Kirk-Othmer Encyclopedia of Chemical Technology.

DIMER ACIDS

The dimer acids [61788-89-4], 9- and 10-carboxystearic acids, and C-21 dicarboxylic acids are products resulting from three different reactions of C-18 unsaturated fatty acids. These reactions are, respectively, self-condensation, reaction with carbon monoxide followed by oxidation of the resulting 9- or 10-formylstearic acid (or, alternatively, by hydrocarboxylation of the unsaturated fatty acid), and Diels-Alder reaction with acrylic acid. The starting materials for these reactions have been almost exclusively tall oil fatty acids or, to a lesser degree, oleic acid, although other unsaturated fatty acid feedstocks can be used (see Carboxylic acids, fatty acids from tall oil; Tall oil).

The basic research that led to these products was done at the Northern Regional Research Center of the USDA: dimer acids research in the 1940s (1–3), C-21 dicarboxylic acid work in 1957 (4), and carboxystearic acid synthetic studies (5, 6) in the 1970s (see Dicarboxylic acids).

1. Physical Properties

The physical properties of polymerized fatty acids are influenced by the basestock, by the dimerization conditions and catalysis, and by the degree to which monomer, dimer, and higher oligomers are separated following the dimerization.

Dimer acids are relatively high mol wt (ca 560) and yet are liquid at 25°C. This liquidity is a consequence of the many isomers present, most with branching or cyclic structures.

Most of the products listed in Tables 1, 2, 3 are based on manufacture from tall oil fatty acids. Dimer acids based on other feedstocks (eg, oleic acid) may have different properties. A European manufacturer recently announced availability of a 44-carbon dimer acid, presumably made from an erucic acid feedstock (7).

2. Chemical Properties

2.1. Structure and Mechanism of Formation

Thermal dimerization of unsaturated fatty acids has been explained both by a Diels-Alder mechanism and by a free-radical route involving hydrogen transfer. The Diels-Alder reaction appears to apply to starting materials high in linoleic acid content satisfactorily, but oleic acid oligomerization seems better rationalized by a free-radical reaction (8–10).

Clay-catalyzed dimerization of unsaturated fatty acids appears to be a carbonium ion reaction, based on the observed double bond isomerization, acid catalysis, chain branching, and hydrogen transfer (8, 9, 11).

It has been shown (12) that different precursors for dimer preparation give quite different structures (Table 4).

Table 1. Properties of Dimer Acid[a]

Physical property	Usual range
composition, %	
dimer acids	82–83
trimer acids (and higher)	14–16
monobasic acids	1–5
neutralization equivalent	285–297
acid number	189–197
saponification number	189–199
unsaponifiables, %	0.5–1.0
color, Gardner (1963)	7–9
viscosity at 25°C, mm^2/s (=cSt)	7500–9000
specific gravity,	
25/25°	∼0.95
100/25°C	∼0.91
density, 25°C, kg/m^3	∼955
refractive index, 25°C	∼1.485
pour point, °C	∼4 to ∼10
flash point (COC) °C	∼300

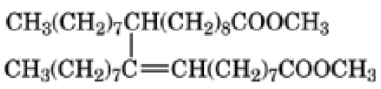
[a] Hystrene series of dimer acids, Humko Chemical Division of Witco Corporation.

Table 2. Properties of Distilled Dimer Acids

	Value	
Physical property	Hydrogenated[a]	Unhydrogenated[b]
Composition, %		
dimer	97	95
trimer	3	4
monomer	trace	1
neutralization equivalent	284–294	286–285
acid number	191–197	190–196
saponification number	193–200	190–202
unsaponifiables, %	0.1	0.5
color, Gardner (1963)	1	∼5
iodine value	∼20	
viscosity at 25°C, mm^2/s (=cSt)	∼5200	7000–8000
specific gravity, 25/25°	0.94	0.9
density at 25°C, kg/m^3	∼950	∼950
refractive index, 25°C	1.475	1.483
pour point, °C	∼12	∼ − 8

[a] Empol series of dimer acids, Henkel Corp., Emery Group (oleic-based, thus of lower viscosity).
[b] Hystrene series of dimer acids, Humko Chemical Div. of Witco Corporation.

The following are three possible structures of the methyl esters of dimer acids.



$$\begin{array}{l} CH_3(CH_2)_7CH(CH_2)_8COOCH_3 \\ \qquad\qquad\;\; | \\ CH_3(CH_2)_7C{=}CH(CH_2)_7COOCH_3 \end{array}$$

(1)

Table 3. Properties of Trimer Acids[a]

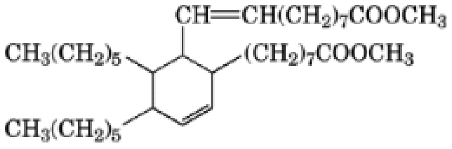
Physical property	Value
composition, %	
dimer	40
trimer	60
monobasic acids	trace
neutralization equivalent	295–330
acid number	170–190
saponification number	170–202
unsaponifiables, %	~1.0
color, Gardner (1963)	dark
viscosity at 25°C, mm^2/s (=cSt)	~30, 000
density at 25°C, kg/m^3	~955

[a] Hystrene 5460, Humko Chemical Div. of Witco Corp.

