

**INDUSTRIAL
FATTY ACIDS
AND THEIR APPLICATIONS**

E. SCOTT PATTISON

Industrial Fatty Acids and Their Applications

Edited by

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**Manager, Fatty Acid Producers' Council
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FOREWORD

This volume has been made possible by the cooperation of technical personnel from more than a dozen members of the Fatty Acid Producers' Council, with the help of other authorities in specialized fields not encompassed by our members.

This cooperation is evidence of a transition, in the industrial production of fatty acids, from a concept of up-grading by-product commodities, to one of offering specialized industrial chemicals. These may be fatty acids of unique composition and purity, or derivatives such as esters or amines.

Increased capital investment is being made for product improvement, because firms in the fatty acid business believe in the future of these long-chain aliphatics as versatile building blocks for resins, surfactants, lube additives and other products as yet unknown.

It is also significant that composition, rather than source, is becoming the frame of reference for evaluation and application. This trend will no doubt be greatly stimulated by advances taking place in the field of gas chromatography, which permits a faster and simpler determination of fatty acid composition, in terms of the chain-length of individual acids.

Interest in the development of fatty acid derivatives exists today both within the industry and among its customers. Our members are particularly grateful to the several chapter-authors outside our industry who have added to the coverage of this book.

A. R. BETHKE

*Chairman, Steering Committee
Fatty Acid Producers' Council*

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1. FATTY ACIDS TODAY AND TOMORROW

E. S. PATTISON

Fatty Acid Producers' Council

The industrial potential of fatty acids and their derivatives is constantly growing. Nature's creative processes, taking place in the fields, farms and forests, act first to build the long aliphatic chains that make up about nine-tenths of the molecular weight of fats and oils. Unfortunately, the synthesis creates mixtures and variations in composition which are troublesome to specialized production techniques. To realize their full economic value, these fatty-acid chains must be processed to provide specific chemical properties and uniform performance. Separation and purification of the fatty acid is the one channel by which the complex fat molecule can be given precise applicability to the closely controlled industrial processes which characterize production of plastics, fibers, surfactants and other high-tonnage chemical products.

As the pressures of population growth enlarge food production, they also broaden the base from which fatty co-products and by-products come. Tallow supplies available for industrial use, for example, now top 3 billion pounds per year in the United States. The need for nonedible uses for vegetable oils and their derivatives is a perennial agricultural problem. Today, too, through the ingenuity of the kraft paper industry, the fatty acid content as well as the rosin content of Southern pine has been made recoverable. All this adds up to an ever-increasing availability of supply.

Agricultural technology, we know, is still open to basic scientific advances. In the future there may be new biochemical or enzymic pathways to build these chains even more strictly to industry's order as to length, reactivity and structure. Thus, in the growth of the chemical industry over the next decade, the products of fatty acid technology will surely have a larger proportionate share.

As this book indicates from Chapter 6 on, fatty acids today have a scope of application extending across the entire industrial horizon. No one field of use represents more than 15 per cent of the total of some 400 million pounds of fatty acids now annually consumed (see Figure 1-1).

This diversity of markets has its problems. The costs of keeping abreast of user technology, and marketing to all these fields, are high for the dollar

