where they are a solid part of a variety of commercial operations. They have found their way into many operations and are finding new and varied uses in industry daily. I feel the future for fatty amines is almost unlimited. They are such a wide variety of compounds because of the extreme number of possibilities available in the fatty acid sources, because of the many chemical reactions that can be made, and because of their particular cationic nature. Ask questions such as:

What chemistry do I need and can a fatty amine perform all or part of it?

What surface do I need modified and will a cationic chemical modify it?

What effect do I need to have in a particular cationic chemical and will a certain homolog distribution accomplish it?

What new chemical can I prepare with a fatty amine as a starting material?

How can I improve the quality or yield of any of the fatty amine products?

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Synthetic Fatty Acids

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ABSTRACT

Manufacture of fatty acids from petroleum and natural gas is a large industry worldwide and has important implications in the U.S. Eastern Europe produces an estimated 1.2 billion pounds by air oxidation of hydrocarbons compared to an estimated 956 million pounds of natural fatty acids from the U.S., in 1978 (exclusive of tall oil fatty acids). The enormous production of SFA's in Eastern European countries and in Russia is done by continuous air oxidation of fresh and recycled mixed aliphatic hydrocarbons. Since the products contain proportions of odd-numbered straight chain acids, they have not been used edibly, but have been applied to the manufacture of industrial products such as soap, lubricants, plasticizers and the like. Another European approach (Liquichimica, Italy) for SFA is the caustic fusion (and oxidation) of branched chain alcohols produced by carbonylation and reduction of olefins. American potential technology is diversified but has not yet been translated to production scale, presumably because of the plentiful supply of natural fats and oils that is available.

Synthetic fatty acids have indeed come of age. The USSR has a very large, thriving synthetic acid industry. France and Germany have important businesses. Italy has a large development. The U.S. does produce many synthetic acids and also does make many derivatives—synthetic alcohols and nitrogen derivatives, for example, that formerly required fatty acids.

In general, synthetics resemble (natural) acids in having at least two major factors in common: both classes are very dependent on byproducts of other industries and both are very energy dependent. Agrichemicals are unique in that their feedstocks are annually renewable. However, agriculture itself is very heavily dependent on petroleum and gas, using in excess of 17% of all the energy consumed in the U.S.

Farmers who raise cattle and hogs need animal feed, the growing of which depends on fertilizers from natural gas. They also need gasoline to run planting and harvesting equipment. The equipment used in agriculture requires large investments in energy: twenty percent of the cost of the steel alone is energy dependent. Food processors also depend on gasoline and fuel oil, all petroleum-derived. In contrast, the whole petrochemical industry uses only 6% of the petroleum and gas consumed in the U.S.—probably only about 5% of total U.S. energy if coal is included—and makes ca. 50 MM tons of primary petrochemicals.

Let's at this point review the current fatty acid industry to set the stage for evaluating synthetics. The agrichemical acids produced in 1978 are shown in Table I. Unsaturated acids (oleic plus tall oil acids) total ca. 58% of the production; coconut fatty acids ca. 9%. Since ca. 85% of natural acids are byproducts of other operations, this means that they will probably be produced and sold at any price, at least until other uses are found for tallow and tall oil. Much of the time, therefore, acids are sold as commodities.

Synthetics would use considerably lower percentages of their raw materials than naturals if produced in equal quantities. Total acids being ca. 600,000 tons requiring ca. 600,000 tons of ethylene, propylene, and paraffin waxes of which over 18,182,000 tons were produced in 1978. Thus, only 3.2% of these raw materials would be needed to replace all natural acids.

Now, what is the commercial status of synthetic fatty acids?

The commercially available petrochemical acids are shown in Table II. About 50,000 tons are commercial in the U.S. now and over 500,000 tons in the USSR and

TABLE I

Agrichemical Acids Production 1978

		Tons	Source
	Stearic	144,530	Tallow and grease
33%	Palmitic	44,600	Soy and palm (tallow)
		6,655	Tallow, palm, lauric oils
	Lauric, myristic	48,018	Coconut, palm kernel, babassu
9.4%	Caprylic, capric	8,396	Lauric oils
	Oleic	143,033	Tallow, grease, tall oil, safflower
58%	Linoleic, linolenic	25,922	Tall oil, soybean, safflower, linseed
	Oleic, linoleic	169,914	Tall oil
	Miscellaneous (Behenic, arichidic, oleic, erucic)	11,060	Fish, rapeseed, cottonseed
	Grand total	602,128	

