shown in Table III, most tall oil fatty acid utilization is now in chemical intermediates where fatty acids are the preferred raw materials.

The intermediate chemicals which account for this rapidly growing share of tall oil fatty acid utilization are the following (A.-E.).

(A.) Dimer Acids. Polymerization of tall oil fatty acids under heat and pressure with a clay catalyst gives a mixture of methyl branched C_{18} monobasic acids, C_{36} dibasic acids (called dimer acids), C_{54} tribasic acids (called trimer acids), plus some higher acids. The products are separated by high vacuum distillation in a thin film.

Hydrogenation of the monobasic acids gives a mixture of stearic acid and a liquid isomer called isostearic acid.

Dimer acids are the highest molecular weight dibasic acids commercially available. They are complex mixtures of isomers, including cyclic structures, with residual carbon-carbon unsaturation. Dimer acids are used mainly in the synthesis of polyamide resins, derived by reaction with various amines. The solid thermoplastic resins are essentially neutral with a wide range of melting points. The lower molecular weight resins are used in solvent-based flexographic printing inks and in thixotropic coatings. The higher molecular weight polyamide resins are used as hot melt adhesives. Liquid polyamide resins with reactive amine groups are used for curing epoxy resins in surface coatings and adhesives. The long chain hydrocarbon structure of dimer acids affords flexibility in the cured resin composition.

Dimer acids are used in the synthesis of polyester resins of improved flexibility; e.g., in oilless alkyds used in coil coatings. Other applications are in hot melt adhesive polyester resins, and in surface coatings based on oil-modified alkyds, epoxy esters or urethanes.

Esters of dimer acids are used in modern industrial lubricants and metal-working compounds to provide both lubrication and rust prevention.

Trimer acids are used as the free acids or as a soap or polyamidoamine in corrosion inhibitors. The polar carboxyl groups are adsorbed onto steel surfaces, and the long chain fatty, hydrophobic part of the trimer acids limits the access of water and other corrosive chemicals. Important applications are in oil well drilling and in petroleum refineries.

(B.) About ten years ago, Hercules started production of oleic and linoleic acids which were obtained by solvent crystallization of tall oil fatty acids. The oleic acid fraction is high quality and one grade, Pamolyn 100-FG, has wide FDA approval for direct food contact. The linoleic acid fraction is further conjugated and used as a replacement for dehydrated castor oil in surface coatings.

(C.) Epoxidized esters of tall oil fatty acids are used as plasticizer-stabilizers for vinyl. The tall oil fatty acid is generally pretreated to remove phenolic impurities, such as dimethoxystilbene, in order to avoid a pink coloration.

TABLE III

Domestic Utilization of Tall Oil Fatty Acids in 1978
(from Pulp Chemicals Association)

	Tons	% of Total
Intermediate chemicals	73,000	49
Surface coatings	34,000	23
Miscellaneous	20,000	13
Surfactants	14,000	9
Flotation	8,000	6
Total	149,000	

(D.) About five years ago, Westvaco pioneered the production of a C_{21} dibasic acid made by the addition of acrylic acid to the linoleic portion of tall oil fatty acids. The unreacted oleic and elaidic acid portions were then stripped off. The two carboxyl groups differ in reactivity and unique surfactants, and other products have been made.

(E.) Low cost byproducts of tall oil fractionation, including heads and pitch, have traditionally been blended together and used in the flotation of phosphate and iron ores. In one stage of the beneficiation process, the fatty acids are used without further processing; but in a subsequent stage, they are used as amidoamine derivatives of the fatty acids.

Union Camp isolates the palmitic acid in tall oil heads by means of solvent crystallization. The purity is sufficiently high for conversion to low odor isopropyl palmitate for use in cosmetics.

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Product Forms and Packaging in the Fatty Acid Industry

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THE FATTY ACIDS INDUSTRY–AN OVERVIEW

Fatty acids, derived from tall oil and fats and oils represent a 1.3 billion pound industry with shipments currently valued at $320 million a year. Twenty-one percent of the fatty acid production is converted into other chemical derivatives by the fatty acids producer. Another 19% is sold on the merchant market to intermediate manufacturers of other chemical derivatives. The remaining 60% of production is sold as free fatty acids for direct use in a wide variety of end uses.