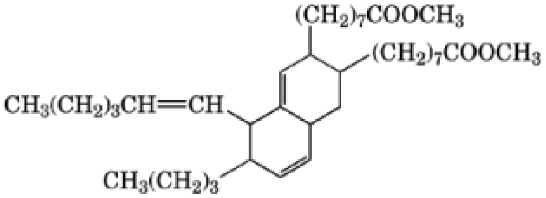
Table 4. Dimer Acid: Feedstock–Structure Relationship

	Dimer structure		
Feedstock	Acrylic	Monocyclic	Polycyclic
oleic[a] or elaidic[b] acid	40	55	5
tall oil fatty acids	15	70	15
linoleic acid[c]	5	55	40

[a] *cis*-9-octadecenoic acid [112-80-1]
[b] *trans*-9-octadecenoic acid [112-79-8]
[c] *cis*-9, *cis*-12-octadecadienoic acid [60-33-3]



(**2**)



(**3**)

The C-18 acid source for the acyclic (**1**) (*E*)-, (*Z*)- [28923-98-0] is the Δ9 acid (oleic or elaidic); for monocyclic (**2**) (*E*)-, (*E*)- [26796-50-9], (*E*)-, (*Z*)- [56636-20-5] it is the Δ9,11-octadecadienoic acid; and for bicyclic (**3**) [32733-04-3] the source is Δ9,11,13-octadecatrienoic acid.

There are a myriad of possible isomers, including positional and geometrical isomers of the double bond(s) as well as structural isomers resulting from head-to-head or head-to-tail alignment of the reacting fatty acids.

Table 5. Nonpolymeric Chemical Reactions of Dimer Acids

Reactions at the double bond and at the α-carbon		Reactions of the carboxyl group	
Reaction	Refs.	Reaction	Refs.
halogenation	14	salt formation	15
epoxidation	14	esterification	(16, 17)
sulfation	14	hydrogenolysis	(18, 19)
sulfonation	14	ethoxylation	(20–23)
hydrogenation	24	amidation	(25–29)
sulfurization	14	ammonolysis, reduction (dimer nitriles, dimer amines)	(30–32)
		isocyanate formation	33

2.2. Chemical Reactions

The reactions of dimer acids were reviewed fully in 1975 (13). The most important is polymerization; the greatest quantities of dimer acids are incorporated into the non-nylon polyamides. Other reactions of dimer acids that are applied commercially include polyesterification, hydrogenation, esterification, and conversion of the carboxy groups to various nitrogen-containing functional groups. Table 5 summarizes the nonpolymeric chemical reactions of dimer acids. Polymerization reactions of dimer acids include polyamidation (34–36), polyesterification (37–39), reactions resulting in polymeric nitrogen derivatives other than polyamides (40–42), and reactions involving dimer diprimary amines (43, 44).

A scan of the literature over the years 1980–1991 shows that most of the current dimer activity involves the reaction of dimer acids to form a huge variety of polyamide and polyester structures to modify their properties for a wide range of industries and uses. Many of these property modifications seem to make use of the flexibilizing properties or adhesion-promoting properties of the dimer structure.

3. Manufacture

The clay-catalyzed intermolecular condensation of oleic and/or linoleic acid mixtures on a commercial scale produces approximately a 60:40 mixture of dimer acids (C_{36} and higher polycarboxylic acids) and monomer acids (C_{18} isomerized fatty acids). The polycarboxylic acid and monomer fractions are usually separated by wiped-film evaporation. The monomer fraction, after hydrogenation, can be fed to a solvent separative process that produces commercial isostearic acid, a complex mixture of saturated fatty acids that is liquid at 10°C. Dimer acids can be further separated, also by wiped-film evaporation, into distilled dimer acids and trimer acids. A review of dimerization gives a comprehensive discussion of the subject (10).

3.1. Thermal Oligomerization

Commercial manufacture of dimer acids began in 1948 with Emery Industries use of a thermal process involving steam pressure. Patents were issued in 1949 (45) and 1953 (46) that describe this process. Earlier references to fatty acid oligomerization, antedating the USDA work of 1941–1948, occur in patents in 1918 and 1919 (47, 48), and in papers written in 1929–1941 (49–51). There appears to still be some small use of this approach to making dimer products.

