TABLE VI
Disintegration Rate of Tablets as a Function of TRT of Granular Sodium Tripolyphosphate

Tablet	TRT of STPP	Disintegration rate
1	6	Over 5 min
2	8	Over 5 min
3	10	5 min
4	11	3 min
5	12	2 min
6	14	2 min

The problem of making a detergent tablet with the proper physical properties is quite frustrating. One must mix the material before tableting in such a way as to give a uniform formulation, which will flow readily and not cause sticking problems in the tableting machine. At the same time, the mixture must have enough tackiness to produce a tablet which has sufficient strength to be handled without breaking. Finally, the housewife buys the product, expects to find it still in one piece, and hard enough to resist breaking if she accidentally drops it; and yet, when she places it in the washing machine, she expects it to disintegrate immediately.

There are several different types of formulations which can be tabulated successfully and since each formulation requires a different type of treatment, a generalization of the properties of granular $Na_5P_3O_{10}$ which are important in making tablets will be given:

Density: The density of the granular $Na_5P_3O_{10}$ can vary from 30–45 lb/cu ft depending upon the amount used and the density of the other materials in the formulation. When the density of the mix, before tableting, is above 50 lb/cu ft, it becomes quite difficult to produce a satisfactory tablet.

Absorption: The absorption of the granular $Na_5P_3O_{10}$ used depends upon the amount of liquids used in the formulation.

Granulation: In general, the coarser the granulation the better it is for tableting, provided there is sufficient tackiness to give good strength to the tablets. The coarser granules provide small voids in the tablets; which, when the tablet is placed in water allow rapid water penetration and increase the rate of disintegration.

TRT: It has been found that when the TRT of the granular $Na_5P_3O_{10}$ is 11 or above, the tablet disintegrates much faster than for lower TRT's. The high heat of hydration and the rapid rate of formation of tripoly hexahydrate, as produced by granular $Na_5P_3O_{10}$ with TRT of 11 or above, causes the tablets to swell when placed in water and disintegration is quite rapid.

Table VI shows the disintegration rate of detergent tablets made from the same formulation, the same tablet weight, and pressure with $Na_5P_3O_{10}$'s having different TRT's. The rate of disintegration was determined by placing the tablet in one liter of water at 120F and visually observing how long the tablet took to completely break apart. No agitation is used during the test.

Thus, it can be seen that the TRT of granular $Na_5P_3O_{10}$ is an important factor in controlling the disintegration rate of a tableted product.

Summary

In summary, the chemistry of the preparation of sodium and potassium polyphosphates, and the properties of importance to their use as detergent builders, such as hydrolysis, hydration rates and solubilities have been discussed. The properties of granular $Na_5P_3O_{10}$, such as density, particle size, frangibility and absorptivity, were discussed in connection with their use in the dry blending and tableting of detergent products.

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Recent Advances in Fatty Amine Oxides. Part I. Chemistry and Preparation

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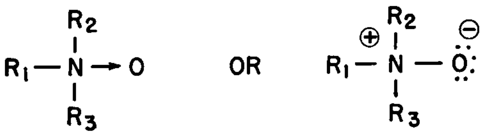
AMINE OXIDES are reaction products of tertiary amines and hydrogen peroxide or peroxyacids. Aliphatic tertiary amines are readily oxidized by hydrogen peroxide, whereas aromatic and heterocyclic amines require the use of peroxyacids. The structure of amine oxides may be represented in either of the following ways:



$$R_1-\overset{R_2}{\underset{R_3}{N}}\rightarrow O \quad \text{OR} \quad R_1-\overset{\oplus\; R_2}{\underset{R_3}{N}}-\ddot{\underset{\cdot\cdot}{O}}\!:^{\ominus}$$

R_1, R_2, and R_3 may be aliphatic, aromatic, heterocyclic or alicyclic. For example, the oxides of triethylamine, pyridine, dimethylaniline and dimethylcyclohexylamine are known as are those of hundreds of other amines in these classes. The amine oxides of interest in detergents are those derived from fatty amines such as dimethyldodecylamine.