The direct consumption of fatty acids, which represents over 800 million pounds a year, is in such consumer product areas as cosmetics, drugs and pharmaceuticals, and specialty soap and detergents. Fatty acids are also directly consumed in many industrial uses and products including metalworking fluids, oilfield chemicals, paints, plasticizers and plastics.

Chemicals derived from fatty acids amount to 539

TABLE I

Forecast U.S. Production of Major Fatty Chemicals 1978-1983[a]

Product	Million pounds 1978	Million pounds 1983	Percent of total 1978	Percent of total 1983	Average annual growth, %
Amines	200	294	5.3	6.8	8.0
Alcohols	715	935	19.0	21.6	5.5
Acids	1,326	1,600	35.4	36.9	3.8
Esters					
Surfactants	230	280			4.0
Plasticizers	30	27			(2.0)
Total	260	307	6.9	7.1	3.4
Glycerin	288	317	7.7	7.3	2.0
Alkanolamides	85	85	2.3	2.0	0.0
Soaps					
Metal stearates	100	138			6.6
Sodium and potassium	780	652			(3.5)
Total	880	790	23.4	18.3	(2.4)
Total	3,754	4,328	100.0	100.0	2.9

[a]Source: Estimates by C.H. Kline & Co. Includes double counting.

TABLE II

End Uses for Free Fatty Acids and Derivatives[a]

End use	Million pounds	Percent of total
Plasticizers and plastics	179	13.5%
Emulsion polymerization	114	8.6
Rubber compounding	108	8.1
Polishes and other cleaners	102	7.7
Soaps	98	7.4
Food	95	7.2
Intermediate chemicals[b]	85	6.4
Household detergents	80	6.0
Coatings	70	5.3
Cosmetics	70	5.3
Other[c]	325	24.5
Total	1,326.0	100.0%

[a]Source: C.H. Kline & Co.

[b]Includes ore flotation, oilfield chemicals and metalworking fluids.

[c]Includes asphalt, candles, lubricants, paper sizes, specialty cleaners, and textile scouring.

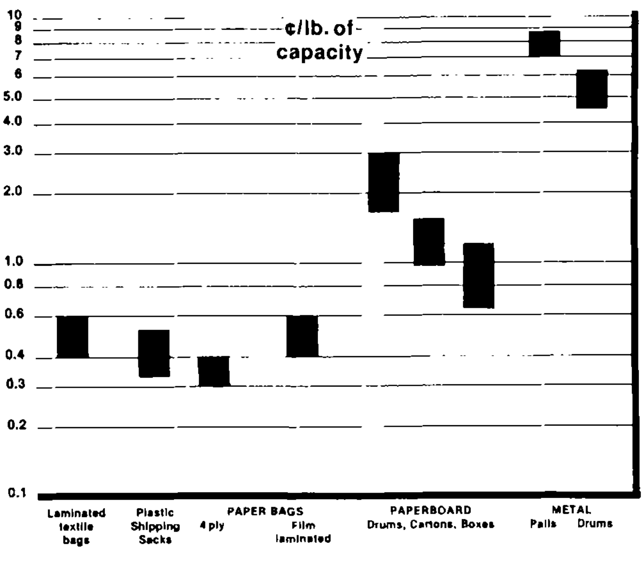

FIG. 1. Relative packaging costs.

million pounds. These derivatives include such specialty products as amines (which are further processed into quaternary ammonium compounds); detergent range alcohols (which are further processed into alcohol ethoxylates and sulfated alcohols), alkanolamides; esters, and soaps.

Fatty chemicals are a family of products that are similar in chemical composition. Table I shows that in 1978 the production of fatty chemicals was 3.75 billion pounds. By eliminating fatty acids and the double counting of fatty acid derivatives, the remaining 1.9 billion pounds is comprised mainly of alcohol, glycerin, and sodium and potassium soaps. We estimate that, over the next 5 years, fatty chemical production will increase at an average rate of 2.9% a year. It is estimated that total fatty acid production will increase at a rate of 3.8% a year, and its share of the total will slightly increase to 36.9% in 1983.

Of the some 25 end uses and products that consume fatty acids, there are 10 major end uses that account for 75.5% of current total production. The leading end uses are shown in Table II.

