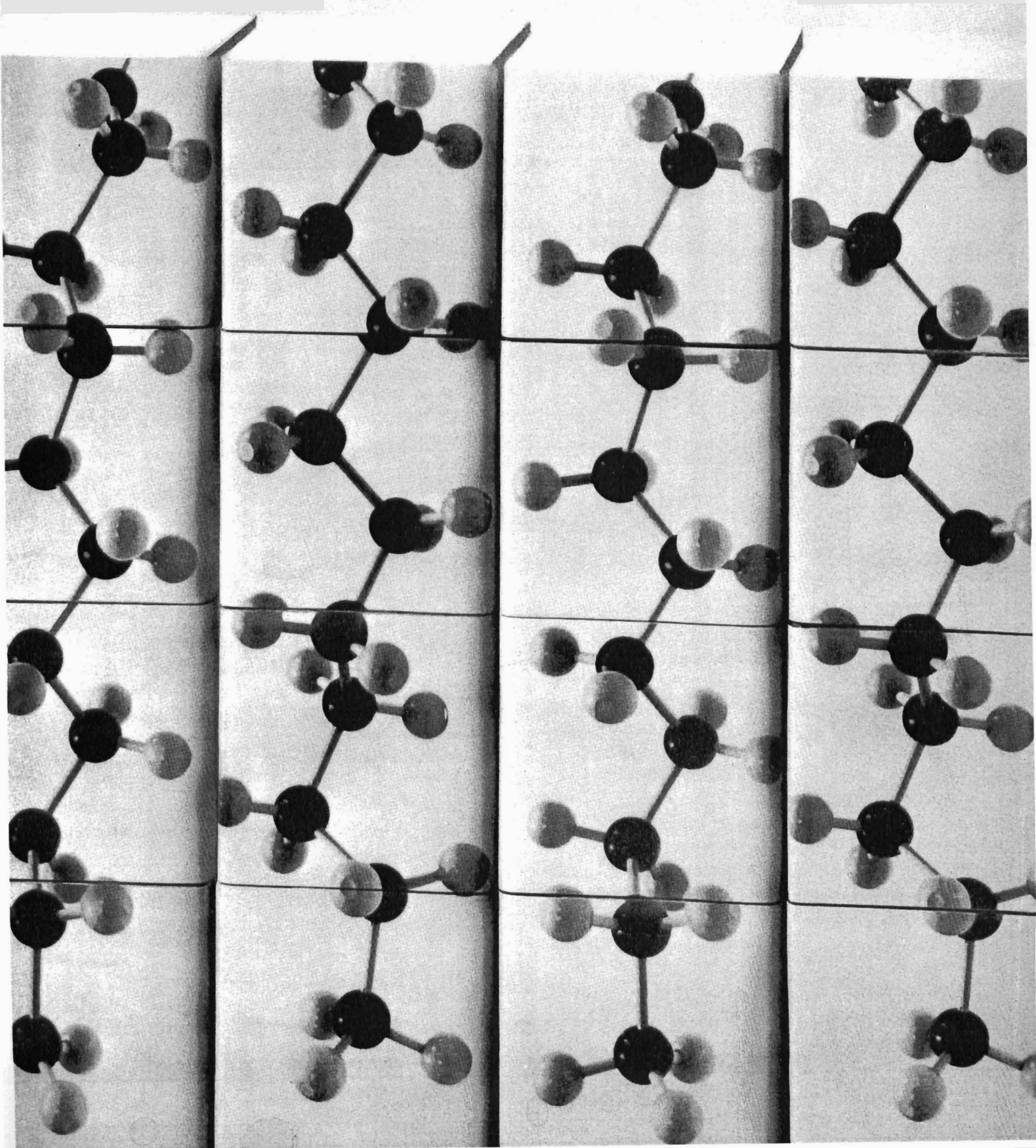


FATTY ACIDS

building blocks for industry



Composition and Characteristics of Some TYPICAL FATTY ACIDS

The approximate composition and value shown are typical of more than 50 different types of acids available to meet the requirements of users. As illustrative examples, they are not intended to describe nor encompass products of individual manufacturers.

For complete product information necessary to serve as a basis of purchase, consult your regular source of supply.

TYPICAL COMMERCIAL FATTY ACIDS	CON ITUENT FATTY ACIDS														RE (DEG. C.)	ACID VALUE	IODINE VALUE
		C — atoms	6	8	10	12	14	16	18	20	22	18	18	18			
		Double Bonds	0	0	0	0	0	0	0	0	0	1	2	3			
STEARIC ACID (T. P. TYPE)							50	48						53.5— 55	205— 210	0.5— 3.0	
STEARIC ACID (S. P. TYPE)						1	51	43				6		52— 54	205— 210	4.0— 6.0	
HIGH PALMITIC							75	20				5		53— 56	207— 215	3.0— 5.0	
SOLID FATTY ACID (Hydrogenated Tallow Type)						2	35	59				4		55— 60	199— 205	3.0— 8.0	
SOLID FATTY ACID (Hydrogenated Vegetable Type)						1	29	68				2		58— 63	199— 205	3.0— 8.0	
SOLID FATTY ACID (Hydrogenated Fish Type)						10	35	28	15	10		2		50— 54	193— 198	6.0— 10	
HIGH LAURIC ACID (Distilled Coconut)		1	7	49	17	9	2					6	2	23— 26	267— 275	6— 14	
OLEIC ACID (RED OIL) (Distilled)						2	7	2				79	10	4— 11	195— 199	85— 95	
OLEIC ACID (Multiple Distilled)						3	5	1				85	6	4— 8	197— 201	90— 95	
ANIMAL FATTY ACID (Distilled)						4	25	15				50	4	38— 44	195— 205	53— 58	
VEGETABLE FATTY ACID (Distilled Cottonseed)						1	24	2				33	39	33— 38	197— 202	90— 110	
VEGETABLE FATTY ACID (Distilled Soybean)							11	4				29	51	25— 30	195— 200	115— 135	
VEGETABLE FATTY ACID (Fractionated Soybean)												39	60	19— 28	196— 203	135— 140	
TALL OIL FATTY ACID							2					51	47	5— 10	192— 196	130— 138	
DISTILLED LINSEED FATTY ACID							6	3				19	24	17— 25	195— 204	155— 190	

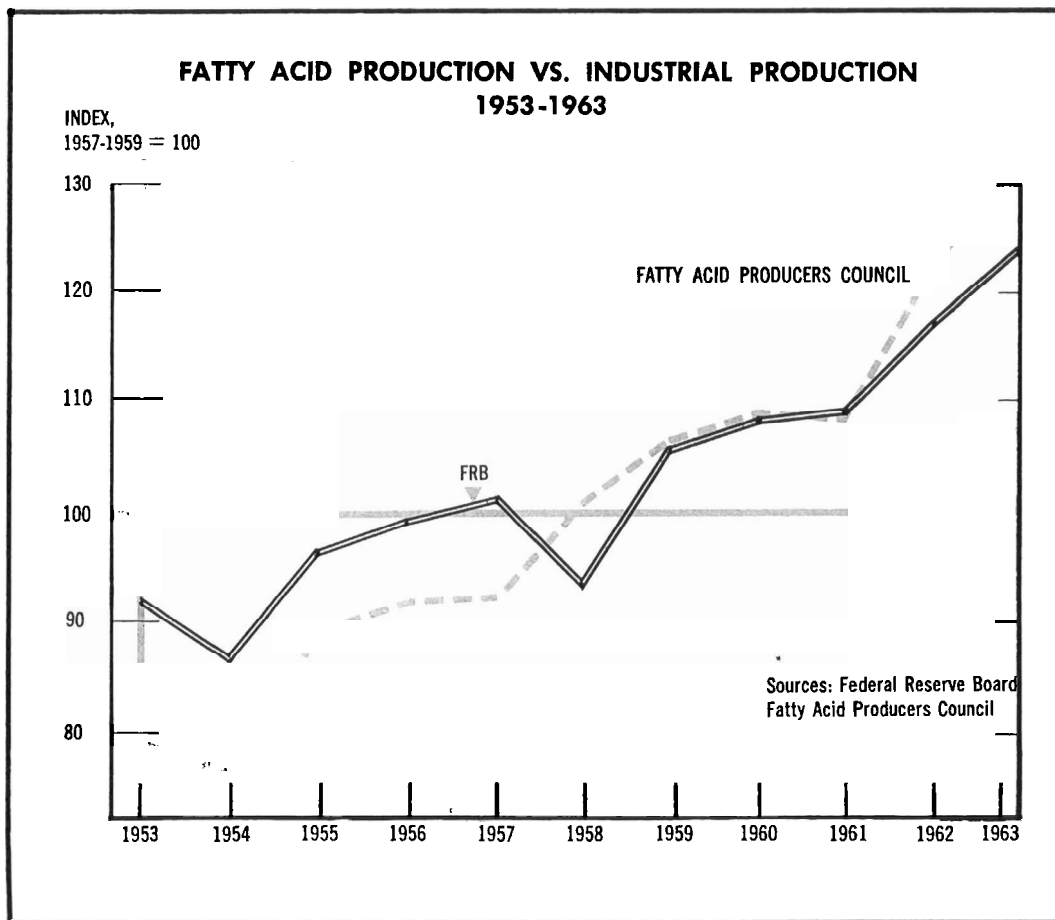
HOW FATTY ACIDS GO NATURE ONE BETTER

Fatty acids and their chemical derivatives have a place in almost every phase of modern living. They add wanted qualities to foods, pharmaceuticals, cosmetics, and other personal products. They improve the performance of paints, plastics, lubricants, textiles, and rubber products. Because their function is mainly to modify other well known materials, they are generally unknown to the ultimate user. Yet the "spread" of a margarine or the "slip" of a shoe-polish may originate with fatty acids.

