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.

REFERENCES

1. Guenther, F., and K. Saftien (I.G. Farbenindustrie A.-G.) U. S. 2,169,976 (1939).
2. Drew, H. F., and R. E. Zimmerer (The Procter and Gamble Co.) U. S. 3,001,945 (1961).
3. Priestly, H. M., and J. H. Wilson (Unilever N.V.) Belgium 603,337 (1961).
4. Huddleston, R. L., and R. C. Allred, presented at The Society for Industrial Microbiology annual meeting, Corvallis, Oregon, Aug. 26–31, 1962.
5. Drew, H. F., and J. G. Voss (The Procter and Gamble Co.) Canada 639,398 (1962).

Anionic Phosphate Surfactants

R. S. COOPER, Victor Chemical Div., Stauffer Chemical Co., Chicago Heights, Illinois

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.

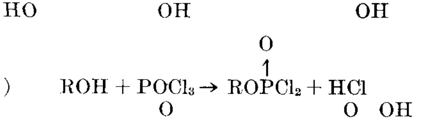
These acid phosphates are readily converted with caustic soda to the sodium salts. Wide variations of surfactant properties are obtained. The monoesters represent a group of surfactants where a single long chain hydrophobic group is attached at one end to a hydrophilic phosphoryl group, while the dialkyl 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

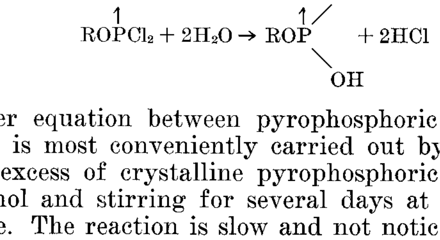
The most popular phosphate surfactants produced commercially are equimolar mixtures of these monoalkyl and dialkyl esters. The perferred method used to manufacture this mixture is to add phosphoric anhydride (P_4O_{10}) to the alcohol with stirring at such a rate that the temperature is kept, by cooling, 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)


$$(HO)_2\overset{\overset{O}{\uparrow}}{P}\text{—O—}\overset{\overset{O}{\uparrow}}{P}(OH)_2 + ROH \rightarrow RO\overset{\overset{O}{\uparrow}}{P}(OH)_2 + H_3PO_4$$

2)


$$ROH + POCl_3 \rightarrow RO\overset{\overset{O}{\uparrow}}{P}Cl_2 + HCl$$

$$RO\overset{\overset{O}{\uparrow}}{P}Cl_2 + 2H_2O \rightarrow RO\overset{\overset{O}{\uparrow}}{P}(OH)_2 + 2HCl$$

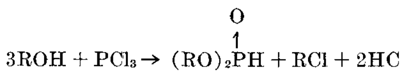
The upper equation between pyrophosphoric acid and alcohol is most conveniently carried out by dissolving an excess of crystalline pyrophosphoric acid in the alcohol and stirring for several days at room temperature. The reaction is slow and not noticeably exothermic. Heating of the reaction mixture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

The reaction mixture is purified by washing out the water solubles and drying the organic layer. Yields vary from 75–90% with purities in the order of 90%.

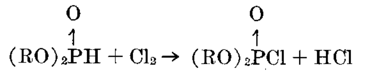
This reaction is not quite as good for higher molecular weight alcohols as the reaction between alcohol and phosphorus oxychloride. This reaction is carried out by adding the alcohol to an excess (100–200%) of phosphorus oxychloride with some cooling at temperatures of 10–20C. When the addition is complete the reaction mixture is allowed to warm, with stirring and a partial vacuum, to room temperature. As soon as the HCl evolution has stopped the excess phosphorus oxychloride is distilled out at 25–30C under vacuum and the crude product is hydrolyzed to the acid by adding to water (60–70C) with good agitation, followed by refluxing to complete the reaction.

After separating and drying, the organic layer yields are normally in excess of 95% and the purity is also usually well above 90%.

