Alpha Sulfo Fatty Esters in Biologically Soft Detergent Formulations

E. A. KNAGGS,[1] J. A. YEAGER, L. VARENYI and E. FISCHER,
Stepan Chemical Company, Northfield, Illinois

Abstract

Salts of α-sulfo tallow and coconut esters were subjected to river die-away, activated sludge and Warburg tests, and results show these derivatives to be biologically soft detergents with disappearance curves approximating those of the fatty alcohol sulfates.

Selection of the proper fatty acid starting material, alcohol of esterification, and alkali for neutralization provides for a high degree of flexibility in tailor-making biologically soft surface active agents for a wide range of applications. Selected compounds have been found which exhibit remarkable foaming, lime soap dispersing, fabric and hard surface detergency, wetting and related surface-active properties. These properties allow the formulation of a variety of synthetic and soap-synthetic combinations.

Primary emphasis is given to the presentation of data on surfactant formulation application studies. Salts of short chain alkyl esters of α-sulfo tallow acid are ideally suited for "combo" soap bar and built heavy-duty detergent applications. Salts of short chain alkyl esters of selected coconut fatty acids are uniquely suitable for light duty liquids, cosmetic and related surfactant applications.

An improved process for the manufacture of these sulfo esters has been developed which produces high yield, high purity and light colored products, and which should provide for their acceptance on a large scale in the detergent field.

Introduction

THE SULFONATION and sulfation of crude oils and fats represents one of the first types of "synthetic" surface-active agents ever developed. This art was practiced as far back as the late 19th century, and the gradual evolution of this sulfonation technology for fats, oils and fatty acids makes it difficult to establish the true originator of long-chain α-sulfo fatty acid derivatives. They appear to have originated in Europe many years ago [England (1) and Germany (2,3)]. Reviews of references to fatty acid sulfonation as well as to processes for their manufacture have been made by Gilbert (4), and Stirton (5).

Ault, Stirton, Weil and Bistline of the Eastern Utilization Research and Development Division of the Department of Agriculture have conducted and published results of extensive studies on the preparation and the surface active and physical properties of pure sulfo acid derivatives based on tallow (5), including the pure sulfo tallow acids (5–12), salts of α-sulfo tallow acids (5,7,12), esters of α-sulfo tallow and pelargonic acids (5,6,13–19), and amides of α-sulfo tallow acids (5,20).

A large number of process patents have appeared in the international patent literature over the last several decades (1,21–40), relating to the sulfonation of oils, fatty acids and the like, but most of the disclosed processes leave much to be desired because of the process complexities, poor yields, high process costs and questionable product quality and purity.

α-Sulfo fatty acid derivatives have not found wide commercial acceptance in the past because of the failure to overcome the afore-cited technological problems of processing, and because of the lack of knowledge concerning their usefulness in detergent formulations.

α-Sulfo palmitic and stearic acids have been promoted as surfactant intermediate raw materials for a number of years (41), but it has only been recently that high quality α-sulfo fatty esters have become commercially available (42–44), due to the development of an improved manufacturing process and extensive application studies by the present authors.

A previous publication by Nussbaum and Knaggs (45) reviewed industry and our company's sulfonation developments, particularly with reference to the development of a continuous SO_3 sulfonation process. This SO_3 sulfonation technology has been successfully applied to the preparation of α-sulfo fatty acid derivatives, with particular emphasis on sulfo-ester derivatives.

Various sulfo fatty acid derivatives have been investigated including sulfo acid salts, esters and amides, but the salts of the short chain alkyl esters of long chain sulfo fatty acids appear to have the greatest overall interest in the surfactant field because: (*a*) they are more water soluble than most of the sulfo acid salts (with the possible exception of certain alkanol-amine salts); (*b*) they can be produced economically; and (*c*) they are excellent detergents and many species are lime soap dispersants allowing their use in a variety of synthetic and soap-synthetic detergent combinations.

While soap was employed almost universally as the major detergent in most cleaning formulations some 20 years ago, its deficiency in hard water with its resultant "tattle-tale grey" deposition problems resulted in the gradual displacement of soap by petroleum-based species, mainly ABS. During the past few years, particularly in Europe, and more recently here in this country, attention has been focused on the contribution of synthetic detergents to water pollution problems, and particularly to the resistance of tetrapropylene derived ABS to biological degradation (44,46,47). The sulfo fatty esters overcome the hard water deficiencies and deposition properties of soaps, are excellent detergents in soft and hard water, and furthermore are readily biodegradable.

It is the purpose of this paper to summarize data we have developed on the biodegradability of α-sulfo fatty ester salts of tallow and coconut fatty acids, and to show how these derivatives can be effectively and economically utilized in the formulation of a wide range of solid and liquid heavy-duty and light-duty biologically soft detergent formulations. Sham-

[1] Presented at the 37th Annual AOCS Meeting, Minneapolis, Minn. Oct. 1, 1963.

