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

E.C. LEONARD, Vice President and Director of R&D, HumKo-Sheffield Chemical,
Division of Kraft Inc., White Station Tower, PO Box 348, Memphis, TN 38101

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.

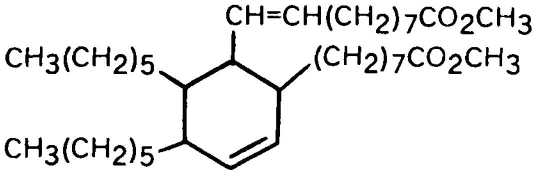
There have been a variety of structures suggested for dimer acids. Dimerization of unsaturated fatty acids has been claimed to lead to cyclic structures by a Diels-Alder reaction, and to linear dimers and higher oligomers by a free-radical route involving hydrogen transfer, particularly in the presence 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.

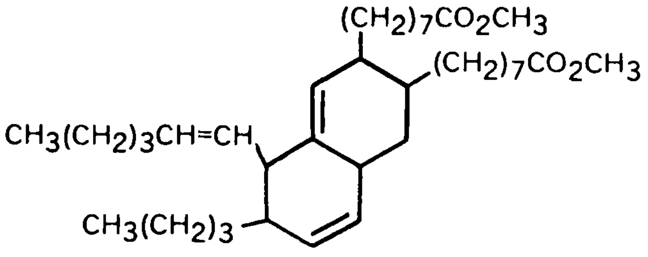
Later, the Northern Regional Research Laboratory of the USDA was one of several research groups that developed dimer acids chemistry. Marketing of dimer acids began at the end of the 1940s. In 1979 US manufacturers are listed in alphabetical order in Table II.

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.

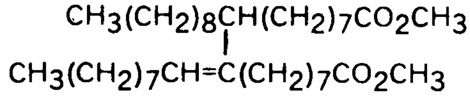
Literature cited in the bibliography of this paper covers commercial procedures as well as noncommercial techniques which have been applied to dimerization—reaction induced at relatively low temperature by corona discharge as an example of the latter. Fractionation of the products after dimerization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



Monocyclic



Bicyclic



$$\begin{array}{l} CH_3(CH_2)_8\underset{|}{C}H(CH_2)_7CO_2CH_3 \\ CH_3(CH_2)_7CH{=}C(CH_2)_7CO_2CH_3 \end{array}$$

Acyclic

FIG. 1. Some possible dimer acid (methyl ester) structures.

TABLE I

Dimer Acids Feedstock/Structure Relationship (%)

	Dimer structure		
Feedstock	Acyclic	Monocyclic	Polycyclic
Oleic or elaidic acid	40	55	5
Tall oil fatty acids	15	70	15
Linoleic acid	5	55	40

TABLE II

U.S. Dimer Acids' Producers

AZS Products
Crosby
Emery Industries
Henkel
HumKo Sheffield Chemical
Union Camp

TABLE III

Commercial Dimer Products

	AZS	Crosby	Emery	HumKo Sheffield	Union Camp
Single-distilled dimer	●	●	●	●	●
Double-distilled dimer			●	●	●
Hydrogenated dimer			●	●	
Monomer	●	●	●	●	●
Isostearic acid			●		●
Trimer			●	●	●

TABLE IV

Properties of Single-Distilled Dimer Acids

	High dimer	Intermediate dimer	High trimer
% Dimer	87	83	75
% Trimer	13	15.5	23.5
% Monobasic acids	trace	1.5	1.5
Acid number	190-198	190-197	189-197
Sap number	195-201	191-199	191-199
% Unsap, max	0.5	1.0	1.0
Color, Gardner max	7	8	9
Viscosity @ 25 C, cSt	8000	8500	9000
Pour point, C	-10	-4	-4

TABLE V

Reactions of Dimer Acids

Commercial	Noncommercial
Polyamidation	Sulfation
Amination	Sulfonation
Esterification	Ethoxylation
Polyesterification	Halogenation
Hydrogenation	Epoxidation
Soap formation	Hydrogenolysis
Isocyanate formation	

Table III shows the range of products offered by unsaturated fatty acid dimerizers. The largest volume commercial product is a single-distilled material, i.e., an entity from which almost all of the monomer has been removed, with the finished product containing ca. 80% dimer, 20% trimer, and a trace of monomer. Double-distilled dimer, trimer, and hydrogenated dimer have relatively small sales outlets in 1979.