3.2. Clay-Catalyzed Oligomerization

Emery Industries modified its commercial process in 1953 and began producing dimer acids by using a combination of thermal- and Montmorillonite clay-catalyzed oligomerization. Such a process has been described in patents (52–55). In general, in present-day commercial practice, 100 parts of the fatty acid, 4 parts of clay, and 2 parts of water are heated in an autoclave under autogenous pressure at approximately 230°C for 4 hours with agitation. After cooling and removal of the clay by filtration, separation of monomeric and polymeric material can be carried out by wiped-film evaporation or molecular distillation. Most current production is based on this type of technology.

In 1991, in addition to Henkel (now including Emery), commercial producers of dimer acids in the U.S. were Arizona Chemical, Schering Berlin, Humko Chemical Division of Witco, and Union Camp Corporation. There are other producers throughout the world.

3.3. Process Modification

Dimer acid process modifications have fallen into three categories (8); those claiming higher dimer:trimer ratios, those utilizing varying types of clays, and those purporting to result in improved yields. Higher dimer:trimer ratios are said to be obtained through use of alkali (56), ammonia or amines (57), aryl sulfohalides (58), 1-mercapto-2-naphthol (59), and a "Texas natural acid clay" (60). Natural or synthetic clay catalysts have included lithium salt–acetic anhydride stabilized clay (61), synthetic magnesium silicate (62), and neutral Alabama bentonite (63). Improved yields of dimer acids are claimed to result from a number of two-step clay-catalyzed procedures (64, 65) and by the addition of low mol wt saturated alcohols to the reaction mixture (66) (see Clays). Clay, lithium salts and phosphoric acid treatment, in one or two stages, are said to yield 63–73% dimer and trimer (67).

Another aspect of process improvement is color improvement. For example, use of phosphoric acid and formaldehyde on the dimer product is said to improve color (68). Other treatments, both on the raw materials and on the finished product, have also been used. Most of these are variations of standard fatty material color reduction techniques.

3.4. Other Polymerization Methods

Although none has achieved commercial success, there are a number of experimental alternatives to clay-catalyzed or thermal oligomerization of dimer acids. These include the use of peroxides (69), hydrogen fluoride (70), a sulfonic acid ion-exchange resin (71), and corona discharge (72) (see Initiators).

3.5. Energy Requirements

The production of dimer acids is quite energy intensive. A standard operating sequence normally results in the expenditure of about 18.6 MJ (17,600 Btu) (equivalent to 0.67 kg coal or 0.33 kg natural gas or fuel oil) to produce each kg of crude dimer and to separate it into monomer, dimer, and trimer. Of this energy it is estimated that 10% is electrical, consumed by the pumps and agitators of the system. The other 90% is fuel-derived, and is consumed mainly for process thermal requirements with some usage for the steam necessary to obtain reduced pressures for certain operations. Energy requirements for the storage and handling of either the raw materials or the products are not included; thus the 18.6 MJ (17,600 Btu) used per kg represents only the energy consumption within the process units themselves.

4. Storage and Handling

Since dimer acids, monomer acids, and trimer acids are unsaturated, they are susceptible to oxidative and thermal attack, and under certain conditions they are slightly corrosive to metals. Special precautions are necessary, therefore, to prevent product color development and equipment deterioration. Type 304 stainless steel is recommended for storage tanks for dimer acids. For heating coils and for agitators 316 stainless steel is preferred (heating coils with about $4\frac{3}{4}$ m^2 (50 ft^2) of heat transfer surface in the form of a 5.1 cm schedule-10 U-bend scroll are recommended for a 37.9-m^3 (10,000-gal) tank. Dimer acid storage tanks should have an inert gas blanket.

316 Stainless steel centrifugal pumps may be used to transfer dimer acid stocks. Pipe, valves, and fittings may be of 304 stainless steel if the liquid temperature is maintained below 107°C. The recommended temperature ranges for transfer (pumping) of dimer acids and related stocks are as follows.

Stock	Range, °C
monomer acids	46–49
dimer acids	54–77 (71 optimum)
trimer acids	77–82

Specific gravities and viscosities for these chemicals, in the recommended temperature ranges for transfer, are shown in Table 6.

Table 6. Specific Gravities and Viscosities at Pumping Temperatures

Stock	Temperature, °C	Specific gravity, t/25°	Viscosity, mm^2/s (=cSt)
monomer acids	49	0.890	23
dimer acids	71	0.923	305
trimer acids	80	0.926	669

The temperature for handling dimers should never exceed 82°C. Even with an inert gas blanket, color deterioration of the products accelerates at higher temperatures. Dimer and trimer acids stored for longer times should be held below 50°C. Tank agitators should be left on or interlocked with the heating cycle of the steam coils so that the agitators will be moving the liquid to prevent discoloration of the material near the coils during heating.