TABLE I
Typical Composition

	TMS product		MMS product	
	Paste form	Solid form	Clear liquid form	Paste form
Solids, %	51.4	99.5	34.0	68.0
Sulfo actives, %	45.0	87.5	30.0	60.0
Alcohol insolubles, %	4.9	9.5	3.1	6.2
Unsulfonated matter, %	1.5	3.0	0.9	1.8
Actives/solids ratio, %	87.5	87.5	88.4	88.4
Alcohol			0.0	5.0
Color, % trans. 420 MU Beckman spectrophotometer 10 mm cell	90 [a]	90 [a]	90 [b]	90 [b]

[a] 5% active solution.
[b] 30% active solution.

poos and other specialty formulation studies are also reviewed.

Before proceeding to the formulation and performance studies, it appears desirable to first: (*a*) review and characterize the sulfo esters investigated; (*b*) summarize biodegradability studies; and (*c*) review most significant properties of the sulfo esters including toxicological and irritancy tests.

Experimental Procedures and Data

Sulfo Esters Investigated

The afore-cited new process developed by our research group has been utilized to produce a wide range of sulfo ester salts. The selection of fatty acid sulfonation feed stock, alcohol of esterification and alkali of neutralization provides extreme flexibility in the design of surfactant molecules for specific applications.

For the purposes of brevity in the ensuing presentation and tables the specific α-sulfo ester salt will be frequently referred to by the combination of letter abbreviations for the fatty radical, ester group, and salts in that order. Thus, α-sulfo hydrogenated tallow methyl ester, sodium salt will be referred to as TMS, and so forth.

Greatest emphasis is placed on the methyl ester of α-fatty acids in preference to other alkyl esters because they are most economical and easiest to manufacture, and for most applications they exhibit superior functionality.

Table I presents typical composition and available physical forms of α-sulfo tallow methyl ester sodium salt (TMS) and α-sulfo myristic methyl ester sodium salt (MMS) capable of being produced by this process.

The properties and formulations of the other sulfo esters used in this study were of the composition equivalent to those shown in Table II.

Biodegradability Studies

The results of some typical river die-away tests are assembled in Figure 1 for a number of surfactant species. These tests were run simultaneously from the same river sampling (Des Plaines River, north of Chicago, 5,000 plate count), seeding with 20 ppm surfactant and aging at 25C aerobically in

TABLE II
Saponification of Esters at 100C—1 Hour

Ester	% breakdown pH 9.7	% breakdown pH 11.0
Methyl palmitate	100.0	100.0
Na-2 sulfo ethyl oleate	62.3	89.7
TMS	0.2	2.1
Di-sodium 2-sulfo ethyl α-sulfo palmitate	8.3	41.2
Na Monoglyceryl ester α-sulfo palmitate	8.8	44.4
Na Monoethylene glycol ester α-sulfo palmitate	4.6	43.9

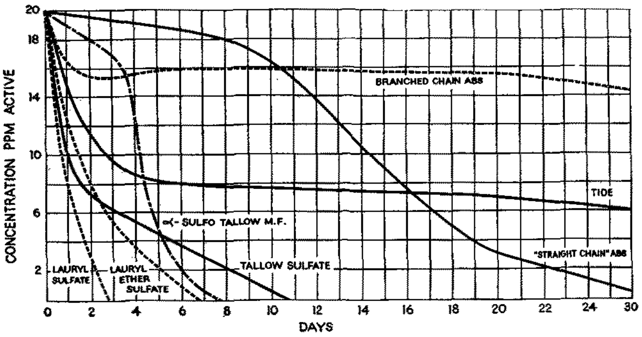

FIG. 1. River die-away test for detergent biodegradability.

the absence of direct sunlight and using the methylene blue test (48). It will be readily observed that the α-sulfo tallow methyl ester salt exhibits a more rapid disappearance curve than both branched and straight chain ABS.

Since the α-sulfo fatty esters are devoid of any aromatic nucleus, they exhibit biodegradability characteristics approximating those for straight chain alkyl sulfates of corresponding molecular weight.

Biological softness of these sulfo esters was further demonstrated by Warburg and activated sludge tests. In the latter study, a laboratory scale activated sludge sewage treatment unit was employed, seeding the unit with activated sludge from a municipal treatment plant.

The detergent and nutrient broth were fed into the unit, and the mixture continuously aerated. Using a 25 ppm anionic feed stock, the α-sulfo tallow methyl ester (TMS) was found to have disappeared completely based on the methylene blue test.

More extensive studies on the biodegradability of sulfo esters has been assembled and reported previously by our research group (42,43).

The foregoing results established the α-sulfo fatty esters as relatively "soft" detergents. Stirton's group (Department of Agriculture) (49), Wayman's group (Department of Interior) (50), and others have confirmed these results.

In passing, it is of more than considerable interest that recent preliminary studies which we have conducted on river die-away type tests using a continuous oxygen free nitrogen purge on the river water has indicated that these same α-sulfo esters exhibit anerobic disappearance curves approximating those of aerobic media. Further studies are underway and are required before final conclusions can be drawn.