TABLE II

Commercial Synthetic Fatty Acids

C_5	Neopentanoic (pivalic), isopentanoic, pentanoic
C_6	2-Ethyl butyric
C_7	Heptanoic
C_8	2-Ethylhexanoic, isooctanoic
C_9	Pelargonic, isononanoic
C_{10}	Isodecanoic, capric, neodecanoic
$C_{10\text{-}20}$	Linear-terminal
$C_{11\text{-}13}$	Linear-terminal and mixed
C_{13}	Iso Tridecanoic
$C_{12\text{-}15}$	Linear and branched
C_{16}	Iso palmitic
C_{16}-C_{19}	Linear and branched
C_{18}	Isostearic acid, iso octadecanoic
C_{11}	Undecylenic

TABLE IV

Commercial Synthetic Fatty Acids
Major Raw Materials

	Source	
	Primary	Byproduct of:
Propylene	---	Ethylene and gasoline
Ethylene		Natural gas, petroleum
N-Olefins		Ethylene, petroleum, natural gas
Iso-Olefins		Gasoline
N-Paraffins		Kerosene, gas oil, petroleum wax, lube oil
Isobutylene		Gasoline and ethylene
Carbon monoxide	Natural gas	
Hydrogen	Natural gas	
Oxygen	Air	

TABLE III

Synthetic Fatty Acid Processes

	Commercial	Potential
Oxidation of straight chain waxes	X	
Oxidation of aldehydes	X	
Oxidation of alcohols	X	
Oxidation of olefins	X	
Hydroformylation of olefins (OXO)	X	
Carbonylation of olefins (Koch)	X	
Ozonolysis of unsaturates	X	
Pyrolysis of castor oils	X	
Dimerization;Oxidation of alcohols	X	
Fermentation		X
Carbonylation of alcohols		X
Addition of acids to olefins		X
Oxidation of diols		X
Addition of HCN to olefins		X
Addition of acrylonitrite to olefins		X
Addition of acrylates to olefins		X
Telomerization of acrylates, formates, acetates with dienes		X
Carbonylation of aluminum alkyls		X

China. Celanese expects to bring an 18,200 ton plant on stream by January 1980. The Liquichimica plant in Italy has been delayed but is still hoped to be operated with a capacity of 91,000 tons. Ruhrchemie's capacity in Germany is 30,000 tons. Monsanto has withdrawn a scheduled 50,000 tonner. Producers also include Emery, Exxon, Hoechst, Ruhrchemie, Henkel, China, Pechiney Ugine Kuhlman, Shell and ICI.

ATO Chimie makes ca. 500 T/mo. of heptanoic acid from castor oil. Ajinomoto has been considering making lube range esters from synacids directly from oxidized paraffins, i.e., not isolating the free acids at all. Hindustan Lever is considering a synthetic acid plant in India for soap range acids (C_{14}-C_{18}). The USSR acids are straight chain, linear acids having 4 to 20 carbon atoms and contain odd- and even-carbon atom acids. Many of the other acids not only contain odd- as well as even-carbon-numbered acids but are nonlinear. There is only one unsaturated acid in the table and it is derived from castor oil. However, there are many liquid acids that can perform in many applications where unsaturates are now needed just because they are liquid.

The major commercial processes used are oxidation of paraffin waxes and hydroformylation of olefins as shown in Table III. The USSR and China oxidize straight chain paraffins from wax and kerosene with manganese catalysts. Therefore most of these acids are straight chain mixtures of odd- and even-carbon numbered molecules. The hydroformylation route is the basis for making both linear straight chain odd-numbered acids and nonlinear branched iso acids. Monsanto and Texaco have patented and Monsanto, PCUK, and Celanese have extensively pilot planted oxo processes to make linear normal acids. Celanese plans to produce high purity heptanoic and pelargonic acids over 94% purity-water white. Pechiney Ugine Kuhlman in

