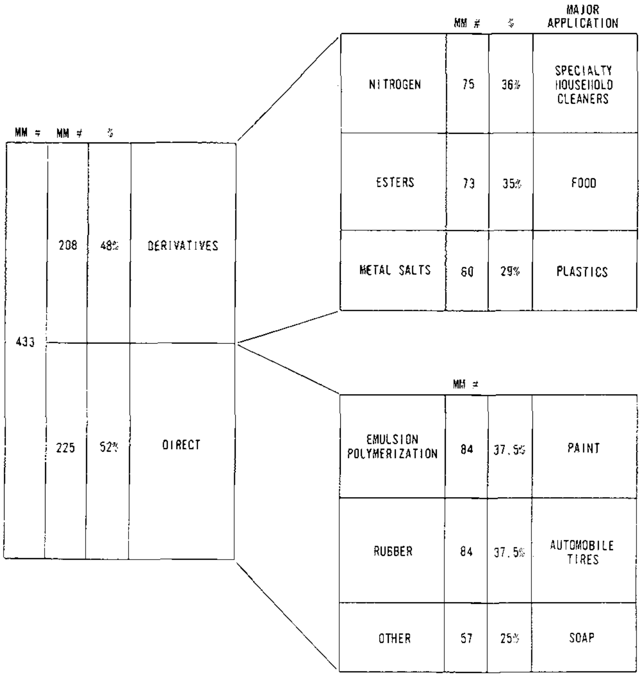

MM #	MM #	%	
433	208	48%	DERIVATIVES
	225	52%	DIRECT

	MM #	%	MAJOR APPLICATION
NITROGEN	75	36%	SPECIALTY HOUSEHOLD CLEANERS
ESTERS	73	35%	FOOD
METAL SALTS	60	29%	PLASTICS

	MM #		
EMULSION POLYMERIZATION	84	37.5%	PAINT
RUBBER	84	37.5%	AUTOMOBILE TIRES
OTHER	57	25%	SOAP

FIG. 20. Estimated 1978 U.S. consumption of hydrogenated tallow and soya fatty acids.

Total Hydrogenated Fatty Acids Consumption

Adding hydrogenated vegetable oil fatty acids (principally soya), plus some split edible tallow, to the inedible tallow source referred to above, brings the total of hydrogenated fatty acids to well over 400 million pounds annually. Their usage is depicted in Figure 20 (21). About half are used directly, with the paint and rubber industries accounting for 75% of this direct consumption. The other half are utilized in three major types of derivatives: nitrogen, esters, and metal salts. Their respective major applications are specialty household cleaners, food, and plastics.

Most of these applications will be discussed in detail in other papers. However, as is evident, hydrogenated fatty acids contribute to our technically based civilization in many and diverse ways.

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Separation of Fatty Acids

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ABSTRACT

Fatty acid separations which do not involve fractional distillation are discussed. Various methods of separating fatty acids from a practical point of view and the most salient facts of each process are described.

HISTORICAL

The first reported separation of fatty acids that appeared in the literature was back in 1828 when a gentleman by the name of Gusserow (1) separated linear saturated fatty acids from linear unsaturated fatty acids by first preparing the lead salt derivative, dissolving the mixed salts in diethyl ether or ethyl alcohol, and then separating the less soluble saturated acids from the more soluble unsaturated acids. Because this method of separation was very efficient, many researchers since that time have prepared various salts of fatty acid mixtures and studied their fractionation in a number of solvent systems.

Separation of fatty acids by this procedure has never become a commercial reality because of process economics. However, before the advent of gas liquid chromatography, this method was frequently used as an analytical tool. In fact, the American Oil Chemists' Society Official Methods describes a lead salt separation procedure (2) for analyzing mixtures of fatty acids.

COMMERCIAL PROCESSES

There are basically five commercial processes for the separation of fatty acid products: panning and pressing; Solexol Process; Emersol Process; Armour-Texaco Process; and the Henkel Process.

Panning and Pressing

In the Panning and Pressing Process (3,4), saturated acids are separated from unsaturated acids by first melting the fatty acid mixture, pouring it into shallow, rectangular aluminum pans, and placing in a cool room to slowly solidify. The formed cakes are removed from the pans, wrapped in burlap or cotton cloth, stacked in vertical presses, and pressure applied to slowly exude the lower melting liquid fraction. In the case of separating tallow fatty acids, the final temperature of the pressed cake determines the titer of the oleic acid fraction and the iodine

TABLE I

Separation of Tallow Fatty Acids by the Panning and Pressing Process

Type of product	IV solid fraction	Titer liquid fraction
Single-Pressed	8-12	6-10 C
Double-Pressed	5-8	2-5 C
Triple-Pressed	1-3	2-5 C

value of the stearic acid fraction.