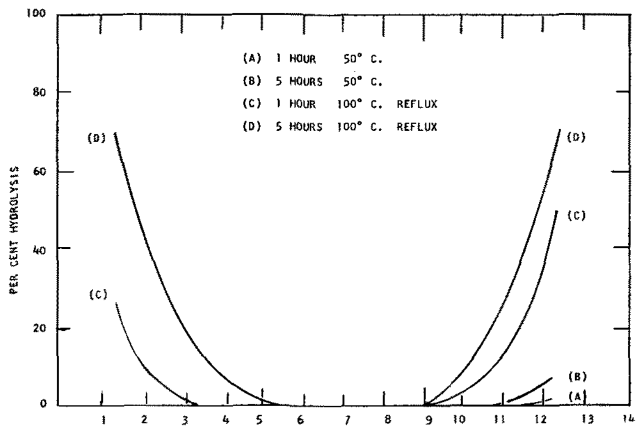

FIG. 2. Hydrolytic stability curves for 1% solutions of bioterge MMS.

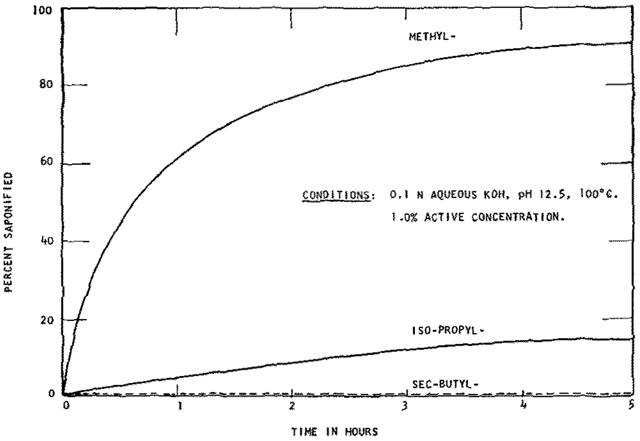

FIG. 3. Saponification curves for Na salts of various alkyl esters of α-sulfo tallowate.

Ester Stability

Esters of α-sulfo fatty acids are significantly more stable than simple esters due to the remarkable stabilizing action of the adjacent sulfo groups, probably reflecting steric hindrance. Stirton and co-workers have reported hydrolysis rate constants on a number of pure esters (5,6,12,14,15).

Figure 3 is a plot of the data on a highly purified sodium α-sulfo tallow methyl ester which was subjected to various alkaline and acidic hydrolysis conditions for 1% active solutions. Sulfuric acid or NaOH were used and appropriately buffered to stabilize pH during these tests. These and comparative data on other esters are illustrated in Figures 3 and 4.

It will be observed that the sulfo tallow methyl ester is quite stable in the pH range of 5 to 10 even under vigorous boiling conditions. On the other hand it is observed that the isopropyl and secondary butyl esters are even more stable and are recommended for applications involving extreme pH conditions.

Table II assembles further comparative saponification data for a number of other esters and sulfo esters.

Table II clearly confirms the stabilizing influence of the sulfo group adjacent to the ester linkage.

Foaming Properties

Table III assembles comparative Ross Miles Foam heights for 0.1% active surfactant concentration in waters ranging from 0 to 1000 ppm hardness.

Inspection of the data reveals that the TMS and TMT species are moderate foamers, whereas the MMS, MMA, MMM, MMT and MMD species are high foamers. It is of special interest to note that foam heights of the sulfo myristate species are quite high over the entire 0 to 1000 ppm range of water hardness.

Synergistic foaming properties are exhibited between blends of sodium lauryl sulfate (SLS), the TEA and magnesium salts, and the sulfo myristic methyl esters (MMS, MMT, etc.).

Ross Miles Foam data at 0.05% and 0.01% actives concentration also shows the sulfo myristic esters to be much more effective than most conventional surfactants.

Some comparative Ross Miles Foam results at 0.01% actives concentration are shown graphically in Figure 5.

TABLE III

Ross Miles Foam Heights
0.1% Active—25C

Product	Initial Foam, MM				
	0 ppm	35 ppm	140 ppm	350 ppm	1000 ppm
ABS (Na) B.C.[a]	172	185	170	175	123
ABS (Na) S.C.[b]	179	179	178	144	112
SLS (Na lauryl sulfate)	186	76	81	74	30
SLES (Na lauryl ether sulfate)	183	180	175	175	154
CES (Na coconut ether sulfate)	150	149	148	145	143
MMS	159	175	180	175	159
HWC-MS	147	150	148	150	131
TMS	137	135	80	48	30
TMT	135	123	90	62	26
MMT	150	172	171	155	152
LMS	150	172	171	155	152
SLS-MMS[c]	166	165	173	170	171
MgLS (Mg lauryl sulfate)-MMS[c]	168	167	172	175	170
MMM	171	138	159	172	168
MMA	170	180	175	180	170
MMD	160	163	171	172	165

[a] Branch chain (B.C.).
[b] Straight chain (S.C.).
[c] 50:50 blends.