Major Forms and Uses of Fatty Acids

Fatty acids are categorized as unsaturated and saturated types. Unsaturated fatty acids are acids having a chain of 18 carbon atoms with either one, two, or three double bonds. They include fractions of tall oil, and oleic acid and acids derived from animal, vegetable and marine oils. Unsaturated fatty acids account for 58.4% of all fatty acid production. Due to their chemical composition, and specifically their point of solidification, almost all unsaturated fatty acids are produced, shipped and used in a liquid state. The major uses of tall oil, which accounts for ca. 31% of all fatty acid production, are ore flotation and oilfield chemicals, in dimer-trimer production, and in paints and soaps. The majority, or ca. 88%, of tall oil fatty acid is used directly with only 12% converted into other derivatives.

Oleic acid accounts for almost 13% of total fatty acid production, and 84% of its production is consumed directly. The major uses are in ozonolysis for the production of pelargonic and azelaic acid, metalworking fluids and textiles. Azelaic acid is the only significant grade of unsaturated fatty acid that is produced and used in such solid form as flakes and powders. Finally, all other animal, vegetable and marine fatty acids, which account for 15% of total fatty acids production, are used as liquids in soaps and detergents, lubricants and in rubber compounding.

TABLE III

Current Prices of Fatty Acids[a]

Type	Form	Price/lb.
Azelaic, tech.	drms, c.l. f.o.b.	$0.76
Coconut, distilled[b]	tanks, f.o.b.	0.52
double distilled	tanks, f.o.b.	0.54
Castor oil acid, dehydrated	drums	0.87
Myristic, pure	bags	0.75
	tanks	0.72
Oleic acid double distilled[b]	drums	0.48
	tanks	0.42
single distilled	drums	0.46
	tanks	0.38
Palmitic 90% tech.	bags	0.45
	tanks	0.42
Pelargonic[b]	tanks, f.o.b.	0.65
Stearic, s.p., d.p., t.p.[b]	bags (ave.)	0.36
Tall oil[b]	tanks	0.21
Tallow distilled[b]	drums, delivered	0.32
	tanks, delivered	0.27
hydrogenated	flake, bags, delivered	0.34
	tanks, delivered	0.34

[a]Source: Chemical Marketing Reporter, June 4, 1979.
[b]Volume grades.

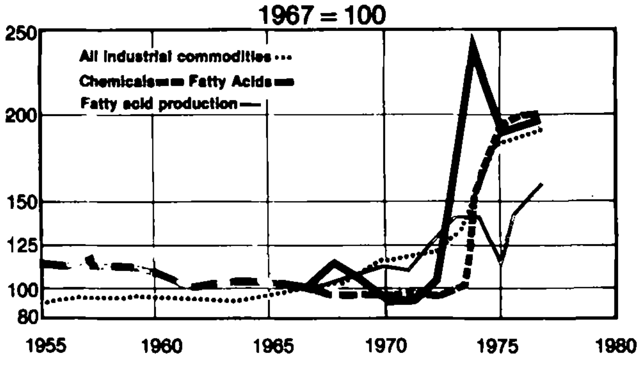

FIG. 2. Producer price indexes 1955-1977.

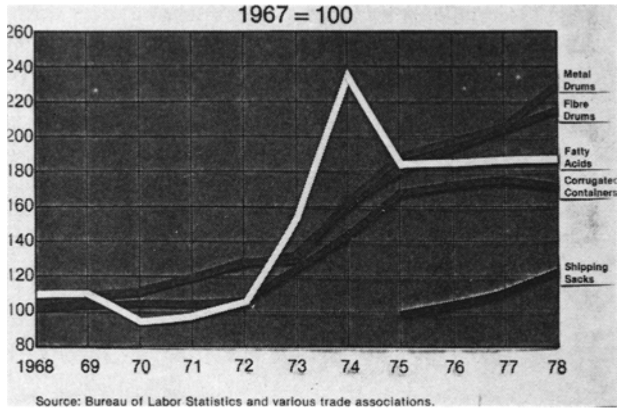

FIG. 3. Producer price indexes of fatty acids and select packaging products 1968-1978.

Saturated fatty acids account for 42% of all fatty acid production. They are straight chain acids that are produced in crystalline form. The largest category is hydrogenated tallow and soya fatty acids which represent 22% of all fatty acid production. Only 50% of hydrogenated acids are consumed directly. Major uses are in rubber compounding (as a flake), in emulsion polymerization, as powdered metal salts in plastics, as liquid esters in foods and as nitrogen derivatives in specialty household cleaners. Based on end use and customer size, several of the saturated grades are also shipped in bulk form, which means they must be liquified for handling and shipping.