Stainless steel or epoxy-lined tank cars and tank trucks are recommended for shipping. Aluminum also has been used. The tank can be flushed with carbon dioxide before loading and blanketed with nitrogen after loading. Drum shipments are recommended in epoxy-lined open-head drums fitted with a bung. Dimer acids and their by-products contaminated with iron or copper show accelerated color deterioration. Exposure to these metals or their salts should be minimized.

5. Economic and Market Aspects

According to one estimate (73), the current capacity for manufacturing dimer acids in the U.S. is around 55,000 t per year. Current demand is estimated at about 33,600 t per year, and is expected to grow at about 2–3% per year to 35,000 t in 1993. The historical growth rate for dimer acids (1980–1989) was 0.8% per year. Prices of tall oil fatty acids, the raw material for over 90% of dimers, currently fluctuates in the $0.55–0.66 per kg range.

The dimer acids themselves are presently selling at about $1.10 per kg for the standard 75–80% dimer acids, and about $2.20 per kg for the distilled (90–95%) dimer acids.

The current market situation for dimer acids includes relatively high raw material costs, high energy costs, slow growth and relatively low prices. It is generally recognized as a mature market, with hopes for future growth hinging on factors such as increased polyamide use and a resurgence of oil drilling, where dimers are used for corrosion inhibition.

6. Analysis

The American Society for Testing and Materials (ASTM) and the American Oil Chemists Society (AOCS) provide standard methods for determining properties that are important in characterization of dimer acids. Characterization of dimer acids for acid and saponification values, unsaponifiables, and specific gravity are done by AOCS standard methods:

Property	Method
acid value	AOCS Te 1a-64
saponification number	AOCS Tl 1a-64
unsaponifiable	AOCS Tk 1a-64
specific gravity	AOCS To 1a-64

Flash and fire points, Gardner color, kinematic viscosity, and pour points are determined by ASTM methods:

Property	Method
flash and fire points	
open cup	ASTM D92-85
closed cup	ASTM D93-85
Gardner color	ASTM D1544-80
kinematic viscosity	ASTM D445-86
pour point	ASTM D97-85

The determination of iodine value (IV), AOCS Tg 1-64, is sometimes used to determine the extent of unsaturation. Because the tertiary allylic hydrogen in the compounds is capable of substitution by halogen atoms, this only approximates a value for the degree of unsaturation.

Currently, there is continuing work on an industry standard method for the direct determination of monomer, dimer, and trimer acids. Urea adduction (of the methyl esters) has been suggested as a means of determining monomer in distilled dimer (74). The method is tedious and the nonadducting branched-chain monomer is recovered with the polymeric fraction. A microsublimation procedure was developed as an improvement on urea adduction for estimation of the polymer fraction. Incomplete removal of monomer esters or loss of dimer during distillation can lead to error (75).

Thin-layer chromatography (76, 77) has been used for the estimation of the amounts of dimer, trimer, and monomer in methyl esters. Both this method and paper chromatography are characterized by lack of precision (78, 79) (see Chromatography).

Microscale distillation techniques have also been used to determine monomer, dimer, and trimer in polymerized fatty acids. Such a method was used for some time, but has been largely replaced by various methods of high pressure liquid chromatography (hplc). Gas–liquid chromatography (glc) has been used for analysis of monomer–dimer–trimer content also. An older approach, packed column chromatography of the methyl ester of the dimer acid with thermal conductivity detection, based on a combination of molecular weight and boiling point separation, was used at one time. Currently, methods of high temperature capillary chromatography of the dimer acid using flame ionization detection and a combination of molecular weight and boiling point for separation find some use in the industry.

Various high pressure liquid chromatographic methods are being widely used for the analysis of dimer acids today. Gel permeation chromatography with separation according to molecular size and response to a refractive index detector as a monomer, dimer, and trimer is currently utilized. Liquid chromatographic separation according to functionality and response to ultraviolet photometric absorption followed by component collection and gravimetric analysis as monobasic, dibasic, and polybasic segments is also currently in use. An AOCS committee is currently working on a liquid chromatography method with separation according to functionality and detection by response to a laser light-scattering mass detector as monobasic, dibasic, and polybasic components.

For production use, once an accurate determination of monomeric, dimeric, and higher oligomeric dimer acids has been established for a specific process and feedstock's oligomerization, subsequent reaction extent can be estimated rapidly by a viscometric method (80).

