New Polymeric Surfactants from Butadiene, Urea and Sulfuric Acid

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Abstract

Butadiene, urea, and sulfuric acid react to form a new sulfated polymer. The sodium salt of the polymer, called BUS, is a good detergent and dispersant; it is practically nontoxic and nonirritating. BUS-soap blends are good detergents for use in hard water. BUS can be precipitated from waste water by heavy metal salts and can be removed by percolation through soil.

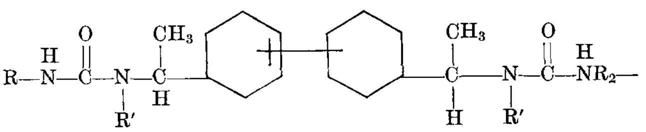
Introduction

Tertiary alcohols and t-olefins react with urea in concentrated sulfuric acid to form N-t-alkylureas and N,N′-di-t-alkylureas (1,2). For example, isobutylene reacts to form N-t-butylurea and N,N′-di-t-butylurea. Nontertiary olefins, such as propylene, 2-butene, and cyclohexene, do not react with urea-sulfuric acid.

Isoprene has one tertiary olefinic group conjugated with a nontertiary olefinic group. If isoprene reacted as a tertiary olefin according to expectations, the product should be t-pentenylurea or, more likely, a polymer containing t-pentenyl units pendant to the chain. When isoprene is added to urea-sulfuric acid, it reacts to form a polymer but not the one expected. The polymer contains few $-NH_2$ groups and therefore few pendant urea groups, some sulfate mono ester groups, olefinic bonds. In addition, infrared analysis shows that the nontertiary olefinic bond of isoprene reacts with urea. Thus a nontertiary conjugated double bond can react with urea. Butadiene, with two nontertiary double bonds, also reacts with urea-sulfuric acid. The polymeric product, isolated as the sodium salt (called BUS), was evaluated as a surface-active agent in a series of screening tests. The structure of BUS and some of its properties are discussed.

Experimental

Preparation of BUS. In a typical reaction the butadiene, C.P., 0.75 moles, was metered into a vigorously stirred mixture of urea, 0.25 moles, 96% sulfuric acid, 0.375 moles, and methylene chloride, 210 ml, during three hours at 15–20C. The mixture was post-stirred for 15 min, then 50 ml of water were added at 20C. The stirrer was stopped, and the layers were separated. The lower clear, colorless, aqueous phase was discarded. The upper organic phase, dark purple and cloudy, was washed twice with 100 ml of water and then neutralized by adding solid sodium bicarbonate. At the neutral point the viscous solution became light yellow. The product BUS was recovered by distilling off the methylene chloride. Weight of BUS corresponded to 50 wt percent conversion of butadiene and urea charged (3).



R = butenyl and $C—\overset{OSO_3—}{\overset{|}{C}}—C—C—$, $CH_3—$, t-butyl, H
R_2 = another polymer unit
R' = H

FIG. 1. Structure of butadiene-urea polymers.

Surface Tension. Measurements were made on a Wilhelmy Tensiometer at 25 ± 0.1C.

Foam Tests. Solutions in 100 ml-stoppered graduate cylinders were shaken vigorously 10 times by hand, and foam volume was recorded at intervals. Foam tests were also run by the ASTM-D-1173-53 procedure.

Detergency Tests. Standard detergency tests were run in a Baker Terg-O-Tometer at 120F and 60 rpm, using American Conditioning House No. 119 soiled cloth. Swatches after washing were dried at 185F for one hour, followed by conditioning 16–24 hours in a constant temperature and humidity room (75F, 40% R.H.) before reflectance measurements were run. Original swatches (before washing) were conditioned in the C.T. room before measuring reflectance.