The cakes remaining in the press are melted and sold as single-pressed stearic acid or remelted and once again poured into pans, solidified, wrapped, and pressed at a higher temperature to yield a double-pressed stearic acid and the corresponding oleic acid. The second stearic acid fraction can be sold as a double-pressed stearic acid or once again put through the panning and pressing process to produce a triple-pressed stearic acid product.

Table I gives the iodine values of the various stearic acid products and the corresponding titers of the oleic acid products when applying this method for separating tallow fatty acid.

It is this method of separating fatty acids wherein the fatty acid industry developed the traditionally used terms single-, double-, and triple-pressed stearic acid. Today only a limited amount of stearic and oleic acids are produced commercially by this process.

Solexol Process

This process involves the use of propane under pressure and is commonly referred to as the Solexol Process (5-11). Mixtures of fatty acids and propane are fed into a column under pressure, and at a selected temperature the more saturated fatty acids are removed from the top of the column; the more unsaturated fatty acids are removed from the bottom of the column. Normally, the saturated acids are more soluble in propane than are unsaturated acids. Temperatures used are 65-82 C and pressures are 350-500 psig. Because of the rapidity with which the solubility of fatty acids changes as the temperature of the solvent is increased, temperature control is critical. At the critical temperature of propane, 97 C, both saturated and unsaturated fatty acids are almost completely insoluble.

Tall oil fatty acids can be separated from rosin acids by the Solexol Process as illustrated in Figure 1. This method of separation was commercially used for manufacturing low-titer oleic acid from tallow fatty acids until the early 1970s.

Emersol Process

In the Emersol Process (12-14) fatty acids are solubilized in methanol, continuously pumped into a multitubular crystallizer equipped with scraper blades, incrementally cooled to -10 C, and filtered on a continuous rotary filter to separate the crystalline higher melting solid fraction from the lower melting liquid fraction. The filter cake is melted and flash-distilled to remove the methanol and recover the higher melting fatty acid. Likewise, the methanol is flash-distilled from the liquid fraction to recover the lower melting fatty acid.

A typical Emersol Process is shown in Figure 2.

Table II summarizes products obtained from the solvent separation of tallow and soybean fatty acids by the Emersol Process.

Armour-Texaco Process

The so-called Armour-Texaco Process (15) is similar to the Emersol Process with the exception that the patent claims the use of anhydrous acetone rather than aqueous acetone or other solvents such as methanol, methyl ethyl ketone, and so forth. Products obtained from the Armour-Texaco Process are comparable to products obtained from the Emersol Process as illustrated in Table III.

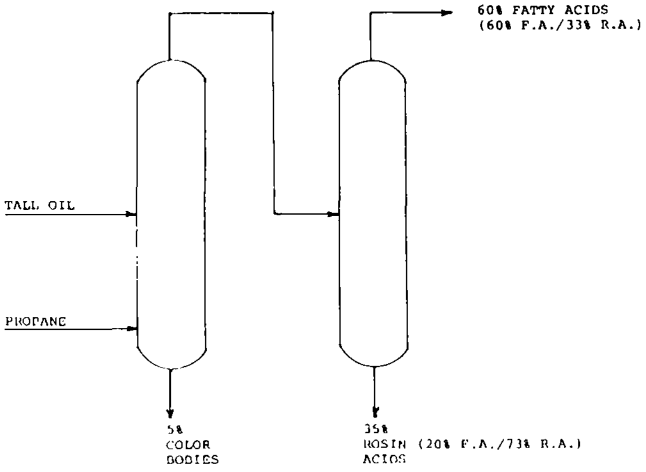

FIG. 1. Fractionation of tall oil by the Solexol Process.

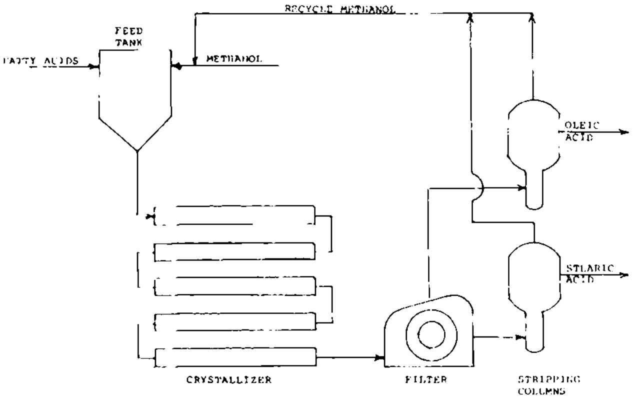

FIG. 2. Emersol solvent separation plant.