7. Health and Safety Aspects

The acute oral toxicity and the primary skin and acute eye irritative potentials of dimer acids, distilled dimer acids, trimer acids, and monomer acids have been evaluated based on the techniques specified in the Code of Federal Regulations (CFR) (81). The results of this evaluation are shown in Table 7. Based on these results, monomer acids, distilled dimer acids, dimer acids, and trimer acids are classified as nontoxic by ingestion, are not primary skin irritants or corrosive materials, and are not eye irritants as these terms are defined in the Federal regulations.

Table 7. Toxicity Data for Dimer Acids and Related Products

Sample	Oral LD_{50}, g/kg	Primary irritation index	Eye irritation
monomer acids	>21.5	1.0	very slight erythema in four rabbits
distilled dimer acids	>21.5	0.50	very slight erythema in four rabbits
dimer acids	>21.5	0.75	very slight erythema in three rabbits
trimer acids	>10.0	0	very slight erythema in six rabbits

7.1. Food Additive and Food Packaging Regulations

Federal regulations do not permit direct use of dimer acids in food products. CFR, however, permits indirect use of dimer acids in packaging materials with incidental food contact. These permitted applications include use of dimer acids as components of polyamide, epoxy, and polyester resins for use in coating plastic films, paper, and paperboard. These regulations 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; and 21 CFR 176.180, dimer acids as components of "resinous and polymeric coatings" for paper and paperboard in contact with dry food.

7.2. Flammability

Dimer and trimer acids, as well as monomer acids derived from dimer acid processing, are neither flammable nor combustible as defined by the Department of Transportation (DOT) and do not represent a fire hazard:

	Flash point, °C		
Product	open cup	closed cup	Fire point, °C open cup
monomer acids	193	154	216
dimer acids	279	246	318
trimer acids	329	299	352

8. Uses

8.1. Nonreactive Polyamide Resins

The non-nylon dimer based polyamide resins are characterized by lack of crystallinity, relatively low softening points, adhesiveness, hydrophobicity and, generally, relatively low transition-temperature ranges. These properties contrast sharply with the crystallinity and high melting temperatures of the nylon polyamides (qv) based on C_6 to C_{12} dibasic acids and are sufficiently unique to carve out large markets of their own (13, 82). About 65% of dimer use is in this area, according to one recent estimate (71).

Dimer-based polyamide resin markets are divided into those for reactive polyamides and those for nonreactive polyamides. The largest volume commercial application of dimer acids is in nonreactive polyamide resins. These resins, solids at 25°C, are manufactured by the reaction of dimer acids (or trimer acids) or their esters with aliphatic diamines. Polyamide resins with a broad spectrum of properties can be obtained, with the transition temperatures (the phase change from a glass to a liquid) being determined by the diamine used, the stoichiometry of the reactants, and the amount and type of short-chain dibasic acids added to increase the melting range. Table 8 shows the melting ranges of typical neutral polyamide resins (34, 36). Dimer acids impart flexibility, corrosion resistance, chemical resistance, moisture resistance, and adhesion to nonreactive polyamides. Hot melt adhesives (qv), the largest commercial application of nonreactive polyamide resins, are thermoplastics that have fairly sharp melting ranges. They are particularly useful in high-speed assembly operations such as packaging, can assembly, bookbinding, and shoe assembly because they can be applied in liquid form, eliminating the need for solvents.

Table 8. Melting Ranges for Typical Neutral Polyamides

Dimer:trimer mol ratio	Diamine	Polyamide melting range, °C
1.7:1	ethylenediamine	96–103
1.8:1	ethylenediamine	108–112
1.7:1	propylenediamine	53–59
1.7:1	hexamethylenediamine	70–80
1.7:1	dimer diprimary amine	liquid at 25°

The dimer acid-based polyamide resins appear best suited to specialized uses requiring high performance. A major application for the dimer acid-based polyamide hot-melt adhesives is in the shoe industry. Here good adhesion and high-temperature properties permit bonding of shoe soles to uppers without the need for stitching with thread. Metal bonding (eg, side-seam welding) and plastic and metal film and foil lamination are other hot-melt adhesive applications of dimer acid-based polyamides.

Flexographic printing inks utilize nonreactive polyamides from dimer acids as resin binders. Polyamide resins are especially well suited for flexographic printing on plastic films and metallic foil laminates because the resins adhere very well to the printed surface, give high-gloss surfaces, and accommodate to substrate deformation (see Inks).

The most important coating application for the nonreactive polyamide resins is in producing thixotropy. Typical coating resins such as alkyds, modified alkyds, natural and synthetic ester oils, varnishes, and natural vegetable oils can be made thixotropic by the addition of dimer acid-based polyamide resins (see Alkyd resins). Specialty high performance coating applications often require the properties imparted by dimer acid components.

8.2. Reactive Polyamide Resins

Another significant commercial application of dimer acids is in reactive polyamide resins. These are formed by the reaction of dimer acids with polyamines such as diethylenetriamine to form polyamides containing reactive secondary amine groups (see Diamines and higher amines, aliphatic). In contrast to nonreactive polyamides, these materials are generally liquids at 25°C.