Four swatches (4 × 4 in.) in the preheated detergent (one liter volume), were washed for 15 min, followed by two separate 3-min rinses. The rinses contained the same hardness as the wash bath.

$$\%\ \text{Increase in reflectance} = \frac{\text{washed swatch R-original R}}{\text{original R}} \times 100$$

where R = reflectance of swatch

Inorganic Ion Tolerance. The Hart method (5) was used. "Standard 0.5% solution of $CaCl_2$ is run from a burette into 100 ml of various percentages of the wetting agent in a 400-ml beaker. The mixture is stirred during the addition. When turbidity appears, enough distilled water is added to bring the volume to within 10–15 ml of a 200-ml mark on the

TABLE I

Product from Reaction of Butadiene with Urea · H_2SO_4 in Cyclohexane · Calcium Salt

Analyses		Average composition per urea	
% C	60.44	C_4 from butadiene	: 5.7
% H	9.18	$—OSO_3^-$	: 0.67
% N	6.24	Ca	: 0.33
% S	4.73	C=C	: 2
→ % Ca	2.83	"H_2O"	: 2
% O	16.59	I.R.	
I_2#	114	$—\overset{O}{\overset{\|\|}{C}}—NH_2$, $\overset{O}{\overset{\|\|}{C}}—NHR$, no $\overset{O}{\overset{\|\|}{C}}—NR_2$	
AN	16		
Empirical formula $C_{71}H_{129}N_6S_2O_{15}Ca$		Internal C=C > terminal C=C	

TABLE II

Foaming Test, ASTM-D-1173-53

% Conc. built detergent	Foam height in mm. at 120F			
	ABS		BUS	
	0 Min	5 Min	0 Min	5 Min
0.01	50	18	23	15
0.05	140	130	58	37
0.10	160	157	74	58
0.15	171	173	74	56
0.20	176	178	82	55
0.25	185	188	82	55
0.30	188	190	88	59

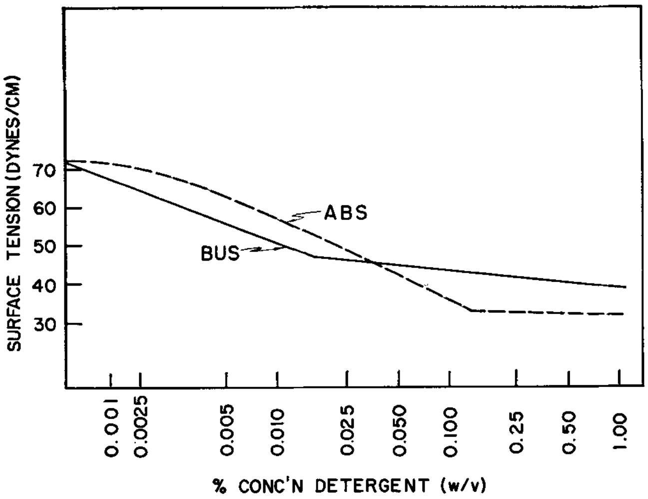


FIG. 2. Surface tension in distilled water at 25C.

beaker. Water and $CaCl_2$ solution are added alternately until the mixture becomes just sufficiently turbid to prevent newsprint (fastened by means of a rubber band to the beaker) from being legible."

Lime-Soap Dispersion Test. The I.G. Farben test (6) was employed. Various amounts of dispersant are added to a solution of sodium oleate. The dispersant-sodium oleate solution is added to 200 ppm hard water. The minimum amount of dispersant necessary to prevent precipitation is determined. A "Lime-Soap Dispersing Value" of one means one gram of dispersant keeps 7.6 grams of lime soap dispersed in a large excess of 200 ppm hard water.

Yellowing Test. A simple test was devised to see if BUS-soap blends would cause yellowing or "tattle-tale gray" when used for repeated washings. Unsized, bleached, scoured, white cotton cloth was cut into 4-in. squares, dried at 85C for one hour in a forced air oven to simulate conditions in a clothes dryer, and then the Yellowness Index was determined.

$$\text{Y.I.} = \frac{\text{amber reflectance} - \text{blue reflectance}}{\text{green reflectance}}$$

Four squares were washed in 200 ppm hard water with 0.25% soap blend in the Terg-O-Tometer and were rinsed twice. Squares were dried at 85C for one hour and pressed with a household iron set for "cotton" (250C), using four passes of 1–2 seconds duration on each side. Y.I. was again measured. This cycle was repeated seven times.

Toxicity and Irritation Index. Acute oral toxicity in mice was determined according to the method of Weil (7) and of Litchfield and Wilcoxon (8). The category of compounds was judged according to the terminology of Hodge and Sterner (9).

