should be pointed out that Figure 2 represents a route which has been tried successfully, and Figure 3 is merely an analog of work successfully carried out on brassylic acid as a source of nylon 13,13.

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Industrial Uses of Palm, Palm Kernel and Coconut Oils: Nitrogen Derivatives

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ABSTRACT

Palm, palm kernel and coconut oils are sources of fatty acids that can be converted to other oleochemicals that have many applications. This paper describes manufacturing procedures, product characteristics and uses for many fatty acids, alcohols, primary amides, monosubstituted amides, diamides, disubstituted amides, nitrites, primary amines, secondary amines, tertiary amines, diamines, quaternary ammonium compounds, amphoterics, amine oxides and polyoxyalkylene alkylamines.

INTRODUCTION

Palm oil, palm kernel oil and coconut oil are excellent sources for fatty acids, alcohols and nitrogen derivatives of 8-18 carbon atoms, when the alkyl moiety is saturated or when the carbon chain is unsaturated with one double bond, as in the eighteen-carbon chain length.

TABLE I

Chain Length Composition of Coconut, Palm Kernel and Palm Oil (%)

Oil	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{18}=
Palm					1	43.5	4.5	40
Coconut	0.5	7.0	6.0	48.0	19.0	9.0	3.0	6.0
Palm kernel		3.5	3.5	48.5	16.5	8.5	2.5	14.5

TABLE II

Chain Length Composition of Tallow (%)

C_{14}	C_{14}=	C_{15}	C_{16}	C_{16}=	C_{17}	C_{18}	C_{18}=	C_{18}==
3.5	1.0	0.5	25.5	4.0	2.5	19.5	41.0	3.0

Table I contains the chain length distribution as it exists in these oils. In the C_{8-14} chain lengths palm kernel and coconut oil have no natural competition in the acid or amine category of derivatives, but there are competitive feedstocks available from petroleum-drived synthetic alcohols and acids. In the C_{16-18} acids and derivatives, there is no significant competition from synthetics. However, in this range competition from tallow is very significant. Table II contains the chain length distribution in tallow, which is the least expensive source for C_{16-18} fatty acids worldwide. In all cases, the end use requirements and economics will dictate the feedstock.

The production of fatty acids worldwide has grown rapidly since World War II. The estimated production is now close to 1.7 million metric tons (MT). Table III shows a breakdown by percentages of the various fields of application. A general overview of the fat and oil industry was presented at Montreaux last year (1).

TABLE III

U.S. Consumption of Fatty Acids by Market Area

Market area	% of total
Personal care products	19.7
Industrial lubricants, corrosion inhibitors, oil additives	18.1
Coatings	13.0
Household cleaners, laundry soaps, fabric softeners	8.0
Plastics	7.6
Textiles	6.7
Emulsion polymerization	5.5
Rubber compounding	5.0
Asphalt	3.4
Mining	1.7
Miscellaneous	11.3

INDUSTRIAL FATTY ACIDS

The raw materials for industrial fatty acid production fall into two quality feedstock classifications:

- Relatively pure triglycerides that are obtained by rendering and extraction and are relatively free of nonfatty materials, and
- Byproduct fat that is recovered from refining, degumming, deodorizing and other operations. The byproduct feedstocks consequently require special processing treatments.

Once a treated feedstock is obtained or a relatively pure triglyceride is used, various processes can be used to hydrolize the fat into free fatty acids and crude glycerine. The Twitchell process is still used in minimal operations, but is being phased out, except in special cases. Batch autoclaving at 180-230 C and 150-450 psi using lime or zinc oxide catalysts and water is still used, but is economically at a disadvantage. The most efficient method is the continuous countercurrent splitting procedure. In this case, the temperature is maintained at 250-260 C, the pressure is 750 psi, and after a residue time of approximately two hours, the fatty acid leaves the reactor at 98% FFA. The sweet water is removed at a concentration of 12-20% glycerine.

In many cases, the crude acids can be used as is. However, high-purity acids can be produced by simple distillation or fractionation. The simple distillation of palm, palm kernel or coconut oil acids will produce a fatty acid mixture as illustrated in Table I.

Fractional distillation of the above acids is now relatively straightforward, and because of the absence of odd chain constituent and of polyunsaturated moieties, the fractionation is less difficult. Table IV lists the boiling points of the referenced fatty acids at various pressures. Purities of 99% plus of each chain length are possible. Table V contains the freezing points of pure saturated acids. Ralston and coworkers in the 1940-1960 era conducted extensive research on fatty acids and derivatives. A great deal of data is available in their book (2).

INDUSTRIAL USES FOR FATTY ACIDS

Soap Production

As mentioned in Table III, the soap, detergent and personal care products markets are the largest usages of fatty acids. Approximately one third of the 1.7 million MT of fatty acids is used in these applications. At one time all soap bars were made in a batch process by simply adding the appropriate amount of caustic to a suitable fat in a soap mill. After thorough neutralization and mixing, the viscous soap is milled, plodded and extruded into bars. When the triglyceride is used as a feedstock, glycerine is produced and is continuously washed out of the system. Three processes: De Laval Centipure, Sharples and Monsavon can be used (3).

Since the advent of continuous fat splitters, soap bars are predominantly produced from distilled fatty acids and caustic or sodium carbonate. The Mazzoni process is probably most widely used. Fatty acid and a caustic solution are continuously fed to preheaters at 50-60 C. Neutralization balance is continuously monitored and fed to a multistage centrifugal mixer. The soap is continuously recirculated at 90 C. The soap is then cooled, extruded and cut into suitable bars. The final product can also be flaked or prilled depending on the end use.

A modification of the Mazzoni process was built by Armour and Co. In this case, the neat soap is spray-dried in a Mazzoni vacuum dryer at 27-28 mm Hg and then extruded into bars. The usual bar of toilet soap can be produced from approximately 85% tallow-derived acids and 15% coco-derived acids. Of course, the feedstocks can vary. The coconut acid feedstock enhances the foaming characteristics of the soap bar.

Liquid soaps are also produced from fatty acid feedstocks. In this case, because of solubility problems, the usual feedstock is mainly coconut acids and unsaturated acids, and the neutralization is done with KOH instead of NaOH. The final concentration of solids is usually 20-25%. Recently, synthetic detergent soap mixtures have been used.