The production and use of fatty acids is a clear-cut chemical partnership between Nature and man. Initial chemical synthesis takes place in the fields and farms and forests where the chain-like

chemical structures of fats are built up. These fatty chemical structures may be of vegetable or animal origin, each with characteristic properties reflecting its particular source. When used for nourishment, fats are generally consumed without chemical change but, industrially, the raw fats are only at the beginning of the series of chemical processes needed to extend their usefulness into many fields.

Nature's chemistry generates mixed combinations of fatty components — including high-value and low-value constituents. To obtain the best utility, these must then be separated and purified to various degrees, and offered as products of uniform composition and predictable



behavior. Fatty acid producers are specialists in this phase of industrial chemistry.

By further chemical modification, fatty acids may be given combinations of properties not heretofore available. From the standpoint of adaptability and cost, they are ideal spring boards for new advances in chemical research and development.

The character and usefulness of all natural fats and oils is largely determined by the fatty-acid components, or chains, which make up about nine-tenths of their molecular weight. The striking difference between tallow, tall oil, and linseed oil, for example, results from different fatty acid structures (see Fig. 1). So too, derivatives built around these character-determining chains carry over these differences—depending upon chain length, degree of saturation, and molecular arrangement. Product characteristics, such as solubility, melting point, and chemical reactivity, are determined and controlled by the acids chosen for use.

The complex natural chemistry which created the fatty acid chain in the fat is utilized and given greater applicability to closely controlled chemical processes. As compared to pure synthesis, this saves money for the user and benefits our whole economy.

For example, giving higher use-value to what would otherwise be an unwanted by-product of meat or edible oil permits a higher total return to the producer of the fat-containing farm product. If new markets are to be found for this class of agricultural surpluses, then fat-splitting—followed by separation and purification is the most likely route to new chemical derivatives.

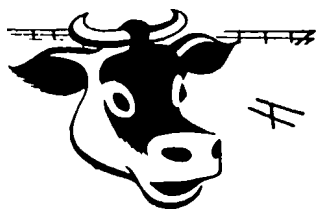
THE ORIGIN OF FATTY ACIDS

Like the soap and the candle industries, out of which it grew, commercial fat-splitting began as an art well before its chemistry was understood. Tallow was the primary raw material and the quality of the finished products were largely determined by the grade of tallow employed.

Batch saponification of the fat, followed by acidulation of the soap, was the original method for separating the acid from the glyceride. Although the principle of high-pressure hydrolysis to split the fatty acid-glyceride molecule was explored as early as 1854, there were then no corrosion-resistant construction materials to make such a process practical. Development of the Twitchell Process (see page 6) and the modern continuous high-pressure splitting methods, not only opened the way to large-scale production, but widened the range of practical source materials.

Top grades of tallow and whole oils, such as coconut oil, offer a starting point for fatty acids with a quality appropriate for food or fine toiletries. However, the economies of upgrading other available materials by more thorough processing has been highly important in broadening the industry's base.

With the growth of the vegetable oil industry, by-products of the refining of these oils for edible use became available, opening up a source of fatty acids with a wide range of characteristics. Coconut, cottonseed and soybean acids have gained in importance and more recently fatty acids from tall oil as



separation methods have developed to enable their constituents to be matched to need.

Acids with highly unsaturated "chains," which exhibit the essential characteristics of drying oils, have their origin in both vegetable and marine sources.

Tall oil, a by-product derived from the digestion of pulpwood, is an important source for unsaturated fatty acids, as well as for rosin.

Origin Versus Properties

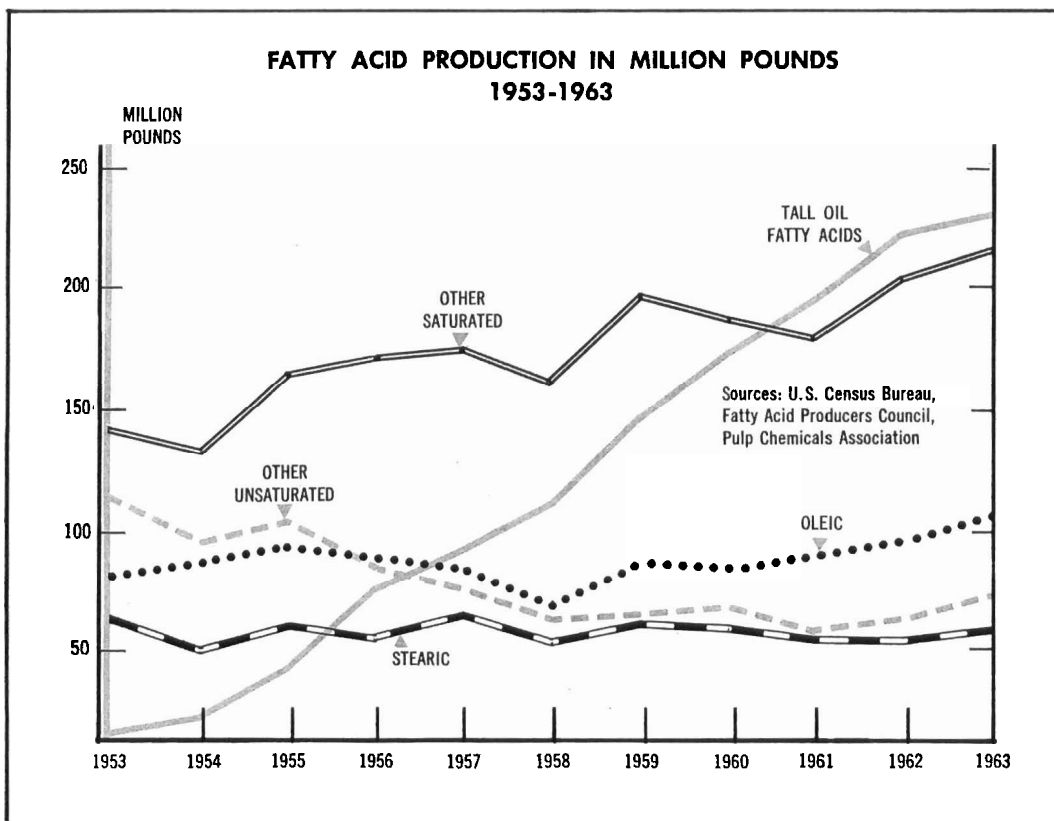
All these natural sources contain mixtures of the chemists' list of individual fatty acids. (See page 2). As we move from one natural source to another, the list of constituent acids generally overlaps. Thus, we have a "moving average" as to the number of carbon atoms in the fatty acid chains to choose from in fitting the product to specific needs. Similarly, the degree of saturation, as determined by the number of double bonds between carbon atoms, gives another overlapping range from one natural source to another.

An important effect on properties, too, arises from the position of these double bonds, which also varies with the source.

In some cases, the properties of a mixed acid of one particular natural source (i.e. cottonseed) may best fit the requirements of a particular use. In other cases, the user may wish to employ a combination of properties which may be met from either of two or more natural sources, depending upon the particular fraction separated and employed. Acids offered today on a specification basis need not always have the same natural sources.

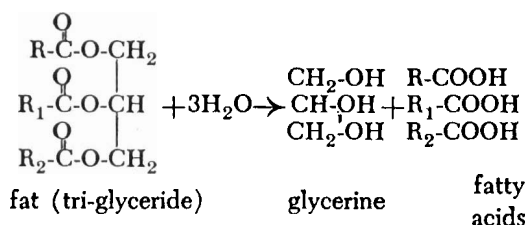
At the same time, processing methods such as hydrogenation, oxidative fission and polymerization may be employed to produce acids with characteristics completely different from those naturally present in a particular source.