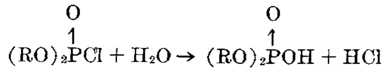
The methods most convenient to use for the preparation of dialkyl phosphates is:



$$3ROH + PCl_3 \rightarrow (RO)_2\overset{\overset{O}{\uparrow}}{P}H + RCl + 2HCl$$



$$(RO)_2\overset{\overset{O}{\uparrow}}{P}H + Cl_2 \rightarrow (RO)_2\overset{\overset{O}{\uparrow}}{P}Cl + HCl$$



$$(RO)_2\overset{\overset{O}{\uparrow}}{P}Cl + H_2O \rightarrow (RO)_2\overset{\overset{O}{\uparrow}}{P}OH + HCl$$

Phosphorus trichloride is added to three molecules of alcohol with good agitation and cooling. The temperature can be held at 30–35C for the higher molecular weight alcohols. The reaction is rapid and quite exothermic. After a short period of stirring, the reaction mixture is cooled to 0–10C and a stoichiometric amount of gaseous chloride added slowly with stirring. The reaction is practically instantaneous so as soon as the addition is complete the crude dialkyl phosphorochloridate can be hydrolyzed, again by adding to hot water. The by-product alkyl chloride and unreacted alcohol are removed by steam distillation and the product is washed and dried to give dialkyl hydrogen phosphate in yields of about 90% and purity of 90–95%. The purity can be improved by distilling the dialkyl phosphonate in vacuo, after the first reaction, before proceeding with the chlorination and hydrolysis steps.

The esters which are included in this discussion were all prepared from either normal alcohols or branched chained commercially available primary alcohols.

Physical Properties

These acid esters may all be converted to the sodium salts by neutralization with caustic soda. In general, the higher molecular weight sodium alkyl phosphates, whether monoesters, diesters, or mixtures made by the phosphoric anhydride process are waxy solids. They are exceptionally stable toward hydrolysis and their rheological properties in some respcets resemble soap.

In general the monoalkyl esters have better sodium salt solubility but poorer calcium salt solubility than those of the corresponding diesters.

We do not want to present voluminous tables here showing the physical and surfactant properties of each of the esters which have been studied. We would rather present some over-all characteristics of these products showing the effects of chain length and branching on the surfactant properties and the relationship of these properties to cotton detergency.

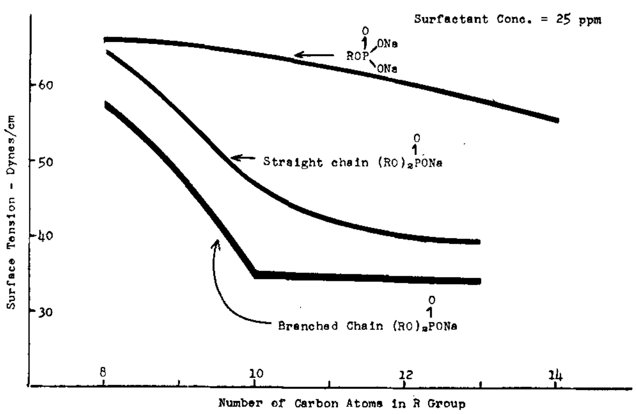


FIG. 1. Surface tension of sodium alkyl phosphates.

Two properties of surfactants which appear to be associated with performance in detergents are surface tension and critical micelle concentrations.

The curves in Figure 1 show the surface tensions of the monoalkyl and dialkyl esters at 25 ppm concentration as a function of the number of carbon atoms in the alkoxy group attached to the phosphorus.

The upper curve gives the values for the monoesters and indicates only moderate surface tension lowering even up to the monoeicosyl ester (not shown).

The two lower curves represent values obtained for the diesters. The upper of these curves gives the values obtained for esters made from straight chain or normal alcohols while the lower curve gives values obtained for the most highly branched chained esters studied. Minimum values of ca. 34 dynes/cm are reached for the branched chain didecyl ester. It is somewhat unusual for surfactants to exhibit such low surface tensions at concentrations of 25 ppm.

Critical micelle concentrations of some of these mono- and diesters are compared in Table I.

The critical micelle concentrations of the monoesters in quite high until the alkyl group is above 13 carbon atoms in length. Values for the monohexadecyl and monoeicosyl esters are about 8.0 and 3.0 x 10^{-3} M, respectively.

Values for the diesters are much lower than for those monoesters with the same alkyl radical. The branched chain didecyl and didodecyl esters have exceptionally low critical micelle concentrations. Even comparing the monoesters with diesters on a mol wt basis, the critical micelle concentrations of the dioctyl and didecyl esters are considerably lower than the monohexadecyl and monoeicosyl esters.

