TABLE IV

Effect of Alcohol mol wt on Foam Stability of DB/ES Liquids

ES portion	% E.O.	Plates washed, 115F, 50 ppm, 0.05% concn.
C_{12}	40	31
C_{14}	40	29
C_{16}	40	20
C_{18}	40	10

These data indicate that as the ethylene oxide content is decreased the foam stability increases. Again, as with detergency, this increase in performance occurs as the alcohol sulfate is approached. At equal ethylene oxide percentages there are no significant differences in foam stability with this formulation between straight-chain petroleum-derived and naturally-derived alcohol ether sulfates.

In light duty liquids the optimum chain length of the alcohol ether sulfates for foam stability is C_{12}, with C_{14} close behind as indicated by data on the DB/ES formulation given in Table IV.

Though the foam stability performance drops at C_{16} and C_{18}, small percentages of these heavier alcohols do not inhibit the effectiveness of more economical broad blends of the alcohols (see Table V).

TABLE V

Foam Stability Performance of Ether Sulfates of Alcohol Blends (DB/ES formulation)

Alcohol distribution				% E.O.	Plates washed at 115F, 0.05% concn.	
C_{12}	C_{14}	C_{16}	C_{18}		50 ppm	300 ppm
55	45	....	....	40	30	32
62	26	12	....	40	30	32
40	30	20	10	40	28	32
....	....	65	35	40	17	....
Nonylphenol				40	26	30

The straight chain alcohol ether sulfates in light duty liquids have advantages over branched-chain ether sulfates in foam stability and solubility in addition to being biodegradable.

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Recent Advances in Fatty Amine Oxides. Part II. Formulation and Use

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ALKYLDIMETHYLAMINE OXIDES as foam stabilizers for detergent formulation have gained considerable interest the last few years. However, amine oxides are excellent detergents in their own right as the sole active ingredient (1,2). For example, in a 20% active heavy duty formulation dodecyldimethylamine oxide (C_{12} DMAO) was compared with alkylaryl sulfonates in foam stability and detergency at 50 and 300 ppm hardness (Table I).

C_{12} DMAO exhibits foam stability between that of dodecyl and tridecylbenzene sulfonates. The detergency of C_{12} DMAO is similar to that of the alkylaryl sulfonates at both hardness levels.

Due to the economics of production, the practical interest in the amine oxides is primarily in the field of foam stabilization, rather than as a major portion of the active content. The amine oxides have been reported as excellent foam stabilizers for light duty liquids (3).

Light Duty Liquids

Light duty liquids in this country are made up of three major types based on their active ingredient: 1) DB/ES type—a blend of alkylaryl sulfonate, usually dodecyl, with an ether sulfate (the sulfate of an ethoxylated alcohol or alkylphenol); 2) DB/NI type—a blend of alkylaryl sulfonate and a nonionic (the ethoxylate of an alcohol or alkylphenol); and 3) Straight ES type—the sole active ingredient is an alcohol ether sulfate.

TABLE I

Active ingredient	Plates washed [a] 115F, 0.125% concn.		Detergency rating [b] 120F, 0.2% concn.	
	50 ppm	300 ppm	50 ppm	300 ppm
C_{12} DMAO	13	19	6.0	5.1
Na dodecylbenzene sulfonate	5	18	5.7	4.4
Na tridecylbenzene sulfonate	17	25	6.3	4.9

[a] Number of uniformly soiled plates washed to obtain an end point of a permanent break in the foam covering the dishpan. Two plates difference is necessary in order to be significant at a 95% confidence level.

[b] One unit difference in detergency rating is necessary in order to be significant (95% confidence). Detergency ratings are relative, rather than absolute, and are obtained from the differences in reflectance between washed and unwashed standard soiled cloths washed in a Terg-O-Tometer.

TABLE II

Formulation	Foam stabilizer	Δ P, difference in plates washed compared with LDEA [a] at 115F, 50 ppm hardness, 0.05% concn.
DB/ES	C_{12} DMAO	−4
DB/NI	C_{12} DMAO	+1
ES	C_{12} DMAO	+6

[a] A difference of two plates is necessary in order to be significant at 95% confidence level.