Today, fatty acid chemistry has become creative, rather than purely extractive. It looks for the structure and specifications of its products for tomorrow's needs of the user.



THE SPLIT THAT OPENS THE DOOR TO IMPROVEMENT

The hydrolysis of a fat into a fatty acid and glycerine is simple in its basic chemical representation.



Actually, the fatty acid radicals (R) present in a natural fat are mixed within the tri-glyceride structure, so that various combinations, differing in composition and in position are formed from R, R₁, and R₂ radicals in the formula shown above. Ordinarily, there will be a physical mixture of different tri-glycerides in the natural fat as well. Some typical fatty acid radicals common in commercial products are shown in Fig. 2.

The practical effect of the "split" thus is always to produce a mixed group of acids, varying — 1) in chain length, 2) in the number of double bonds, 3) in the position of the double bonds, and sometimes 4) in the mode of juncture of the two portions of the molecule on either side of the double bond.

Batch-Type Splitting

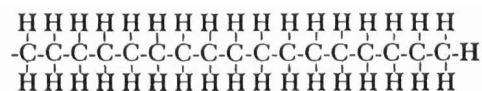
Heat and pressure alone (500° F.-725 psi), in the presence of water, will produce the hydrolysis or "split". However, catalysts have been widely employed and are essential to splitting at atmospheric pressures. The most common reagent for this purpose is the basis of the Twitchell Process, which was the dominant method of fat splitting up to World War II. Acid-washed fat, diluted with 25-50% water, is steam-boiled in open vessels for 24 to 36 hours, in the presence of about 1% of an aromatic sulphonic acid (Twitchell reagent). In its modern application, the process is usually carried on in 2 to 4 stages.

Autoclave splitting is favored by some producers. Constructed of modern, corrosion-resistant metals, these high pressure splitting cylinders produce light-colored acids and a high grade of glycerine.

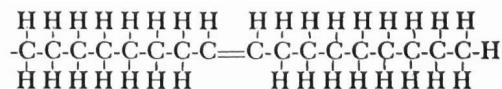
LAURIC



STEARIC



OLEIC



LINOLEIC

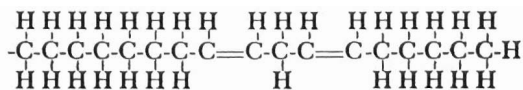


Fig. 2

Continuous High-Pressure Splitting

Continuous hydrolysis is carried on in a tower structure in which finely dispersed water flows downward while hot fats are charged at the bottom of the column, and pass up and out the top as fatty acids. This is the fundamental continuous splitting principle which is employed as an initial step in continuous soap-making and which is now used by most fatty acid producers. Steam heating is applied at critical levels in the tower, and pressures of some 725 psi are employed. Rapid removal of the acids from the tower, once they are hydrolized, is an important quality factor.

Normally, no catalyst is employed and a contact time of 3 to 5 hours or less is sufficient to produce a 97-99% split.

The key to economical operation is the highly developed thermal efficiency of the "splitter" and other integrated parts of the complete process. The key to the quality and color of the acids produced is the extensive use of stainless steel and other non-corrosive metals throughout the processing equipment. Operating flexibility results from automatic process control and centralized instrumentation. Towers now in operation range in throughput from three to five thousand pounds per hour.

Various other splitting methods differing in their mechanics are also employed. Essentially, however, they all provide a mixed group of acids whose composition is determined by the original fat charge and whose output is subsequently distilled or otherwise separated to provide the desired commercial products or fractions.

SEPARATION PROCESSES THAT YIELD SPECIFICATION PRODUCTS

Two functions are essential to convert the output of the splitting process to commercial products favored for a particular use: 1) *Purification* — removing from the fatty acids the non-volatile constituents, unhydrolized oil, color bearing bodies, etc.; and 2) *Separation* — dividing up the mixture of acids on the basis of chain length, saturation or some other factor of significance to the user.

Distillation under vacuum, either batch or continuous, is widely employed for purification. Stripping distillation, for example, is usually practical in connection with separation by direct-pressing. Stripping distillation permits the removal of undesirable non-fatty components. With continuous operation at high vacuum and relatively low temperatures, the fatty acids are not exposed to extreme heat, thereby reducing the development of decomposition products which are sometimes responsible for instability and odor.

Distillation is sometimes, but not universally, employed for the separation step. Fractional distillation serves to separate materials of different boiling points which do not form constant boiling mixtures. It is effective in separating fatty acids from rosin acids when tall oil is the source.

Separation by Pressing

The original separation process for tallow-based fatty acids takes advantage of the appreciable difference in titer (or melting point) between the saturated stearic-palmitic portion and the unsatu-

rated oleic-linoleic acid portion. After distillation, the mixed acids are cooled to about 40° F. and partial solidification takes place. A "pressing" of the cakes so formed removes the entrapped liquids. By two or three subsequent melting-cooling-pressing cycles, followed by a bleaching operation, a commercial stearic acid fraction of high purity is obtained.

A characteristic crystal structure develops as the stearic-palmitic product is slowly pan cooled. This structure in cakes of commercial stearic acid (55 palmitic-45 stearic) is regarded by some as a guide to product quality.

Because of the poor crystallinity of mixtures substantially higher or lower in stearic acid content, separation by pressing is practical only for animal fatty acids with this particular ratio of composition.

Solvent Crystallization

More recently, continuous-process fractional crystallization, using a solvent such as methanol, has put this separation on a more economical large-scale basis. The methanol solution of the fatty acids is pumped continuously through a multitubular crystallizer fitted with agitator scraper blades and cooled to about -15°C. Cooling is accomplished by circulating refrigerated methanol through the jackets of the crystallizer tubes. During chilling the solid fatty acids crystallize from the solvent solution to form a slurry which is fed to a rotary vacuum filter. The solid acids filter to form a cake which is continuously washed with fresh 90 per cent methanol and then discharged from the filter. This filter cake containing approximately 40 to 60 per cent methanol is melted and pumped to a solvent recovery still in which the solvent is removed from the fatty acids and

returned to the system. The solid acids are discharged from the still ready to be finished and packaged as commercial stearic acid.

The filtrate containing the liquid acids is passed through a heat exchanger to a solvent recovery still. The discharged liquid acids from the still are ready for finishing and packaging into commercial oleic acid.

Fractional Distillation

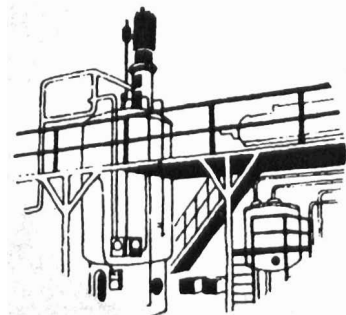
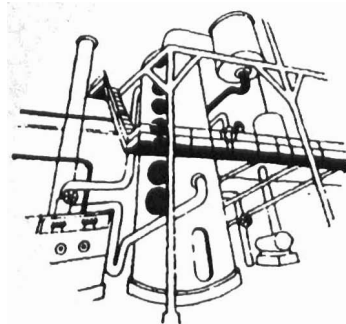
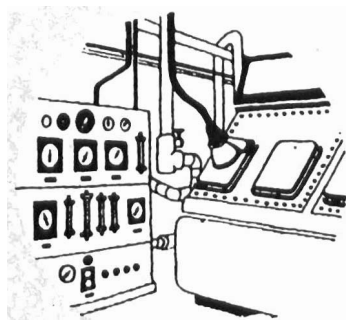
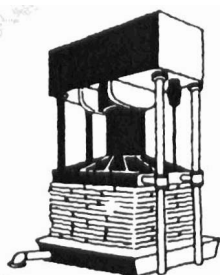
Used alone or in combination with other methods, fractional distillation has particular application where useful separation can be made of acids of different boiling points. Temperatures in the 400-450° F. range are normally employed at pressures as low as 2mm. Hg.

Coconut oil fatty acids, for example, are successfully separated by fractionation to provide the individual acids, such as caprylic, capric, lauric, myristic, palmitic, stearic, etc. at a purity of 90% or more.

In certain mixtures of acids, such as those derived from fish oil, the unsaturated components generally consist of somewhat longer chains (C_{20} , C_{22}) than the saturated portion. Thus, vacuum distillation provides effective separation and provides a product with highly desirable "drying" properties, as indicated by a high "iodine value." (See page 15).