The quality and composition of the commercial oleic acids produced by low temperature solvent separation depend primarily upon the composition and quality of the raw materials that are separated: e.g., tallow fatty acids contain ca. 3.0% myristic acid, 1.0% myristoleic acid, 26% palmitic acid, 2.5% palmitoleic acid, 22.5% stearic acid, 43.0% oleic acid, 1.5% linoleic acid with traces of other acids. This raw material upon solvent fractionation yields a stearic acid having a typical composition of 2.5% myristic acid, 50% palmitic acid, 37% stearic acid, and 8% oleic acid, whereas the oleic acid fraction contains 3% myristic acid, 2% myristoleic acid, 6% palmitic acid, 6% palmitoleic acid, 74% oleic acid, and 8% linoleic acid.

As expected, stearic and oleic acids prepared from edible tallow are better quality products than the same acids produced from bleachable fancy tallow.

Henkel Process

The Henkel Process (16-19) is sometimes better known as the "rewetting, hydrophilization or water separation" process. In this process, mixtures of fatty acids, such as tallow fatty acids in their neat form, are subjected to controlled cooling in a heat exchanger equipped with scraper blades to yield a slurry of saturated acids and unsaturated acids. The slurry is first mixed with an aqueous solution of a wetting agent such as sodium lauryl sulfate followed by the addition of an aqueous solution of an electrolyte like magnesium sulfate. The dispersion is separated in a centrifuge to yield a lighter oil fraction of unsatu-

TABLE II

Typical Raw Materials and Emersol Products Processed from Them

Raw material	Acid product	Yield %	Titer °C	Iodine value
Tallow fatty acids	Stearic	51	54.0	8.0
	Oleic	49	3.0	93.0
Soybean fatty acids	Palmitic	15	49.0	50.0
	Linoleic	85	3.0	144.0

TABLE III

Products from the Solvent Separation of Tallow Fatty Acids in Acetone

Raw material	Acid product	Yield %	Titer °C	Iodine value
Tallow fatty acids	Stearic	50	54.0	5.0-8.0
	Oleic	50	0.4	95

TABLE IV

Characteristics of Stearic and Oleic Acids Derived from Tallow Fatty Acids via the Henkel Process

Raw material	Acid product	Yield %	Titer °C	Iodine value
Tallow fatty acids	Stearic	41	---	10
(52.5 IV)	Oleic	59	6-8	82
Tallow fatty acids	Stearic	48	--	17
(52.3 IV)	Oleic	52	3-5	85

rated fatty acids and a heavier aqueous fraction which is a suspension stearic acid. The suspension is heated to liquify the stearic acid and separated from the aqueous phase. Both the saturated and unsaturated fractions are further refined to yield stearic and oleic acids. Table IV gives some of the characteristics of these acids derived from tallow fatty acids.

The data in the table illustrate the fact that the process can be manipulated in a manner to obtain the desired oleic or stearic acid products. Several modifications of the Henkel process are now used commercially to produce stearic and oleic acids.

NEWER METHODS FOR SEPARATING FATTY ACIDS

These five processes constitute the fatty acid separation processes that have become commercial realities.

Now let me briefly discuss some of the newer methods that have appeared in the literature within the past nine years which someday may also become commercial processes. They include: Air Entrainment Method; Selective Adsorption; Methyl Formate Solvent Process; Transesterification-Fractionation Process; and Lithium Soap Separation.

Air Entrainment Method

In 1976 a patent (20) was granted wherein a fatty acid mixture is first heated to an elevated temperature until it becomes clear and limpid. The melted acids are poured into a pan and cooled to form a cake as previously described in the Panning and Pressing Process. The cake is removed, placed in a blender, whipped, and macerated in the presence of air to produce a liquified, pourable, and pumpable slurry. The slurry is then vacuum-filtered to yield a solid acid fraction and a liquid acid fraction. As with other processes, the iodine value and titer of the two fractions vary according to the temperature of crystallization. The process is stated to be applicable to a variety of feedstocks such as tallow fatty acids, soybean fatty acids, and coconut fatty acids.