Amine oxides were evaluated as foam stabilizers in each of these types of formulations. The actual formulations were:

DB/ES	18% sodium DB sulfonate, 12% sodium lauryl ether sulfate, 5% foam stabilizer
DB/NI	18% sodium DB sulfonate, 12% lauryl alcohol ethoxylate (62.5% E.O.), 5% foam stabilizer
ES	25% sodium lauryl ether sulfate (3 mole ethylene oxide adduct), 5% foam stabilizer

Cursory foam stability evaluations of each of these formulations comparing C_{12} DMAO with LDEA (lauric diethanolamide) are give in Table II.

These results indicate that the best potential for the amine oxides in light duty liquids was in the ES type formulation.

The effect of molecular weight on foam stability was studied to determine optimum carbon chain length. C_{10} through C_{18} DMAO were prepared from the appropriate petroleum-derived straight chain alcohols and compared with LDEA (Table III).

The optimum DMAO for foam stability in this

TABLE III
Light Duty Liquid (ES Type) Foam Stability

Foam stabilizer	Plates washed at 115, 0.05% concentration	
	50 ppm	300 ppm
C_{10} dimethylamine oxide	15	17
C_{12} dimethylamine oxide	21	24
C_{14} dimethylamine oxide	21	23
C_{16} dimethylamine oxide	18	18
C_{18} dimethylamine oxide	9	13
LDEA	16	16

formulation is between C_{12} and C_{14} at both hardness levels. The C_{14} thru C_{18} amine oxides are better than LDEA.

Though the C_{12} was only equal to conventional amide in the DB/NI formulation, a molecular weight study was made to determine if a different carbon chain length oxide would give much better results. Table IV gives results of this study:

TABLE IV
Light Duty Liquid (DB/NI) Foam Stability

Foam stabilizer	Plates washed at 115F, 0.05% concentration	
	50 ppm	300 ppm
C_{10} dimethylamine oxide	18	21
C_{12} dimethylamine oxide	18	19
C_{14} dimethylamine oxide	15	15
C_{16} dimethylamine oxide	9	9
C_{18} dimethylamine oxide	6	7
LDEA	18	20

The optimum for DB/NI liquid foam stability in this formulation is C_{12} to C_{10} or less; however, these optimum chain lengths are not significantly better than LDEA.

Therefore, of the three major types of formulations, the straight ES type is the only one which exhibits foam stability advantages with the amine oxides evaluated here. Table V gives an example of the efficiency of the amine oxide in this type of formulation. In this study both the alcohol ether sulfate and the amine oxide were derived from "ALFOL" 1214 alcohol* (55% C_{12}, 45% C_{14}).

Table V data indicate that a formulation with good foam stability can be obtained with amine oxides by either decreasing the amount of foam stabilizer or by reducing the active. The most effective way of reducing formulation cost and maintaining high quality product is by using 2½% DMAO, which gives a foam stability of seven plates more than obtained with 5% LDEA.

TABLE V
ES Light Duty Liquid Foam Stability

% Ether sulfate	Foam Stabilizer	Plates washed at 115F, 0.05% concn., 50 ppm hardness
30	5% 1214 DMAO	29
30	2½% 1214 DMAO	26
30	5% LDEA	19
30	5% 1214 DMAO	29
20	5% 1214 DMAO	22
15	5% 1214 DMAO	21
30	5% LDEA	19

TABLE VI
Heavy Duty Foam Stability
(DB sulfonate system)

Foam Stabilizer 2%	Plates washed at 115F, 0.125% concentration	
	50 ppm	300 ppm
C_{10} DMAO	7	22
C_{12} DMAO	19	27
C_{14} DMAO	24	25
C_{16} DMAO	17	16
C_{18} DMAO	16	14