Vegetable oil fatty acids, such as cottonseed and soybean, also respond to fractional distillation, as the linoleic and other unsaturated acids have a somewhat higher boiling point than the palmitic acid present. Highly efficient continuous fractionating stills are employed.

In addition to fractional distillation of the acids themselves, certain derivatives such as methyl esters may be distilled to provide individual fractions of high purity.



OTHER PLANT PATHWAYS TO PRODUCT IMPROVEMENT

A fatty acid is "improved" as it comes closer to the ideal specifications for a particular use, regardless of whether it is a "purer" acid in the strict chemical sense. In one case, this may call for "unsaturant enrichment," in another it may call for concentration on color-stability, or high uniformity as to titer (solidification point).

In addition to customary methods of product improvement, such as acid-boil or deaeration of the stock before distillation, removal of polymerized material, decolorization, etc., certain basic product improvements are a result of special processing now widely employed. They include the following:

Hydrogenation

Hydrogenation of the fat before splitting, or of the fatty acids themselves, has become of great economic significance in recent years, and some 50% of the saturated acids now produced are of the hydrogenated type. Basically, the purpose is to fill-in the ethylenic linkages (double-bonds) to produce a more highly saturated and a higher melting mate-

rial. Other selective effects of hydrogenation include the shifting of double bonds, and the production of isomers with characteristics differing to some degree from the normal. The proper choice between a naturally saturated acid, and one in which saturation is made more complete by hydrogenation will generally be determined by the particular conditions of use.

Oxidative Cleavage

Oxidation of unsaturated fatty acids under controlled conditions produces dihydroxy acids, and if carried further has a rupture effect at a double bond position. Thus, oleic acid yields pelargonic and azelaic acids. The latter acids have important applications along with sebacic, adipic and the family of saturated dicarboxylic acids.

Polymerization

When unsaturated acids, such as linoleic, are heated under carefully controlled pressure conditions in the presence of water, it is possible to combine two or more molecules into a complex structure. Commercial production of a dibasic or "dimer" acid follows this procedure. These products are low in volatility and have high heat stability. They have found wide application in surface coatings and in the formation of polyesters and other polymers.

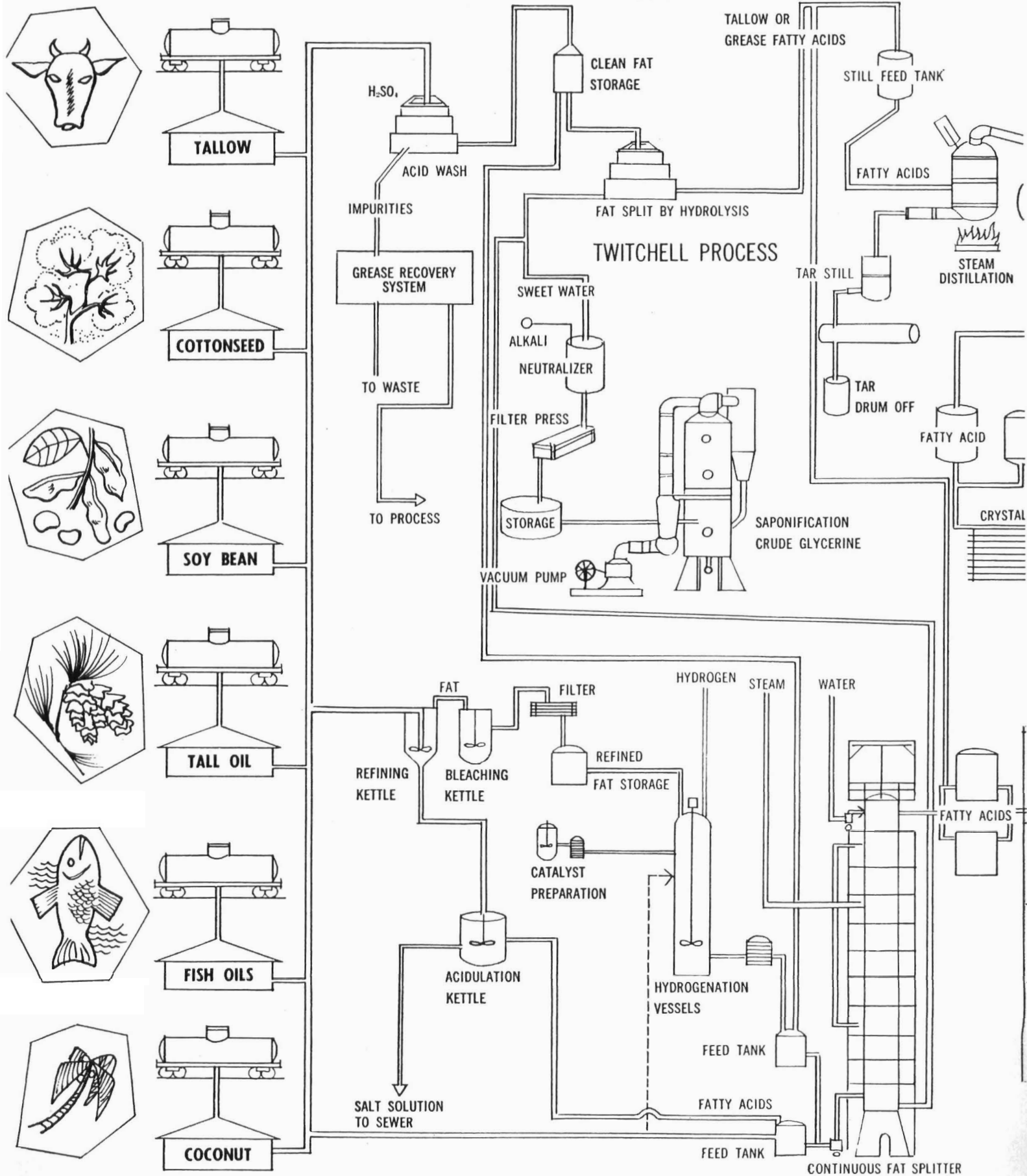
Chemical Derivatives

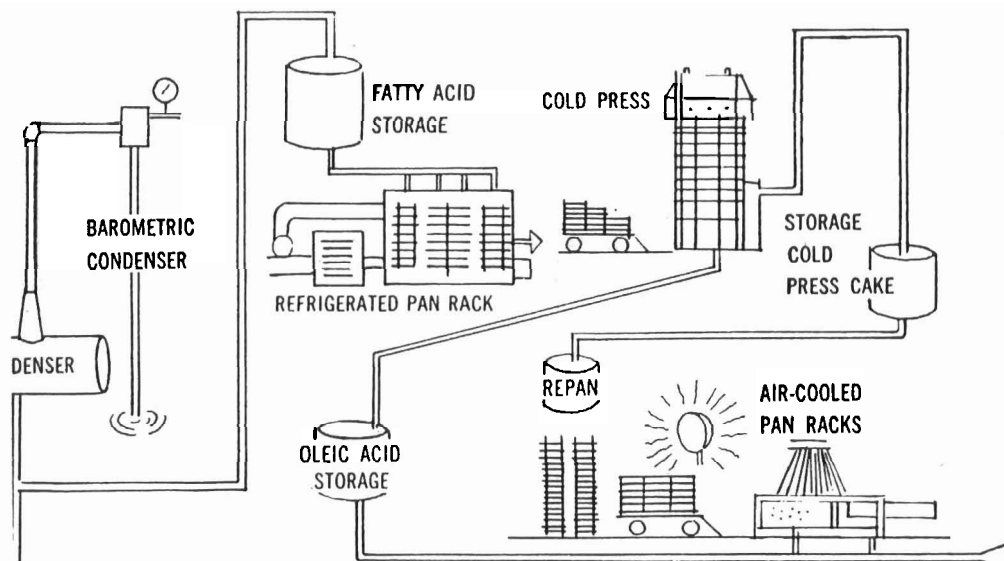
Chemical reactions involving the carboxyl radical of fatty acids produce families of related products, such as fatty alcohols, amides, amines and nitriles. Other processes used to modify the integral chain structure by addition include sulphonation and chlorination, and various chain addition and substitution reactions.

These products have valuable characteristics of their own which in a strict sense, puts them outside the fatty acid industry. Nevertheless, their increasingly wide range of applications suggests further possibilities for the user of fatty acids in chemical combinations still to be explored.