Wetting Properties

Comparative Draves Wetting Test results are plotted in Figure 6, where it will be observed that MMS is an outstanding wetting agent particularly at low concentrations. In tap water MMS exhibits a Draves Wetting time of 5.5 seconds at 0.1% active concentration.

Table IV assembles further Draves Wetting results which demonstrate synergistic wetting action of the sulfo ester (MMS) in combination with soap or lauryl sulfate (SLS).

Lime Soap Dispersing Properties

Table V assembles comparative lime soap dispersant properties of sodium N-menthyl N-tallow acid taurate and a series of tallow and coconut sulfo esters using a Modified Borghetty Method (42).

It is of interest to note that salts of α-sulfo methyl palmitate exhibits optimum lime soap dispersant properties of the sulfo esters studied.

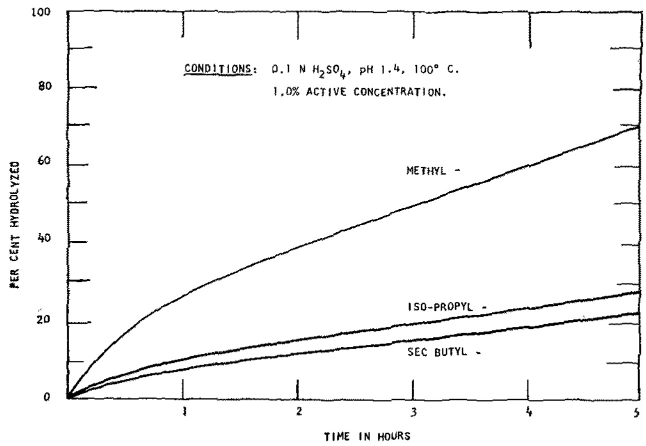

FIG. 4. Acid-hydrolytic stability curves for various alkyl esters of Na α-sulfo tallowate.

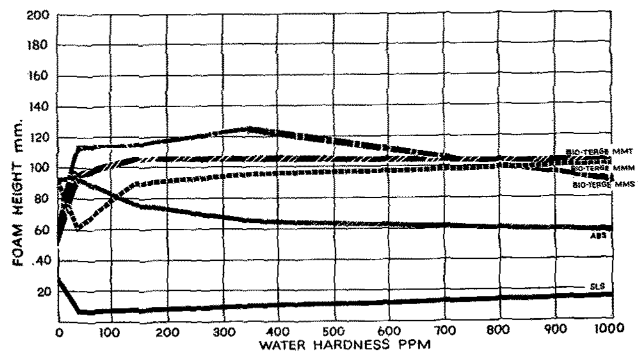

FIG. 5. Ross Milles foam heights (initial) at 25C with varying water hardness 0.01% active concentration.

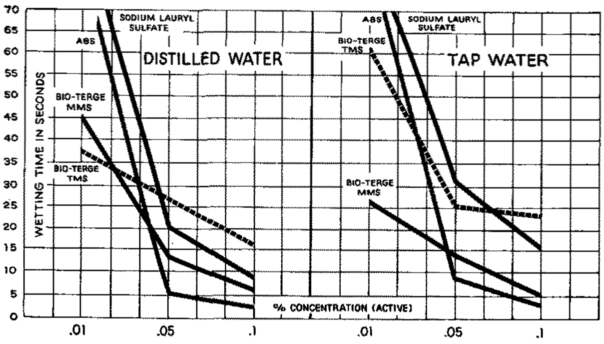

FIG. 6. Draves wetting test at 25C.

Both the palmitic and myristic homologues show quite favorable LSD performance properties compared to the tallow taurate species.

Somewhat surprisingly, the calcium and magnesium salts as well as the sodium and potassium sulfo tallow and myristic methyl esters exhibit excellent LSD properties.

The excellent LSD properties of some of these sulfo esters suggests their use for a wide number of soap-synthetic detergent formulations, including "combo" bar soaps, heavy duty formulations, shampoos, etc.

Toxicological and Irritancy Properties

Preliminary work conducted at the Department of Agriculture and reported by Weil (49) indicates that pure α-sulfo fatty esters including those types under present discussion exhibit lower acute oral toxicity than ABS based on rat feeding experiments. LD_{50} values in excess of 3.0 g/kg were reported for the pure sulfo esters of short chain alcohols based on tallow and coconut. At the 3.0 g/kg feeding level no animals had died, and this level was the maximum tested due to reported limitations in introducing the sulfo ester into the animals' stomachs.

Primary skin irritation properties have been preliminarily evaluated (51) applying some of the sulfo esters derived from our process to rabbit skin. The results indicate they are milder than most cosmetic and detergent species.

A number of salts of α-sulfo methyl myristate have been evaluated for eye irritation properties according to the Draize Method (52).