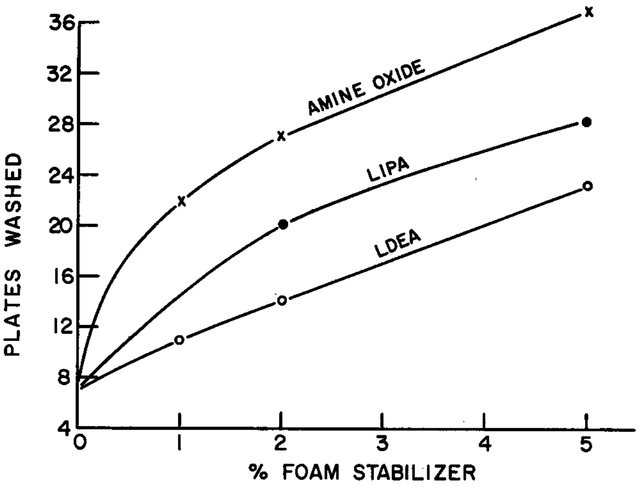

FIG. I HEAVY DUTY FOAM STABILITY
50 PPM HARDNESS

Heavy Duty Formulations

The amine oxides are excellent foam stabilizers in heavy duty formulations, both solid and liquid. Though some of the amine oxides decompose at temperatures above 100C, it is possible to drum dry or spray dry finished formulations containing amine oxides without decomposition or loss of foam stability.

A molecular weight study (Table VI) shows that for a DB sulfonate formulation (20% sodium DB sulfonate, 50% phosphate (STPP), 15% sodium sulfate, 5% sodium silicate, 8% water, and 2% foam stabilizer) the optimum foam stability is exhibited by the C_{14} DMAO at 50 ppm hardness. At 300 ppm hardness the optimum is closer to C_{12}.

Table VI results indicate that a blend of C_{12} and C_{14} chain lengths should be very good for this type of active and formulation. Figs. 1 and 2 below give foam stability curves for a C_{12}-C_{14} DMAO (55% C_{12}, 45% C_{14}) compared with LDEA and LIPA (lauric isopropanolamide) in the same DB active duty formulation.

At 50 ppm hardness, 1% amine oxide is a better foam stabilizer than 2% LIPA and is similar in performance to 5% LDEA. At 300 ppm hardness, LIPA

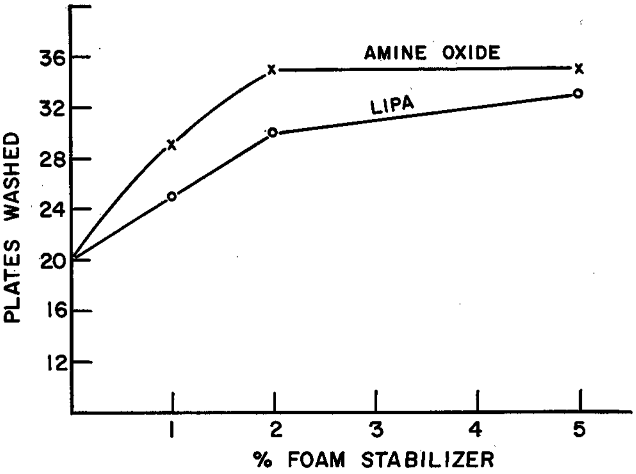

FIG. 2 HEAVY DUTY FOAM STABILITY
300 PPM HARDNESS

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* Registered trademark.

and LDEA are almost identical in foam stability. The differences between the amine oxide and the amides are not nearly so great at this higher hardness, but 1% amine oxide continues to perform as well as 2% amide.

Detergency tests were run on the entire molecular weight range from C_{10} thru C_{18} DMAO as the sole active ingredient (20% active formulation). These data in Table VII were obtained at 120F, 0.2% solids concentration at 50 and 300 ppm hardness.

TABLE VII
Heavy Duty Detergency

Active	Detergency Rating	
	50 ppm	300 ppm
C_{10} DMAO	4.5	3.5
C_{12} DMAO	6.0	5.1
C_{14} DMAO	8.9	8.0
C_{16} DMAO	9.4	9.0
C_{18} DMAO	8.7	9.0
Na DB sulfonate	5.7	4.4

The C_{14} thru C_{18} amine oxides are better in detergency than DB sulfonate; the C_{10} DMAO is poorer. Therefore, adding foam stabilizer quantities (5% or less) of C_{12} to C_{18} DMAO will not hinder detergency. Tests run with 2% amine oxide added show no effect upon the detergency of the total formulation.