They are used extensively to react with epoxy or phenolic resins, yielding adhesives that are useful in casting and laminating, in structural work, for patching and sealing compounds, and for protective coatings. The amount used in epoxy applications far exceeds the use with phenolic resins.

8.3. Miscellaneous Commercial Applications

Dimer acids are components of “downwell” corrosion inhibitors for oil-drilling equipment (see Petroleum; Corrosion and corrosion inhibitors). This may account for 10% of current dimer acid use (71). The acids, alkyl esters, and polyoxyalkylene dimer esters are used commercially as components of metal-working lubricants (see Lubrication). Dimer estershave achieved some use in specialty lubricant applications such as gear oils and compressor lubricants. The dimer esters, compared to dibasic acid esters, polyol esters and poly(α-olefin)s, are higher in cost and of higher viscosity. The higher viscosity, however, is an advantage in some specialties, and the dimer esters are very stable thermally and can be made quite oxidatively stable by choice of proper additives.

Other dimer acid markets include intermediates for nitriles, amines and diisocyanates. Dimers are also used in polyurethanes, in corrosion inhibition uses other than for downwell equipment, as a “mildness” additive for metal-working lubricants, and in fiber glass manufacture.

BIBLIOGRAPHY

“Dimer Acids” in *ECT* 3rd ed., Vol. 7, pp. 768–782, by Edward C. Leonard, Humko Sheffield Chemical.

Cited Publications

1. J. C. Cowan, W. C. Ault, and H. M. Teeter, *Ind. Eng. Chem.* **38**, 1138 (1946).
2. L. B. Falkenburg and co-workers, *Oil Soap* **22**, 143 (1945).