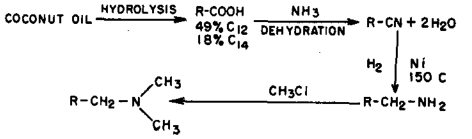
Amine oxides were first studied in the last decade of the nineteenth century but little was done at that time toward defining their properties or finding practical applications. In the 1930's and '40's, investigators found evidence of amine oxide structures in alkaloids and other naturally occurring materials, and the widespread occurrence of amine oxides in nature was soon recognized. Chemotherapeutic investigations showed that alkaloid amine oxides retained the physiological and therapeutic effectiveness of the parent bases but were much less toxic. This, plus the mild antibacterial activity shown by certain amine oxides, prompted extensive investigations resulting in numerous publications and patents relating primarily to heterocyclic and heteroaromatic amine oxides. Examples of successful ventures resulting from this work are diazepine oxide tranquilizers and pyridine oxide antibacterials.

The utility of aliphatic amine oxides as surfactants was first noted by Du Pont, who obtained a patent in 1939 relating to dialkylaminoacid oxides for use as detergents and foam stabilizers (1). A U.S. patent granted to I. G. Farbenindustrie A. -G. later the same year disclosed dimethyldodecylamine oxide as a wetting, cleansing, and dispersing agent (2). This oxide has found a limited market in the textile industry, and has been offered by Onyx Chemical Corp. for the past several years under their "Ammonyx" trademark. In 1956, a patent assigned to Firestone Tire & Rubber Co. described the use of dimethyldodecylamine oxide as a foam stabilizer in the production of foam rubber articles (3). The cationic activity of amine oxides was first mentioned in 1958 by British workers, who suggested that the oxides have the same advantages and disadvantages as quaternary ammonium compounds (4). It was not until 1961, 22 years after the Du Pont and I. G. Farben disclosures, that attention was focused on fatty amine oxides for household detergent uses. In September 1961, new liquid detergent formulations based on amine oxides were disclosed in patents (5,6) assigned to Procter & Gamble Co. Subsequent patents and publications have intensified the interest in fatty amine oxides in both detergent and non-detergent applications. Fatty amine oxide products have been introduced on a development scale by several chemical manufacturers.

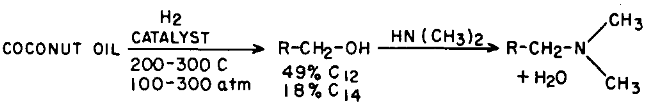
Routes to Fatty Amines

The fatty tertiary amine precursor to the oxide can be made in a variety of ways starting from naturally occurring materials such as coconut oil and tall oil or from petrochemicals such as the "Alfol"* alcohols.

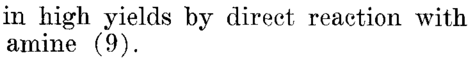
A well-established route to fatty amines involves classical fat hydrolysis, reaction of the free fatty acids with ammonia, and hydrogenation of the resulting nitriles (7). The primary amines so obtained can then be alkylated to tertiary amines.



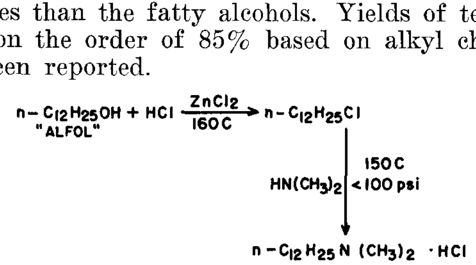
An alternate route to these tertiary amines is hydrogenolysis of the fat followed by reaction of the fatty alcohols with dimethylamine (8). Both steps require rigorous conditions.



Straight chain primary alcohols derived from petrochemical raw materials are potentially lower in cost than fatty alcohols from natural sources. These new "Alfol" alcohols can be converted to tertiary amines in high yields by direct reaction with a secondary amine (9).



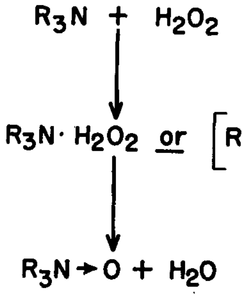
A more convenient route involves intermediate formation of alkyl chlorides (9). The chlorides react with secondary amines at lower temperatures and pressures than the fatty alcohols. Yields of tertiary amine on the order of 85% based on alkyl chloride have been reported.



Amine Oxidation

Conversion of the fatty tertiary amine to amine oxide is a relatively straightforward reaction. However, published procedures for tertiary amine oxidations have specified the use of a large excess of hydrogen peroxide or the use of a peracid system. Since none of these published procedures appeared commercially feasible, we have attempted to define optimum conditions for producing fatty amine oxides on a commercial basis. The results discussed below are based principally on dimethyldodecylamine oxidation, but can be applied generally to fatty dialkylamines in the C_8–C_{18} series.