The more important physical properties of single-distilled dimer acids are shown in Table IV. All of the commercial products are liquid at 25 C (except monomer, which is a slush). They have low vapor pressures, are noncrystallizable, and have viscosities ranging from highly mobile to molasses-like, with higher trimer contents producing higher viscosities.

Monomer, dimer, and trimer acids are classified as nontoxic by ingestion. In addition, they are considered neither primary skin irritants nor eye irritants, as these terms are defined by the Federal regulations dealing with toxic substances. The bibliography for this monograph gives references containing data on storage, handling and safety of dimer acids. It also refers to the Federal regulations which permit use of the products in packaging materials with indirect food contact.

In a nutritional study (using rats), it was found that the short term metabolic effects of cyclic dimers do not appear to be serious. The purpose of this study was to assess, by inference, the possible effects on human metabolism of fried (and thus polymerized) fats—a diet component which Americans ingest at relatively high levels compared to both their own history and compared to the diets of those in less developed countries. It was found that, for the most part, the ring moiety of dimer is excreted rather than absorbed through the intestine. The question of long term effects was left unanswered.

Monomer, dimer, and trimer acids are not flammable or combustible, again as these terms are defined in Federal regulations. Thus, the products do not constitute a fire hazard. The chemical reactions of dimer acids may take place at the carboxyl function, at the double bond, or at the α-carbon atom.

Table V lists the chemical reactions of dimer acids, in

TABLE VI

U.S. Consumption of Dimer-Based, Nonreactive Polyamides (Metric Tons)

	1976	1972
Hot melt adhesives	4500	3600
Printing inks	3600	3150
Surface coatings	450	900
Other	450	450
Total	9000	8100

TABLE VII

U.S. Consumption of Dimer-Based, Reactive Polyamide Resins (Metric Tons)

	1976	1972
Surface coatings	4500	4050
Adhesives	1350	900
Potting and casting	450	450
Other	900	900
Total	7200	6300

decreasing order of commercial importance, with the order being somewhat judgmental. By far the most important reaction, from a commercial standpoint, is polycondensation with multifunctional amines to form polyamides.

The analysis of dimer acids is covered in the bibliography. It has been our experience, after examining microdistillation, gas liquid chromatography and paper chromatography, that liquid chromatographic techniques offer the fastest, most accurate method for analysis of dimer mixtures and the sharpest plant control tool.

In 1977, it was estimated that annual production of dimer acids was ca. 40 MM lbs./yr, with capacity far in excess of that figure. Recent market growth has been low, probably in the range of 1 to 3% per year.

By far the largest market for single- and double-distilled dimer acids is in the production of polyamide resins. It is estimated that 70-80% of dimer production is consumed in that application. All six producers of dimer acids also produce these nonnylon polyamide resins, as do a number of companies which do not produce dimers–Lawter, Cooper Polymers, USM, Celanese and Reichhold, among others. Two companies, Emery and Union Camp, are vertically integrated in the sequence: tall oil fatty acids, dimer products, polyamides. Emery is a joint venture partner in tall oil fatty acids.

Dimer acid-based polyamides are divided into reactive and nonreactive types. Nonreactive polyamides are reaction products of dimer acids and diamines in approximately stoichiometric amounts. If more diamine or a polyfunctional amine such as diethylenetriamine is used, reactive polyamides with residual amine functionality are obtained.

