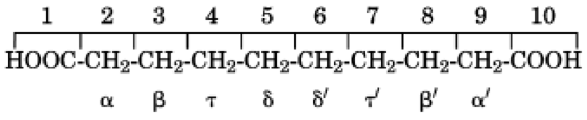
Kirk-Othmer Encyclopedia of Chemical Technology.

DICARBOXYLIC ACIDS

The diacids are characterized by two carboxylic acid groups attached to a linear or branched hydrocarbon chain. Aliphatic, linear dicarboxylic acids of the general formula $HOOC(CH_2)_nCOOH$, and branched dicarboxylic acids are the subject of this article. The more common aliphatic diacids (oxalic, malonic, succinic, and adipic) as well as the common unsaturated diacids (maleic acid, fumaric acid), the dimer acids (qv), and the aromatic diacids (phthalic acids) are not discussed here (see Adipic acid; Maleic anhydride, maleic acid, and fumaric acid; Malonic acid and derivatives; Oxalic acid; Phthalic acid and other benzene-polycarboxylic acids; Succinic acid and succinic anhydride). The bifunctionality of the diacids makes them versatile materials, ideally suited for a variety of condensation polymerization reactions. Several diacids are commercially important chemicals that are produced in multimillion kg quantities and find application in a myriad of uses.

1. Nomenclature

Unsubstituted aliphatic dicarboxylic acids, $HOOC(CH_2)_nCOOH$, are most often referred to by their trivial names for $n = 2$ to 10 (see Table 1). Higher homologues are named using the IUPAC system by adding the suffix dioic to the parent hydrocarbon. Older literature may refer to compounds using a system whereby the name is formed by adding the suffix dicarboxylic acid to the name of the hydrocarbon skeleton. Note that carbons from the carboxyl groups are not included in formulating the name of the base hydrocarbon in this latter system. By way of illustration, the compound



$$\begin{array}{cccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ \text{HOOC-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{CH}_2\text{-} & \text{COOH} \\ & \alpha & \beta & \tau & \delta & \delta' & \tau' & \beta' & \alpha' & \end{array}$$

is designated sebacic acid, decanedioic acid, and 1,8-octanedicarboxylic in the respective systems. Locations of substituents are specified by numbers as shown in the illustration or by Greek letters where the carbons adjacent to the carboxyl groups are designated α and α' as illustrated.

2. Physical Properties

Detailed summaries of physical properties are given (1, 2). The diacids are colorless, crystalline solids that melt somewhat higher than monoacids of the same molecular weight. For diacids of even carbon number, melting points decrease sharply for numbers 2–10 and remain relatively constant for numbers 12–20 (see Table 1). There is a marked alternation in melting point and other physical properties with changes in carbon number from even to odd within the series. Odd members exhibit lower melting points, and higher solubility.

Table 1. Physical Properties[a] of C_2–C_{21} Aliphatic Dicarboxylic Acids

IUPAC name	CAS Registry Number	Common name	Mp, °C	Bp, °C[b]	Water solubility,[c] g/100 mL	Density, g/mL
ethanedioic	[144-62-7]	oxalic	187 (dec)		9.5	
propanedioic	[141-82-2]	malonic	134–136 (dec)		152	1.619
butanedioic	[110-15-6]	succinic	187.6–187.9		8.35	1.572
pentanedioic	[110-94-1]	glutaric	98–99	200[d]	130	1.424
hexanedioic	[124-04-9]	adipic	153.0–153.1	265[e]	3.08[f]	1.345
heptanedioic	[111-16-0]	pimelic	105.7–105.8	272	5.0	1.287
octanedioic	[505-48-6]	suberic	143.0–143.4	279	0.16	1.270
nonanedioic	[123-99-9]	azelaic	107–108	286.5[e]	0.214	1.235
decanedioic	[110-20-6]	sebacic	134.0–134.4	294.5[e]	0.10	1.231
undecanedioic	[1852-04-6]		110.5–112[g]		0.003	
dodecanedioic	[693-23-2]		128.7–129.0	254[h]	0.004	1.16
tridecanedioic	[505-52-2]	brassylic	114			
tetradecanedioic	[821-38-5]		126.5[i]			
pentadecanedioic	[1460-18-0]		114.7[i]			
hexadecanedioic	[505-54-4]	thapsic	125[i]			
heptadecanedioic	[2424-90-0]		117–118[j]			
octadecanedioic	[871-70-5]		124.6–124.8[k]			
nonadecanedioic	[6250-70-0]		118–119.5			
eicosanedioic	[2424-92-2]		124–125[l]			
heneicosanedioic	[505-55-5]	japanic	118–120[i]			