The mechanism of amine oxidation by aqueous hydrogen peroxide as first proposed by Wieland (10) in 1921 involves the formation of an amine perhydrate or ammonium peroxide. The peroxide then decomposes to the oxide with loss of water.



Confirmation of this mechanism was recently obtained by A. A. Oswald and D. L. Guertin of Esso Research (11), who isolated ammonium peroxide intermediates formed from trialkylamines and then converted them to the corresponding amine oxides by heating. Oswald and Guertin also confirmed that amine oxides themselves form perhydrates with excess hydrogen peroxide. This ease of perhydrate formation perhaps accounts for the frequent patent and literature references to the oxidative power of amine oxides. For example, they have been cited both as polymerization initiators and as bleaching agents. Pure amine oxides should not be classified as oxidizing agents, whereas the perhydrates would be.

On investigating the effect of hydrogen peroxide concentration on conversion of dimethyldodecylamine to its oxide, we found that 35% aqueous hydrogen peroxide gave a faster reaction and more complete conversion than 70% peroxide (12). The results shown in Figure 1 are consistent with earlier work (13) showing that water is a unique solvent in ter-

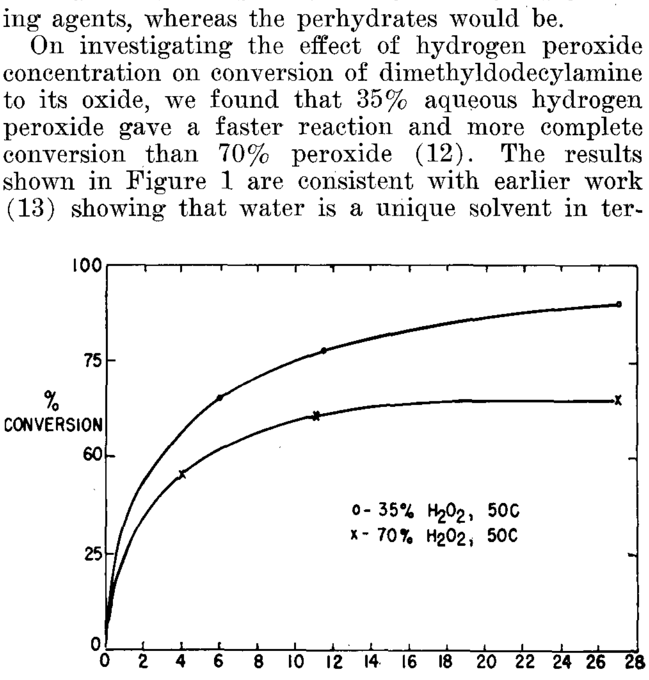


FIG. 1. Oxidation of dimethyldodecylamine without added solvent.

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* Registered trademark of Continental Oil Co.

tiary aliphatic amine oxidation and enhances the rate of oxide formation. The addition of water as the reaction proceeds accelerates the oxidation and also is required to prevent gel formation and permit continued agitation. However, if the dilution water is combined with the Hydrogen peroxide to give an initial hydrogen peroxide concentration of much less than 35%, the reaction rate is reduced significantly. In our preferred method for oxidizing dimethyldodecylamine and similar fatty amines, water is added stepwise as the reaction proceeds to give a 30–40% solution of amine oxide at 100% conversion.

The procedure is as follows: the amine is preheated to 60C, and 35% aqueous hydrogen peroxide is added over a one-hour period with good agitation. The reaction mixture is kept at 60–65C during peroxide addition; at temperatures much above this the solution becomes yellow, and at lower temperatures a longer reaction time is required. During the one-hour period while peroxide is being added, the mixture will gel unless water is also added. The water required for dilution is added in portions just sufficient to keep the reaction mixture fluid. After all the peroxide has been charged, the remaining dilution water to give the desired final concentration is added and the temperature of the reaction mixture is raised to 75C. Conversions approaching 100% can be realized in an additional three to four hours at the higher temperature. The solution is cooled and the unreacted hydrogen peroxide is destroyed by adding a stoichiometric amount of sodium sulfite.