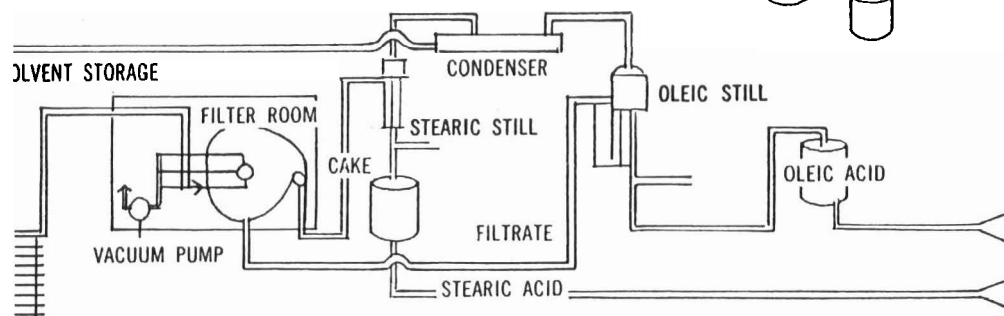
REFINING

SPLITTING

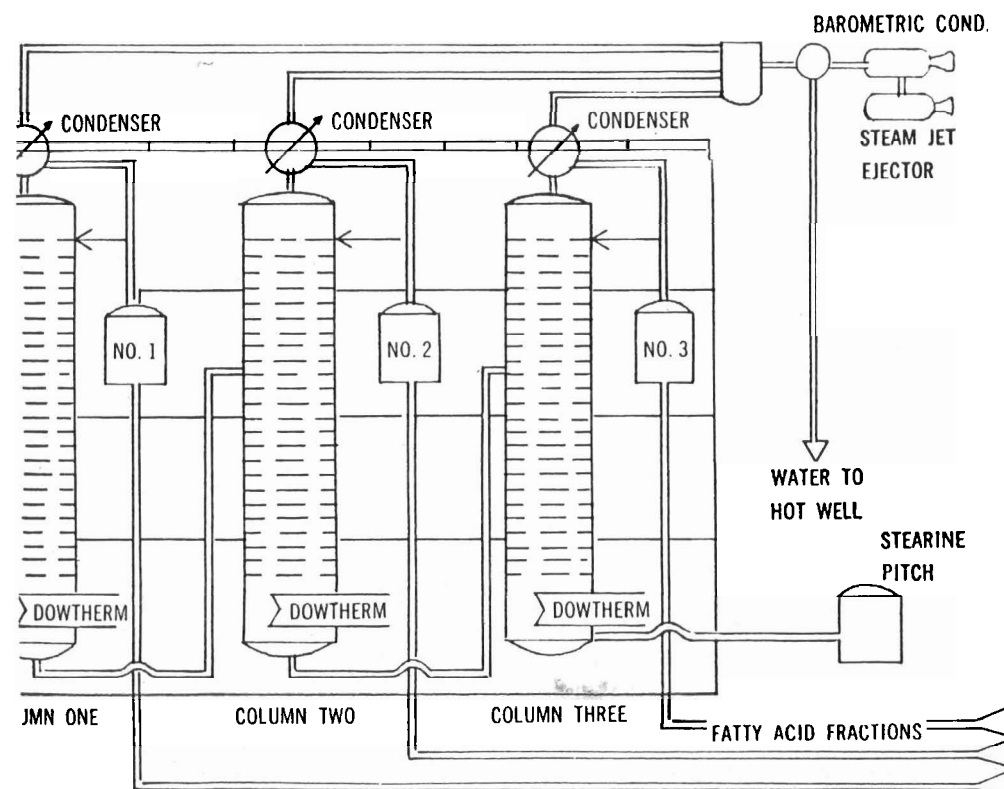




PRESSING



SOLVENT CRYSTALLIZATION



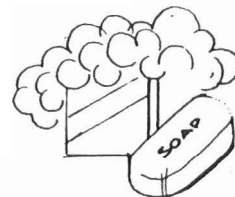
FRACTIONAL DISTILLATION

OLEIC ACID	LINOLEIC ACID
PALMITIC ACID	STEARIC ACID
CAPRIC ACID	CAPRYLIC ACID
LAURIC ACID	MYRISTIC ACID
SOYA FATTY ACID	CORN FATTY ACID
FISH FATTY ACID	COTTONSEED ACID



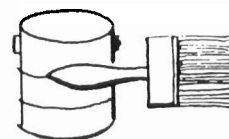
COSMETICS AND TOILETRIES

SOAPS AND DETERGENTS



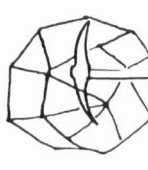
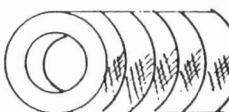
TEXTILES

LUBRICATING GREASES & OILS



PAINTS AND PROTECTIVE COVERS

RUBBER GOODS



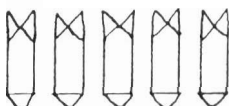
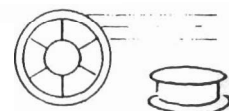
MINING

METAL WORKING



LEATHER GOODS

COMMUNICATION TYPEWRITER RIBBON



MILITARY USE NAPALM BOMBS

FIELDS OF USE FOR FATTY ACIDS

Few products have a wider range of application than fatty acids, yet their versatility in entering combinations in which they lose their identity leaves them unknown to the ultimate user. In this general booklet, we can only highlight some of the outstanding uses that typify the properties they provide. For specific application data and choice of type or grades, we suggest you consult the manufacturers listed on page 20.

Cosmetics and Toiletries

Many bland and soothing preparations for personal use obtain their body and "feel" from characteristics inherent in the fatty acid chains present. Use on the body is a natural application, as the fats which normally exist on the skin are of related structure. In the preparation of such products, the acids may be added directly to the mix and there be partially or completely saponified; or again, soaps, esters or other derivatives may be produced separately to become components of the final mixture.

Almost any desired level of oiliness, soapiness, waxiness or moistness may be achieved by the balance of the acids used, and the bases with which they are saponified, or combined. The ranges of melting points, softening points and viscosities available from common fatty acids have a natural relation to body temperatures, so that creams and lotions which soften and spread smoothly on application are easily produced. Surface-active and emulsifying properties, as well as cleansing properties, come naturally to the family of fatty acid derivatives. Many of them serve as a bridge between water-solubility and oil-solubility. And where water-repellent qualities are desired in the formula, insoluble metallic soaps based on fatty acids come into the picture.

Stearic acid in the grade suitable for

pharmaceutical and edible products, and meeting USP requirements, is notable for its white color, mild odor and high stability. Also important to toiletries are high lauric content fatty acids, derived from coconut oils, which provide exceptional lathering qualities for shaving creams and shampoos. All acid groups undesirable for personal use are removed from the lauric acid composition. These high lauric fatty acids are now being combined in many surface active and detergent compositions suitable for personal use, such as sodium lauryl sulphate.

Multiple distilled oleic acid (white oleine) is also available to meet USP standards, and has a wide range of uses in cosmetics, cleansing creams, and skin protection preparations — generally of the liquid or free-flowing type. Here again new esters and condensation products with emulsifying properties are finding increased usefulness.

Metallic salts of fatty acids, of which zinc stearate is an outstanding example, are used in pharmaceutical products of the dry, water-repellent type.

Once the formula for a cosmetic or toilet preparation has been established, the use of fatty acids of known chain-length composition goes a long way to assure uniform product composition and to simplify quality control. Impurities and "unstabilizers" are removed from the raw material, and never enter the user's plant to necessitate later removal.

Foods

Foods and food packaging use fatty acids and fatty acid esters as emulsifiers, defoaming agents, stabilizers, surface active agents, lubricants and plasticizers. In foods themselves they find application in ice creams, bakery products as so called shortening extenders, candy and chewing gums, shortenings and margarine.

For polyglycerol esters up to and including the decaglycerol esters, Food & Drug Administration approval has been granted in the United States and Great Britain. The polyglycerol esters such as stearates, palmitates, etc. are used in margarine, special dietary fats, shorten-



ings, icings and salad oils. Of recent years the use of polyunsaturated fatty acids have been popularized and are widely used in shortenings and margarines.

Soaps and Synthetic Detergents

The decisions as to whether to produce a soap by saponification of a glyceride (natural fat or oil) or by saponification of the corresponding fatty acids is primarily an economic one, but frequently many of the hidden costs of starting with the glyceride are overlooked in the analysis. When using fatty acids there are savings in steam, labor and in the capital investment necessary for a certain output. In addition, greater flexibility is possible in the choice of the composition of raw materials. Saponification or esterification takes place predictably and completely even in combination with weak bases. Adaptation of the product to changing demands also supports the trend to greater usage of fatty acids. This applies as much to the field of specialty and industrial soaps as to toiletries.