[a] Data from Ref. 1 except as noted.
[b] At 13.3 kPa = 100 mm Hg unless otherwise noted.
[c] At 20–25°C unless otherwise noted.
[d] At 2.7 kPa = 20 mm Hg (2).
[e] Ref. 3.
[f] At 34.1°C.
[g] Ref. 4.
[h] At 2.0 kPa = 15 mm Hg (5).
[i] Ref. 6.
[j] Ref. 7.
[k] Ref. 8.
[l] Ref. 9.

Theoretical treatments have been developed to correlate these physical properties (6, 10). The alternating effects are the result of the inability of odd carbon number compounds to assume an in-plane orientation of both carboxyl groups with respect to the hydrocarbon chain (1). Other properties showing these alternations are decarboxylation temperature and index of refraction. Boiling point, heat of combustion, density, and dielectric constant do not show the alternating effect and vary, predictably, with the ratio of methylene to carboxyl groups within the molecule. Alternating effects can be quite pronounced as illustrated by glutaric acid which melts lower than succinic or adipic (see Table 1). Such alternation persists throughout the series with odd-numbered acids always melting lower than their neighbors; the effect diminishes as the number of carbons increases (Fig. 1). These effects have practical consequences in the selection of material for a given preparation since acid melting point, decarboxylation temperature, and solubility are often key considerations. The effects persist in derivatives based on the diacids, particularly polyamides (qv), polyurethanes, and polyesters (qv) (11–13) (see Urethane polymers).

The temperature at which decarboxylation occurs is of particular interest in manufacturing processes based on polymerization in the molten state where reaction temperatures may be near the point at which decomposition of the diacid occurs. Decarboxylation temperatures are tabulated in Table 2 along with molar

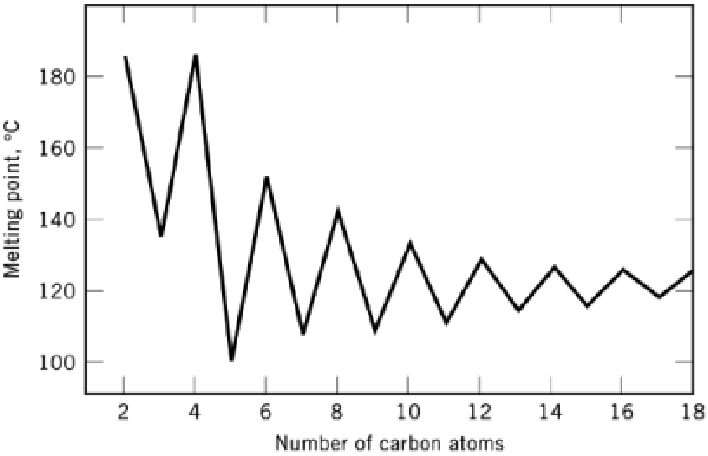


Fig. 1. Melting points of linear saturated aliphatic dicarboxylic acids.