Fatty acids and fatty acid esters are used in a very large variety of cosmetic formulations. The oleophilic nature of these compounds makes them valuable as emollients, creams, lotions, moisturizing agents, etc. The endproducts and formulations are too numerous to include, but can be

TABLE V

Freezing Points of Saturated Acid (° C)

No. of carbon atoms	F.P.
6	−3.24
7	−6.26
8	16.30
9	12.25
10	31.24
11	28.13
12	43.92
13	41.76
14	54.10
15	52.54
16	62.74
17	60.94
18	69.60

TABLE IV

Boiling Points of n-alkyl Acids (° C)

Pressure (mm)	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic
1	61.7	87.5	110.3	130.2	149.2	167.4	183.6
2	71.9	97.9	121.1	141.8	161.1	179.0	195.9
4	82.8	109.1	132.7	154.1	173.9	192.2	209.2
8	94.6	121.3	145.5	167.4	187.6	206.1	224.1
16	107.3	134.6	159.4	181.8	202.4	221.5	240.0
32	120.8	149.2	174.6	197.4	218.3	238.4	257.1
64	136.0	165.3	191.3	214.6	236.3	257.1	276.8
128	152.5	183.3	209.8	234.3	257.3	278.7	299.7
256	171.5	203.0	230.6	256.6	281.5	303.6	324.8
512	192.5	225.6	254.9	282.5	309.0	332.6	355.2
760	205.8	239.7	270.0	298.9	326.2	351.5	376.1

found in many publications. Frequently the soaps or surfactant esters will provide emulsifying properties to the cosmetic formulation. The following is a list of cosmetic applications where fatty acids and/or derivatives are used in various formulations.

- Hand creams and lotions
- Emollient creams and lotions
- Liquid and cream shampoos
- Shaving soaps and creams
- Face powders and bath powders
- Rouges
- Hair dressings
- Hair conditioners
- Hair colorants and tints
- Aromatic products
- Deodorants and antiperspirants
- Eye creams and mascara
- Baby toiletries

Metallic Soaps

Metallic soaps are another class of fatty acid derivatives that are used extensively. The combination of acids and metal compounds to produce this specialty class of soap is almost limitless. However, the metallic stearates are the largest commercial class.

The methods of production are also many and varied, but the general reaction is fatty acid neutralization with CaO. The reaction is usually conducted at 150-200 C, and the fused mass is allowed to solidify. It may then be ground, powdered or pelletized before packaging. It should be emphasized that the soap may be derived from many fatty acids and metallic constituents.

Following is a list of applications for metallic soaps. Time does not permit details on the applications.

- Driers for paints, varnishes and printing inks
- Catalysts in condensation reactions
- Stabilizers for PVC resins
- Fungicides
- Lubricants
- Mold release agents
- Lubricants in paper coating
- Lubricants for drawing ferrous metals
- Antiblocking and anticaking agents
- Water repellants
- Cosmetic formulations
- Lubricating greases

A large list of other applications for fatty acids can be found in reference (3).

Rubber Application

Another market for fatty acids that are produced from the subject oils is the rubber industry. They can be used for manufacturing of synthetic elastomers as the emulsifiers in polymerization, and in compounding to obtain optimum processing and vulcanization characteristics. Fatty acids perform several functions when compounded into rubber. They act as softeners or plasticizers so that the rubber formulation can be handled more easily during mixing and subsequent forming operations such as calendering, extrusion and molding. The fatty acids also act as lubricants and release compounds to prevent the rubber sticking to the molding equipment.

The main role of the fatty acid is in the vulcanization reaction. Vulcanization is done by heating plasticized rubber with sulfur and other vulcanizing agents including accelerators, zinc oxide, long-chain saturated fatty acids or the zinc soap of these acids. The object is to cross-link the rubber molecules and the fatty acid or its derivative.

Table VI illustrates the value of fatty acid additions. Beyond 10 PHR additional acid has no effect. Lauric acid does not have to be the acid of choice. The acid used will be based on availability and cost, which is why stearic acid, of 70-90% C_{18}, is usually used.

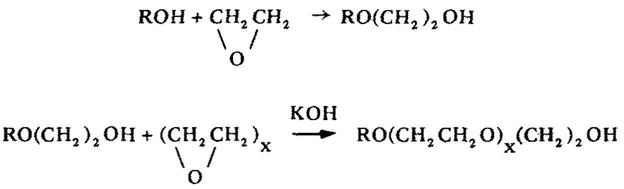
Fatty Derived Alcohols

Fatty alcohols can be produced from a wide variety of fats. The chain length can be from 8 to 22 carbon atoms. The detergent alcohols are usually 12-18 carbon atoms in length, with 12-14 dominating. Fatty alcohols compete directly with a large number of petrochemically derived alcohols of similar chain lengths, and again economics play the major role as to which alcohol is used. The primary use for fatty alcohols is in the surfactant market which is dominated by alkylbenzenes at 65%. The remaining 35% of the surfactants are alcohol-derived, with 21% synthetic and 14% natural.

The natural alcohols come from three sources: coconut oil, palm kernel oil and tallow. Natural alcohols in the C_{16-18} range are produced predominantly from tallow. Most of the natural alcohols are produced by reduction of methyl esters, but fatty acids also can be reduced to alcohols. Currently about 500 mill MT of natural alcohols are produced worldwide, with detergent producers dominating the market (1).

As surfactants, the alcohols are sulfated with SO_3 and then neutralized, usually with NaOH. The resultant sodium sulfate then can be used in a large variety of detergent and cleaning formulations. A typical heavy-duty liquid example is shown in Table VII.

Nonionic surfactants are also derived from alcohols by ethoxylation:



$$ROH + \underset{O}{CH_2CH_2} \rightarrow RO(CH_2)_2OH$$

$$RO(CH_2)_2OH + (\underset{O}{CH_2CH_2})_x \xrightarrow{KOH} RO(CH_2CH_2O)_x(CH_2)_2OH$$

TABLE VI

Effect of Lauric Acid Concentration on Cross-Linking Reaction in MBT[a] Accelerated Natural Rubber Sulfur Systems (4)

Lauric acid conc., phr	0	2	4	8	10	15
Stress at 200% elongation, psi	25	100	200	250	300	300

[a] MBT = Mercaptobenzothiazole.

The basic recipe was natural rubber, 100.0 phr; zinc oxide, 10.0 phr; MBT, 2.0 phr; sulfur, 1.0 phr.

Similar effects were observed at sulfur levels of 0.50 and 0.65 phr.