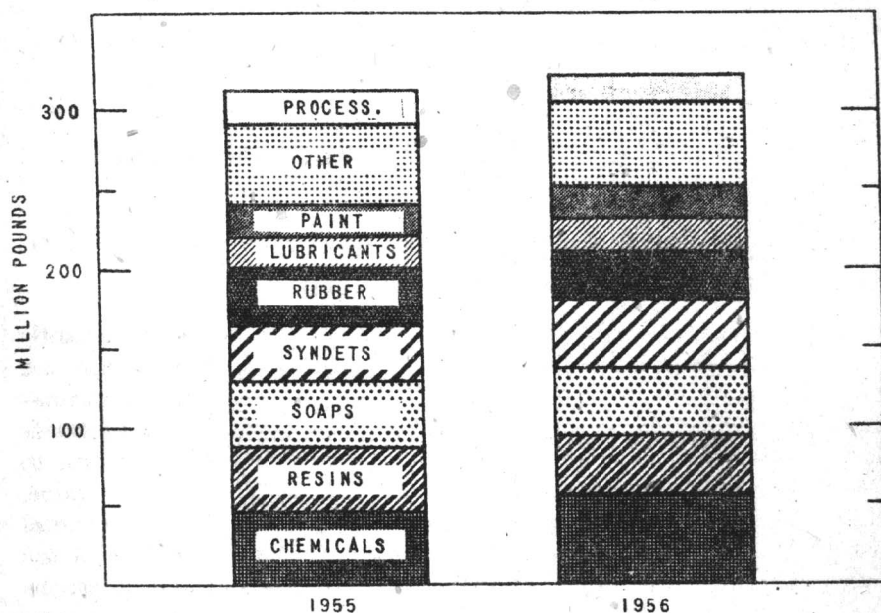


Figure 1-1. Fatty acid end-use (excluding unsaturated unhydrogenated animal).

	1955		1956	
	Quantity (Mil. lb)	% of Total	Quantity (Mil. lb)	% of Total
Total consumption	315.5	100.0	322.9	100.0
Used in:				
Chemicals	48.4	15.4	57.9	17.9
Resins and plastics	40.8	12.9	37.5	11.6
Soaps	40.3	12.8	43.5	13.5
Syndets	37.4	11.8	42.6	13.2
Rubber products	35.0	11.1	30.0	9.3
Lubricants	19.3	6.1	19.9	6.2
Paint and varnish	18.8	6.0	21.8	6.7
Other inedible and edible	53.4	16.9	54.9	17.0
Processing	22.1	7.0	14.8	4.6

Finished fatty acids consumed in factories, excluding mixed animal fatty acids going largely into "processing" (hydrogenation-pressing, etc.). 1956 consumption shown represents 63.2% of U. S. production as compiled by the Census Bureau.

volume involved. But the diversity also offers opportunity. Any such broad pattern of technical service increases the contacts and possibilities out of which tomorrow's new big-volume uses are most likely to come.

From the standpoint of biochemistry, fatty acids have a basic importance in the body's metabolic processes which we cannot even touch on in this volume. Food fats are hydrolyzed and the acids oxidized for fuel, while at

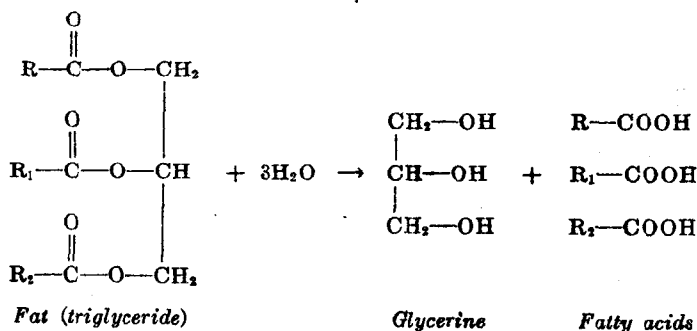


Figure 1-2. Hydrolysis of a fat to fatty acids and glycerine.

the same time, other fats characteristic of the particular organism are being synthesized within the body tissue. It has not been found possible to modify to any significant extent the fat composition of a specific animal or oil-bearing plant. For our industrial materials, therefore, we must start with the balance of mixed glycerides which nature makes available.

Hydrolysis, or fat-splitting, is the starting point for most fatty acid manufacture; tall oil, which is not a glyceride, is the only exception. It is only after the three-pronged glycerol linkage, typical of all fats (see Figure 1-2), has been severed that separation of the individual monobasic acids can be begun. This is because "chains" of different structure are randomly linked in the same fat (triglyceride) molecule, in addition to the mixture of different triglyceride molecules usually present in the fat. A completely pure and homogeneous fat molecule, such as triolein (triglyceride of oleic acid) is a synthetic laboratory curiosity.