We have found that the rate and extent of conversion depend markedly on the purity of the starting amine (12). The importance of this is shown in Figure 2. When a commercial grade of dimethyldodecylamine was oxidized with a 10% molar excess of hydrogen peroxide, the conversion in two hours was about 80%. Increasing the peroxide excess 2½ times raised the conversion only to about 87%. But when the commercial amine was distilled through a one-foot Vigreux column before oxidation, the two-hour conversion with a 10% molar excess of hydrogen peroxide was 99.2%. Purifying the amine, using a 10% molar excess of hydrogen peroxide, and following the recommended procedure should ensure a product essentially free from unreacted amine. This is desirable since the amine may be troublesome in some end uses.

A practical advantage of the aqueous hydrogen peroxide oxidation system just described is that the resulting 30–40% aqueous solution of amine oxide can be used directly in many applications, thus eliminating the cost of isolation and purification. Carrying out the oxidation in aqueous isopropanol permits the production of more concentrated amine oxide solutions but may result in lower conversions.

Amine Oxide Properties

Fatty amine oxide molecules are highly polar. The oxygen atom is linked to the nitrogen by a semipolar bond, with the electron density greater at the oxygen atom. The dipole moment of 4.38 calculated for the N → O bond is larger than the moments of other semipolar bonds such as P→O or S→O (14). Studies by Oswald and Guertin (11) of the infrared absorption spectra of adducts of various tertiary amine oxides with hydrogen peroxide and water have shown the existence of strong hydrogen bonding. As a result, fatty amine oxides are very hygroscopic and difficult to dry.

Anhydrous dimethylododecylamine oxide can be isolated with great difficulty by prolonged vacuum drying over a desiccant. The waxy solid has a mild, pleasant odor and melts with decomposition at about 120C.

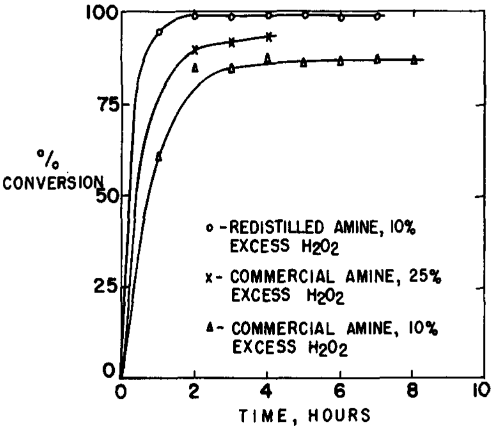
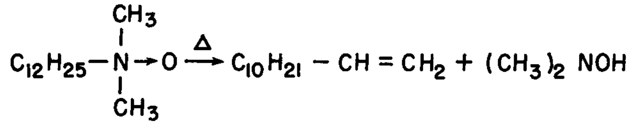


FIG. 2. Oxidation of dimethyldodecylamine by 35% hydrogen peroxide at 75C.

Although amine oxides are less basic than the parent amines they will form salts with strong acids. The sulfate of dimethyldodecylamine oxide can be dried more readily than the amine oxide itself. Our studies with this salt indicate that it can be spray dried.

An important factor in the chemistry of fatty amine oxides is their relative thermal sensitivity. This is typified by the well-known Cope elimination reaction (15).



$$C_{12}H_{25}-\underset{CH_3}{\overset{CH_3}{N}}\rightarrow O \xrightarrow{\Delta} C_{10}H_{21}-CH=CH_2+(CH_3)_2NOH$$

Dr. Cope's extensive studies of aliphatic and alicyclic amine oxides have shown that pyrolysis generally leads to the lower dialkylhydroxylamine and the longer chain or cyclic olefin.

In our studies, a 30% solution of dimethyldodecylamine oxide showed no change in amine oxide content or color after 5 days at 75C. However, the same solution heated at 100C lost about 2.8% of its original amine oxide content per day. Thermal sensitivity is not believed to be a serious problem in the liquid detergent end use.

Analytical Methods

The analytical procedure developed by Brooks and Sternglanz (16) is most commonly recommended for determining amine oxide purity. This method is based on the reduction of amine oxide with an excess of titanium trichloride. The excess titanous ion is back-titrated with ferric sulfate solution.

An acidimetric method developed more recently by Armour Industrial Chemical Co. (17) is somewhat simpler and equally reliable. In the Armour procedure, one sample is titrated potentiometrically with standard hydrochloric acid to establish total alkalinity. Potentiometric titration of a second sample after quaternization of unreacted amine with methyl iodide gives the alkalinity due to amine oxide, and the difference between the two titers affords a measure of free amine content.