TABLE VII

Example of Heavy Duty Liquid Cleaning Formulation

Component	% by weight
Sodium alkylsulfate	30
Ethanol	6.5
Triethanolamine	10.0
Whitener	0.3
Water, perfume and dye	q.s.
Total	100

The additional moles of ethylene oxide added to the alcohol are varied. Properties of the resultant nonionic surfactant will depend on the chain length of the starting alcohol and the number of moles of ethylene oxide. Figure 1 represents typical detergency data that can be obtained by varying both parameters (5).

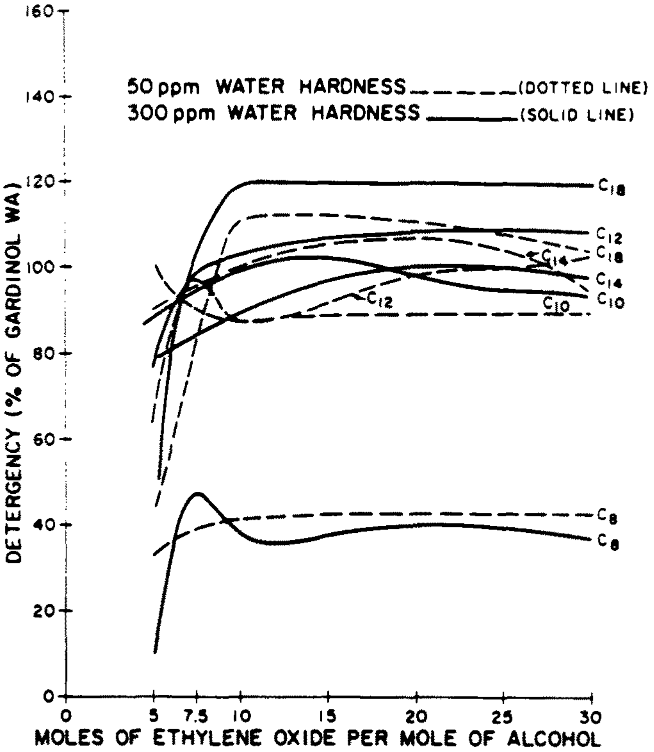


FIG. 1. Detergency of oxyethylated straight-chain alcohols on active basis at 0.2% concentration in hard water.

The solid lines represent cotton detergency expressed as percent GARDINOL WA (DUPONOL WA, trademark of E.I. DuPont de Nemours & Co.) in 300 ppm water hardness, 0.2% concentration as determined in Launder-Ometer at 60 C by eight replicate swatches (6). The dotted lines represent cotton detergency expressed as percent GARDINOL WA in 50-ppm water hardness, 0.2% concentration as determined in Launder-Ometer at 60 C by eight replicate swatches.

From Figure 1 it is evident that the poorest detergents for cotton are the n-octanol-EO adducts which have the lowest molecular weight alcohol as a starting raw material. It may also be deduced that the best detergents are based on n-octadecanol-EO adducts, which are the alcohols of highest molecular weight used in this study. These trends are not only true for detergency in 50 but also in 300-ppm hardness. No significant difference between the EO adducts of C_{10}, C_{12} and C_{14} alcohols has been observed except that the C_{12} adduct appears to increase slightly with EO addition, whereas the C_{10} and C_{14} alcohol adducts level off at 10 moles of ethylene oxide, in line with the general behavior of nonionic surfactants. In general, it can be seen from Figure 1 that once a maximum in detergency is obtained, the further addition of ethylene oxide has little effect on the detergency values.

While the major use for fatty alcohol is in the surfactants described above, it should be recognized that these alcohols can be and are used for scores of other products, such as esters and other chemical intermediates.

NITROGEN DERIVATIVES OF FATTY ACIDS

Primary Amides

Introduction of the nitrogen atom into fatty acids opened up a large spectrum of fatty nitrogen derivatives. Again, Ralston and coworkers (2) have done extensive research on these compounds. Simple amides are usually prepared in industry by the reaction of the fatty acid with anhydrous ammonia (7). In this process, the ammonia and fatty acid are reacted at 180-200 C at a slight pressure (50-100 psi) for 10-12 hr. Ammonia and water are continuously removed from the reactor. The ammonia is recovered and recycled. Boric acid has been used as a catalyst in the amidation of fatty acid by Benbasat and coworkers (8). Other catalysts include AL_2O_3 (9), Ti and Zn alkoxides (10).

Primary amides can also be produced from methyl esters of fatty acids by the reaction with ammonia at high temperatures (220 C) and pressures (1800 psi). The reaction time can be as low as one hour.

Uses of Amides

Solubilities of saturated primary amides are shown in Table VIII, and melting points in Table IX.

Solubility characteristics of the simple amides lead to their main use, the most important of which is as an antislip and antiblock additive for polyethylene film. For this use, octadecenamide and docosenamide are the most important. Unfortunately, the feedstock for docosenamide is not available from palm or coconut oil feedstocks.

Usually fatty amides are added to polyolefins using the master batch technique. A polyolefin master batch will be made by adding 5% of the amide to the resin and then adding the master batch to the resin at a rate so that 0.1-0.5% of amide is in the final resin, but even at these concentrations the color stability of the amide is important. The use of these additives is permitted in food packaging materials by FDA regulations.

TABLE VIII

Solubilities of Amides of Saturated Acids at 30 C

No. of C atoms in amide	Grams per 100 g solvent					
	Benzene	Tetrachloromethane	Acetone	Methanol	95% ethanol	Acetonitrile
8	0.6	0.4	7.8	53.0	32.8	5.4
10	0.8	0.2	3.8	15.2	12.0	1.4
12	1.0	0.4	3.4	12.4	11.4	0.9
14	0.4	0.1	1.0	2.7	3.8	0.6
16	0.4	0.1	0.8	1.2	1.5	0.3
18	0.4	0.1	0.5	0.7	0.8	0.2

TABLE IX

Melting Points of n-alkylamide

Carbon atoms	Melting point (°C)
6	101
8	105.9[a]
10	98.5[a]
12	102.4[a]
14	105.1[a]
16	107[a]
18	109.7[a]
20	108
22	111
$18^=$	70-78[b]
$22^=$	76-86[b]

TABLE X

Monosubstituted Amides

Compound	MP C
R'CONHR $R'=22^=$ $R=18$	72-75
R'CONHR $R'=22^=$ $R=22^=$	55-58
R'CONHR $R'=16$ $R=18^-$	69-72
R'CONHR $R'=18$ $R=18$	92-95
R'CONHR $R'=18$ $R=22^=$	72-75

Because of the long fatty chain and the polar nature of the amide function, the fatty amides will orient at the surface of the resin with the polar function above the surface to provide the slip properties.