Cotton Detergency

A comparison of these esters' performance in cotton detergency has also been made with a standard

TABLE I
Critical Micelle Concentrations of Sodium Alkyl Phosphates

R Radical	Critical micelle concentration	
	$RO\overset{\overset{O}{\uparrow}}{P}(ONa)_2$	$(RO)_2\overset{\overset{O}{\uparrow}}{P}—ONa$
n-Octyl	$>30 \times 10^{-3}$ M	2.0×10^{-3} M
Dimethyl hexyl	$>30 \times 10^{-3}$ M	6.1×10^{-3} M
n-Decyl	$>30 \times 10^{-3}$ M	....
Trimethyl heptyl	$>30 \times 10^{-3}$ M	1.5×10^{-3} M
Dodecyl	$>30 \times 10^{-3}$ M	1.6×10^{-3} M
Tridecyl	$>30 \times 10^{-3}$ M	....
Hexadecyl	$\sim 8.0 \times 10^{-3}$ M	....
Eicosyl	2.9×10^{-3} M	....

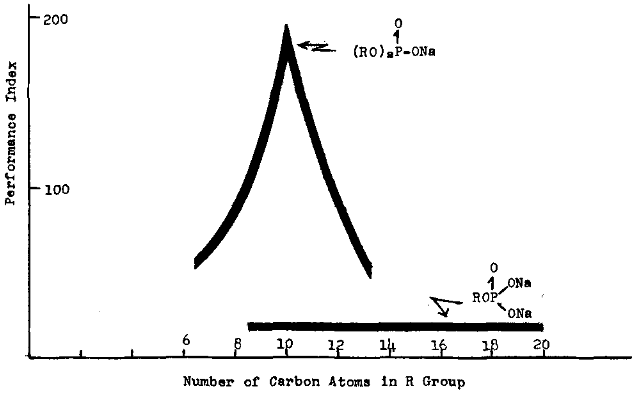


FIG. 2. Relative performance of sodium alkyl phosphates in cotton detergency.

Terg-O-Tometer procedure. A commercial type of soiled cloth, prepared from artificial soil composed of carbon black, bentone, mineral oil, coconut oil and coconut oil fatty acids, was used. The detergent composition was 50% sodium tripolyphosphate, 8% sodium metasilicate, and 0.5% sodium carboxymethyl cellulose. The surfactant concentration was varied from 5–40% while the remainder of the detergent was sodium sulfate.

All detergency tests were carried out with 15 cycle washes at 140 cycles per min agitator speed at 120F in water of 175 ppm hardness. The total detergent concentration was 2.0 gm/liter which is about the equivalent of 4 oz of detergent in a 16 gal washing machine. The pH was 10.0 ± 0.1. Comparative performances of the monoalkyl and dialkyl esters are shown in Figure 2.

These curves compare performance of these surfactants as a function of the number of carbon atoms in the alkyl radical R.

Performance Index represents the amount of soil removed divided by the minimum concentration of surfactant required to give maximum performance.

The lower nearly horizontal line gives the relative performance of the monoalkyl esters, which is uniformly very poor from the monoctyl through the monoeicosanyl. Some improvement in the performance of these monoesters can be obtained by increasing the sodium tripolyphosphate and surfactant concentrations to excessively high levels.

Performance of the dialkyl esters is much different. The dioctyl ester is fairly poor but performance improves very rapidly as the mol wt increases to a very sharp maximum at the didecyl ester, then recedes again as the chain length get longer.

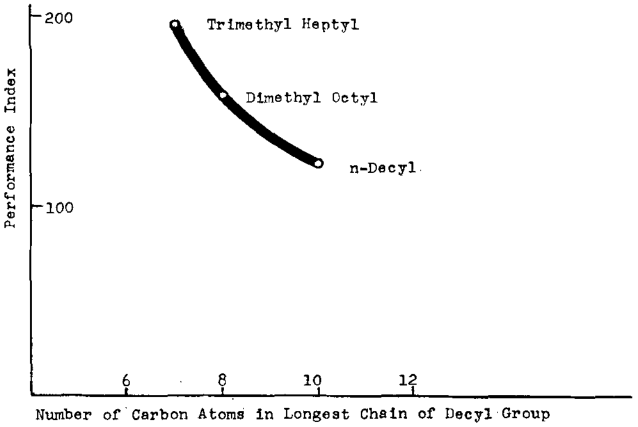


FIG. 3. Relative performance of sodium didecyl phosphates in cotton detergency.