Nonreactive polyamide resins are tough, flexible, with excellent adhesive properties. Their melting behavior, their solubility in ink vehicles, and their compatibility with other resins make them useful for hot melt adhesives, particularly shoe adhesives, and for printing inks. Nonreactive dimer-based polyamides are also used for surface coatings, as sealants, and in textile applications.

Reactive polyamides are liquids and, as the name signifies, are capable of linkage with functional groups that can chemically react with amines. They are used primarily as a component of thermosetting epoxy systems, but some reactive polyamides are also incorporated into phenolic resins. Epoxy-polyamide resins are hard, corrosion resistant and flexible; the phenolic-polyamide resins are solvent and heat resistant.

Reactive polyamides are consumed, as epoxy or phenolic curing agents, in surface coatings for marine finishes, for swimming pool paints, and as primers for coatings for metals, masonry, and plastics.

Adhesive use of reactive polyamides is most familiar in the consumer do-it-yourself two-part epoxy adhesive package. In the consumer and in the industrial market, these adhesive systems are used for wood, glass, metal, and plastic assemblies. Composites involving epoxy-polyamide adhesives have journeyed as far as the moon as part of the space program.

Tables VI and VII summarize the recent market status of the reactive and nonreactive, dimer-based polyamide resins.

There are three other applications of dimer acids that deserve special mention. Several million pounds per year of dimer products are used in oilfield chemical manufacture. These chemicals are used for corrosion inhibition in petroleum production equipment, mostly as imidazolines.

The synthetic lubricant field utilizes straight and branched chain alkyl esters of dimer acids as basestocks for industrial lubricating oils, particularly gear oils. The esters, protected with the appropriate additive package, are characterized by good lubricity, good viscosity characteristics at both ends of the temperature-use spectrum, and by surprisingly good high temperature oxidation stability. It is estimated that this application now consumes less than two million pounds per year of dimer acids.

One dimer nitrogen chemical family, imidazolines, has already been mentioned. Dimer diamines and derivatives of dimer diamines have found some use as corrosion inhibitors and as components of polymer systems. Again, volume is thought to be less than 2 MM pounds per year.

Other applications of dimer acids include use as components of polyester resins for surface coatings, as surface active agents in the form of alkali metal soaps, as components of polyurethane coatings, as heavy metal soap greases, and in miscellaneous corrosion inhibition applications.

Dimer producers predict that market growth rate for dimer acids will remain relatively flat if polyamide resins continue to be the major outlet, although hot melt adhesives based on dimers may have some modestly increasing relative cost advantage in the future compared to petrochemically based adhesives such as ethylene-vinyl acetate copolymers. If, however, dimer esters can carve out a substantial niche as a major component of industrial lubricants, the dimer acids business will become much more attractive.

In April, the 1979 list price, in bulk, for single-distilled dimer acids was ca. $0.60/lb. Low rosin tall oil fatty acids ranged in price from $0.25 to $0.285/lb., depending on the grade. Assuming dimer sale at list and assuming ca. 60% yield of single-distilled product, every 1,000 pounds of input results in about $100 (not counting byproduct credit) to cover labor, utilities, costs related to investment, and profit. Sale of byproduct monomer, of course, adds to this revenue. Monomer can be hydrogenated and separated into liquid and solid (25 C) components, the liquid portion being called isostearic acid. Isostearic acid, in its turn, is used to manufacture a lubricant for 2-cycle engines. It is also used as an intermediate to isostearyl alcohol, which is a cosmetic ingredient.

Westvaco Corporation is now marketing a dimer acid variant–a C_{21} dicarboxylic acid manufactured by reacting the linoleic acid of tall oil fatty acids with acrylic acid. This material is said to have application as a surface active agent and as a component of polyamide resins. Volume is small compared to that for dimer acids.

REFERENCES AND BIBLIOGRAPHY FOR FURTHER STUDY

Chemical Properties

A description of the chemical properties of dimer acids is given in "The Dimer Acids," Edited by E.C. Leonard, HumKo Sheffield Chemical, Memphis, TN, 1975. A copy of this monograph may be obtained by writing the author (c/o HumKo Sheffield Chemical, Box 398, Memphis, TN 38101).

den Otter, M.J.A.M., Fette, Seifen, Anstrichm. 72:667 (1970); Ibid. 72:875, 876 (1970).