Stearic and Oleic Acids

To avoid confusion of terms, it is necessary to distinguish between fatty acids, as defined by the organic chemist and as commercially produced and sold. The term "stearic acid" is an example of this confusion.

Here the commercial product name has priority, going back to the splitting of tallow for the manufacture of hard, high-melting candles, before individual acids of definite composition had been isolated or identified. Historically, commercial stearic acid has been a crystalline combination of the chemist's palmitic and stearic acids in a 55 % to 45 % ratio, with some small percentage of unsaturated acids. This ratio is that which naturally occurred in the mixed acid derived from splitting tallow, after most of the liquid acids were removed by the original pressing method (see Chapter 2). The liquid acids so removed are known as oleic acid, or red oil.

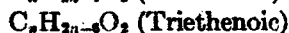
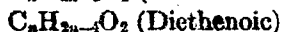
Other commercial acids have been identified by origin—say, coconut fatty acid or cottonseed fatty acid—terms reflecting the characteristic

ratio in which the component acids exist when released from the glycerides of these oils. Fractionation to separate or enrich the wanted acids, however, has made identification by origin obsolete as a means of characterizing many of today's acids. Blends and "cuts" are offered to meet particular market demands such as drying characteristics in paint films. Composition expressed in terms of component acids as the chemist defines them is now finding its way, more and more, into product descriptions and specifications.

In scientific work, the term "fatty acid" is often applied to the entire family of straight chain acids terminating in a single carboxyl group (monobasic, aliphatic acids) including the short-chain acids, such as acetic, which have the same molecular ratios. This group begins with the fully saturated fatty acids, (having the formula $C_nH_{2n}O_2$) where the chain may have as many as 30 carbon atoms. Only those with C_8 or higher are associated with natural fats or the fatty acid industry as such.

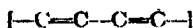
In general, the *saturated* acids having 12 to 18 carbon atoms are of major commercial concern. Their uses tend to reflect the stability or lack of easy reactivity at any point along the chain except at the carboxyl (acid) position. The highly stable metallic soaps are an example of useful derivatives (see Chapter 8). Saturated acids, including those saturated by hydrogenation, comprise slightly more than half of all fatty acids commercially produced. Saturated acids produced by hydrogenation, though differing in some respects from naturally saturated constituents separated from mixed acids, are one of the fatty acid industry's major products today.

Acids of reduced hydrogen content, having one or more double-bonds between carbon atoms along the chain, constitute the other main fatty acid family of high commercial importance. The *unsaturated* acids of the ethylenic family are made up of a number of separate series of the following general compositions:



Because linkage with other chemical radicals is readily made at the double-bond position, the possibility of many different derivative compounds is opened up. Oxidation becomes a factor to be reckoned with, both constructively to yield epoxy and cleavage products, and as a threat to stability.

The chemical reactivity and utility of unsaturated fatty acids in various polymeric or "drying" reactions is determined in part by the number of double bonds along the carbon chain. These double bonds also introduce



(a) Conjugation— as present in elaeostearic acid, an isomer of linolenic acid and a major constituent of tung oil.



(b) Nonconjugated double bonds, characteristic of regular linolenic acid.

Figure 1-3. Conjugated form of fatty acids

different properties arising from their location along the chain, i.e., conjugated and nonconjugated fatty acids (Figure 1-3). A different structure also results from a reversed positioning of those parts of the molecule on either side of the double bond, known as *cis* and *trans* isomerism.

The one double bond of the most important unsaturated acid (oleic acid) always occurs between the ninth and tenth carbon atom in an 18-carbon chain. It exists in natural fats as a *cis* acid, although a *trans* form (elaidic acid) may be artificially produced. Thus, despite the wide range of theoretically possible variations, the predominant "one-double-bond" acid, when purified by distillation, is one of specific composition and performance.

As to acids containing two or more double bonds, most of those being marketed fall into a few specific structural types. Linoleic and linolenic acids are the main "drying-type" constituents of mixed acids derived from vegetable oils. (The term "drying-type" as applied in paint technology, refers to an oil in which oxidation will spontaneously cause the chains to cross-link at the double bonds to form a hard, resistant polymer.) Commercial products containing linoleic acid, particularly, whether derived from cottonseed, soybean or tall oil sources, have found high acceptance in the protective coatings field.