Table 2. Decarboxylation Temperatures and Molar Heats of Combustion of Dicarboxylic Acids

Dicarboxylic acid	Decarboxylation temp[a], °C	Molar heat of combustion[b], kJ/mol[c]
oxalic	166–180	246
malonic	140–160	864
succinic	290–310	1492
glutaric	280–290	2151
adipic	300–320	2800
pimelic	290–310	3464
suberic	340–360	4115
azelaic	320–340	4778
sebacic	350–370	5429
dodecanedioic		6740

[a] Refs. (14–16).
[b] Refs. 17, 18.
[c] To convert J to cal, divide by 4.184.

heats of combustion. The diacids become more heat stable at carbon number four with even-numbered acids always more stable. Thermal decomposition is strongly influenced by trace constituents, surface effects, and other environmental factors; actual stabilities in reaction systems may therefore be lower.

Order of thermal stability as determined by differential thermal analysis is sebacic (330°C) > azelaic = pimelic (320°C) > suberic = adipic = glutaric (290°C) > succinic (255°C) > oxalic (200°C) > malonic (185°C) (19). This order is somewhat different than that in Table 2, and is the result of differences in test conditions. The energy of activation for decarboxylation has been estimated to be 251 kJ/mol (60 kcal/mol) for higher members of the series and 126 kJ/mol (30 kcal/mol) for malonic acid (1).

Lower members of the series are water soluble; solubility falls off sharply above adipic acid. Alternating effects are again expressed with acids of odd carbon numbers being the most soluble (see Table 1). Dibasic acids are ionized in aqueous solution to varying degree depending upon the proximity of the carboxyl groups within the individual structures. The carboxyl group, being electron-withdrawing, causes the neighboring carboxyl hydrogen to be more readily dissociated. With more than one interspersed methylene group the pK_a approaches

Table 3. Ionization Constants[a] of Dicarboxylic Acids

Dicarboxylic acid	K_1	K_2	References
oxalic	5.36×10^{-2}	5.42×10^{-5}	20
malonic	1.42×10^{-3}	2.01×10^{-6}	19
succinic	6.21×10^{-5}	2.31×10^{-6}	21
glutaric	4.58×10^{-5}	3.89×10^{-6}	22
adipic	3.85×10^{-5}	3.89×10^{-6}	23
pimelic[b]	3.19×10^{-5}	3.74×10^{-6}	23
suberic[b]	3.05×10^{-5}	3.85×10^{-6}	(23–25)
azelaic	2.88×10^{-5}	3.86×10^{-6}	(23–25)
sebacic	3.1×10^{-5}	3.6×10^{-6}	25
dodecanedioic[c]	2.0×10^{-6}	2.5×10^{-7}	25
tridecanedioic[c]	1.6×10^{-6}	2.9×10^{-7}	25

[a] In water at 25°C unless otherwise noted.

[b] At 18°C.

[c] In ethanol : water = 40 : 60·

that of the monocarboxylic acids of similar molecular weight. Ionization constants are tabulated in Table 3.

3. Chemical Properties

The dibasic acids undergo the reactions typical of monocarboxylic acids (see Carboxylic acids). The dibasic acids respond to heat by either losing one carboxyl group, yielding a monocarboxylic acid, or dehydration to a cyclic or polymeric anhydride. A carbon suboxide, having a bis-ketene structure, may be formed under some conditions. Cyclic anhydrides are formed by glutaric acid on heating or dehydrating with acetic anhydride or acetyl chloride. Heating adipic acid results in a high molecular weight polymeric anhydride that can be vacuum distilled to an unstable cyclic anhydride. Polyanhydrides are formed from all of the diacids of six carbons or higher when these are heated with acetic anhydride (26).

Cyclization with loss of one carboxyl takes place in the presence of metal oxides, notably barium and thorium. Thus adipic acid yields cyclopentanone, carbon dioxide, and water (Dieckmann reaction).