It has been proposed (12) that vapor-liquid partition chromatography may be useful for determining amine oxide content. This is based on the observa-

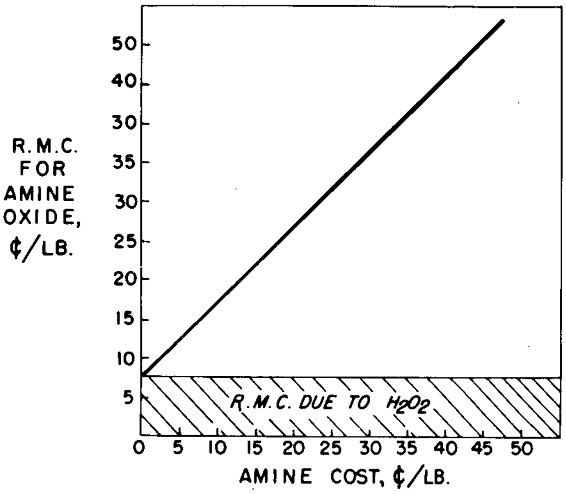


FIG. 3. Raw materials cost for dimethyldodecylamine oxide. (10% molar excess of H_2O_2; 98% conversion).

tion that thermal degradation occurs in the chromatograph column. If Cope elimination is quantitative under chromatograph conditions the peak for the olefin formed should afford a measure of amine oxide content.

Some difficulty in determining the amine oxide content of formulated detergents has been reported. The alkaline builders commonly included in detergent formulations interfere with the acidimetric procedure described above. However, the reductometric method of Brooks and Sternglanz has been found to give reliable results if the sample is first neutralized with concentrated hydrochloric acid.

Economics

The economics of fatty amine oxides depend primarily on cost of the parent amines. Figure 3 shows the raw materials cost per pound of dimethyldodecylamine oxide as a function of dimethyldodecylamine cost. With hydrogen peroxide available at 45.7¢ lb (100% basis), peroxide cost is 7.5¢ per pound of amine oxide assuming use of the recommended 10% molar excess. To realize a total raw materials cost of around 30¢/lb for the oxide, dimethyldodecylamine must be charged in at 20–25¢/lb. A raw materials cost of 30¢/lb for amine oxide should permit a selling price below 50¢/lb (100% basis). At this price level, fatty amine oxides should find broad market acceptance.

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Alpha-Olefins in the Surfactant Industry

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RELATIVELY SMALL SCALE commercial quantities of straight chain α-olefins have been available from animal fats and vegetable oils for many years. However, large scale production from this source is hindered by the relatively high cost of the natural starting materials and the expense of the saponification, reduction, and dehydration processes required. Therefore, up to the present α-olefins have not found extensive favor in the surfactant industry, except for low-volume, high-cost specialty products.

Recently, however, large scale production from petroleum of high-quality, low-cost α-olefins was announced. Thus, the surfactant industry now has the incentive to investigate present and potential uses of these reactive compounds. α-Olefins not only provide opportunities for commercial development of entirely new surfactants, but in addition, these new raw materials may give improved properties in many types of products and processes now based on highly branched olefins. For instance, surfactants prepared from α-olefins undergo much more rapid biodegradation than the analogous branched-chain products.

Of particular interest for surfactants are the higher molecular weight α-olefins (C_{11}–C_{20} carbons atoms) because these materials are easily convertible into surface-active products. However, the lower molecular weight olefins (C_6–C_{11}) offer potential advantages in plastics, polymers, hydrotropes, and many types of specialty products related to the detergent industry.

Some of these new large-volume α-olefins from petroleum are available in development quantities as single carbon number cuts at a permium price. However, of much greater interest to the surfactant industry are various blends of higher molecular weight olefins. In most detergent applications, these blends offer satisfactory properties and equivalent or superior performance as compared to single molecular weight material, as well as being more economical. Some of these blends are analogous to the fat-based olefins in that only even-numbered carbon chains are present. On the other hand, some large volume petroleum-based olefins contain both even- and odd-numbered carbon chains in approximately equal amounts. The optimum blend type and molecular weight split should be considered individually for each application, based on performance and availability.

In view of the foregoing, it appears worthwhile to present the chemistry of some of the most interesting surface active agents which may be derived from α-olefins. Properties and performance characteristics of some of these surfactants are also discussed.

Reactivity

Many types of reactants, both organic and inorganic, easily add across the terminal double bond of long-chain α-olefins. Addition reactions may be of either the ionic or free radical-type, depending on the particular reactants and conditions. For purposes of illustrating these types of addition (ionic and free