In Table 1-1 are listed the 12 basic types in which the most important commercial fatty acids are commonly classified, and the constituent acids from which their properties are derived.

The chemist extends the name fatty acids to a few members of the acetylenic family having one or more triple bonds. At the moment, these are of little commercial interest.

In addition to the saturated and unsaturated acids of the straight, monobasic chain structure, however, fatty acid technology does encompass related *hydroxy* acids, of which ricinoleic acid—derived from castor oil—is the most important. These are acids in which a hydroxyl (OH) group is substituted for a hydrogen atom at a specific location. Dibasic acids derived from the processing of fatty acids, such as sebacic acid and azelaic acid, as well as self-polymerized fatty acids, are generally considered within

TABLE 1-1. SOME EXAMPLES OF COMMERCIAL FATTY ACIDS SHOWING TYPICAL PERCENTAGES OF CONSTITUENT ACIDS.

	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Ricinoleic	Other	Titler-°C	Iodine Value	Acid Value
	Carbon atoms														
	6	8	10	12	14	16	18	18	18	18	18				
	Double bonds														
	0	0	0	0	0	0	0	1	2	3	1				
Stearic acid (triple-pressed type)					1	50	48	1					55	1.0	210
Stearic acid (double-pressed type)					1	51	43	6					54	6	210
Solid fatty acid (hydrogenated tallow type)					2	35	59	4					57	5	205
Solid fatty acid (hydrogenated vegetable type)					1	29	68	2					62	2	201
Coconut acid (distilled type)	1	7	49	17	9	2	6	2					24	9	270
Lauric acid (fractionated type)			2	96	2								42	0.5	280
Oleic acid (distilled type)					2	7	2	79	10				9	95	196
Oleic acid (multi-distilled type)					3	5	1	85	6				5	95	200
Vegetable fatty acid (distilled cottonseed)					1	24	2	33	39	1			35	100	200
Vegetable fatty acid (distilled soybean)					11	4	29	51	5				28	130	200
12-Hydroxystearic acid								15				85	73	60	180
Tall oil fatty acid						2	46	44	3			4	10	138	192
Tall oil fatty acid (minimum rosin type)						1	50	46	2			1	5	130	196

the family and are so discussed here. In the widening field of derivatives described in this book, of course, products based on chains modified by sulfonation, epoxidation, and halogenation are also covered, along with esters and other compounds linked at the carboxyl position.

Fatty Source Materials

Animal fat, principally in the form of inedible tallow, is the largest single source material for fatty acids. In 1957 some 56 per cent of our commercial fatty acids originated from this source.

Prior to World War II, soapmaking used over 70 per cent of the domestic production of inedible tallow, and production of animal fatty acids as industrial chemicals took a relatively insignificant part of the tallow market—some 100 million pounds, as compared to 2 billion pounds for soap. Most of the tallow for fatty acids was split by the Twitchell Process (see Chapter 2) and separated by distillation and “pressing” to stearic and oleic acids. The conventional names single-pressed, double-pressed, triple-pressed, in a literal sense, were applied to stearic acid at that time, although they have now come to imply a quality specification regardless of the actual production cycle.

The hydrolysis of animal fats with steam on a continuous basis in high-pressure towers (high-pressure splitting) was first introduced to produce fatty acids for soapmaking, prior to its application to fatty acids for commercial sale. Here, long runs on a particular type of fat were the rule. Furthermore, the demand for glycerine in World War II favored a method of soapmaking in which glycerine was recovered as salt-free “sweetwater”, rather than as spent lye solution from the soap kettle.

Regulations were put into effect at the time limiting the use of fat in soapmaking processes in which glycerine was not recovered. This opened up new markets for fatty acids as a starting point for the specialty soap manufacturer. The greasemaker, too, found that fatty acids were more uniform than the glycerides then available. A rise in annual fatty acid production from about 100 million to over 300 million pounds took place in the decade 1941–1951. This rise was closely tied in with the emergence of continuous high-pressure fat splitting as a major production tool for the producer of industrial fatty acids.