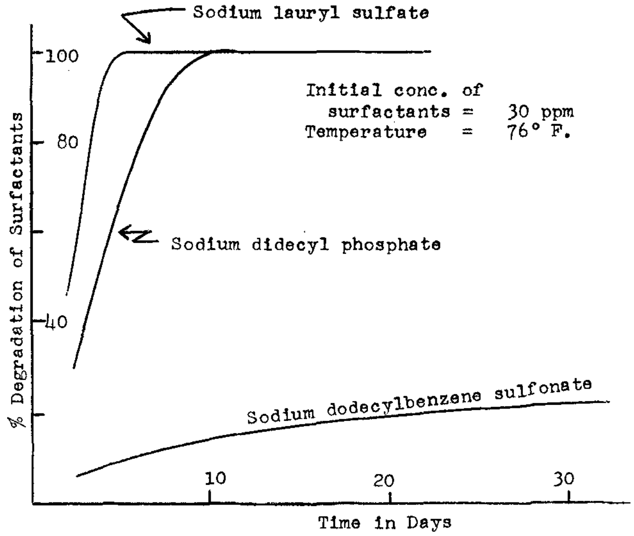


FIG. 4. Biodegradation of surfactants.

The number of carbon atoms in the alkyl radical of these dialkyl esters is not the only factor influencing performance. Chain branching has a very marked influence on performance.

Figure 3 gives an indication of the effect of chain branching on the detergency performance of the didecyl esters. Here the Performance Index is compared with the longest chain in the alkoxy group. The performance of the most highly branched chain, the trimethylheptyl ester, is much better than that of the dimethyl octyl which is in turn better than the n-decyl ester.

It should be emphasized that these branched chain esters were made with commercial alcohols. For instance, the trimethyl heptyl ester is made from commercial decyl alcohol produced by the oxo process, the major constituents of which are isomeric trimethyl heptanols.

Biodegradability

Any discussion of surfactants today must take into account their biodegradability. Within a very few years there is little question but that surfactants used in volume products such as heavy duty detergents will have to be degradable biologically for both aesthetic, sanitary, and probably legal reasons.

In Figure 4 the loss of surface activity of sodium didecyl phosphate is compared with two commercial surfactants, sodium lauryl sulfate and sodium dodecylbenzene sulfonate using the River Water Die-Away Test. In this particular test we measured the increase of surface tensions of solutions of these surfactants over a period of time. As these curves show, the surface activity of sodium lauryl sulfate is destroyed in ca. five days, that of sodium didecyl phospate in about 10 days, while only about 20% of the surface activity of sodium dodecylbenzene sulfonate is lost in 30 days.

Comparison of Sodium Didecyl Phosphate with Commercial Surfactants

Thus far we have compared some of the surfactant and detergency properties of sodium monoalkyl and dialkyl phosphates. The data have shown that the branched chain didecyl ester has exceptional properties, particularly in respect to use in built detergents.

In order to give all of these data some perspective it should be of some interest to compare the data obtained for the branched chain sodium didecyl phosphate with some commercial surfactants.

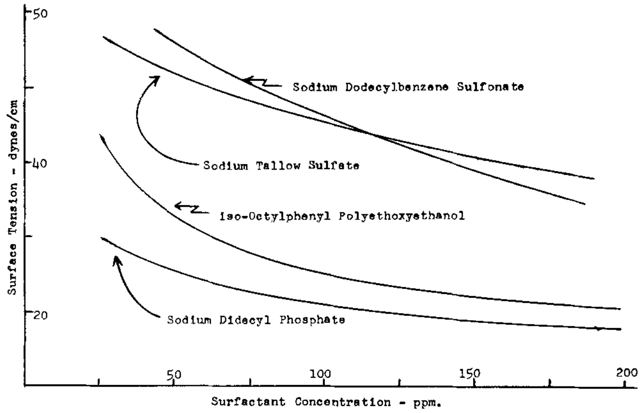


FIG. 5. Comparison of the surface tension of solutions.