McMahon, D.H., and E.P. Crowell, JAOCS 51:522 (1974).

Chemical Reactions

Leonard, E.C., "The Dimer Acids," HumKo Sheffield Chemical, Memphis, TN, 1975.

Kulkarni, M.V., and R.L. Scheribel, (to General Mills), US patent 3,595,887, July 27, 1971.

For a general reference describing fatty acid salt formation, see: Levy, J., in "Fatty Acids and Their Industrial Applications," Edited by E.S. Pattison, Marcel Dekker, Inc., New York, 1968, p. 209.

Manufacture

Goebel, C.G., (to Emery Industries, Inc.), US patent 2,483,761, September 27, 1949.

Goebel, C.G., (to Emery Industries, Inc.), US patent 2,664,429, December 29, 1953.

Kappelmeier, C.P.A., *Farben-Ztg.* 38:1018, 1077 (1933).

Bradley, T.F., and W.B. Johnston, Ind. Eng. Chem. 33:86 (1941); Bradley, T.F., and D. Richardson, Ind. Eng. Chem. 32:963, 802 (1940).

Barrett, F.O., C.G. Goebel, and R.M. Peters, (to Emery Industries Inc.), US patent 2,793,219, May 21, 1957.

Morimoto, M., M. Saito, and A. Gouken, (to Kao Soap Co.), US patent 3,773,806, November 20, 1973.

Scharrer, R.P.F., (to Arizona Chemical Co.), US patent 3,925,342, December 9, 1975.

Miller, S.E., (to General Mills, Inc.), US patent 3,412,039, November 19, 1968.

Wheeler, D.H., (to General Mills, Inc.), US patent 3,444,220, May 13, 1969.

Berman, L.U., (to Kraftco Corp.), US patent 3,732,263, May 8, 1973.

Conroy, N.H., (to Arizona Chemical Company), US patent 3,632,822, January 4, 1972.

Dieckelmann, G., and H. Rutzen, (to Henkel), US patent 3,507,890, April 21, 1970.

Croston, C.B., H.B. Teeter, and J.C. Cowan, (to the United States Department of Agriculture), US patent 2,670,361, February 23, 1954.

Arlt, H.G., (to Arizona Chemical Co.), US patent 3,367,952, February 6, 1968.

Coffman, J.A., and W.R. Browne, (to General Electric Co.), US patent 3,533,932, October 13, 1970.

Dimer Acids–Economics

"Fatty Acids–North America, A Multiclient Market Survey," Hull & Company, Bronxville, NY, 1975, p. 528.

Analysis

AOCS Methods: Acid value (AOCS Te 1a-64); Saponification value (AOCS Tl 1a-64); % Unsaponifiables (AOCS Tk 1a-64); Specific gravity (AOCS To 1a-64).

ASTM Methods: Flash and fire points (ASTM D92-72); Gardner color (ASTM D1544-63T); Kinematic viscosity (ASTM D445-65); Pour point (ASTM D97-66).

Firestone, D., W. Horowitz, L. Friedman, and G.G. Shue, JAOCS 44:465 (1961); Firestone, D., S. Nesheim, and W. Horowitz, J. Assoc. Off. Anal. Chem. 38:253 (1961).

Firestone, D., JAOCS 40:247 (1963).

Rost, H.E., Fette, Seifen, Anstrichm. 65:463 (1963); Ibid. 64:427 (1962).

Frankel, E.N., C.D. Evans, D.G. McConnell, E. Selke, and H.J. Dutton, J. Org. Chem. 26:4663 (1961); Frankel, E.N., C.D. Evans, H.A. Moser, D.G. McConnell, and J.C. Cowan, JAOCS 38:130 (1961); Evans, C.D., D.G. McConnell, E.N. Frankel, and J.C. Cowan, Ibid. 42:764 (1965).