TABLE V

Fatty Acid Economics – 1979

Capacity, tons, 22,700	Natural coconut	Synthetic	
		Alcohol[a] oxidation	Oxocarbonylation
Capital, $MM			
Fixed plant	7.6	23.2	25.6
Working	5.7	6.0	5.3
Raw materials	$/Ton	$/Ton	$/Ton
Coconut oil @ 1100	1210	—	—
C_{12} Olefin @ 516	—	484	475
Others[b]	—	210	64
	1210	694	539
Utilities	36	86	27
Labor-related	35	58	30
Capital-related			
Dep., maintenance, tax, Ins.	67	204	226
Profit	117	257	272
Sell., Admin., Res.	150	188	125
Transfer Price, Bulk, FOB	1615	1487	1219
Credit	—	-33[c]	-54[d]
Net, $/Ton	1615	1454	1165
¢/Lb.	73	66	53

[a] Caustic oxidation of tridecyl alcohol.

[b] Syngas, hydrogen, carbon monoxide, caustic soda, sulfuric acid, catalysts.

[c] Salt cake @ $75/ton, .136 tons recovered.

[d] Hydrocarbons @ $399/ton.

France also is producing the pure heptanoic acid via an oxo process.

A Russian patent claims 82% yield of pelargonic acid by carbonylating trioctyl aluminum with CO_2. I used to believe that an air leak in an aluminum alkyl plant could produce acids.

Iso acids (branched acids) are commercially based on oxo or Koch chemistry. Ruhrchemie, Hoechst, and PCUK convert olefins to aldehydes and/or alcohols and then oxidize the aldehydes or alcohols to acids. Koch chemistry is used by Exxon to carbonylate olefins to their neo-acids. Shell in Europe makes their version of Versatic acids via Koch chemistry. PCUK makes the Cekanoic acids via oxo chemistry. Most of the iso- and neo-acids in Table II are made via the oxo and Koch route except the isostearic acid.

In hydroformylation carbon monoxide and water or hydrogen are added to the double bond of an olefin. Usually the catalysts are cobalt or rhodium types. Depending on the catalysts, the products may consist of linear acids or branched acids. Even when using linear alpha olefins this is true. When hydrogen is used rather than water, the products are aldehydes which are then further oxidized to acids. Alcohols are also produced via this chemistry, and they are also further oxidized to acids. Water can be replaced by methanol, and the products will then be methyl esters.

In Koch chemistry carbon monoxide and water are added to the double bonds also, but very strong acids are used; e.g., conc. H_2SO_4 in the large excesses or BF_3. Because of this, no matter what olefin is used, the products are always highly branched. Extensive isomerization of the chain takes place. The Liquichimica process also is basically an oxo route. Normal olefins from n-paraffins are hydroformulated to alcohols which are then oxidized with caustic soda. The Monsanto process reputedly converts olefins to acids in one step via oxocarbonylation chemistry. This technology is considered viable, but Monsanto has no immediate plans to commercialize it. Their development work has concentrated on mixtures of C_{11}-C_{12}-C_{13}, containing 90% linear, terminal acids. They also did work with ca. 50% linear acids. It is even possible to make unsaturated linear acids or esters by cooligomerizing butadiene and methyl acrylate.

The major raw materials for petroacids are derived from petroleum and natural gas—mostly byproducts. Ethylene is made from LPG, a byproduct of the natural gas industry, and naphtha or gas oil, ca. 25% of the oil barrel. The raw materials for the petrochemical products are shown in Table IV.

All the major raw materials are 100% energy related; all except oxygen are fuels as well as feedstocks for the acids. But remember that agriacids are fairly dependent on the same fuels for energy too. Internal transfer prices were estimated for coco range synthetic acids (Table V). Plant size is 22,700 tons in brand new sites. Costs are in 1979 dollars and are useful for making comparisons. They are not intended to represent any specific producer's costs; rather they are meant to represent U.S. conditions and situations in general. The synthetics cover conversion of olefins to alcohols and oxidation with caustic to acids plus the one step direct oxo carbonylation process. It is significant that 55% of the costs are entirely energy—the olefins, carbon monoxide plus hydrogen, hydrogen and utilities. That is in contrast to the ca. 25% for agri-acids. Using a one-step conversion of olefins directly to acids can reduce costs of production (the internal transfer price) considerably using the same olefin prices (Table V). Capital is higher than in the two-step process, but raw materials are less. The one-step process costs are $1165/ton vs. $1454 for the two-step process.