3. J. C. Cowan, A. J. Lewis, and L. B. Falkenburg, *Oil Soap* **21**, 101 (1944).
4. H. M. Teeter and co-workers, *J. Am. Oil Chem. Soc.* **22**, 512 (1957).
5. E. N. Frankel and E. H. Pryde, *J. Am. Oil Chem. Soc.* **54**, 873A (1977).
6. N. E. Lawson, T. T. Cheng, and F. B. Slezak, *J. Am. Oil Chem. Soc.* **54**, 215 (1977).
7. *Unichema International News Bulletin*, Vol. **3**, Unichema North America, Chicago, Spring/Summer 1991.
8. R. W. Johnson in E. H. Pryde, ed., *Fatty Acids*, American Oil Chemists Society, Champaign, Ill., 1979.
9. M. J. A. M. den otter, *Fette Seifen Anstrichm.* **72**, 667, 875, 1056 (1970).
10. R. W. Johnson in R. W. Johnson and E. Fritz, eds., *Fatty Acids in Industry*, Marcel Dekker, Inc., New York, 1989.
11. R. W. Johnson, *Clay Catalyzed Dimerization of Fatty Acids*, American Oil Chemists Society Meeting, Chicago, 1991.
12. D. H. McMahon and E. P. Crowell, *J. Am. Oil Chem. Soc.* **51**, 522 (1974).
13. E. C. Leonard, ed., *The Dimer Acids*, Humko Sheffield Chemical, Memphis, Tenn., 1975.
14. *Empol Dimer and Trimer Acids*, technical bulletin, Emery Industries, Inc., Cincinnati, Ohio, 1971, p. 8.
15. J. Levy in E. S. Pattison, ed., *Fatty Acids and Their Industrial Applications*, Marcel Dekker, Inc., New York, 1968, p. 209.
16. U.S. Pat. 2,673,184 (Mar. 23, 1954), A. J. Morway, D. W. Young, and D. L. Cottle (to Standard Oil Development Co.).
17. U.S. Pat. 2,849,399 (Aug. 26, 1958), A. H. Matuzak and W. J. Craven (to Esso Research and Engineering Co.).
18. U.S. Pat. 2,347,562 (Apr. 25, 1944), W. B. Johnston (to American Cyanamid. Co.).
19. U.S. Pat. 2,413,612 (Dec. 31, 1946) E. W. Eckey and J. E. Taylor (to The Procter and Gamble Co.).
20. U.S. Pat. 3,173,887 (Mar. 16, 1965), T. E. Yeates and C. M. Thierfelder (to the U.S. Dept. of Agriculture).
21. U.S. Pat. 2,473,798 (June 21, 1949), R. E. Kienle and G. P. Whitcomb (to American Cyanamid Co.).
22. U.S. Pat. 2,758,976 (Aug. 14, 1956), G. E. Barker (to Atlas Powder Co.).
23. U.S. Pat. 3,429,817 (Feb. 25, 1969), M. J. Furey and A. F. Turbak (to Esso Research and Engineering Co.).
24. U.S. Pat. 3,595,887 (July 27, 1971), M. V. Kulkarni and R. L. Scheribel (to General Mills, Inc.).
25. U.S. Pat. 2,537,493 (Jan. 9, 1951), and U.S. Pat. 2,470,081 (May 10, 1949), J. T. Thurston and R. B. Warner (to American Cyanamid Co.).
26. U.S. Pat. 2,992,145 (July 11, 1961), C. Santangelo and B. H. Kress (to Quaker Chemical Products Corp.).
27. U.S. Pat. 3,256,182 (June 14, 1966), G. F. Scherer (to Rockwell Manufacturing. Co.).
28. U.S. Pat. 2,965,591 (Dec. 20, 1960), J. Dazzi (to Monsanto Chemical Co.).
29. U.S. Pat. 3,219,612 (Nov. 23, 1965), E. L. Skau, R. R. Mod, and F. C. Magne (to the U.S. Dept. of Agriculture).
30. U.S. Pat. 2,526,044 (Oct. 17, 1950), A. W. Ralston, O. Turinsky, and C. W. Christensen (to Armour & Co.).
31. U.S. Pat. 3,223,631 (Dec. 14, 1965), A. J. Morway and A. J. Rutkowski (to Esso Research and Engineering Co.).
32. U.S. Pat. 3,010,782 (Nov. 28, 1961), K. E. McCaleb, L. Vertnik, and D. L. Anderson (to General Mills, Inc.).
33. U.S. Pat. 3,481,959 (Dec. 2, 1969), G. Egle (to Henkel).
34. D. E. Floyd, *Polyamide Resins*, 2nd ed., Reinhold Publishing Corp., New York, 1966, p. 11.
35. L. B. Falkenburg and co-workers, *Oil Soap* **22**, 143 (1945).
36. U.S. Pat. 2,450,740 (Oct. 12, 1948), J. C. Cowan, L. B. Falkenburg, H. M. Teeter, and P. S. Skell (to the U.S. Dept. of Agriculture).
37. U.S. Pat. 2,411,178 (Nov. 19, 1946), D. W. Young and E. Lieber (to Standard Oil Development Co.); U.S. Pat. 2,424,588 (July 29, 1947), W. J. Sparks and D. W. Young (to Standard Oil Development Co.); U.S. Pat. 2,435,619 (Feb. 17, 1948), D. W. Young and W. J. Sparks (to Standard Oil Development Co.).
38. U.S. Pat. 3,492,232 (Jan. 27, 1970), M. Rosenberg (to The Cincinnati Milling Machine Co.).
39. U.S. Pat. 3,769,215 (Oct. 30, 1973), R. J. Sturwold and F. O. Barrett (to Emery Industries, Inc.).
40. U.S. Pat. 3,217,028 (Nov. 9, 1965), L. R. Vertnik (to General Mills, Inc.).
41. U.S. Pat. 3,281,470 (Oct. 25, 1966), L. R. Vertnik (to General Mills, Inc.).
42. U.S. Pat. 3,235,596 (Feb. 15, 1966), R. Nordgren, L. R. Vertnik, and H. Wittcoff (to General Mills, Inc.).
43. U.S. Pat. 3,231,545 (Jan. 25, 1966); U.S. Pat. S3,242,141 (Mar. 22, 1966), L. R. Vertnik and H. Witcoff (to General Mills, Inc.).
44. U.S. Pat. 3,483,237 (Dec. 9, 1969), D. E. Peerman and L. R. Vertnik (to General Mills, Inc.).
45. U.S. Pat. 2,483,761 (Sept. 27, 1949), C. G. Goebel (to Emery Industries, Inc.).