Determination of irritation to rabbit skin and eyes was done by the procedure outlined in "Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics" (10). A 60% aqueous solution of the detergent was used. Interpretation of scoring of irritation to the eyes was made by the terminology of Kay and Calandra (11).

TABLE III

Foaming Tests wtih BUS and BUS-Alkanolamine Sulfate (100-ml Stoppered Graduate)

Concentration wt.		Foam volume, ml.		
BUS	TAS	0 Min	5 Min	20 Min
0.1	0	31	27	25
0.1	0.01	48	42	40
0.1[a]	0	33	12	5
0.1[a]	0.01	48	38	22

[a] Built detergent: BUS, 15%; STPP, 39%; Metso, 10%; sodium carbonate, 39%; NaCMC, 1%.

[b] TAS is a trialkanolamine sulfate (Pilot's TAS-50). Metso is Philadelphia Quartz Company's sodium metasilicate.

Results and Discussion

Properties and Structure of BUS

The sulfate mono ester groups of butadiene-urea polymer can be neutralized by any base. Since the calcium salt is not soluble in water and is more readily purified than the sodium salt, some calcium salts were made for analysis. Results of analyses and the calculated composition of a calcium salt are shown in Table I. It will be noted that there are only two olefinic groups per urea but an average of 5.7 C_4 units from butadiene. This means part of the polymerization reaction consumes more double bonds than cationic polymerization can.

For surfactant studies, butadiene-urea-sulfate polymers were isolated as sodium salts. The light-tan sodium salt, BUS, of about 2,000 average molecular weight, melts at 110–130C and is soluble in water, methanol, methylene chloride-methanol (10:1 to 1:10), pyridine, and other polar solvents.

Monomeric ureas are easily hydrolyzed by acid or by base, but BUS is remarkably stable to hydrolysis. It is not appreciably hydrolyzed by boiling aqueous KOH, boiling 50% sulfuric acid, boiling 60% phosphoric acid, or by KOH in glycol at 160C. A few terminal groups are removed by these treatments, but the polymer is not generally decomposed. This unexpected hydrolytic stability was a handicap in structure studies but, by trying increasingly severe conditions, it was found that BUS decomposed completely when fused with 85% KOH at 300–350C. Figure I shows a reasonable structure of BUS, deduced from a study of the amines formed by KOH fusion and from the observed effect of reaction variables. It will be noted that R can be t-butyl if a mixture of butadiene and isobutylene (called BIUS; mole ratio given before name) is reacted with urea-H_2SO_4. Co-reaction of butadiene and other tertiary olefins with urea-H_2SO_4 gives copolymers which are soluble in nonpolar solvents such as hexane, tetrachloroethylene, etc.

Consideration of all the known facts about structure

TABLE IV

Effect of Concentration and Water Hardnesss on Detergent Properties of Built Detergents[a]

% Conc. built detergent	% Increase in Reflectance											
	Distilled H_2O			100 ppm hard H_2O			200 ppm hard H_2O			500 ppm hard H_2O		
	ABS	BUS	BIUS[b]	ABS	BUS	BIUS[b]	ABS	BUS	BIUS[b]	ABS	BUS	BIUS[b]
0.05	130	131	127	73	62	55	67	72	70	33	32	33
0.10	132	128	124	105	104	99	81	88	86	43	41	39
0.15	150	147	150	104	110	103	93	90	75	48	46	47
0.20	150	147	146	101	110	111	96	74	72	77	57	54
0.30	144	149	146	104	111	104	104	97	96	105	67	64

[a] Detergent, 15%; sodium carbonate, 39%; STPP, 35%; Metso, 10%; NaCMC, 1%.

[b] 9:1 Butadiene:Isobutylene mole ratio in charge.