Another use of long-chain saturated amides is as intermediates in the production of water repellents for textiles of the Zelan or Velan type. The products of reaction of the amide with formaldehyde, pyridine, and hydrochloric acid are water-soluble quaternary salts which are applied to the fabric and heated to form a water-repellent film, probably diamide in structure.

Films of fatty acid amides are deposited from a variety of formulations as mold-release agents. A solution of the amide is usually sprayed onto the mold. With rubber goods, the saturated amide is added to the rubber mix before curing and assists in curing and improvements of the mechanical properties.

Fatty acid amides improve the properties of printing ink by assisting slip, reducing gloss, reducing block and tack, and improving resistance to scuffing, scratching, and rub-off. Better spreading properties at the ink-paper interface are obtained along with improved adhesion of the ink to the paper.

The ability of fatty acid amides in hydrocarbon solvents to adhere to metal surfaces makes them valuable additives to lubricants. They increase the wear characteristics of the lubricant and leave no carbon deposits on the metal surface. Both saturated and unsaturated amides may be used for this purpose.

Monosubstituted Amides

Monosubstituted amides (RCONHR) can be produced from a variety of acids and primary amines. R or R' or both can be derived from a fatty source. The main products usually produced from a C_{16-22} fatty acid are amines that are saturated or unsaturated. Again, the main uses for these compounds are for slip additives, lubricants or mold-release compounds. Table X contains the melting points of a series of monosubstituted amides that are commercially available.

Diamides

The main diamide produced from fatty acids is ethylene bisstearamide [$RCONH(CH_2)_2NHCOR$] prepared by the reaction of 2 moles of stearic acid with ethylenediamine. The reaction is run at 180-185 C under slight pressure with continual removal of water and under a nitrogen blanket.

The main products of this structure that are produced commercially are N,N-ethylene bisstearamide, which has a melting point of 135 C. These products are hard, waxy materials and find uses as lubricants, mold release agents and defoamers.

Disubstituted Amides

A very important series of commercial surfactants is produced by the reaction of fatty acids and esters with ethanolamines. The estimated U.S. production is 50 MT; the reactions between acids and/or esters is complicated by the competing functional groups. The reaction product of equimolar amounts of fatty acid and diethanolamine are water-insoluble, but it was noted by Kritchevsky that when 2 moles of diethanolamine were reacted with one mole of fatty acid at 140-170 C, a water-soluble surfactant was produced. The following reaction describes the mixture of products produced:

$$\begin{array}{rrr} RCO_2H + 2HN(CH_2CH_2OH)_2 & \rightarrow RCONH(CH_2CH_2OH)_2 & 65\% \\ & RCO_2(CH_2)_2NH(CH_2)_2OH & 5\% \\ & RCO_2(CH_2)_2NH(CH_2)_2O_2CR & 5\% \\ & RCO_2^-N^+H_2(CH_2OH)_2 & 2\% \\ & HN(CH_2CH_2OH)_2 & 23\% \end{array}$$

The percentages listed are appropriate, and the endproduct is a mixture that depends somewhat on the reaction conditions. In spite of the mixture produced, this process continues to be used commercially.

More recently, superamides were introduced. This process uses essentially equimolar quantities of methyl ester and diethanolamine (11). The reaction is conducted at atmospheric pressure at 100-110 C using sodium methylate as a catalyst with the constant removal of methanol. The final product is essentially 90% fatty diethanolamide [$RCONH(CH_2CH_2OH)_2$]. The preferred chain length is C_{12-14}, although in some cases to obtain a more oil-soluble surfactant longer chain lengths will be used.

The main use for these surfactants is in liquid detergent formulations. A typical example is shown in Table XI. The amides enhance detergency and are excellent foam boosters.

Another series of alkoxylated amides is of commercial significance. These are produced by the reaction of primary amides with an alkylene oxide such as ethylene oxide. The

TABLE XI

Typical Dishwashing Formula

20%	Sodium dodecylbenzenesulfonate
10%	Ammonium salt of sulfated polyoxyethylenenonylphenol
5%	Coco Diethanolamide
65%	Water, dye, perfume

general properties of this type of product are similar to those of previously described amides, and they find specific uses.

Other disubstituted amides are produced, with N,N-dimethylamide [$RCON(CH_3)_2$] a typical example. Using rather mild conditions, dimethylamine will react with fatty acids at 30 C in a relatively short time. The methyl esters can also be used. Higher dialkylamines require higher temperatures to form N,N-dialkylamides. The N,N-dialkylamides are excellent solvents and are used in a number of formulations.

AMINE DERIVATIVES OF FATTY ACIDS

The production of amine derivatives of fatty acids results in literally hundreds of commercially used endproducts. Almost all these uses depend on the cationic nature of the amine derivatives. Most amines start with a nitrile base which is produced by the reaction of fatty acids. Nitriles are the building block for amine derivatives. When producing primary amine via reduction, nickel catalysts, using an ammonium suppressant to prevent excess secondary formation, are most commonly used. Secondary amines are produced by venting off the ammonia. From the primary or secondary amines, a very large variety of tertiary amines can be produced. The most widely produced tertiary amines are the dimethylalkylamines, methyl dialkylamines and the alkoxylated amines. These amines have end uses of their own, and are also used as intermediates to a wide variety of cationic surfactants. Discussion in this article will include primary, secondary and tertiary amines plus many derivatives of these amines, such as quaternary ammonium compounds, alkoxylated derivatives, amphoterics and amine oxides. In recent years, there have been many publications describing these products (12-16).

Nitriles

Nitriles have been produced from fatty acids for the last 50 years. Commercially today, the production is done by either a batch or a continuous process. The reaction is run at 280-360 C and frequently uses a metallic oxide catalyst. The overall reaction is:

$$RCO_2H + NH_3 \rightarrow RC{\equiv}N + 2H_2O$$

While this reaction appears to be quite simple, several equilibrium reactions should be considered as taking place:

$$RCO_2H + NH_3 \rightleftarrows RCO_2NH_4 \rightleftarrows RCONH_2 + H_2O \rightleftarrows RC{\equiv}N + H_2O$$

In the reaction sequence, the water of reaction must be removed continuously to minimize undesirable impurities in the finished nitrile (17-22). The most undesirable contaminants are aliphatic amides.