In the purification steps which follow splitting, as well, the trend from batch to continuous methods was pushed farther. This involved introduction of fractional distillation, fractional crystallization, liquid-liquid solvent separation and others (see Chapter 3).

Fractional distillation in stainless steel equipment in particular, brought about important quality improvement in fatty acids from sources other than from animal fats—those from vegetable oils and their soapstocks, and those from tall oil, specifically.

Vegetable Sources

Normally, the splitting of edible whole oils such as soybean or cottonseed is not economically justified. In the alkali-refining of these oils, how-

TABLE 1-2. PRODUCTION OF COMMERCIAL FATTY ACIDS.

	In Million Pounds			
	1952	1955	1957	1958 ^b
Saturated ^a	175	225	237	218
Unsaturated ^a	190	194	158	157
Tall oil F.A.	NR	47 ^a	92 ^a	66 ^a 39 ^a
				105
Grand total	365	466	485	400

^a AASGP—Fatty Acid Monthly Census.

^b Estimated.

^c Bureau of Census—Facts for Industry—(Low rosin fatty acids—20% or less).

^d AASGP—Tall oil fatty acids (Less than 2% rosin).

^e Calculated from Census Bureau Tall Oil Fatty Acids less AASGP fraction.

ever, soaps of the free fatty acids present are removed along with other impurities from the treated oils. These so-called soapstocks containing some unreacted oil as well, when acidulated and concentrated, become a source of the same acids which characterize the oil. From soybean oil sources totalling over 3 billion pounds in 1957, soapstocks yielding some 35 million pounds of fatty acid were made available. Distilled and fractionated fatty acids comprising 50 per cent or more linoleic acid, offering particular advantages in resin manufacture, are the major product. Removal of the saturated acid (mostly palmitic) from the vegetable source boosts its drying characteristics to the level equal or exceeding linseed oil, and makes it more desirable from a color retention standpoint.

Cottonseed soapstocks, although somewhat lower in linoleic acid, are similarly employed as a starting point for drying-type fatty acids of substantial volume (see Table 1-3). Recently, there have been limitations to the wider use of soapstocks for fatty acid production, because of improvements in methods of oil extraction and refining that lower the amount of recoverable acid therein, in proportion to the original oil. Also some soybean soapstock has been found acceptable for animal feeding, thus creating competition for a limited raw material.

At the same time, a new source for drying-type acids having the same major constituents—linoleic and oleic acids—has originated in the kraft paper industry, with the increased availability of tall oil. Production at a level rising to 100 million pounds a year is predicted by 1960 for fatty acids from tall oil, fractionated to reduce rosin content to less than 5 per cent.

The modern stainless steel fractionating still (see p. 36) opens the way

TABLE 1-3. RAW MATERIALS USED IN PRODUCING COMMERCIAL FATTY ACIDS, 1952 AND 1957

Materials	1952		1957	
	Million Pounds	Per Cent	Million Pounds	Per Cent
Tallow and grease, inedible	187	45.4	284	38.5
Coconut oil, crude	48	11.6	45	6.1
Vegetable foods, total:	143	34.7	89	12.1
a—Cottonseed*	(57)	(13.8)	(31)	(4.2)
b—Soya*	(48)	(11.7)	(36)	(4.9)
c—Other*	(38)	(9.2)	(22)	(3.0)
Tall oil, crude	—	—	264	35.8
Other	34	8.3	55	7.5
Total	412	100.0	737	100.0

* Estimated.

Sources: Actual figures—U. S. Bureau of the Census.

Estimated figures—Association of American Soap & Glycerine Producers, Inc.

to separate relatively pure rosin acids from the fatty acids, and to reduce the rosin content of the fatty acid to 1 per cent or so, if economically required.