TABLE V

Detergent Blends Containing BUS (0.25% Conc. Built Detergent, 200 ppm Hard Water)

	Built Detergent Composition					
% BUS	% Second detergent	% STPP	% Metso	% Na_2CO_3	% Na CMC	Relative efficiency
0	15 ABS	35	10	39	1	100
15	0	35	10	39	1	106
7.5	7.5 ABS	35	10	39	1	101
7.5	7.5 MYRJ® 52 Ethoxylated Stearic Acid[a]	35	10	39	1	104
14	7.1 RENEX® 690 Ethoxylated Nonyl Phenol[a]	32.6	9.3	36.3	0.93	101
14	7.1 C_{15}–C_{20} Paraff. Sulfonate, Na[b]	32.6	9.3	36.3	0.93	100
14	7.1 C_{10}–C_{20} Paraff. Sulfate, Na[b]	32.6	9.3	36.3	0.93	104
14	7.1 RENEX® 20 Ethoxylated Tall Oil[a]	32.6	9.3	36.3	0.93	104

[a] Atlas Chemical Industries Inc.

[b] Oronite Division, Chevron Chemical Company.

TABLE VI

Inorganic Ion Tolerance of Detergents (Hart Method) (5)

	ABS			BUS		
Detergent conc., %	ppm Ion	Ion: detergent ratio	pH	ppm Ion	Ion: detergent ratio	pH
		Calcium ion				
1	273	0.027	8.4	233	0.023	8.4
0.025	107	0.428	6.1	577	2.308	5.6
		Magnesium ion				
0.1	82	0.082	6.0	589	0.589	4.7
0.025	116	0.464	6.0	2235	8.94	....
		Ferric ion				
0.1	15	0.015	3.4	17	0.017	3.0
0.025	27	0.108	2.7	14	0.056	3.1

TABLE VII

I. G. Farben Lime Soap-Dispersion Test (6)

Surfactant	Lime soap-dispersing value[a]
BUS	1+
BRIJ® 35, polyoxyethylene (23) lauryl ether[b]	1+
1:1 BUS-BRIJ® 35	2+
RENEX® 35, polyoxyethylene (12) tridecyl ether urea complex [b]	3
1:1 BUS-RENEX® 35	3−
19:1 BIUS[e]	4+
Igepon T-51[c]	15
Sodium dodecylsulfate	30
Atlas G-3300®, alkyl/aryl sulfonate[b]	>40
ABS[d]	>>40

[a] Concentration of surfactant needed to keep calcium oleate in dispersed form.

[b] Atlas Chemical Industries Inc.

[c] General Aniline and Film's N-methyl-N-lauryltaurate.

[d] Atlantic Refining Company's Ultrawet K.

[e] Charge gas to urea-H_2SO_4 reaction was 19:1 (moles) butadiene: isobutylene.

TABLE IX

Yellowing Test

Y. I.[a] after N wash-dry-iron-cycles	Ivory Snow	70% Ivory Snow 10% BUS 20% Na_2CO_3	Built ABS
0	0.025	0.022	0.023
5	0.076	0.068	0.052
7	0.115	0.074	0.073
Visual	Lt. yellow-gray	Whitest	Sl. off-white

[a] Yellowness Index = $\frac{\text{amber reflectance—blue reflectance}}{\text{green reflectance}}$

and reaction variables indicates that BUS is formed by a series of unique reactions which must occur in order (4). a) One molecule of butadiene reacts with one of the urea-NH_2 groups to form monobutenylurea. The t-olefins, if present, react with monobutenylurea formed in this first step. Some of the $-NH_2$ groups remaining react with another molecule of butadiene to form N,N′-dibutenylurea. b) Some butenylurea groups are sulfated by the reversible addition of sulfuric acid. c) Unsulfated butenyl groups undergo Diels-Alder reaction with butadiene to form cyclohexenylureas. Thus butenylureas are strong dienophiles, capable of reacting with butadiene below 25C. d) Cyclohexenylurea groups are joined by cationic chain-lengthening reactions, probably involving some molecules of butadiene.

Surface-Active Properties of BUS

Surface Tension. The surface tensions of aqueous solutions of BUS are plotted in Figure 2. BUS solutions have lower surface tension than ABS (Ultrawet K) below 0.03% concentration, but above 0.03% ABS solutions have lower surface tension.

Foaming. BUS is a low foamer. It gives about one-third to one-fifth as much foam as ABS in ASTM D-1173-53 (Table II). Foaming was built to moderately high levels by blending with alkanolamine sulfates (Table III).