Commercially the continuous reactors are run in thousands of pounds per hour, and this depends strictly on the size of the production equipment. The continuous process is really used by one company and is the invention of Potts (23-28). In this method fatty acids are fed continuously to a reactor column countercurrently with ammonia. Excess ammonia and water are removed at the top of the column, and the stream is sent to an ammonia absorber for recovery and recycling. The product nitrile is removed from the reactor column as a vapor and is condensed and used as is. Usually no additional distillation is needed.

The batch or liquid phase procedure can take as long as 24 hours and the endproduct is usually distilled before further use. Reactor sizes can vary, but seldom are less than 2,000 gallons. Unsaturated feedstocks have a tendency to polymerize at higher temperatures, so they are usually run at lower temperature, but require a longer reaction time. Catalysts such as ZnO or $Mn(CH_3CO_2)_2$ at 0.1-0.25% by weight can be used. The ammonia rate is adjusted to the rate of reaction, and usually about two moles per mole of acid are required. The excess ammonia, of course, has to be recovered and purified for recycling.

Primary Amines

Many methods for the preparation of amines are known, but commercial production is usually based on hydrogenation of a nitrile in either a batch or a continuous process. Several nickel and cobalt catalysts are used for this purpose. Caustic and/or ammonia metal soaps have been used to suppress the formation of secondary amine in the Raney nickel- or cobalt-catalyzed hydrogenation of fatty nitriles to primary amines (29-30). These alkalis, however, are reported to yield an undesirable residue during hydrogenation. This can be avoided by using ammonia and a small amount of water instead of alkali. Waddleton (31) has obtained over 96% yield of primary amine by hydrogenating a nitrile at 130-140 C with a partial pressure of ammonia of 2.07 MPa (300 psi) and a total pressure of 3.45 MPa (500 psi) with hydrogen in the presence of Raney nickel catalyst. Other catalysts include mixtures of Ni, Al, Co oxides (32), Zn-Al_2O_3 or Zn-Cr oxides (33), and Cu-Cr-alkali (34), but they generally produce mixtures of primary, secondary and tertiary amines. In continuous processes for making primary amines, both Raney cobalt and nickel catalysts are useful. Ammonia, lower alkylamines, or substances yielding hydroxyl ions are used as suppressants of secondary amine formation. Other procedures include recycling partially converted primary amines, nitrile, ammonia, and hydrogen over a cobalt catalyst bed (35) and introducing hydrogen in small fractions at regular intervals along the reaction zone using Raney nickel catalyst (36). The unsaturation can be preserved during cobalt- or nickel-catalyzed hydrogenations or unsaturated nitriles under certain conditions (37-39).

Fatty acids can be converted directly to primary amines by catalytic hydroammonolysis at high temperatures (300 C) and pressures (30.4 MPa or 4400 psi) in the presence of nickel and/or cobalt (40) or zinc and/or chromium (41) or rhenium (42). Similarly, methyl esters (43) and fatty acids glycerides (44) can be directly converted to amines. In a continuous manufacturing process for diamines, dicarboxylic acids react with excess ammonia in the presence of hydrogen and powdered cobalt oxide at high temperature and pressure (45). The physical properties of primary amines were extensively studied by Ralston et al. (2) in the 1940-1960 era.

Since the initial uses for primary amines were due to their solubilities, cationic nature and characteristics of their salts, much physical data on these matters were collected. The melting points are shown in Table XII.

Primary Amine Uses

Primary amines of the saturated higher members are used as hard rubber mold release agents, and dodecylamine is used in reclaiming both natural and synthetic rubber. The amines and their salts are effective flotation agents for concentrating lower grades of phosphate rock and are effective collectors for mica, feldspar and silica. Amines are the basis for formulations used in protecting hygroscopic materials against atmospheric moisture. They can be used in anticaking granular and blended fertilizers and in the single salts of ammonium nitrate, sylvite, sodium nitrate, ammonium sulfate and urea. The fatty amines are of considerable value in the petroleum industry at all stages, from the well head through the finished product. The inherent oil solubility, affinity for metal surfaces, oiliness properties, and acid neutralizing and bactericidal activity are of value for lubricating additives, corrosion inhibitors and fuel and gasoline additives. The amines are used extensively as intermediates in the manufacture of salts, quaternaries, ethoxylated derivatives and isocyanates.

Secondary Amines

Secondary amines can be easily manufactured from either nitriles or primary amines. The formation of an intermediate imine in the hydrogenation of a nitrile to a secondary amine is suggested (46). Young (47) has shown that by continuously removing ammonia during the reaction, nitriles can be converted to secondary amines in good yields. Thus dodecanitrile was hydrogenated at 200 C and 10.3 MPa (1500 psi) over Cu-SiO_2-Na catalysts to a product containing over 90% secondary amine (48).

Shapiro (49) has developed a two-stage reaction starting from hydrogenation of nitrile to primary amine at low temperature and moderate pressure followed by a second stage of reductive deamination at high temperature and low pressure. Catalysts such as cobalt or nickel (50) can be used for the first stage, and cobalt or CU-Cr (51) for the deamination. The Raney nickel-catalyzed deamination of primary amine to secondary amines also involves the formation of an intermediate imine (52). The unsaturation could be preserved by using Cu-Cr catalyst (53).

Table XIII shows the melting points of symmetrical secondary amines.

Tertiary Amines

Most of the industrially useful aliphatic tertiary amines are either symmetrical amines, methyl dialkyl amines or dimethyl alkyl amines, or those derived by the reaction of primary or secondary amine with alkylene oxides, which find use in manufacture of quaternaries and other derivatives.