Stearic acid, the second largest saturated fatty acid, accounts for 10% of all fatty acid production and 75% of its production is directly consumed. Principal end uses for stearic acid are in cosmetics, drugs and pharmaceuticals, polishes, soaps, and as an ester in foods. Stearic acid is generally produced and used in powder and flake form. High palmitic acid grades with at least 60% palmitic content account for less than 1% of fatty acid production and are used in flake production of soaps and cosmetics.

The last important type of saturated acid is coconut oil which accounts for almost 9% of all fatty acid production and has only 15% consumed directly. In liquid form, the major end uses for coconut oil fatty acids are as nitrogen derivatives in household detergents, in soaps, in the conversion into alcohol and surfactants. Coconut oil is also fractionated in flake form into lauric and myristic acid, used in textiles and cosmetics.

Fatty Acids Packaging

Packaging should be designed to protect the purity, color and stability of the acids. This may require the use of such specialty materials as aluminum, 304 stainless steel, coated drums, or plastic-lined shipping sacks or cartons. The manufacturer must also consider the capacity of the package, set up requirements and, of course, the filling costs. In some cases, the manufacturer will choose additional packaging techniques such as strapped or film-stretch wrapped palletizing. Finally, packaging must meet the customer handling and use requirements, such as for stacking, mixing and package disposal.

Fatty acids produced and used in solid form are more popularly produced as flakes, powders or beads. These grades are typically packaged in 50, 80 or 100 pound capacity paper, plastic or woven bags, 55 gallon metal or fiber drums, or in 500 pound or larger capacity bulk boxes. Larger forms such as bars-slabs or cakes-chunks are typically packaged in 100 pound cartons or woven bags. And, finally, shipments of solid fatty acids in bulk are liquified and shipped in 4,000, 6,000 or 8,000 gallon tank wagons, or 4,000, 6,000, 8,000, 10,000 or 20,000 gallon tank cars.

Semisolid and liquid fatty acids such as oleic, linoleic, and tall oil acids, are all shipped as liquids in either 55 gallon drums (lined or unlined), in tank cars which may be lined or made of aluminum or just plain steel, and in stainless steel or aluminum tank wagons.

Product, Package and Shipping Costs

Recognizing that packaging prices vary with the selection of material, the type of construction and capacity, Figure 1 visually shows the variation in the cost/lb. of capacity of a select group of packaging containers. As seen, heavy duty shipping sacks, regardless of composition and construction, generally cost between 0.3-0.6¢/lb., followed by paper board drums, cartons, and boxes at 0.6-3.0¢/lb. The most expensive containers used are metal pails and drums at costs ranging from 5-8¢/lb. of capacity.

Reviewing the costs of shipping fatty acids between New York and Chicago shows that a 30,000 pound unit shipment (packaged in drums, bags or cartons), costs $2.65/hundred lb. in full truck loads and $2.66/hundred lb. in boxcars. Naturally, the cost for packaging of such shipments must be added to these rates to compare accurately shipping and packaging costs with bulk methods of shipping. When shipping by tankcar, a 30,000 pound load of fatty acids costs $2.66/hundred lb. Tank wagon shipments, which have the ability to utilize various constructions and several compartments, cost $3.38/hundred lb. As you would expect, tank wagon costs are higher as they are the fastest mode for bulk shipping and offer the customer the greatest off-loading flexibility.

The current prices for fatty acids are shown in Table III. Prices per pound vary with product grade, package type and method of shipment. As shown, the prices range from 20 to 30¢ for the high volume grades and up to 50 to 70¢/lb. for the lower volume or specialty grades. It is interesting to note that the difference between a drum or tankcar shipment generally decreases from 12 to 15¢/lb. in favor of bulk shipments, and that the price differential between bags and tankcar shipments is only about 8 to 10¢.

Historical Pricing–a Review

For many years the prices of fatty acids, as with other chemical and industrial commodities, varied within a narrow band. However, the composite price index for fatty acids increased dramatically by 150% in 1973-74. This increase occurred about one year before the 100% increase in the price index of all chemicals. These changes over the last 8 years are shown in Figure 2 along with an index of fatty acid production. The rapid and high increase for prices of fatty acids can be generally attributed to elimination of price controls, and the rapid price increase in such basic fatty acid feed stocks as tallow, tall oil and coconut oil. As shown, fatty acid demand peaked in this period (possibly due to false purchasing), and supplying was fairly constant. We believe these factors are the reasons for the rapid and sudden rise in fatty acid prices.