Detergency Tests. Detergency of BUS, 9:1 BIUS (butadiene-isobutylene-urea-sulfate) and ABS as a function of concentration and water hardness is compared in Table IV. The built detergents contained 15% detergent, 39% sodium carbonate, 35% STPP, 10% Metso, and 1% Sodium CMC. The significant conclusion is that BUS and BIUS are roughly comparable with ABS except in 500 ppm hard water at concentrations of 0.2–0.3% of built detergent, where they are inferior. Other BIUS compositions, in which the amount of isobutylene which was incorporated varied considerably, were comparable with the 9:1 BIUS shown in Table IV. This is surprising since the HLB of such compositions must be significantly different.

TABLE VIII

Detergency of Soap-BUS-Builder Blends (0.25% Conc. Blend, 200 ppm Hard Water)

Ivory Snow %	BUS %	Deterg. # 2	%	Na_2CO_3 %	Na_2SO_4 %	STPP %	TSPP %	Relative efficiency
67.5	3				4.5		25	107
70		ABS	20	10				106
70	10	Mannitol	5	15				104
70	10			20				103
70	20			10				102
80	5			15				102
10	5			39		35[a]		90
12	3			39		35[a]		97
13.5	1.5			39		35[a]		105
		ABS	15	39		35[a]		100
80				20				98

[a] Plus 10% Metso and 1% Na CMC.

TABLE X

Pigment-Dispersing Properties of BUS

Lbs./100 Gal. dispersing and/or wetting agent				Hunter white reflectance	Contrast ratio	Color acceptance DuPont phthalo green	
						Flocculation rating	Hunter reflectance
TAMOL 731[c]	BUS	RENEX® 690[d]	KTPP	H[a]	H[a]	L[b]	L[b]
2	..	3	..	78.7	0.889	6	73.4
..	2	3		83.1	0.912	3	56.6
..	2	..	3	82.8	0.919	4	63.3

[a] High reading preferred.
[b] Low reading preferred.
[c] Sodium polyacrylate, Rohm and Haas Company.
[d] Polyoxyethylene (10) nonylphenol, Atlas Chemical Industries Inc.

TABLE XI

Precipitation of Detergents by Inorganic Salts

Detergent		Concentration inorganic salt, ppm			
ppm	Name	50	150	300	500
		Calcium chloride (pH 5.5–6.7)			
500	ABS	1	3	3	3
500	BUS	0	0	1	4
50	ABS	0	0	0	0
50	BUS	0	0	0	2
		Ferric chloride			
500	ABS	0	1	4	4
500	BUS	4	5	5	5
50	ABS	1	0	0	0
50	BUS	2	2	2	3
		Aluminum sulfate			
500	ABS	0	1	1	1
500	BUS	4	4	4	4
50	ABS	1	1	1	1
50	BUS	2	2	2	2

(0 = none, 5 = heavy precipitate)

BUS can be blended with other detergents. Table V shows data which illustrate the high efficiency of blends of BUS with various anionics and nonionics.

Inorganic Ion Tolerance. Table VI compares the tolerance of BUS and ABS with calcium, magnesium, and ferric ions. BUS has a greater tolerance for calcium and magnesium ions, and lower tolerance for ferric ion, than ABS.

BUS-Soap Blends. The excellent calcium and magnesium ion tolerance of BUS and the fact that BUS is a polyelectrolyte indicated that BUS might be a good ingredient in general-purpose soap blends. Table VII shows that BUS efficiently disperses hard-water soap scum. BUS, BRIJ 35 [polyoxyethylene lauryl ether (12)], RENEX 35 [polyoxyethylene ether alcohol complexed with urea (12)], and blends of these are in a class by themeslves as far as lime soap-dispersing ability is concerned. Various detergent-soap blends were evaluated in the Terg-O-Tometer. The results are in Table VIII. Several formulations were slightly better detergents than built ABS or soap-sodium carbonate mixtures. Table IX contains results of the repeated wash-dry-iron cycle tests on BUS-soap blend. After seven cycles there was no visual or reflectance indication that hard-water scum was accumulating on the cloth.