Striking examples of extra flexibility in adjusting products to different and rapidly changing market needs are showing up in the field of detergents derived from fatty acids. In a recent list of surface active agents, about 200 products out of some 700 are identified as derivatives of fatty acids or containing typical fatty chain groups. These include esters, condensation products with polyhydric alcohols, various fatty acid amide derivatives, sulphates and sulphonates. While fatty acid-based products are not currently dominant in the low-price, general-purpose field, they are being employed in increasing quantities for special purpose detergent applications.

The familiar water-soluble soaps of fatty acids, along with sodium and potassium salts of fatty acid derivatives are in the anionic class of detergents. Other derivatives, such as ethylene oxide condensation products, are nonionic, and still others, such as the quaternary ammonium group, are cationic. Thus, fatty acids have application "across the board" in the preparation of detergents or deter-

gent intermediates. As before, they also offer definite quality control advantages over the use of oils and soapstocks as starting points for the detergent producer.

Textile Industry Applications

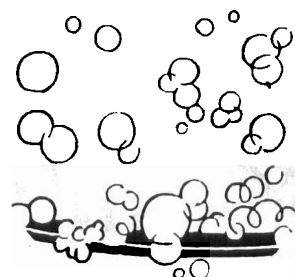
Among the industrial fields in which fatty acids and their derivatives have application, the textile industry ranks high. To begin with, they serve as wetting agents, generally in the form of neutral soaps chosen to fit each particular fiber and processing step. Uniform dyeing characteristics are imparted by a related group of fatty acid products. Textile lubricating agents produced from sulphonated acids serve another key requirement. As manufacturers of textile soaps and conditioning agents have increased the degree of specialization of products, they have increased their preference for fatty acids as a starting point.

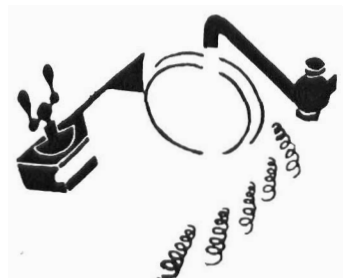
In contrast to wetting and cleansing agents, heavy-metal insoluble "soaps" of fatty acids are applied to give water repellency to textiles. Resins containing fatty acids or fatty acid derivatives are also finding increased application for waterproofing, moldproofing and other coating purposes.

Lubricating Greases and Oils

Important advances in the formulation of lubricating grease have taken place — particularly to meet the needs of military equipment — by approaching it as a chemical problem, rather than as a compounding art. In these advances, the substitution of fatty acids, or metallic soaps of fatty acids, for natural fats, has done much to assure grease of uniform lubricating and bodying characteristics and which will not separate on long-term exposure to temperature extremes in storage. Closer control and less time loss in the saponification reaction, and more productive use of plant equipment, also result from the use of fatty acids.

Improvement of lubricating oils for special purposes by fatty acid additives is of less commercial importance, but their use to increase film strength and impart polar characteristics to the oil films finds some application. Of greater





significance is the development of special wide-temperature-range lubricants from dibasic fatty acids as a complete replacement for the petroleum lubricant. Esters of sebacic, adipic and azelaic acids are under investigation here.

Paints and Protective Coatings

The entire field of drying oils is changing character as polymerization of films becomes better understood. Greater usage of fatty acids is a natural consequence, as they assist the manufacturer to choose and regulate the "functionality" of reacting compounds. Resynthesized drying oils provide combinations of drying speed and film qualities impossible with natural oils, and have provided products in plentiful supply for certain scarce natural drying oils.

Fractionated fatty acids derived from soybean oil and tall oil can be "enriched" from an unsaturant standpoint, and fish fatty acids can be freed from saturated components. Some acids can be dimerized, paralleling the effect of bodying an oil.

In the manufacture of alkyd resins, fatty acids of various degrees of unsaturation are widely employed to modify the glycerol phthalate molecule. Here, too, the processor has found increased precision in the use of fatty acids as compared to natural oils.

Fatty acids are also reacted with maleic anhydride to form adducts or maleinized oils with greater functionality than the original acid possessed. Some of the resulting maleic resin derivatives are finding increased usage in the water-dispersible type of paint.

Metallic salts of fatty acids, such as linoleates, have a further application as paint driers, and metallic stearates as flattening agents. A whole range of other plasticizing, emulsifying and modifying functions for fatty acids are employed in special finishes.

Rubber Manufacture

Fatty acids have been found essential over the past 50 years for vulcanizing and compounding natural rubber into a commercially useful commodity. They

assist the action of the accelerators, help solubilize the zinc oxide activators, aid in the dispersion of pigments, and lubricate the product during milling and extruding. Stearic, lauric and various hydrogenated vegetable and animal fatty acids are employed in quantities exceeding 50 million pounds per year.

Polymerization of synthetic rubber takes place in an emulsion generally built around a potassium fatty acid soap. Improved quality of synthetic rubber resulting from cold processing (5°C or less) has required close control of constituents of the emulsion bath and various activators and modifiers. In some formulations, fatty acids are providing the basis for accurately controlled emulsion polymerization.

Many specialty applications as plasticizers, mold release compounds, softeners in rubber reclaiming, and the like add to the wide range of fatty acid usage associated with the rubber industry.

Mining

Fatty acids play an essential role in the concentration of certain minerals by froth flotation. Phosphates, barites, hematites, spodumene, feldspar, fluorospar, and specific sulphides are enriched or selectively separated by these flotation techniques. In petroleum production, too, fatty acids are used as surface active agents for drilling muds.

Metal Working

Cutting oils and coolants on which the entire metal-working industry depends are generally emulsions of oil in water, with fatty acid soaps as the emulsifying agent.

Stamping and drawing compounds, buffing and polishing compounds and many other applications in metal fabrication, use fatty acids or products in which their lubricating and emulsifying properties are applied. Core oils, used to bind sand molds, are sometimes compounded with fatty acids.

Leather

Fat-liquoring, an essential step in softening leather after tanning, requires substantial quantities of fatty acids for for-

mulating the emulsions employed. Many of the compounds for dressing, treating and polishing leather are highly dependent upon fatty acids.

Communications

Fatty acids and their derivatives cut across the entire field of communications — pencil "lead," typewriter ribbons, carbon paper, printing ink, stencil wax, and various paper coatings. In the electronics field, fatty acids are used in wire insulation, insulating varnishes and various plastics and resins.

Fatty acids have application too in the field of phonographic and photographic supplies.

Military

As in civilian life, there are hundreds of essential yet indirect applications for fatty acids serving military purposes. They range from paints and mold-proofing compounds all the way to hospital supplies. An important direct use of fatty acids, however, is in the preparation of Napalm, or jellied gasoline, which is based on the aluminum soaps of naphthenic, oleic and coconut-oil fatty acids.

COMMON TERMS AND TESTS USED IN SPECIFYING FATTY ACIDS

The table on page 17 shows numerous other uses to which fatty acids are being applied, from long-established applications such as candles to new types of emulsifiers, plasticizers and chemical intermediates. As a result of research work now in progress, many of the minor uses shown are expected to become increasingly important.

There are two ways to approach the problem of getting the particular fatty acid that best suits a user's need. One is

by considering the wanted properties; titer, color, stability, drying characteristics and the like. The other is by considering the wanted composition in terms of the component acids of various chain-lengths, degrees of unsaturation, and molecular structure. Major properties are determined by the ratio of particular acids present, but many significant variations will depend on the degree of freedom from impurities, and the character of minor constituents.

Composition

(by gas chromatography)

In the past ten years, a revolution has occurred in the ease with which mixed fats, fatty acids or their esters can be separated and identified. By the analytical technique known as gas liquid chromatography (GLC), it has become possible to measure the individual constituents in fatty mixtures having as many as 40 components, including isomers or rare structural types present in minor amounts (0.5% or less).

The typical gas chromatograph consists of a packed column for separating the components, on the basis of their relative rate of movement in a stream of carrier gas. As the separated fractions emerge, some responsive type of detector and recorder is used which automatically plots a curve. The position of the peaks along the curve identifies a component; the area under the curve, its quantity. Figure 3 shows a typical curve of the methyl esters of a mixed fatty acid, with the "peaks" corresponding to particular chain lengths identified.

As a tool for research and for process control, the gas chromatograph has given the producer of fatty acids a far more exact means for determining the composition of minor components affecting quality. New concepts of uniformity have become possible by using the gas chromatograph to monitor processing operations. Research quantities of individual acids at a purity above 99% can be separated and their properties determined, thus helping to determine the justification for large-scale separation of pure fractions for special uses.

Some fatty acid companies are now offering typical chromatographic analyses of their commercial products, along with the more routine specifications as given below.