4. Manufacture, Preparation, and Processes

4.1. Glutaric Acid

Until 1990–1991 glutaric acid was available commercially from Du Pont as a by-product in the production of adipic acid. It is no longer available, but Du Pont produces dimethyl glutarate and mixtures of dimethyl succinate and dimethyl glutarate, as well as mixtures of dimethyl glutarate and dimethyl adipate; these esters are known commercially as DBE (dibasic esters). Du Pont fractionates DBE into 99% dimethyl glutarate (DBE-5) and 98% dimethyl adipate (DBE-6) as well as mixtures of the two (DBE-2 and DBE-3). Also available is DBE-9, which contains 66% dimethyl glutarate and 33% dimethyl succinate. Physical properties of these methyl esters are published in Du Pont's technical bulletin on dibasic esters (DBE) (27).

Several procedures for making glutaric acid have been described in *Organic Syntheses* starting with trimethylene cyanide (28), methylene bis (malonic acid) (29), γ-butyrolactone (30), and dihydropyran (31). Oxidation of cyclopentane with air at 140° and 2.7 MPa (400 psi) gives cyclopentanone and cyclopentanol, which when oxidized further with nitric acid at 65–75° gives mixtures of glutaric acid and succinic acid (32).

4.2. Pimelic Acid

This acid is manufactured by Tateyama Chemical Company in Japan in quantities of about 1000–2000 kg/yr, and by Heinrich Mock Nachf in Germany. The method or process they are using has not been disclosed. Pimelic acid is available in small quantities with purities of 98% from laboratory chemical supply companies. The preparation of pimelic acid has been described in *Organic Syntheses*; cyclohexanone condenses with diethyl oxalate, followed by decarboxylation to ethyl 2-keto-hexahydrobenzoate, and then cleavage of the β-keto ester with strong alkali (33). It has also been made from salicylic acid by reduction and subsequent cleavage with sodium in isoamyl alcohol (34). A potential commercial method has been described in which ϵ-caprolactone reacts with carbon monoxide and water in the presence of a catalyst such as palladium, and a co-catalyst such as hydriodic acid. Pimelic acid was obtained in yields as high as 46.7% (35). Other synthetic routes to pimelic acid have been described (36).

4.3. Suberic Acid

This acid is not produced commercially at this time. However, small quantities of high purity (98%) can be obtained from chemical supply houses. If a demand developed for suberic acid, the most economical method for its preparation would probably be based on one analogous to that developed for adipic and dodecanedioic acids; air oxidation of cyclooctane to a mixture of cyclooctanone and cyclooctanol. This mixture is then further oxidized with nitric acid to give suberic acid (37).

Another method that appears to have commercial potential is the ozonolysis of cyclooctene. Ozonolysis is carried out using a short chain carboxylic acid, preferably propanoic acid, as solvent. The resultant mixture is thermally decomposed in the presence of oxygen at about 100°C to give suberic acid in about 60–78% yield (38–40). Carboxylation of 1,6-hexanediol using nickel carbonyl as catalyst is reported to give suberic acid in 90% yield (41).

There are several laboratory methods useful for the preparation of suberic acid. One starting material is 1,6-hexanediol which can be converted to the dibromide with HBr. Reaction of the dibromide with NaCN gives the dinitrile which can be hydrolyzed to suberic acid. The overall yield is 76% (42). Another laboratory method is the condensation of 1,3-cyclohexanedione with ethyl bromoacetate followed by reductive cleavage to give suberic acid in 50% yield (43).

4.4. Azelaic Acid

This acid is produced by the Emery Group of Henkel Corporation in Cincinnati, Ohio in multimillion kg quantities. The process that is currently used is based on the ozonolysis of oleic acid (from grease or tallow) followed by the decomposition of the ozonide with oxygen. Oleic acid [112-80-1] and pelargonic acid [112-05-0] are fed into an ozone absorber countercurrent to a continuous flow of oxygen gas containing about 2% ozone. The pelargonic acid serves as a solvent or diluent to help moderate the reaction. Since the reaction is highly exothermic the ozone absorber is cooled and usually maintained at a temperature of 25–45°C. The reaction mixture is then fed into reactors maintained at about 100°C and sparged with oxygen gas where the ozonides are decomposed and oxidized rapidly. Manganese salts are used to catalyze the oxidation of any aldehydes that were formed to acids. The product at this stage contains pelargonic, azelaic, and palmitic and stearic acids that were present in the feed and high molecular weight materials such as esters and dimer that were formed during ozonization.