TABLE XII

Removal of Detergents from 5-ppm Aqueous Solutions by Ferric Chloride

$FeCl_3 \cdot 6 H_2O$, conc., ppm	% Detergent removed	
	BUS	ABS
5	39	24
10	64	39
15	67	42
25	49	11
50	45	11
0[a,c]	30	4
10	74	7
0[b,c]	34	2
10	61	10

[a] Solutions prepared individually.
[b] Stock solutions, portions used for each test.
[c] 1,000-ppm dirt added.

TABLE XIII

Toxicological Properties of the Detergents

	Acute Oral Toxicity		Primary Irritation to Rabbit Skin	
Detergent	LD_{50} g/kg of body weight	Category of compound	Irritation index	Degree of irritation
ABS	2.24 g	slightly toxic	5.58	severe
BUS	7.4 g	practically nontoxic	0.34	mild
BIUS (3:1)	>19.9 g	relatively harmless	0.25	mild
BIUS (9:1)	>22.4 g	relatively harmless	0.08	mild

BUS as a Paint-Pigment Dispersant. Since BUS was an effective suspending agent for lime soaps, BUS was tested as a dispersant. It was an efficient dispersant for organic pesticides, such as Sevin, and for pigments in rubber-based paints. Typical results obtained when BUS was used to suspend and disperse pigment in a polyvinyl acetate paint are shown in Table X.

Removal of BUS from Waste Water. The low tolerance of BUS to ferric chloride and to alum indicated that BUS can be precipitated easily from waste effluents. Table XI shows that ferric chloride and alum precipitate BUS much more readily than ABS. Table XII shows that ferric chloride removes twice as much BUS as ABS from 5-ppm solutions and four times as much from 25-ppm solutions. The efficiency of Delaware soil for removing BUS from solution was determined by a simple slurry-filter test. Table XII also shows that 1,000 ppm of soil will remove 30% of the BUS from a 5-ppm solution. The addition of 10 ppm of ferric chloride more than doubles the amount of BUS removed. These results suggest that BUS will be removed from cesspool effluents and from ground water very easily, by simple percolation through the soil. Percolation tests gave no evidence that BUS will plug the pores of the soil. Thus BUS probably can be used in homes which have domestic waste systems without becoming dissolved in the ground water which feeds wells in the same area. The ions and dirt normally present in waste treatment plants should precipitate most BUS even if ferric chloride or alum is not added.

Toxicity and Irritation Index. BUS and BIUS are practically nontoxic, or relatively harmless, and are much less toxic than ABS. They are also much less irritating than ABS. Data are in Table XIII. BUS and BUS-containing blends can thus be considered for cosmetics, face soaps, and toothpastes.

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REFERENCES

1. Harvey, M. T., and Caplan, S. (Harvel Corporation), U.S. 2,247,495, July 1, 1941; Chem. Abstr. *35*, 6267 (1941).

2. Brown, H. C. (Standard of Indiana), U.S. 2,548,585, April 10, 1951; Rutledge, T. F. (Atlas Chemical Industries Inc.) U.S. 3,297,752, January 10, 1967.

3. Atlas Chemical Industries Inc., Netherlands Application 6,500,872, July 26, 1965; Chem. Abstr. *64*, 6838 (1966).

4. Details of structure determinations and reaction mechanisms, to be published in Journal of Organic Chemistry.

5. Hart, R., American Dyestuff Reporter *23*, 646 (1934).

6. Baird, W., E. B. T. Brown and G. R. Perdue, PB Report 32565, p. 43.

7. Weil, C. S., Biometrics *8*, 249 (1952).

8. Lichtfield, J. T. Jr., and F. Wilcoxon, J. Pharm. Expt'l. Therapy *95*, 94 (1949).

9. Hodge, H. C., and J. H. Sterner, Ind. Hyg. Quart. *10*, 93 (1949).

10. Association of Food and Drug Officials, U.S., "Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics," 1959.

11. Kay, J. H., and J. C. Calandra, J. Soc. Cosmetic Chem. *13*, 285–286 (1962).

12. Atlas Chemical Industries Inc., Wilmington, Del.

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