46. U.S. Pat. 2,664,429 (Dec. 29, 1953), C. G. Goebel (to Emery Industries, Inc.).
47. Brit. Pat. 121,777 (1918), J. Craven.
48. Brit. Pat. 127,814 (1919), (to De Nordiske Fabriker).
49. J. Scheiber, *Farben, Lacke, Anstrichst.*, 585 (1929).
50. C. P. A. Kappelmeier, *Farben Ztg.* **38**, 1018, 1077 (1983).
51. T. F. Bradley and W. B. Johnston, *Ind. Eng. Chem.* **33**, 86 (1941); T. F. Bradley and D. Richardson, *Ind. Eng. Chem.* **32**, 963, 802 (1940).
52. U.S. Pat. 2,347,562 (Apr. 25, 1944), W. B. Johnston (to American Cyanamid Co.).
53. U.S. Pat. 2,426,489 (Aug. 26, 1947), M. De Groote (to Petrolite Corp.).
54. U.S. Pat. 2,793,219 (May 21, 1957), F. O. Barrett, C. G. Goebel, and R. M. Peters (to Emery Industries, Inc.).
55. U.S. Pat. 2,793,220 (May 21, 1957), F. O. Barrett, C. G. Goebel, and R. M. Peters (to Emery Industries, Inc.).
56. U.S. Pat. 2,955,121 (Oct. 4, 1960), L. D. Myers, C. G. Goebel, and F. O. Barrett (to Emery Industries, Inc.).
57. U.S. Pat. 3,076,003 (Jan. 29, 1963), L. D. Myers, C. G. Goebel, and F. O. Barrett (to Emery Industries, Inc.).
58. U.S. Pat. 3,773,806 (Nov. 20, 1973), M. Morimoto, M. Saito, and A. Gouken (to Kao Soap Co.).
59. U.S. Pat. 3,925,342 (Dec. 9, 1975), R. P. F. Scharrer (to Arizona Chemical Co.).
60. U.S. Pat. 3,157,681 (Nov. 17, 1964), E. M. Fischer (to General Mills, Inc.).
61. U.S. Pat. 3,412,039 (Nov. 19, 1968), S. E. Miller (to General Mills, Inc.).
62. U.S. Pat. 3,444,220 (May 13, 1969), D. H. Wheeler (to General Mills, Inc.).
63. U.S. Pat. 3,732,263 (May 8, 1973), L. U. Berman (to Kraftco Corp.).
64. U.S. Pat. 3,110,784 (Aug. 13, 1963), C. G. Goebel (to Emery Industries, Inc.).
65. U.S. Pat. 3,632,822 (Jan. 4, 1972), N. H. Conroy (to Arizona Chemical Co.).
66. U.S. Pat. 3,507,890 (Apr. 21, 1970), G. Dieckelmann and H. Rutzen (to Henkel).
67. Brit. Pat. 2,172,597 (Sept. 24, 1986), K. S. Hayes (to Union Camp Corp.).
68. Jpn. Pat. 62,022,742 (Jan. 30, 1987), Arimoto and co-workers (to Harima Chemicals, Inc.).
69. U.S. Pat. 2,964,545 (Dec. 13, 1960), S. A. Harrison (to General Mills, Inc.).
70. U.S. Pat. 2,670,361 (Feb. 23, 1954), C. E. Croston, H. B. Teeter, and J. C. Cowan (to the U.S. Dept. of Agriculture).
71. U.S. Pat. 3,367,952 (Feb. 6, 1968), H. G. Arlt (to Arizona Chemical Co.).
72. U.S. Pat. 3,533,932 (Oct. 13, 1970), J. A. Coffman and W. R. Browne (to General Electric Co.).
73. "Chemical Profile: Dimer Acid", in *Chem. Mark. Rep.* (May 15, 1989).
74. D. Firestone and co-workers, *J. Am. Oil Chem. Soc.* **44**, 465 (1961); D. Firestone, S. Nesheim, and W. Horwitz, *J. Assoc. Off. Anal. Chem.* **38**, 253 (1961).
75. A. Huang and D. Firestone, *J. Assoc. Off. Anal. Chem.* **52**, 958 (1969).
76. A. K. Sen Gupta and H. Scharmann, *Fette, Seifen, Anstrichm.* **70**, 86 (1969).
77. G. Billek and O. Heisz, *Fette, Seifen, Anatrichm.* **71**, 189 (1969).
78. D. Firestone, *J. Am. Oil Chem. Soc.* **40**, 247 (1963).
79. H. E. Rost, *Fette, Seifen, Anstrichm.* **64**, 427 (1962); **65**, 463 (1963).
80. R. P. A. Sims, *Ind. Eng. Chem.* **47**, 1049 (1955).
81. J. M. Cox and S. E. Friberg, *JAOCS* **58**(6), 743–745 (1981).
82. R. W. Johnson and co-workers in J. L. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **11**, 2nd ed., Wiley-Interscience, New York, 1988, 476–489.

General References

83. R. W. Johnson in E. H. Pryde, ed., *Fatty Acids*, American Oil Chemists Society, Champaign, Ill., 1979.
84. E. C. Leonard, ed., *The Dimer Acids*, Humko Sheffield Chemical, Memphis, Tenn., 1975.
85. E. C. Leonard in E. H. Pryde, ed., *Fatty Acids*, American Oil Chemists Society, Champaign, Ill., 1979.
86. E. H. Pryde and J. C. Cowan, Wiley-Interscience, New York, 1972.
87. R. W. Johnson in R. W. Johnson and E. Fritz, eds., *Fatty Acids in Industry*, Marcel Dekker, Inc., New York, 1989.

THOMAS E. BREUER
Humko Chemical Division of Witco Corporation

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