Preliminary screening tests run on the sodium and alkanolamine salts all fell within the nonirritating to mildly irritating classification following the technique and scoring recommended by Draize (52).

The DEA salt (MMD) was more extensively evaluated at 12% active concentration, and was classified as nonirritating at a pH range of 6 to 7. In these tests no irideal or corneal irritation or damage was observable after one hour of application. Moderate initial conjunctivities cleared up completely within the 7-day observation period, and in most instances much sooner.

TABLE IV

Synergistic Wetting of MMS in Draves Wetting Test
Concentration—0.1% Active

Detergent	Water: tap (140 ppm)
	Temperature: 25C
	Wetting time in seconds
A. MMS	5.5
B. Sodium lauryl sulfate	17.0
C. Potassium cocoate	35.5
D. 60% MMS—40% coco soap	7.4
E. 65% MMS—45% SLS	6.6

TABLE V

Comparison of Lime Soap Dispersant Properties
Modified Borghetty Method [a]
(80% Tallow—20% Coconut Soap)

Specie	% L.S.D.
Na N-methyl N-tallow acid taurate	30
HWC-MS (α-sulfo hydrogenated whole coconut—methyl ester, Na)	>50
LMS (α-sulfo methyl laurate, Na)	>50
MMS (α-sulfo methyl myristate, Na)	30
MMK (α-sulfo methyl myristate, K)	30
PMS (α-sulfo methyl palmitate, Na)	25–30
PPS (α-sulfo iso-propyl palmitate, Na)	25–30
SMS (α-sulfo methyl stearate, Na)	40
SMK (α-sulfo methyl stearate, K)	40
Tallow MS (α-sulfo methyl tallowate, Na)	30
Tallow MK (α-sulfo methyl tallowate, K)	30
Tallow MC (α-sulfo methyl tallowate, Ca)	30
Tallow MM (α-sulfo methyl tallowate, Mg)	30

[a] Reference 42 describes method.

Heavy-Duty Detergent Studies

The literature contains reference to some laboratory results for a number of "unbuilt" sulfo esters (17), but none for "built" systems.

Table VI presents laboratory Terg-o-tometer detergency and redeposition results for a number of "built" heavy duty formulations containing various sulfo ester salts as the main organic detergent. Also included are 50:50 blends of sulfo ester and 80:20 tallow-coco soap.

It will be observed that the sodium, calcium, magnesium salts of α-sulfo tallow methyl, isopropyl and sec-butyl esters all show good detergency and antiredeposition properties.

Of even greater significance from an economic point of view, is the observation that 50:50 blends of these sulfo esters and soap also exhibit good detergency and antiredeposition properties.

To determine whether appreciable lime soap curd might be deposited on cotton during the wash cycle,

TABLE VI

Terg-o-tometer Cotton Detergency Tests [a]

Detergent	% Conc.	% Soil removal			Redeposition		
		ppm			ppm		
		35	140	350	35	140	350
1. TMS	0.1	31.6	27.4	27.9	+0.5	−0.8	−1.3
2. MMS	0.1	24.7	24.4	17.6	−0.1	−1.7	−2.0
3. TMC	0.1	32.6	......	26.3	0.0	....	−1.0
4. TMM	0.1	31.2	.....	21.3	+0.9	....	−1.8
5. TBS	0.1	27.5	......	22.8	+0.6	....	−0.2
6. TPS	0.1	29.0	......	23.4	+0.7	....	0.0
7. ABS	0.1	28.7	24	21	+0.2	−1.2	−0.6
8. TMS/soap [b]	0.1	36.0	25.4	19.2	−0.5	....	−1.3
9. MMS/soap [b]	0.1	35.1	25.3	13.7	−1.8	−0.9	−3.5
10. TMC/soap [b]	0.1	33.6	......	17.2	+0.1		−0.5
11. TMM/soap [b]	0.1	34.3	......	17.1	−0.2		−1.4
12. TBK/soap [b]	0.1	36.1		21.9	+0.4		+0.4
13. TPK/soap [b]	0.1	36.6		21.4	+0.8		0.0

Formula: 20% organic detergent (including 1.5% LIPA), 45% STPP, 4.5% silicate, 0.8% CMC, 19.7% Na_2SO_4, 10% H_2O, 0.05% brightener.
[a] 30 min at 120F, 100 rpm test fabric soiled swatch.
[b] 50:50 blend.

TABLE VII

Soap Curd Deposit on Cloth During Washing

1. Soap (80% tallow, 20% coco)	1845
2. TMS	30
3. Formula SP II (1:1 ratio soap—TMS)	95
4. 2 Soap:1 TMS	105

cotton swatches were washed in the Terg-o-tometer using the laboratory procedure of Knowles (53) involving the use of 0.5% detergent in 360 ppm wash water and subsequent wash rinses.

These results are assembled in Table VII, where it will be observed that 1:1 and 2:1 ratios of soap: TMS in built systems do not show high deposition values.