TABLE XII

Melting Points of Saturated Primary Amines (R—NH_2)

R=	M.p.C°	R=	M.p.C°
CH_3	−92.5	$C_{11}H_{23}$	16.5
C_2H_5	−80.6	$C_{12}H_{26}$	28.0
C_3H_7	−83.0	$C_{13}H_{27}$	27.0
C_4H_9	−50.5	$C_{14}H_{29}$	37.9
C_5H_{11}	−55.0	$C_{15}H_{31}$	37.3
C_6H_{12}	−19.0	$C_{16}H_{33}$	46.2
C_7H_{15}	−23.0	$C_{17}H_{35}$	49
C_8H_{17}	− 0.4	$C_{18}H_{37}$	51.8
C_9H_{19}	− 1.0	$C_{20}H_{41}$	57.8
$C_{10}H_{21}$	15.0	$C_{22}H_{45}$	62.7

TABLE XIII

Melting Points of Symmetrical Secondary Amines

Amine	Melting point (°C)
Dihexyl	1.2
Dioctyl	26.7
Didecyl	41.5
Didodecyl	47.0
Ditetradecyl	60.62
Dihexadecyl	67.03
Dioctadecyl	72.3

There are several methods for the preparation of tertiary amines. One of the oldest procedures is the Leuckart reaction (54,55) using formaldehyde and formic acid for alkylation. Shapiro (56) developed the industrial reductive alkylation of primary and secondary amines with formaldehyde. N,N-dimethylamides can be reduced to tertiary amines at high temperature and pressure in the presence of Cu-Cr catalyst (57). Long-chain alcohols can be converted directly to N,N-dimethylalkylamines (58) by treating with dimethylamine at 360 C in the presence of $TH(SO_4)_2$ catalyst. Alkyl halides (59) and sulfates (60), when autoclaved with dimethylamine, yield tertiary amines. Alkylation of long-chain amines with short-chain alcohols (61-62) leads to tertiary amines. Adkin's catalyst (CU-Cr-Ba) was used in such reactions (63). Similarly, alkylation of long-chain amines to high molecular weight tertiary amines is achieved by treating the amine with a long-chain alcohol under hydrogenation conditions with Raney nickel or Cu-Cr catalyst (64), or with a catalyst such as Cu (65). Fatty tertiary amines are also produced from esters and tertiary amines. Ethyldodecanoate and triethylamine, under hydrogenation conditions, gave N,N-diethyldodecanamine (66). Secondary amines treated with olefins, carbon monoxide, and hydrogen in the presence of group VIII metal catalyst (e.g., rhodium) produce high yields of tertiary amines (67). Disproportionation of secondary amines by heating with catalyst amounts of ruthenium complexes gave mostly tertiary amines (68). Many other modified fatty tertiary amines are produced commercially.

Diamines

A fourth class of fatty amines produced commercially is the n-alkyl-1, 3 diaminopropanes manufactured by the following reactions:

$$RNH_2 + CH_2{=}CHC{\equiv}N \rightarrow RNH(CH_2)_2C{\equiv}N$$

$$RNH(CH_2)_2C{\equiv}N + RNH(CH_2)_3NH_2$$

The quality of the final product depends on the cyanoethylation procedure. This reaction can be carried to 98% (69).

The diamine applications depend on their cationic properties. In this case two amino functions are available which give these products excellent bonding ability on surfaces such as metals, textiles, plastics and minerals. They find many applications as corrosion inhibitors, pigment wetting agents, mineral flotation and floculation, asphalt emulsification, and antistrippers, biocides and petroleum additives. The diamines can also be further derivatized into numerous other compounds which will be discussed later.

QUATERNARY AMMONIUM COMPOUNDS

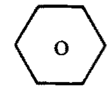
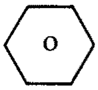
An almost infinite number of quaternary ammonium compounds can be produced because the available reactants are many and varied. The most convenient reaction is combining a suitable tertiary amine with an alkylating reagent. Table XIV describes the most commonly used alkylating agents and the structure of final quaternary ammonium compound.

The tertiary amines that can be used are found in the section on tertiary amines. Quaternary ammonium compounds can also be prepared from primary or secondary amines, but the process is used only to a limited extent because of the need for excess alkylating reagent and the difficulty of removing the produced salt.

Quaternary ammonium compounds have scores of uses

TABLE XIV

Quaternary Structure Obtainable from Various Alkylating Agents

Tertiary amine	Alkylating agent	Final quaternary ammonium salt	
R_3N	CH_3Cl	$R_3\overset{+}{N}CH_3$	Cl^-
R_3N	$(CH_3)_2SO_4$	$R_3\overset{+}{N}CH_3$	$CH_3SO_4^-$
R_3N	$(C_2H_5)_2SO_4$	$R_3\overset{+}{N}C_2H_5$	$C_2H_5SO_4^-$
R_3N	 CH_2Cl	$R_3\overset{+}{N}CH_2$ 	Cl^-

because of their affinity for negatively charged surfaces (70). Their single largest market is as fabric softeners, which accounts for 40,000 metric tons of 75% active material and is increasing at an annual rate of 4-5%. There are three types of consumer products. The original product is 3-8 wt % dispersion of quaternary and is added to the rinse cycle of the washing process. The second product developed is a quaternary formulation applied to a nonwoven sheet or a polyurethane foam, which is added with the wet clothes into the dryer. The formulation contains a transfer agent, usually a fatty-acid ester, which allows the quaternary to transfer from the substrate to the clothes. The latest innovation is the introduction of combined detergent, softener, and antistatic formulations, which allow the introduction of all ingredients in the wash cycle. In all cases, the benefits to the users are fabric softening, antistatic properties, ease of ironing, and odor improvement, the latter because of the addition of perfumes to the formulation. The most widely used and most effective products are dimethyldi(hydrogenated tallow)ammonium chlorides or methyl sulfates. The imidazolinium and amidoamine quaternaries are not as effective and cause fabric yellowing.

The second largest market for quaternary compounds is in the manufacture of organomodified clays. The main use for compounds of this type is in the addition of organomodified clay to drilling mud to improve the lubricity and rheology of the systems. With a rapid increase in well drilling and greater depths of drilling, use of the organoclays has grown rapidly. Current estimates are that about 14,000 tons of quaternaries are used annually in the organoclay market. Production of organoclays is by an ion-exchange reaction. The clay compound is dispersed in water and then combined with an equivalent amount of quaternary dispersion under thorough mixing conditions. The positively charged quaternary ions replace the positively charged inorganic ions on the clay surface. The organoclay product is then removed from the dispersion, dried, and ground to the proper particle size. There are three main quaternaries used for this reaction: dimethyldi(hydrogenated tallow)ammonium chloride, dimethyl(hydrogenated tallow)benzylammonium chloride, and methyldi(hydrogenated tallow)benzylammonium chloride. Besides drilling mud, the organoclays are used as thixotropic agents in paints, various coatings, grease additives, foundry additives, cosmetics (qv), resins, and printing inks. The properties desired in each specific system dictate the organoclay needed.