The mixed oxidation products are fed to a still where the pelargonic and other low boiling acids are removed as overhead while the heavy material, esters and dimer acids, are removed as residue. The side-stream contains predominately azelaic acid along with minor amounts of other dibasic acids and palmitic and stearic acids. The side-stream is then washed with hot water that dissolves the azelaic acid, and separation can then be made from the water-insoluble acids, palmitic and stearic acids. Water is removed from the aqueous solution by evaporators or through crystallization (44, 45).

Chromic acid was used by Emery to oxidize oleic acid on a commercial scale in the late 1940s and early 1950s until it was replaced by the ozone route. The process was relatively expensive in spite of the fact that the spent chromic acid solutions were regenerated in electrolytic cells. Pelargonic acid was removed from the oxidation mixture by distillation at reduced pressure. Azelaic acid was recovered from the residue by recrystallization from hot water. The resulting azelaic acid contained lower molecular weight dibasic acids that resulted from degradation during the oxidation reaction (46, 47).

A good laboratory method for preparing azelaic acid is the permanganate oxidation of oleic acid (48). Less degradation occurs as only small amounts of suberic acid are formed. When the oxidation is carried out in acetone, an azelaic acid yield of 83% is reported (49). Nitric acid oxidations of oleic acid have been studied by a number of investigators (50–52). The main disadvantage of using nitric acid is that it leads to degradation of azelaic acid, resulting in relatively large amounts of suberic acid being formed. Typically, oxidation products contain 65% azelaic acid and 35% suberic acid. Like nitric acid oxidation, air oxidation has been studied extensively, and the azelaic acid thus obtained contains other dibasic acids, mainly suberic acid. Generally, a cobalt catalyst is used and yields are usually no higher than 15% (53, 54).

A U.S. patent describes the reaction of commercial oleic acid with hydrogen peroxide in acetic acid followed by air oxidation using a heavy metal compound and an inorganic bromine or chlorine compound to catalyze the oxidation. Excellent yields of dibasic acids are obtained (up to 99%) containing up to 72% azelaic acid (55).

A novel route to azelaic acid is based on butadiene. Butadiene is dimerized to 1,5-cyclooctadiene, which is carbonylated to the monoester in the presence of an alcohol. Hydrolysis of this ester followed by a caustic cleavage step produces azelaic acid in both high yield and purity (56).

4.5. Sebacic Acid

This acid is produced commercially by Union Camp in Dover, Ohio, by Hokoku Oil Company in Japan, and by a state enterprise in the People's Republic of China (57). The process used in each case is based on the caustic oxidation of castor oil or ricinoleic acid [141-22-0] in either a batch or continuous process. The castor oil or ricinoleic acid and caustic are fed to a reactor (usually Monel or nickel) at a temperature of 180–270°C where the ricinoleic acid undergoes a series of reactions with evolution of hydrogen to give disodium sebacate and capryl alcohol (58). When the reaction is complete, the soaps are dissolved in water and acidified to a pH of about 6. At this pH, the soaps of the monobasic acids (C-16 to C-20 plus dimer acids) are converted to free acids that are insoluble in water. The disodium sebacate is only partially neutralized to the half acid salt which is water soluble. The oil and aqueous layers are separated. The aqueous layer containing the half salt is acidulated to a pH of about 2 causing the resulting sebacic acid to precipitate from the solution. It is then filtered, water washed, and finally dried (59).

A number of process improvements have been described, and include the use of white mineral oil having a boiling range of 300–400°C (60) or the use of a mixture of cresols (61). These materials act to reduce the reaction mixture's viscosity, thus improving mixing. Higher sebacic acid yields are claimed by the use of catalysts such as barium salts (62), cadmium salts (63), lead oxide, and salts (64).

