	5	5	5	5	5	5	5
Octylphenol · 9–10 ETO	5	....	10	....	5	....	10	....
Sodium hydroxystearate		5	....	10	....	5	....	10
Water	60	60	60	60	60	60	60	60
	Dishes washed to foam end point							
	a	b	c	d	e	f	g	h
2-grain water	8	9	9	11.5	11	8.5	9	6.5
15-grain water	7	10	9	10	....	....	....	....

Dishwashing test results are shown in Table V. The formulations shown are not necessarily representative of commercial practice, but are indicative of the effect of sodium hydroxystearate on foam stability in the presence of food soil. One series of formulations consisted of LAS in combination with an alkanolamide and either an ethoxylated octylphenol or sodium hydroxystearate. The presence of the soap increased the number of dishes washed to a foam end point. In a second series, sodium lauryl sulfate was used in place of LAS. Here, the hydroxystearate soap had a deleterious effect.

Built liquid compositions can be readily compounded with the hydroxystearate soap. For example, a composition consisting of 20% of ABS and tetrapotassium pyrophosphate, 2% of lauryl diethanolamide and the remainder water separated on standing into two layers of approx equal volume. The same result was obtained when one-half of the ABS was replaced by sodium oleate, potassium oleate or sodium 12-hydroxystearate. However, when the partial replacement was made with either the sodium or potassium salt of isomeric hydroxystearate a single phase, viscous solution resulted.

Conclusions

The experimental data clearly demonstrate that these isomeric hydroxystearate soaps can play a significant role in this new era of biodegradable detergent compositions. They can be used to replace a substantial proportion of the synthetic surfactants in both liquid and solid detergent compositions, without any loss in performance properties. In some instances these properties are enhanced. Compatibility is improved when these soaps are incorporated into built liquid compositions. Since these materials exhibit the usual response of soaps to pH change and to divalent cations, there is complete assurance that they will be inactivated under all treatment conditions and that they will not find their way into wells or the effluent from sewage treatment plants.

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