Figure 3 shows the changes in price index of fatty acids along with several of the containers used in their shipment. In 1973-74, the price of fatty acids increased at a rate greater than that for its containers. However, since 1975, fatty acid prices have stabilized and are now increasing at a rate much less than the rate for metal and fiber drums and multiwall shipping sacks.

Packaging Developments

Several developments in fatty acid packaging are: (a.) corrugated cartons are less frequently used as the bulk of solid fatty acid shipments are in flake, powder or bead form; (b.) the packaging of fatty acids in 50 and 100 pound plastic shipping sacks which are then loaded into Banbury mixes is being evaluated by the rubber industry; and (c.) there may be an opportunity to use 500 to 2,000 pound capacity bulk boxes for the semibulk shipment of fatty acids.

Polymerization–Dimer Acids

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ABSTRACT

Dimer acids are the commercial products resulting from clay-catalyzed, high temperature polymerization of unsaturated fatty acids, usually tall oil fatty acids. The products have been commercially available since the 1950s and now, in all forms, represent 40-50 million pounds per year sales in the United States. The products are high boiling, mobile to viscous liquids. Their most important chemical property is carboxyl multifunctionality, which allows conversion to high polymers, mostly polyamides in commercial practice. Dimer-based polyamides have sizeable application as hot-melt adhesives and as reactive components of epoxy resins. There are much smaller uses in other polymer systems. Dimer acids are relatively nontoxic, and are not flammable. In February 1979, single-distilled dimer acids sold in tankcar quantities in the range $0.45-0.55/lb. There were six producers in the business, with one almost entirely a captive consumer.

INTRODUCTION

Polymerized fatty acids, along with fatty esters, amines and amine derivatives, amides, alcohols, and metallic stearates, are important commercial fatty acid derivatives. Dimer acids is the general term applied to products obtained by the intermolecular reaction of two or more molecules of unsaturated fatty acids or unsaturated fatty acid esters. For the most part, the unsaturated fatty acids used commercially in manufacture are those which have 18-carbon atoms and are mixtures of oleic and linoleic acids. As a result, the finished products are mostly 36-carbon entities. In commercial products, the degree of fractionation determines the level of trimer and higher oligomers, as well as the trace percentages of unpolymerized, or structurally altered, 18-carbon, monocarboxylic acids.

There have been a variety of structures suggested for dimer acids. Dimerization of unsaturated fatty acids has been claimed to lead to cyclic structures by a Diels-Alder reaction, and to linear dimers and higher oligomers by a free-radical route involving hydrogen transfer, particularly in the presence of oxygen. Clay-catalyzed dimerization of unsaturated fatty acids appears to be predicated on carbonium ion reaction involving double bond isomerization, acid catalysis, hydrogen transfer, and chain branching. Some idealized possible structures for dimer acid methyl esters are shown in Figure 1. Table I relates final product structure to the type of fatty acid precursor.

In the United States, in the 1970s, ca. 80% of the feedstock for dimer acid industrial production has been tall oil fatty acids. The first serious experimental work on tall oil fatty acid dimerization began in Norway in the second decade of this century. This led to the realization that unsaturated fatty acid dimerization could easily result in an inexpensive, carboxyl reactive, difunctional, noncrystalline, nonvolatile chemical entity.

Later, the Northern Regional Research Laboratory of the USDA was one of several research groups that developed dimer acids chemistry. Marketing of dimer acids began at the end of the 1940s. In 1979 US manufacturers are listed in alphabetical order in Table II.

The manufacturing process for dimer acids seems to be quite standard through the industry. A fairly typical set of reaction conditions, taken from published literature are 4% montmorillonite clay catalyst at 230 C for 6 to 8 hr and finally bleached with 2% clay and H_3PO_4.

Literature cited in the bibliography of this paper covers commercial procedures as well as noncommercial techniques which have been applied to dimerization–reaction induced at relatively low temperature by corona discharge as an example of the latter. Fractionation of the products after dimerization is generally done by some form of wiped-film evaporation or molecular distillation.