It is obvious from Table V that synthetics could be competitive with $1100/ton coconut oil. There are other evaluators around and other evaluations. Some would find that a new producer may lose money! There are several major factors that can lower costs for all processes: size of plants, pricing the raw materials at byproduct values vs. alternate use values, use of government funds at very little

TABLE VI

Use of Fatty Acids[a]

Detergents and soaps	About 30% (ca. 41% of coc. fat. acids) Toilet bars Sulfated and alkoxylated alcohols Nitrogen derivatives Sulfated G.M.E.
Rubber	About 20%
Fatty nitrogens	About 18% (CFA 28%) Quats Imidazolines Diamines Alkylol Amides
Ozonolysis (short chain and dibasic acids)	About 10% Note: About 1/3 of oleic acid is used for ozonolysis – ca. 13% each for cutting oils, lubes, dimer acids and paints.
Plastic additives	About 9% Stabilizers – metal salts, Ba, Mg, Ca, Zn, Cd Catalysts
Textiles	About 5% Water repellants – metal salts
Cosmetics	About 5% (CFA – ca. 60%)
Lubricants	About 5%
Protective coatings	About 4% – SBO, CSO, LO, Fish, CFO (About 20% of TOFA)
Intermediates	About 45% of TOFA – dimers, azelaic, pelargonic CFA alcohols ca. 21% – ca. 6% for all alcohols.
Paper additives	Sizing agents

[a] Much of this data is derived from Hull and Co., "Fatty Acids of North America" study published in December 1975.

cost, and government regulations. These cost estimates assume 100% sale of product on day one of start-up and excellent luck for start-up. These are brand new processes and products vs. agri-acid processes which are well experienced and agri-acids which are well known. Cost/performance will have a major influence on their relative values. Natural acids are, of course, linear, even-carbon-numbered, terminal carboxy acids. The synthetics for which the costs are given are odd carbons, and are not entirely linear.

CF acids today are ca. 79¢/lb. Celanese projects 55¢ for heptanoic, 63¢ for pelargonic, very competitive with the above.

Uses of natural fatty acids and where petrochemicals fit are shown in Table VI.

The single biggest use of naturals is in soap and detergents' manufacture. Synthetics have already absorbed much of this territory; in the USSR synthetic acids are large volume raw materials for soaps and plasticizers. Metal soaps for protective coatings and plastics' additives already have large synthetic inroads. Lubricants use all the synthetic acids they can get; the Celanese acids will go into these markets. Ugine Kuhlman (PCUK) produces them already and so does the USSR.

Fatty nitrogen derivatives consume an estimated 18% of agrichemical acids in the form of quaternaries, imidazolines; alkylolamides, diamines. Most of these derivatives are vulnerable to petrochemicals. As a matter of fact, most fatty nitrogens don't really require fatty acids for their manufacture; some are already being made from petro alcohols and olefins. Detergent and plasticizer alcohols which were once made from fats now are ca. 75% derived from ethylene and olefins. Most liquid and phosphate free detergents are based on petroalcohols. Rubber additives, mainly so-called rubber grade stearic, are known to be able to use petroacids. Most paper additives uses could be replaced by synthetics.

The real restraint for an immediate large volume petroacid industry is probably the relatively small volumes of products required, the slow growth, plus the byproduct nature of much of the natural acid production–tallow from beef and tall oil from paper production. The economics of petrochemicals require large plants, large volumes, few products. That is why we see really large petro acid plants so far only in countries where beef and paper are not big enough industries.

In the U.S. we see high priced synthetics such as pelargonic acid, heptanoic, pentanoic, octanoics, decanoics. Ethyl Corporation's dimethyl alkylamines are replacements for some natural amines. They are made from olefins. The uses for unsaturated acids that depend on the presence of the double bonds–such as ozonolysis and dimerization–seem relatively secure with present know-how. However, liquid nitrogen derivatives (a major use for unsaturates) can be obtained from branched acids and alcohols. Liquid amides can be obtained from butadiene and formamide. Pelargonic and heptanoic acids can be synthesized as described.