Greaves, J.H., and B. Laker, Chem. Ind. (London), 1709, 1961.

Paylor, R.A.L., R. Feinland, and N.H. Conroy, Anal. Chem. 40:1358 (1968).

Chang, T.L., Ibid. 40:989 (1968).

Sims, R.P.A., Ind. Eng. Chem. 47:1049 (1955).

Dimer Acids Safety

The regulations (Title 21 CFR, revised as of April 1, 1977) in which dimer acids are mentioned are:

21 CFR 177.1200–dimer acids as a component of polyamide resins for coating cellophane;

21 CFR 175.300–dimer acids as a component of epoxy, polyester, or polyamide resins for "resinous and polymeric coatings" that come into contact with food;

21 CFR 175.390–dimer acids as a component of zinc-silicon dioxide matrix coating which is the food contact surface of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food;

21 CFR 177.1210–dimer acids as components of "resinous and polymeric coatings" used in closures with sealing gaskets for food containers;

21 CFR 176.200–dimer and trimer acids as defoaming agents in coatings ultimately destined for food use;

21 CFR 175.380–dimer acids as components of "resinous and polymeric coatings" used as adjuvants for other resins used in food-contact coatings;

21 CFR 175.320–dimer acids as components of polyamide resins used as coatings for food-contact polyolefin films;

21 CFR 176.180–dimer acids as components of "resinous and polymeric coatings" for paper and paperboard in contact with dry food.

Flash points and firepoints of dimer acids and related products (data obtained by HumKo Sheffield Chemical):

	Open cup flash point
monomer acids	193 C (380 F)
dimer acids	279 C (535 F)
trimer acids	329 C (625 F)

	Closed cup flash point
monomer acids	154 C (310 F)
dimer acids	246 C (475 F)
trimer acids	299 C (570 F)

	Open cup fire point
monomer acids	216 C (420 F)
dimer acids	318 C (605 F)
trimer acids	352 C (655 F)

Taubold, R.T., Dissertation, University of Illinois, Urbana, from Diss. Abstr. Int. B 38(10):4737, 1978. This work covers studies on the synthesis and metabolism (in the rat) of dimeric fatty acids.

Applications

Leonard, E.C., "Dimer Acids Applications," American Oil Chemists' Society Convention, Higher Molecular Weight Dibasic Acids Symposium, New York City, May 12, 1977. Copies of this paper may be obtained by writing the author.

Wolfe, A., in "Chemical Economics Handbook," Stanford Research Institute, Menlo Park, CA, June, 1977, pp. 580.1031L, 580.1032M.

deMeer, W.E.A., and R.J. Bellamy, Polym. Paint Colour. J. p. 233, (March 27, 1974).

Reading List

Leonard, E.C., "The Dimer Acids," in the Kirk/Othmer "Encyclopedia of Chemical Technology," 3rd edition, Volume 8, Wiley-Interscience, New York, November, 1979.

"The Dimer Acids," Edited by E.C. Leonard, HumKo Sheffield Chemical, Memphis, TN, 1975.

Leonard, E.C., "The Higher Aliphatic Di- and Polycarboxylic Acids," "Fatty Acids," Edited by E.H. Pryde, American Oil Chemists' Society, (In press).

Johnson, R.H., "Dimerization and Polymerization," Ibid.

Pryde, E.H., and J.C. Cowan, "Aliphatic Dibasic Acids," in "Condensation Monomers," Wiley-Interscience, New York, 1972.

Wolfe, A., "The Nonnylon Polyamides," in "Chemical Economics Handbook," Stanford Research Institute, Menlo Park, CA, 1977.

Sonntag, N.O.V., "Dehydration, Pyrolysis, and Polymerization," in "Fatty Acids," 2nd edition, Edited by K.S. Markley, Interscience, New York, 1960, 1961.