Figure 5 compares the surface tension of solutions of sodium didecyl phosphate with three surfactants used in or recommended for use in built detergents. The surface tension of sodium didecyl phosphate solutions, up to a concentration of 200 ppm is far below that of either sodium dodecylbenzene sulfonate or sodium tallow sulfate and significantly lower than that of the nonionic surfactant, iso-octylphenyl polyethoxyethanol, particularly at very low concentrations.

Performance of built detergents containing these surfactants is compared in Table II. The test methods were the same as were used in comparing the alkyl phosphates. Our data indicate that sodium didecyl phosphate is about 20% more effective than sodium tallow sulfate, nearly twice as effective as sodium lauryl sulfate and three times as effective as sodium dodecyl benzene sulfonate when used in a built detergent.

TABLE II
Comparative Performance of Commercial Surfactants in Cotton Detergency

Surfactant	Performance index	% Surfactant required for maximum performance
Sodium didecyl phosphate	195	8%
Sodium tallow sulfate	155	10%
Soduim lauryl sulfate	118	14%
Sodium dodecyl benzene sulfonate	76	25%

Conclusions

A study of the sodium monoalkyl phosphates and sodium dialkyl phosphates has shown that the dialkyl esters, in general, possess markedly superior surfactant and detergent properties compared to the monoalkyl esters. This is true whether we are comparing equivalent mol wt mono- and diesters or when comparing those made from the same alcohols.

The branched chain didecyl ester, in addition to giving aqueous solutions of exceptionally low surface tensions and possessing a very low critical micelle concentration, also performs exceptionally well in built detergents. In fact, our data indicate that its performance characteristics are considerably better than commercial surfactants used today in these types of products.

The Nation's Water Pollution Problem — Detergent's Role in It

M. M. COHN, Consultant, New York, New York

THE petroleum industry, like others, has been importuned to conduct its industrial operations in a manner that will prevent processing wastes from polluting our water resources—from the well, to the refinery, to the petrochemical production phases of industrial operation. It is the sanitary engineering profession which has been pleading the cause for steam pollution control. I hope in the course of my presentation today to plead for your Society's active interest in this worthwhile national endeavor.

Your industry has done as well as any in pollution control. In fact, you have done more than many other basic industries to clean up pollution from your complex operations. But, there are things which you have done which should not have been done, in terms of pollution, and things you have left undone which your industry should have done, in the interests of water pollution control.

I make this point, lest it be assumed that I am placing sole responsibility for the nation's pollution problem on the doorstep of the oil chemists' profession. This I am not doing because other industries have been equally remiss; in fact, we all have! It is my earnest plea, however, that we can do better than we have done in preventing the despoliation of the nation's rivers, lakes and coastal waters and that, together, we can clean up the pollution problem which threatens the ultimate value and usefulness of the nation's greatest asset—its water resources.

I have been tempted to retitle my address, "Between the Devil and the Deep Blue Sea," because that is the dilemma your industry faces in attacking your part of the nation's water pollution control problem. On one hand, you are being pressed to prevent pollution from your various operations—which I term "back door" pollution conditions. I refer to the discharge of industrial by-products or waste materials which are the result of internal operations of product manufacture in your industry. This industrial wastes problem is so much a part of the overall threat to our water resources that the oil industry must maintain vigilant control of everything that goes out its "back door." On the other hand, you are, indeed, in the position of being between the devil and the deep blue sea, because in addition to being concerned about your "back door" wastes, you are being urged to do something about your "front door" products. I refer, of course, to detergent products.

The "Front Door" Problem . . . and the "Back Door" Problem

What makes the "front door" problem more vexing than your "back door" control problem is a two-fold situation that can be equally frustrating to scientists and industrialists:

1) You are dealing with lawmakers, not scientists, and they are being whipped into a "frenzy over foam" by well-meaning protectors of water quality—people who advocate laws which would be the first prohibition imposed on the manufacture and sale of a product with a "head" since the Volstead Act!
2) You make cleansing products to keep America clean—only to find that they are accused of making America dirty!