Lauric Acid Types

In the case of coconut oil, soapstocks made available in refining for edible use are small in amount, as this oil finds its major outlet directly for soapmaking. At the same time, the demand for fatty acids and derivatives of these saturated C_{12} and C_{14} chains is above 50 million pounds per year. As a result, crude coconut oil becomes a primary raw material, along with available soapstocks.

After splitting, the differences in molecular weight of the mixed chains are of sufficient magnitude to permit practical fractionation either of the acids or of their methyl esters. Detergents and other surface-active materials based on lauric acid of 90 per cent purity or more have had wide acceptance.

Fatty acids from linseed oil, castor oil, corn oil, and from various fish and whale oils have specialized applications—particularly in the coatings field—but they have not in themselves emerged as substantial articles of commerce in the United States.

Industry Trends

Historically, fatty acid production was associated with candlemaking and soapmaking. Some companies entered the business as a means of up-

grading by-products from other plant operations. With the coming of continuous splitting, fractional distillation and other technically advanced high capital-cost operations, the economics of the industry has been changed. Today, even those plants that are affiliated with meat packing or other interrelated fields are being operated on a decentralized basis as producers of industrial chemicals. They are becoming research-oriented, rather than raw-materials-oriented, and are turning more of their attention to specialty products resulting from such research and development.

These new chemicals include upgraded varieties of the standard types of fatty acids, but they do not stop there. Specialty products derived from fatty acids, such as esters and amines, are being developed and marketed within the industry on an increasing scale (see Chapters 11 and 12). In 1957, approximately 15 per cent of fatty acid production entered captive use by these producers. In addition, research in fatty chemicals applications by customers has been encouraged. Development departments, operating independently of regular sales staffs, have offered fatty chemicals for experimental use, with the objective of breaking through to new mass outlets. The fatty acids themselves are coming more and more to be the starting points rather than the end-products of this "industry in transition".

In the past, most of the companies concerned with producing and marketing fatty acids have tended to concentrate on a particular type of raw material—some on animal fats, some on vegetable stocks, some on tall oil source material. The trend of the future, however, seems definitely in the direction of diversity of raw material sources, unified through a common technology and quest for new markets for the common offspring of chain molecules. Today, thanks to research and development, the fatty acid industry is greater than the sum of its parts.

2. PRODUCTION OF FATTY ACIDS. I

RALPH H. POTTS

Armour and Company

RAW MATERIALS

Raw materials for the production of fatty acids fall into two quality classifications: (1) oils and fats obtained by rendering and extraction, which are relatively free of nonfatty materials and contain but small amounts of free fatty acids; and (2) by-product fat which is recovered from refining, degumming, deodorization, bleaching, and other recovery and purification operations. By-product fats are generally high in free fatty acids and impurities, and consequently require special treatment in processing.

Chief among these by-product raw materials are the foots obtained from the caustic refining of soya, cottonseed, coconut, corn and peanut oils. Foots from the refining of linseed, safflower, rapeseed, etc., are available in relatively small quantities.

These foots or soapstocks vary greatly in composition depending upon the refining process. Improvement in refining processes obviously reduces their quality, leaving less neutral oil and a correspondingly greater amount of impurities. Soapstocks from solvent-extracted oils contain a much greater quantity of oxidized fatty acid. Batch-refined, hydraulic-expressed oils contain the greatest amount of triglycerides as well as the highest amount of total fatty acid. Raw foots usually contain between 25 and 50 per cent of total fatty acid, the balance being water and impurities. These are usually acidulated at the refinery to save the expense of transporting water. The acidulated foots usually contain about 95 per cent total fatty acids, the oxidized fatty acid content varying between 3 to 16 per cent. The free unoxidized fatty acids may run between 55 to 85 per cent.²⁰

In processing acidulated fats, the fatty acid manufacturer has several choices open to him. If the free fatty acid content is high, he can distill before splitting and split the residue; or, as is the usual case, he can treat and split by any of the methods of hydrolysis to be described.

In addition to the grade of fat, the manufacturer selects fat as to source. Different recovery and refining procedures are usually required for fats of different composition; the degree of unsaturation especially requires the