Origin

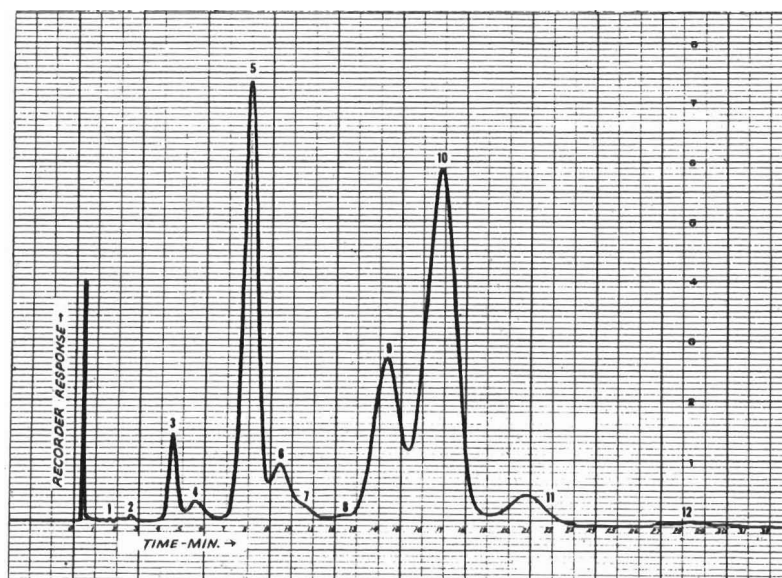
The particular source of the fat or oil from which a fatty acid is produced helps to define its characteristics and applicability to some uses. Users may feel their requirements are best met by specifying acids from animal fats, coconut fatty acids, cottonseed fatty acids, tall oil, soya bean fatty acids, or fish oil fatty acids, as offered in various degrees of purity. Actually, of course, this is merely an optional way of specifying properties within the limits of composition set by Nature, as each source has its characteristic balance of acids.

Sometimes, a product formulation may be critically affected by minor constituents which differ in acids derived from oils of different origin. In such cases customers will want to know the origin —

and to be aware of any change of origin — of fatty acids whose physical specifications come within their acceptable range. Economically, however, it is important that a requirement as to source should have a reason behind it other than mere tradition.

Titer

Titer, or solidification point, is probably the most widely used and most explicit fatty acid specification. It is commonly expressed in degrees Centigrade, as determined by standard methods established by the American Oil Chemists' Society. Titer is a function of the chain length, and the degree of saturation of the component acids. Commercial stearic acid (45% stearic — 55% palmitic) with virtually no unsaturants will have a titer as high as 55°C. and a "straight stearic acid (95%) as high as 67°C. Highly unsaturated acids may be liquid at -5°C. Short-chain acids, even if saturated, have relatively low titer points; a typical caprylic acid (90%) for example has a



THE CURVE WAS PREPARED ON AN F AND M MODEL 500 PROGRAMMED TEMPERATURE GAS CHROMATOGRAPH EQUIPPED WITH A BROWN RECORDER, MODEL No. Y143 X (58)-(VB)-11-111-(27). THE COLUMN WAS 8 FT. LONG, 1/4" OUTSIDE DIAMETER STAINLESS STEEL, PACKED WITH 60/80 MESH CHROMOSORB W; THE LIQUID SUPPORT BEING 20% DIETHYLENE GLYCOL SUCCINATE. THE COLUMN TEMPERATURE WAS 180° C. THE INJECTION PORT TEMPERATURE WAS 325° C. THE DETECTOR BLOCK TEMPERATURE WAS 300° C.

METHYL ESTERS OF TALLOW FATTY ACIDS

- | | |
|--|---|
| 1) Methyl Caprate < 0.1% | 7) Methyl iso-Palmitate (C ₁₆) < 0.1% |
| 2) Methyl Laurate < 0.1% | 8) Methyl iso-Stearate (C ₁₈) < 0.1% |
| 3) Methyl Myristate (C ₁₄) 2.9% | 9) Methyl Stearate (C ₁₈) 18.0% |
| 4) Methyl Myristoleate (C ₁₄) 1.1% | 10) Methyl Oleate (C _{18 1}) 40.5% |
| 5) Methyl Palmitate (C ₁₆) 28.3% | 11) Methyl Linoleate (C _{18 2}) 3.9% |
| 6) Methyl Palmitoleate (C _{16 1}) 4.3% | 12) Methyl Arachidate (C ₂₀) 0.8% |

titer of 16°C. Dibasic acids are higher in titer than monobasic acids of the same chain-length and degree of saturation.

It should be noted that fatty acids are polymorphic, and may solidify in different crystal forms with somewhat different solidifying and melting points. Also, eutectic mixtures may be formed. Blended fatty acids may have similar titers, and yet vary widely in composition.

Acid Value

Acid value or neutralization value, is determined by the number of milligrams of potassium hydroxide required to neutralize one gram of the acid. This amounts to complete saponification in the case of high-quality products. Oleic acid and stearic acid from animal fats will have acid values in the range of 195–210. Shorter chain coconut acids will have an acid value of 260 or higher. Of course, the presence of saponifiable matter, unsaponifiable also, other than free fatty acids, will distort the acid value as an indicant of the type of acids present. Conversely, acid value is a guide to purity only when the acids present are identified.

Free Fatty Acids (as oleic)

The composition of fatty acids, particularly those in the oleic group, is sometimes calculated on the basis of an assumed combining weight equivalent to that of oleic acid. (One unit of acid value equals 0.503% free fatty acids). Obviously, low molecular weight acids will have an apparent free fatty acid content in excess of 100%. On this scale, a typical coconut acid will show a free fatty acid content of 130% expressed as oleic. This is an evaluation now mainly applied to raw glycerides to indicate the amount of fatty acids released.

Saponification Value

By determining the number of milligrams of potassium hydroxide necessary to convert all saponifiable constituents into potassium soap, we measure the combined as well as the free fatty acids present. In commercial fatty acids, saponification value is generally a few percentage points higher than the acid value, and the difference (sometimes

called "ester value") may be significant. Saponification value is determined primarily to permit exact calculation of the average molecular weight of free and combined fatty acids after accounting for unsaponifiable constituents.

Iodine Value

The absorption of iodine is an effective measure of the degree of unsaturation of fatty acids, and of their reactivity and drying characteristics as used commercially for resin manufacture and other industrial processes. Standard methods for this iodine titration (such as Wijs) have been established by the American Oil Chemists' Society and the A.S.T.M. The method has limitations, however, as applied to acids such as those from tung oil, containing conjugated double bonds, and here alternative methods are employed.

The presence of polyunsaturated acids, such as linoleic, and linolenic, can boost the iodine value of a drying type acid to 140 or more. A highly purified stearic acid may have an iodine value less than 3.0.

Color

Because specifications for color of fatty acids have grown out of the requirements of different consuming industries, no universally-accepted scale of color ratings is yet in use. Among the ratings employed are Lovibond, Gardner, Fat Analysis Committee (F.A.C.), National Petroleum Association (N.P.A.) and the Spectrophotometric method (A.O.C.S.). Some suppliers and consumers now use spectrophotometric transmission readings. Light colors are associated with good quality. In general, multiple-distilled saturated acids come close to true white, and multiple-distilled unsaturated acids a very pale yellow to the eye.

A clear distinction must be maintained between product color and color stability. They are not directly related, and in many cases, color stability at elevated temperatures (say 205°C.) is the more effective guide to the ultimate color of the end-product. A minimum color change under appropriate condi-

tions as to heat, time, etc., is often accepted as the more important proof of good quality.

Unsaponifiable Matter

This specification measures the non-fatty acid matter (other than moisture and insolubles) present in fatty acids. Included in unsaponifiables will be hydrocarbons, higher alcohols, sterols and waxy matter which may be objectionable contaminants, as well as diluents of the fatty acid content.

Other Physical and Chemical Tests

Specific gravity, refractive index, viscosity, flash point, fire point, hardness, cloud point and numerous other properties help to determine the suitability of specific acids to particular uses. The

crystal structure of solid fatty acids is frequently used as a guide to quality by experienced buyers.

Oxidation stability, as measured for a saturated acid such as stearic, is based on the time required for oxygen to be absorbed by the sample.

Ultraviolet absorption, as measured spectrophotometrically, is used to measure conjugated and non-conjugated molecular structure in unsaturated acids. It permits calculation of the percentages of polyunsaturated acids present.

Acetyl value, as applied to acids containing hydroxyl groups, and which are free from mono- and di-glycerides, gives a measure of the hydroxyl groups present.