To provide substantiation to our laboratory detergency studies, washing machine tests were conducted in our laboratory as well as machine tests in a home panel study and at a laundromat.

Two heavy-duty formulations were spray dried for use in this study, and their general compositions are shown in Table VIII and designated SP I and SP II. The major organic surfactant in SP I was TMS, whereas in SP II it was a 50:50 blend of TMS and soap.

Results of comparative machine tests run in our laboratory are shown in Table IX, where SP I and SP II exhibited detergency results quite comparable to a leading commercial detergent.

In a home panel test involving 33 families employing and comparing SP II and their regular detergent, the results again show formula SP II to be comparable to present day commercial products. The composite score for the average reflectance increase using the commercial laundry detergent was 14.90% whereas SP II had a 14.93% average increase.

The same panel also ran a clean white cloth through five washday cycles comparing SP II and their regular product. These results show SP II to have a significant edge on antiredeposition. SP II had only an 0.5% loss in reflectance compared to the commercial detergent with a 2.5% decrease.

Extensive laundromat studies also add confirmation to the laboratory and machine panel studies already reported. The general consensus on reviewing questionaires from this study was that SP II was at least equal to their regular product, and many commented that their clothes felt softer. Formula SP II was rated as a moderate foamer.

Further machine testing was conducted on washing and drying a series of wash cloths, carbon swatches and white-unsoiled cotton along with a load of soiled bath towels.

This study was devised to determine detergency, lime soap deposition and yellowness build-up and included 10 wash and dry cycles.

These results are assembled in Table X. It will be observed that SP II again exhibited good detergency, low "yellowness" build-up, and did not show significant lime soap curd deposits.

TABLE VIII

Spray Dried Laundry Detergents

Formulation	SP I	SP II
1. Sodium tripolyphosphate, ANH., %	45.0	45.0
2. Sodium sulfate, %	16.4	16.4
3. Silicate (1 Na_2O:2.4 SiO_2), %	4.5	4.5
4. CMC, %	0.8	0.8
5. Optical brightener, %	0.05	0.05
6. TMS (actives), %	17.7	8.85
7. Soap (tallow), %	0.0	8.85
8. Lauric isopropanolamide, %	1.5	1.5
9. Moisture (retained), %	10.0	10.0
Total organics, %	20.0	20.0

TABLE IX

Washing Machine Detergency Tests

Soil	0.025% Bandy black clay
Water	Lake Michigan tap (140 ppm) 130F
Test cloths	Test fabric carbon soil
Load	12 Clean bath towels

Detergent	% Conc. (Solids)	% Detergency (3 Run average)
Commercial Product A	0.15	19.1
Formulation SP I	0.15	18.2
Formulation SP II	0.15	19.8
Commercial Product A	0.10	15.8
Formulation SP I	0.10	16.0
Formulation SP II	0.10	15.6

Thus laboratory, machine tests, home panel and laundromat studies all show formulation SP II (sulfo ester and soap blend) to be an excellent laundry product.

Light Duty Detergent Formulations

The outstanding detergent, wetting and foaming properties over a wide range of water hardness, makes the sulfo ester salts based on myristic and coconut fatty acids ideally suited for use in a variety of light duty biodegradable detergent formulations.

These sulfo esters also contribute synergistic wetting foaming, grease removal and emulsification properties when properly blended with other surfactants.

In light duty liquid detergent systems the sodium, magnesium and ammonium salts of α-sulfo methyl myristate and cocoate appear to be of greatest interest, although some of the alkanolamine salts being more soluble may find special application even though somewhat more expensive.

The sulfo methyl coconut salts in many aspects are similar to the coconut alcohol sulfates, particularly with regard to solubility, fine creamy-like stable bubble quality, and general response to foam boosters and stabilizers.

Extensive formulation and application studies have been conducted on a number of light-duty formulations. Unfortunately time permits only a brief summary.

Dishwashing tests were conducted using the classical manual laboratory dishwashing test of Mayhew (55), recording the number of soiled dishes to break the foam layer initially generated.

Performance results of a number of the more outstanding formulations are assembled in Table XI,

TABLE X

Washing Machine Tests [a]
0.15% Built Detergent, 140F Water
(Sears Lady Kenmore Automatic-Model 800)
1–10 Wash and Dry Cycles

Formulation		SP II	Built ABS	Built ABS/TAS
Total organic content		20%	26%	20%
Cotton detergency [b]				
1-cycle	140 ppm	35.6	20.6	28.5
	350 ppm	21.3	27.2	17.0
Cotton yellowing [c]				
10-cycles	140 ppm	3.9	4.5	3.6
(NBS units)	350 ppm	6.0	6.8	6.9
Lime soap deposit [d]				
10-cycles	140 ppm	65	60	30
	350 ppm	45	38	38
Foaming rating				
	140 ppm	Moderate	Moderate	High
	350 ppm	Moderate	Very high	High

[a] Soil load 12 bath towels (8 lb) soiled by immersion in 0.05% bandy black clay, wrung "dry."
[b] Test fabric soiled swatch.
[c] Tri-stimulus colorimetry. National Bureau of Standards circular C-429.
[d] LSD method, JAOCS, 4/52, p. 158–161 (54).