Selective Adsorption

Several patents (21-23) have been issued on the separation of saturated fatty acid methyl esters from monounsaturated fatty acid methyl esters and monounsaturated fatty acid methyl esters from polyunsaturated fatty acid methyl esters which comprises contacting the methyl ester mixture with a particular zeolite containing selected cations at exchangeable cationic sites, thereby selectively adsorbing one methyl ester in preference to the other. One type of zeolite is used for separating saturated from monounsaturated fatty acid methyl esters, and another zeolite is used for separating monounsaturated from polyunsaturated fatty acid methyl esters. One patent in the series describes the separation of a mixture of saturated, monounsaturated, and polyunsaturated methyl esters employing a two-stage zeolite solid bed adsorbent treatment. The idea for these patents came from the well known method of using crystalline aluminosilicates for fractionating normal paraffins from branched chain paraffins and paraxylene from other isomers.

Table V illustrates the selectivity of specific zeolites for separating fatty acid methyl esters according to their degree of unsaturation. The efficiency of fractionation varies both with temperature and pressure. Temperature ranges from 20 to 250 C and pressures from atmospheric to 500 PSIG.

TABLE V

Selectivities of Zeolites' Adsorbents for Separating Fatty Acid Methyl Esters According to the Degree of Unsaturation (Desorbent-Free Basis)

	Adsorbent			
Methyl esters	K-Cu-X	K-Cu-Y	Na-X	K-X
$C_{18:1}/C_{16:0}$	13.5	20.0	1.7	6.7
$C_{18:1}/C_{18:0}$	18.0	40.0	2.5	14.5
$C_{18:2}/C_{18:1}$	—	—	1.4	3.2

Methyl Formate Solvent Process

Another patent (24) describes the use of methyl formate or aqueous methyl formate for separating saturated fatty acids from unsaturated fatty acids comprising dissolution of the fatty acid mixture in methyl formate at elevated temperatures, cooling the solution to slightly above room temperature, and separating the crystallized fatty acids from the mother liquor, evaporating the solvent from the two fractions, and obtaining the desired acids. A real plus to this process is that the separation is conducted at crystallization temperatures substantially higher than those employed in the Emersol and Armour-Texaco solvent crystallization processes.

Transesterification-Fractionation Process

Although this paper does not describe fractional distillation, I would like to take the liberty of discussing one method of fractionating lower molecular weight saturated acids from higher molecular weight unsaturated fatty acids using a transesterification-fractional distillation process (25).

As reported in the literature, palm oil is transesterified with methyl alcohol and fractionally distilled to yield a methyl palmitate product and a methyl oleate product containing ca. 20% methyl linoleate. The methyl oleate fraction is then interesterified with palm oil while methyl palmitate is continuously removed using fractional distillation techniques. The final products are methyl palmitate, which can be hydrolyzed to the acid, and a liquid palm oil, which has salad oil properties. Correspondingly, the methyl palmitate can be interesterified with palm oil to yield methyl oleate and tripalmitin. The flowsheet presented in Figure 3 schematically illustrates the process.

Lithium Soap Separation

Relative to the deluge of patents and literature that have appeared within the past ten years on the synthesis of fatty acids from petrochemical feedstocks wherein they are primarily mixtures of linear and nonlinear monocarboxylic acids, I felt it worthy to briefly comment on a method for separating such a mixture.

The lithium soap process (26) converts a mixture of C_{16}-C_{19} monocarboxylic acids into their lithium soaps by reacting them with an aqueous solution of lithium sulfate above room temperature, whereupon the lithium soaps of the linear monocarboxylic acids begin to precipitate. The temperature is lowered to ambient temperature and the solid fraction separated by filtration. Acidulation of the solid fraction yields linear acids of 98% purity, and acidulation of the mother liquor yields the nonlinear acids of 94% purity.

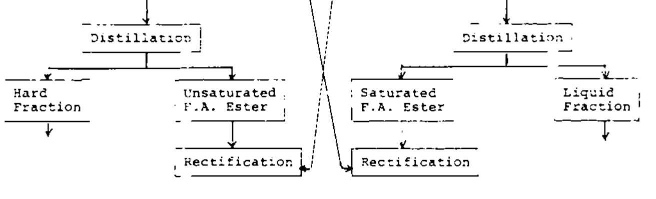

FIG. 3. Flowsheet representing the fractionation of palm oil by transesterification-fractionation.

OTHER METHODS OF SEPARATING MIXTURES OF FATTY ACIDS

It was my intention to discuss only those methods of separation which have appeared in the literature since 1970. However, there are earlier literature references which I, personally, feel are worthwhile reviewing if an individual is interested for the first time in the separation of fatty acids. These methods are: Liquid Thermal Diffusion (27); Urea Separation (28-36); Nitropropane Solvent Crystallization Process (37); Dichloroethane Process (38); Trendex Leaching Process (39); and the Citiosol Process (40).

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