HOW TO HANDLE FATTY ACIDS

One important advantage of the use of fatty acids, as compared to whole oils, is that type-for-type they are more reactive and permit faster and more complete saponification, esterification or other reactions.

The precautions used to protect the purity, color and stability of the acids are simple. Generally, all that is called for is the use of corrosion-resistant vessels and piping of the types now favored for any quality-controlled chemical reaction.

Fatty acids may be handled in aluminum vessels and in stainless steel (#304) nickel-alloy or glass-lined equipment. For some high temperature operations, type 316 stainless steel, with a molybdenum content of approximately 2.5% has been found desirable. For the fatty acids of lower molecular weight (myristic, etc.), a preferred material of construction is Inconel. Duramet alloy and nickel, as well as types 347 and 316 stainless steel, have also been successfully used.

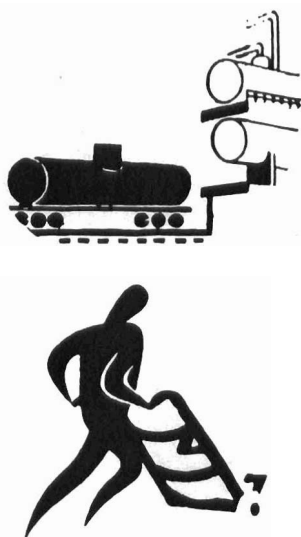
Shipment and storage in lacquer-lined drums is satisfactory, although long-term storage of partially used drums is not recommended. Iron, black or galvan-

ized, copper and most copper alloys are unsuitable for fatty acid handling or storage, particularly if color is a factor.

Solid fatty acids in cake, flake, or powder form are easily handled and stored in paper cartons, multi-wall bags, or fiber drums. Tank-car quantities are supplied from specially lined cars equipped with heating coils, and storage tanks equipped with external heating coils or jackets are recommended. The more reactive low-titer acids are shipped in lacquer lined steel drums, or in aluminum or other specially lined tank cars. Because heat may be a cause of discoloration and instability, it is important that in transfer to and from storage tanks heat be evenly distributed and not excessive.

Although fatty acids are inflammable, the flash point of typical acids is high, so that no critical problems of fire protection are created, beyond normal precautions for handling fats and oils.

Most fatty acids are harmless to the skin, although the lower molecular fractions, such as capric and caprylic, are irritating and direct contact should be avoided.



WHERE FATTY ACIDS ARE USED

	STEARIC ACID (Pressed Grades)	PALMITIC ACIDS (Over 60%)	COCONUT ACIDS	HYDROGENATED SOLID ACIDS	OLEIC ACID (Red Oil)	ANIMAL FATTY ACIDS	VEGETABLE FATTY ACIDS (Semi-Drying)	VEGETABLE & FISH FATTY ACIDS (Drying Types)	STEARIC ACID (Pressed Grades)	PALMITIC ACIDS (Over 60%)	COCONUT ACIDS	HYDROGENATED SOLID ACIDS	OLEIC ACID (Red Oil)	ANIMAL FATTY ACIDS	VEGETABLE FATTY ACIDS (Semi-Drying)	VEGETABLE & FISH FATTY ACIDS (Drying Types)
ADHESIVES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
BELT DRESSINGS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
BUFFING COMPOUNDS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CANDLES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CARBON PAPER	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CEMENTS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CHEMICAL INTERMEDIATES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CORE OILS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
COSMETICS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CRAYONS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
CUTTING OILS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
DETERGENTS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
DISINFECTANTS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
DRYCLEANING SOAPS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
DUPLICATING STENCILS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
DYES AND DYEING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
EMULSIFIERS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
FLOOR COVERING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
FLOOR WAXES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
FLOTATION AGENTS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
FRUIT COATINGS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
FUNGICIDES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
GERMICIDES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
INKS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
INSECTICIDES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
LEATHER	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
LEATHER, ARTIFICIAL	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
LUBRICATING GREASE	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
LUBRICATING OILS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
METAL POWDERS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
MOISTURE PROOFING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
NAPALM	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PAINTS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PAINT DRIERS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PAPER	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PAPER COATINGS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PHARMACEUTICALS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PLASTICS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PLASTICIZERS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
POLISHES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PUTTY	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
RESINS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
RUBBER (Compounding)	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
RUBBER (Synthetic)	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
SHORTENING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
SOAPS	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
SOAPS (Metallic)	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
TANNING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
TEXTILES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
VARNISHES	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
WIRE DRAWING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
WIRE INSULATION	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
WOOL SCOURING	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●

MAJOR USE ●

MINOR USE •

THE INDUSTRY BEHIND THE PRODUCT

In the past twenty years, total domestic fatty acid production has risen from less than 200 million pounds to almost 500 million pounds. A continued widening in the number and range of products has taken place.

Today the industry is comprised of some 20-25 companies. In cases where they are divisions of larger establishments, they are generally operated as independent units, with concern for the future progress of fatty acid usage equal to that of companies concentrating solely in this field. Included are "full-line" organizations that can meet any fatty acid need, and others who have

preferred to concentrate on special types with exceptional experience in the narrower range.

The important additions to capacity since World War II, and the extensive modernization programs carried on, have been based on two broad convictions: 1) that natural fats and oils, considered as a chemical starting point, furnish untapped technical possibilities and a stable, economic base, and 2) that the availability of these natural "chains" in the form of easily reactable acids of fully identified composition will broaden and stimulate their use.

Every member of the fatty acid industry is moving in the direction suggested by quality-minded and research-minded thinking. In some cases, research is taking the form of new derivatives and secondary products. In other cases, it is being concentrated on application aid to present and potential fields of fatty acid use.

If your own possibilities for product improvement or product development call for the properties furnished by fatty chemicals, we suggest you check with any of the organizations listed below.

The producers of fatty acids came together in 1951 to carry on activities which would be of general benefit to immediate and ultimate consumers of fatty acids, to the producers, and to those directly or indirectly supplying their raw materials.

Statistical, technical and educational projects aimed at encouraging more effective use and broader application of fatty acids come within the scope of the organization's objectives. General information as to the status of the industry, its materials, methods and fields of application is made available from time to time from the Association office. For complete information as to products, product specifications, and performance, consult the individual companies listed below:

**FATTY
ACID
PRODUCERS'
COUNCIL**

ACME-HARDESTY COMPANY
3512 Cedar St., Philadelphia 34, Pa.
ARCHER-DANIELS-MIDLAND COMPANY
733 Marquette Ave., Minneapolis, Minn.
ARMOUR INDUSTRIAL CHEMICAL CO.
110 N. Wacker Dr., Chicago 6, Ill.
BAKER CASTOR OIL COMPANY
40 Avenue A, Bayonne, New Jersey
CAPITAL CITY PRODUCTS COMPANY
P.O. Box 569, Columbus, Ohio 43216
CROSBY CHEMICALS, INC.
P.O. Box 460, Picayune, Mississippi
DARLING & COMPANY
4201 S. Ashland Ave., Chicago 9, Ill.
DREW CHEMICAL CORPORATION
522 Fifth Ave., New York 36, N. Y.

EMERY INDUSTRIES, INC.
4300 Carew Tower, Cincinnati 2, Ohio
GENERAL MILLS, INC., CHEMICAL DIV.
South Kensington Road, Kankakee, Ill.
THE GLIDDEN COMPANY
Organic Chemical Division
P.O. Box 389, Jacksonville 1, Florida
A. GROSS & COMPANY
295 Madison Ave., New York 17, N. Y.
HARCHEM DIV., WALLACE & TIERNAN, INC.
P.O. Box 178, Newark 1, New Jersey
HERCULES POWDER COMPANY
900 Market St., Wilmington 99, Del.
HUMKO PRODUCTS,
DIV. NATIONAL DAIRY PRODUCTS
P.O. Box 398, Memphis, Tennessee
LEVER BROTHERS COMPANY
390 Park Ave., New York 22, N. Y.
THE PROCTER & GAMBLE COMPANY
P.O. Box 599, Cincinnati 1, Ohio
SWIFT & COMPANY
115 W. Jackson Blvd., Chicago 4, Ill.
WEST VIRGINIA PULP & PAPER COMPANY
230 Park Ave., New York, N. Y.
WILSON & COMPANY, INC.
Wilson-Martin Division
Snyder Avenue & Swanson Street
Philadelphia 48, Pennsylvania
WOBBURN CHEMICAL CORPORATION
1200 Harrison Ave., Harrison, New Jersey

THE SOAP AND DETERGENT ASSOCIATION, 295 Madison Avenue, New York, N. Y. 10017