TABLE XI
Dishwashing Performance

	Formulation:	Conc. %	Dish End Point ppm 8	35	140	350
A	Commercial det.	0.04	7	12	13	13
B	MMS	0.04			11	10
C	MMS	0.02			7	7
D	80% MMS—20% L-DEA	0.02			8	
E	80% MMS—20% L-MEA	0.025	7	9	14	12
F	80% MMS—20% L-MEA—2 E.O.	0.025	9	12	14	11
1.	65% B.C.—ABS—25% B.C.—NPES 10% L-DEA	0.04	7	12	13	12
2.	65% S.C.—ABS—25% MMS 10% L-MEA	0.035	8	11	13	12
3.	65% S.C.—ABS—25% MMS 10% L-MEA—2 E.O.	0.035	8	11	13	12
4.	65% S.C.—ABS—25% MMM 10% L-MEA—2 E.O.	0.035	10	12	14	12

utilizing only biodegradable species.

Formulation A compares the dishwashing performance of a present day high quality liquid detergent based on biologically "hard" anionics with a number of biologically soft detergents formulated with high proportions of sulfo esters (B, C, D, E, F).

It will be noted that the superior efficacy of the sulfo esters when formulated with the proper foam booster allows their use at 50–60% of the concentration of commercial detergent formulations.

Formulation 1 compares the performance of a classical present day dishwashing formulation comprising 65% branched chain ABS, 25% branched chain nonyl phenol polyethoxy ethyl ammonium sulfate, 10% lauric diethanolamide with a number of formulations based on straight chain ABS (2–4).

It will be observed that the myristic sulfo esters function excellently in the straight chain ABS-amide system, contributing to improved detergency, grease removal and grease emulsificaton. The observed effectiveness of these sulfo esters particularly in light duty application is due to their superior wetting and foaming performance at the low concentration of 0.02 to 0.04%.

Extensive light duty formulation studies underline the importance of "tailoring" the foam stabilizer system to the other components in order to achieve optimum performance.

The most suitable solvent and/or hydrotrope system to insure adequate cloud point properties for these light-duty formulations is dependent on the salt content of the ABS, the selection of cations for the ABS and sulfo ester, and the physical characteristics of the foam stabilizer. In general, the sulfo esters appear to formulate easier than present day "hard" species.

The excellent performance and efficiency obtained using these formulations containing the prescribed sulfo esters provides biodegradable products with projected costs equivalent or lower than present day "hard" formulations.

Shampoos and Specialties

The exceptional cleansing and foaming properties of the sodium, DEA and TEA salts of α-sulfo methyl myristate together with their extreme mildness make them ideal detergents for hair shampoos.

Ross Miles Foam results already presented clearly demonstrate the markedly superior foam properties of MMS and homologues over sodium lauryl sulfate commonly used in shampoos.

Synergistic-foaming properties of MMS suggests a number of high-foaming shampoo applications.

The effectiveness of MMS and homologues as lime soap dispersants also suggests the formulation of combinations with soap where economy is important.

The broad pH stability range of the sulfo esters, particularly on the lower side allows their formulation at the pH of skin to help insure maximum mildness and to insure greater fastness properties to dyed hair.