Although Table V indicates that petro acids could be very competitive today with short chain acids–coconut range or heptanoic or pelargonic–this doesn't necessarily mean the petrochemical industry will try to compete in the whole fatty acid range. Coconut oil is a primary product and so is castor oil from which heptanoic acid is obtained, so synthetic's further prospects are better in these areas. However, coconut oil is used mainly as a food fat throughout the world, and prices are not affected much by U.S. usage.

There are some signals that indicate synthetics will become more important to industry. The future relationship of the costs for the two types of acids is hard to forecast. However, present indications are that raw material prices for both will go up by a factor of two. This could be interpreted as a slight pitch in favor of agri-acids. However, synthetic acids and derivatives are already quite important in the market place and have a chance of breaking through into much larger volumes. Another factor is the effect of TSCA on new product innovation! The latest estimates are that ca. $235,000 of testing will be needed to commercially introduce a brand new product! That's a restraint of large magnitude and will have an effect.

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Fat-Based Detergent Additives

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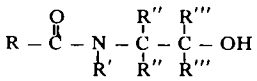
ABSTRACT

The function of several of the coco-based alkanolamide additives in detergents today varies depending upon the particular product. It could be foam-boosting, foam stabilization or a variety of other supplementary effects. Tracing the development of the Ninol detergent through to the advent of the "superamides" is illustrative of the kind of progress that has been made in the utilization of this type of fatty acid derivative in the large detergent industry.

The designation additive is a bit diffuse. Whether a given compound is an "additive" or, in fact, a principal component can depend on its function or often on the level at which it is present in a fully formulated product. The compounds discussed here fall into the latter category. They are additives, but at the same time they possess all of the elements which qualify them as surfactants in their own right.

Let us begin with alkanolamides. The general formula for these compounds is:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R'}{|}}{N}-\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle R''}{|}}{C}}-\underset{\underset{\displaystyle R'''}{|}}{\overset{\overset{\displaystyle R'''}{|}}{C}}-OH$$

In this general formula, written in a manner suggesting a patent application,

R = alkyl
R' = hydrogen, alkyl or hydroxyalkyl
R'' and R''' = hydrogen or alkyl.

There are three important structural elements. First is the acyl group derived from the – long chain – fatty acid, principally coconut fatty acid for our purposes. This places the length of the fatty acid chain at 12-14 carbon atoms. The second is the amide grouping, involving an oxygen, a carbon and a nitrogen atom. Finally, the third element is the presence of at least one 2-hydroxyalkyl group with a backbone where a hydroxyl group is separated from an amide nitrogen by two carbon atoms.

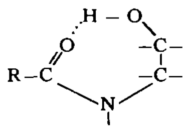
The manner in which all three of the structural elements are combined is of interest and gives us some insight into the special properties of alkanolamides which make them so important as a class of compounds. Not unlike many other commercially important developments, the insight afforded by the consideration of structure should more properly be referred to as hindsight. The first commercial preparation of alkanolamides, as we shall see, was made without benefit of detailed structural considerations.

In examining the structural elements, we note in the first place that the amide linkage is associated with a structural rigidity, as evidenced by relatively high melting points. The framework for this assertion is a consideration of the series of acetic acid, acetyl chloride, acetate esters and acetamide, not to mention other 2-carbon chain derivatives such as ethyl alcohol or the ethyl halides. Except for acetamide, all of the 2-carbon derivatives are liquids or gases.

The long carbon chain of the acyl group is also associated with a certain measure of rigidity and elevated melting points, but much less so than the amide group. More importantly, the chain confers a good measure of water insolubility. Two of the three structural groupings, then, would make for a rigid, water insoluble molecule.

With the introduction of an hydroxyl group in the third structural element, water solubility is enhanced. Hydroxyl groups are powerful water-solubilizing groups through hydrogen bonding with water molecules. The ability of hydroxyl groups to confer water solubility through this mechanism is diminished when the possibility exists to form hydrogen bonds *within* the same molecule or with another molecule. When this is possible – and thermodynamically preferred – crystallinity rather than water solubility is promoted. Five- and six-membered ring structures are "thermodynamically preferred," and internal hydrogen bonding often takes place when the resulting structure is a six-membered ring.

Internal hydrogen bonding of alkanolamides would lead to a seven-membered ring, which is difficult to form:



A hydrogen bonding arrangement involving two molecules of alkanolamides leads to an eight-membered ring, also