Properties other than foam stability give an added luster to the potential of the amine oxides. Solubilities of the amine oxides are excellent (e.g., a 30% solution of 1214 DMAO is water white and has a cloud point of 39F). Throughout the molecular weight range studied here the amine oxides were found to be biodegradable in a shake flask culture test (4) using surface tension as a method of analysis. It is also reported (5) that amine oxides are exceptionally mild to the skin.

Though the alkyldimethyl amine oxides do not appear to be appropriate foam stabilizers for all types of products, the foam stabilizing properties are so exceptional in some formulations that these compounds should be an interesting addition to the surfactant industry.

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Anionic Phosphate Surfactants

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NUMEROUS ANIONIC ORGANOPHOSPHORUS surfactants are being marketed in the United States by about a dozen companies. The total annual volume for these products is about four million lb. These surfactants are used in or recommended for use in textile finishing, dry cleaning detergents, foaming agents, emulsion polymerization, floor cleaning concentrates and other specialty uses.

None of the anionic phosphate surfactants have ever been used to any appreciable extent in heavy duty laundry detergents; furthermore, little information is available in the literature on either the surface active or detergency properties of either monoalkyl sodium phosphates or dialkyl sodium phosphates.

We propose to discuss both the preparation and properties, particularly those properties related to detergency performance, of the mono- and dialkyl esters of phosphoric acid.

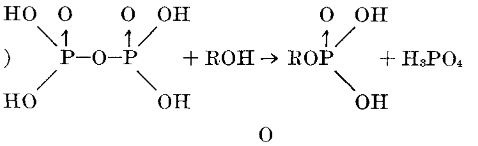
These acid phosphates are readily converted with caustic soda to the sodium salts. Wide variations of surfactant properties are obtained. The monoesters represent a group of surfactants where a single long chain hydrophobic group is attached at one end to a hydrophilic phosphoryl group, while the dialkyl esters have two hydrophobic groups with the hydrophilic moiety in the center of the molecule. This major difference in these two types of anionic phosphate surfactants will be compared in this discussion but is emphasized now because of the processes used to manufacture these surfactants.

Methods of Preparation

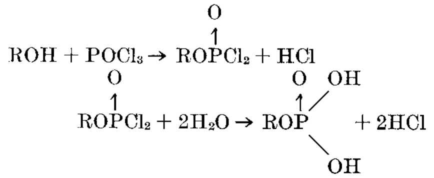
The most popular phosphate surfactants produced commercially are equimolar mixtures of these monoalkyl and dialkyl esters. The perferred method used to manufacture this mixture is to add phosphoric anhydride (P_4O_{10}) to the alcohol with stirring at such a rate that the temperature is kept, by cooling, about 50C. Some care must be taken during this addition since the reaction is quite exothermic. The reaction mixture is then held at about 50C until the reaction is complete. Assuming anhydrous conditions, the mono- and diesters are prepared in equimolar amounts in nearly quantitative yields.

For the obvious reasons that raw material costs are moderate, yields are excellent and there is virtually no processing required, this method is used today to manufacture in excess of 75% of the phosphate surfactants sold in this country. As we shall see later, however, when we examine the surfactant properties of the mono- and diesters, there are wide differences in these properties because of the structural and molecular weight differences.

The pure monoesters may be prepared in a variety of ways, two of which are shown in the following equations:

1)


$$\mathrm{(HO)_2P(\rightarrow O)\!-\!O\!-\!P(\rightarrow O)(OH)_2 + ROH \rightarrow ROP(\rightarrow O)(OH)_2 + H_3PO_4}$$

2)


$$\mathrm{ROH + POCl_3 \rightarrow ROP(\rightarrow O)Cl_2 + HCl}$$

$$\mathrm{ROP(\rightarrow O)Cl_2 + 2H_2O \rightarrow ROP(\rightarrow O)(OH)_2 + 2HCl}$$

The upper equation between pyrophosphoric acid and alcohol is most conveniently carried out by dissolving an excess of crystalline pyrophosphoric acid in the alcohol and stirring for several days at room temperature. The reaction is slow and not noticeably exothermic. Heating of the reaction mixture is not advisable since dehydration of the alcohol can occur as a side reaction.