REFERENCES

1. Levinstein, I., Brit. 16,577 (1913).
2. Gunther, F., U.S. Department of Commerce, O. T. S. Report, PB 30,081 (1932).
3. Gunther, F., and J. Hetter (to I. G. Farben Industrie A. G.) U.S. 1,926,442 (Sept. 12, 1933).
4. Gilbert, E. E., "The Reactions of Sulfur Trioxide and Its Adducts" Allied Chemical & Dye Corporation, Morristown, Pa., 1962.
5. Stirton, A. J., JAOCS *39*, 490–496 (1962).
6. Stirton, A. J., J. K. Weil, and R. Bistline, JAOCS *31*, 13–16 (1954).
7. Weil, J. K., R. G. Bistline and A. J. Stirton, "Organic Synth.sis," Vol. 36, John Wiley and Sons, New York, 1956, pp. 83–86.
8. Weil, J. K., R. G. Bistline and A. J. Stirton, JAOCS *34*, 100–103 (1957).
9. Weil, J. K., A. J. Stirton, E. W. Maurer, W. C. Ault and W. E. Palm, JAOCS *35*, 461–465 (1958).
10. Weil, J. K., A. J. Stirton, R. Bistline and W. Ault, JAOCS *37*, 679–682 (1960).
11. Weil, J. K., A. J. Stirton and E. W. Maurer (to the Secretary of Agriculture) U.S. 2,867,586 (1959).
12. Stirton, A. J., J. K. Weil and E. W. Maurer (to the Secretary of Agriculture) U.S. 2,915,473 (1959).
13. Weil, J. K., R. Bistline and A. J. Stirton, JAOCS *32*, 370–372 (1955).
14. Weil, J. K., G. Bistline, A. J. Stirton, J. Am. Chem. Soc. *75*, 4859 (1953).
15. Bistline, R., A. J. Stirton, J. K. Weil and W. S. Port, JAOCS *33*, 44–45 (1956).
16. Stirton, A. J., R. Bistline, J. K. Weil and W. Ault, JAOCS *39*, 55–58 (1962).
17. Stirton, A. J., R. Bistline, J. Weil, W. Ault and E. Maurer, JAOCS *39*, 128–131 (1962).
18. Weil, J. K., A. J. Stirton and R. Bistline, JAOCS *37*, 295–297 (1960).
19. Weil, J. K., and A. J. Stirton (to Secretary of Agriculture) U.S. 2,806,044 (1957).
20. Weil, J. K., A. J. Stirton and R. Bistline, JAOCS *37*, 295–297 (1960).
21. Flesch, C. (to Farb-Und Gerbstoffwerke), Brit. 284,206 (1927).
22. I. G. Farbenind, A. G., Brit. 288,127 (1927).
23. Bohme, H. T. (to Chemische Fabrik), Fr. 637,338 (1927).
24. Stockhausen, H., F. Schlotterbeck, C. Cremer and A. Hecking, Can. 285,772 (1928).
25. I. G. Farbenind A. G., Brit. 288,612 (1926).
26. Chemische Farbriek Servo and M. D. Rozenbroek (to N. V. Chem. Fabr.), Brit. 312,283 (1928).
27. Bertsch, H. (to H. T. Bohme), U.S. 1,801,189 (1931).
28. Bohme, A. G., Fr. 701,187 (1930).
29. Bohme, A. G., Brit. 351,013 (1929).
30. Johnson, J. Y. (to I. G. Farbenindustrie A. G.), Brit. 377,249 (1924).
31. Chemische Fabriek Servo and M. D. Rozenbroeck (to N. V. Chem Fabr), Dutch 30,316 (1932).
32. Horwitz, A., U.S. 1,939,169 (1933).
33. Moyer, W. (to Solvay Process Company), U.S. 2,195,186; 2,195,-187; 2,195,188 (1940).
34. Datin, R. C., and D. C. Bardwell (to Solvay Process Company), U.S. 2,324,199 (1939).
35. I. G. Farbenindustrie A. G., Ger. 583,686 (1933); 591,196 (1934); 642,414 (1937); 717,384 (1942).
36. I. G. Farbenindustrie A. G., Fr. 645,819 (1928).
37. N. V. Chemische Fabriek Servo and M. D. Rozenbroek, Fr. 688.637 (1930).
38. Societe Des Laboratories de Recherches Pour Applications Industrielles, Fr. 984,456 (1951).
39. Crittenden, E. D. (to Solvay Process Company), U.S. 2,195,145 (1940).
40. Crowder, J. A. (to Solvay Process Company), U.S. 2,268,443 (1941).
41. Armour Industrial Chemical Company, Technical Bulletin G-7 (1956).
42. Stepan Chemical Company, Technical Bulletins I-G & II-G: "Biodegradable Detergent Developments" Dec. 5, 1962 and May 15, 1963.
43. Stepan Chemical Company, Technical Bulletin: "Light Duty Biodegradable Detergent Studies" August 1, 1963.
44. Chem. Eng. News, *41*(11), 102–114 (1963).
45. Knaggs, E. A. and M. Nussbaum, Soap Chem. Specialties, May, June and July (1962).
46. "Synthetic Detergents in Perspective" The Soap & Detergent Association publication, 39 pages, 1962 (New York, New York).
47. Speel, H. C., JAOCS *40*, 4, 12–13, 15 (1963).
48. Standard Methods for the Examination of Water & Waste Water, American Public Health Assoc., 11th Edition, p. 246–251.
49. Weil, J. K., and A. J. Stirton, JAOCS *41*, 355–358 (1964).
50. Wayman, C. H., "Biodegradation of Surfactants Under AEROBIC and ANOEROBIC Conditions" Paper presented at the New York A.C.S. Meeting, September 10, 1963.
51. Code of the Federal Regulations, Part 191, Title 21, Reprinted from Federal Register of Aug. 12, 1961; 26 F.R. 7333.
52. Draize, J. H., G. Woodward and H. O. Calvery, J. Pharmacol. Exp. Ther. *82*, p. 377 (1944).
53. Knowles, J., J. Berch and M. Schwartz, JAOCS *29*, 158–161 (1952).
54. "Tristimulus Colorimetry," National Bureau of Standards Circular C-429.
55. Mayhew, R. L., C. F. Jelinek and A. Stefcik, Soap Chem. Specialties, *31*(7), 37 (1955).

[Received January 29, 1965—Accepted March 8, 1965]