The third largest use for quaternaries is in the bactericidal or sanitizer market. The most popular types are those prepared from the reaction of benzyl chloride and dimethylalkylamine, wherein the alkyl group is C_{12}-C_{16}. These compounds in high concentration are viscous liquids, but they are usually sold as aqueous solutions. A wide variety of these solutions is used as sanitizing agents for cleansing eating utensils and food-processing equipment and as cleaning compounds in restaurants, dairies, and hospitals. They have advantages over phenols and chlorine-containing disinfectants in that they are nonirritating and odor-free and have relatively long activity. Quaternary ammonium compounds containing three methyl groups and one long alkyl chain, e.g., trimethyloctadecylammonium chloride, also exhibit excellent germicidal activity. The only drawback may be in their formulation. Compounds containing two methyl groups and two alkyl groups, such as those derived from coconut-oil fatty acids, are most effective against anaerobic bacteria, e.g., those that occur in oil wells. These bacteria are sulfate reducers, and their growth frequently causes severe corrosion problems in oil wells as well as plugging of formations. The surface-active property of quaternary ammonium compound also helps in removing oil from the sandstone formation.

The advent of pollution concern and the rising price of petroleum products have also increased the use of cationic emulsifiers in producing water-based asphalt emulsions for road building and maintenance. Compounds such as the trimethyl quaternaries are particularly useful for a noncorrosive cationic system. The cationic emulsions can be produced without any polluting solvents and can be designed to break on contact with the negatively charged aggregates used in road maintenance (71).

Quaternary ammonium compounds are usually prepared in stainless steel or glass-lined equipment. The amine and solvent, e.g., isopropyl alcohol, water or both, are loaded into the reactor and heated to the proper temperature (usually 80-100 C), and then the alkylating reagent is added. In the case of methyl chloride, the system is under pressure. The reaction is exothermic and cooling is required. The resulting product, after reaction, is analyzed, the activity and pH is adjusted, and usually any insolubles are removed by filtration.

A unique type of quaternary ammonium compound can be prepared from the reaction of alkylene oxides with amine salts, in which the anion can be one of a variety of possibilities and can be chosen to be noncorrosive (76).

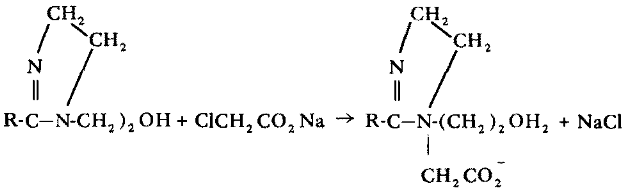
AMPHOTERICS

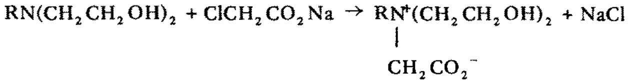
Another important class of cationic surfactants are amphoterics. This is a relatively small segment of the nitrogen fatty derivative business, but these specialty products have utility. They can function in acid or basic pH systems. At their isoelectric point, they exhibit special behavior of minimum solubility, foaming and wetting. Anionic properties are found in basic systems and cationic properties in acid systems. At the isoelectric range, these products are truly amphoteric.

Amphoterics are produced from a variety of tertiary amines, by dissolving the amine in a polar solvent in which sodium chloride is essentially insoluble, usually low molecular weight alcohols, and then adding the sodium chloracetate. The salt then precipitates and is removed by filtration.

One of the most common series of betaines produced is in the following reactions:

$$RN(CH_3)_2 + ClCH_2CO_2Na \rightarrow RN^+(CH_3)_2CH_2CO_2^- + NaCl$$





$$RN(CH_2CH_2OH)_2 + ClCH_2CO_2Na \rightarrow \underset{\displaystyle CH_2CO_2^-}{RN^+}(CH_2CH_2OH)_2 + NaCl$$

Amphoterics are also manufactured by the reaction of fatty amines with methyl acrylate at 110 C via the following reactions:

$$RNH_2 + CH_2{=}CHCO_2CH_3 \rightarrow RNH(CH_2)_2CO_2CH_3$$

$$RNH(CH_2)_2CO_2CH_3 + NaOH \rightarrow RN^+H(CH_2)_2CO_2^-$$

The endproduct desired can be the salt of the amphoteric or, if neutralized to the isoelectric point, a zwitterion is obtained.

A different type of amphoteric is produced by the reaction of primary amines with crotonic acid.

$$RNH + CH_3CH{=}CHCO_2H \rightarrow RN^+HCH(CH_3)(CH_2)_2CO_2^-$$

Again the endproduct can be the true zwitterion at the isoelectric point or the salt at a basic pH. The products are usually used in basic media in water solutions. Because of their structure, these compounds are frequently referred to as glycinates.

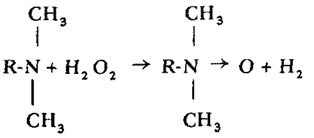
AMINE OXIDES

Fatty-derived aliphatic oxides are a class of nitrogen derivatives that can be classified as weak cationic surfactants. Almost all production is done from tertiary amines that have a long-chain aliphatic group and two methyl groups or two hydroxyethyl groups. Amine oxides are hydroscopic compounds that have large dipole moments and are soluble in polar solvent, but relatively insoluble in nonpolar solvents.

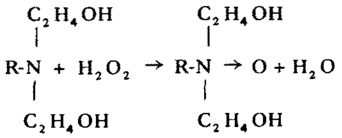
Aliphatic amine oxides behave as typical surfactants in aqueous systems. Below the critical micelle concentration (CMC), dimethyldodecylamine oxide exists as a simple basic molecule. In the presence of an anionic surfactant such as sodium dodecylbenzenesulfonate any protonated amine oxide present will form an insoluble salt (74). Salt formation results in an increase in the pH of the remaining solution due to protonation of more amine oxide by water, with a consequent increase in hydroxide ion concentration. At the CMC, a mixed micelle is formed containing a 3:2 ratio of oxide:sulfonate. Above the CMC, the micellar system solubilizes any of the salt that is present. For all oxides of commercial interest, physical data are usually available only as industrial specifications for solutions of these materials, although some studies have been made of phase behavior and chain mobility in various mesomorphic phases (75).

Manufacture

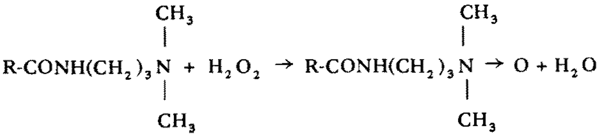
The largest-volume industrial amine oxides are derived from alkyldimethylamines, alkylbis(2-hydroxyethyl) amines and amidoamines. All cases contain the alkyl group which may have 8-20 carbon atoms and may or may not be unsaturated. The three general reactions are as follows:



$$R\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} + H_2O_2 \rightarrow R\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} \rightarrow O + H_2$$



$$R\text{-}\overset{\displaystyle C_2H_4OH}{\underset{\displaystyle C_2H_4OH}{N}} + H_2O_2 \rightarrow R\text{-}\overset{\displaystyle C_2H_4OH}{\underset{\displaystyle C_2H_4OH}{N}} \rightarrow O + H_2O$$



$$R\text{-}CONH(CH_2)_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} + H_2O_2 \rightarrow R\text{-}CONH(CH_2)_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} \rightarrow O + H_2O$$

Most frequently, the commercially available amines are homologous mixtures. The procedure employed for oxidation consists essentially in adding aqueous hydrogen peroxide to a well-stirred solution or dispersion of the amine at 60-80 C. Since the reaction is exothermic, cooling may be necessary during addition of the hydrogen peroxide. However, when addition is complete, it is usually necessary to supply heat in order to maintain the desired temperature during a digestion period.

With isopropyl alcohol or aqueous isopropyl alcohol as the solvent, concentration of amine oxide up to 65-70% can be attained. When a strictly aqueous system is employed, final concentrations of amine oxide should be limited to 35% since higher concentrations tend to gel and prevent good mixing. Because hydrogen peroxide is sensitive to heavy metals and because amine oxides are readily decomposed by iron salts, sequestering agents are generally added to the reaction mixture, particularly when water is the solvent.

Applications of fatty amine oxides in detergents and cosmetics depend primarily upon their surfactant properties. Such properties were first disclosed in 1939 when these materials were described as wetting, cleaning and dispersing agents.

However, it was not until the 1960's that these materials were used in detergent formulations and shampoos. The first product that used significant quantities of amine oxides was a liquid household detergent formulation for dishwashing. In this application, the amine oxides replaced fatty alkanolamides as foam boosters.

A general formulation for an emollient dishwashing detergent is shown in Table XV.

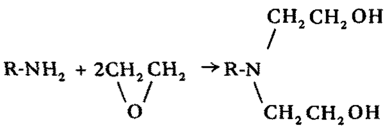
The detergent, foaming, antistatic and antiseptic properties of amine oxides are of interest for shampoo formulations. Owing to these properties shampoos containing amine oxides not only clean the hair but give it body and luster, as well as making it more manageable. A shampoo formulation incorporating amine oxide is shown in

Table XVI. Other formulations using amine oxides in shampoos, detergents, bubble baths and shaving creams have been published.

POLYOXYALKYLENE ALKYLAMINES

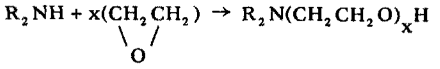
Preparation of ethoxylated amines was first published in 1934. Since that time, literally hundreds of variations have been described, starting with a large variety of fatty amine compounds with reactive hydrogens. Included in the great variety of commercially available ethoxylation products are also poly-functional amines. While the polyoxyethylene alkylamine surfactants are cationic in nature, the cationic activity decreases as the ethylene oxide chain increases.

The reaction of ethylene oxide with primary amines first occurs at 100 C by addition of 2 moles of ethylene oxide to the two active hydrogens without any added catalyst.



$$\mathrm{R\text{-}NH_2} + 2\underset{\setminus\;\mathrm{O}\;/}{\mathrm{CH_2CH_2}} \rightarrow \mathrm{R\text{-}N}\begin{matrix}/\;\mathrm{CH_2CH_2OH}\\ \setminus\;\mathrm{CH_2CH_2OH}\end{matrix}$$

Additional ethoxylation requires a basic catalyst and temperatures above 150 C. As the mole addition ethylene oxide increases, the water solubility increases.



$$\mathrm{R_2NH} + x(\underset{\setminus\;\mathrm{O}\;/}{\mathrm{CH_2CH_2}}) \rightarrow \mathrm{R_2N(CH_2CH_2O)_xH}$$

The use of secondary amines to produce ethoxylated derivatives is also possible. In this case, only a single ethylene oxide chain is produced. Table XVII gives the surface tension solutions of ETHOMEENS in distilled water at 25 C. The trade name had to be used in this data because the data was generated using these compounds.

The nature of fatty acids from which compounds in Table XVII are derived has a direct bearing on surface tension and wetting. Starting with coco-derived compounds (e.g., C_{15}), we see that an increase in EO chain length results in increased surface tension and wetting time. Unsaturated compounds have lower surface tension and faster wetting times than similarly saturated derivatives.

Applications

Polyoxyethylene alkylamines have a great variety of end uses as emulsifiers in neutral and acid solutions, as foaming or frothing agents, as corrosion inhibitors, emulsion breakers, wetting agents, mud-drilling additives, leveling agents for dyes and textile-finishing agents. They can also be neutralized with organic and inorganic acids to form a new series of surfactants with different general properties. Neutralization with inorganic acids will result in greater water solubility, whereas neutralization with organic acids increases oil solubility.

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TABLE XV

Emollient Dishwashing Detergent

Substance	Wt. %
Alkyl ether sulfate	25
Alkyl sulfate	15
Cetyl alcohol	3
Dimethylcocoamine oxide	2.5
Acetic acid	3.2
Sodium acetate	8
Ethanol	8
Water and miscellaneous	35.3

TABLE XVI

Shampoo Formulation

Substance	Wt. %
Dimethyldodecylamine n-oxide	7
Sodium salt of sulfated condensation product of 1 mole of coconut (dodecyl alcohol with 3 moles of EO	7
Dodecanoyldiethanolamide	5
Perfume, color, citric acid to pH 7.9, water	Balance

TABLE XVII

Surface Tension and Wetting Time of Solutions of ETHOMEENS in Water

	Surface tension of solutions (25 C) dynes/cm		Canvas-disc method		Official (Draves) method
Derivative	0.1%	1.0%	0.1%	1.0%	0.5%
ETHOMEEN C/15	33	33	90	3	3.5
ETHOMEEN C/20	39	38	115	11	14
ETHOMEEN C/25	41	41	173	49	
ETHOMEEN T/15	34	33	226	12	23
ETHOMEEN T/25	41	40	157	27	53
ETHOMEEN S/15	33	33	269	23	28
ETHOMEEN S/20	40	39	179	25	29
ETHOMEEN S/25	43	43	198	67	
ETHOMEEN 18/25	34	Gel	360	Gel	

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