An electrooxidation process was developed by Asahi Chemical Industry in Japan, and was also piloted by BASF in Germany. It produces high purity sebacic acid from readily available adipic acid. The process consists of 3 steps. Adipic acid is partially esterified to the monomethyl adipate. Electrolysis of the potassium salt of monomethyl adipate in a mixture of methanol and water gives dimethyl sebacate. The last step is the hydrolysis of dimethyl sebacate to sebacic acid. Overall yields are reported to be about 85% (65).

Another alternative method to produce sebacic acid involves a four-step process. First, butadiene [106-99-0] is oxycarbonylated to methyl pentadienoate which is then dimerized, using a palladium catalyst, to give a triply unsaturated dimethyl sebacate intermediate. This unsaturated intermediate is hydrogenated to dimethyl sebacate which can be hydrolyzed to sebacic acid. Small amounts of branched chain isomers are removed through solvent crystallizations giving sebacic acid purities of greater than 98% (66).

The electrochemical conversions of conjugated dienes into alkadienedioic acid have been known for some time. Butadiene has been converted into diethyl-3,7-decadiene-1,10,dioate by electrolysis in a methanol–water solvent (67). An improvement described in the patent literature (68) uses an anhydrous aprotic solvent and an electrolyte along with essentially equimolar amounts of carbon dioxide and butadiene; a mixture of decadienedioic acids is formed. This material can be hydrogenated to give sebacic acid.

In another method based on butadiene, it is dimerized in the presence of sodium to form an isomeric mixture of disodiooctadiene (69). Carbonation of the mixture using dry ice gives the unsaturated acids, 3,7-decadienedioic acid, 2-vinyl-5-octenoic acid, and 2,5-divinyladipic acid in a ratio of about 3.5:5:1, respectively. Hydrogenation of this mixture gives the saturated dibasic acid product consisting of approximately 51% 2-ethylsuberic, 38% sebacic, and 11% 2,5-diethyl-adipic. Sebacic acid is separated by fractional crystallization in about 35% yield. By-product acids, consisting of 72–80% 2-ethylsuberic, 12–18% diethyladipic, and 5–10% sebacic acids are obtained and referred to as isosebasic acid (70).

4.6. Dodecanedioic Acid

Dodecanedioic acid (DDDA) is produced commercially by Du Pont in Victoria, Texas, and by Chemische Werke Hüls in Germany. The starting material is butadiene which is converted to cyclododecatriene using a nickel catalyst. Hydrogenation of the triene gives cyclododecane, which is air oxidized to give cyclododecanone and cyclododecanol. Oxidation of this mixture with nitric acid gives dodecanedioic acid (71).

Other methods have been described to produce dodecanedioic acid. Cyclododecene is prepared from cyclododecatriene by partial hydrogenation. Ozonolysis of the cyclododecene followed by oxidation of the intermediate ozonides gives dodecanedioic acid (72). Hydrogenation of ricinoleic acid gives 12-hydroxystearic acid, which upon treatment with caustic at high temperatures, 325–330°C, gives a mixture of undecanedioic and dodecanedioic acids. The use of a catalyst such as cadmium oxide increases the yield of dibasic acids to about 51% of theoretical. The composition of the mixed acids is about 75% C-11 and 25% C-12 dibasic acids (73). Reaction of undecylenic acid with carbon monoxide using a triphenylphosphine–rhodium complex as catalyst gives 11-formylundecanoic acid, which, upon reaction with oxygen in the presence of Co(II) salts, gives 1,12-dodecanedioic acid in 70% yield (74).

Another process for the production of dodecanedioic acid is by oxidation of cyclododecene using a two-phase system in which ruthenium tetroxide serves as the oxidizing agent in the organic phase, and is regenerated in the second phase, an aqueous phase containing cerium(IV) ions (75).

4.7. Brassylic Acid

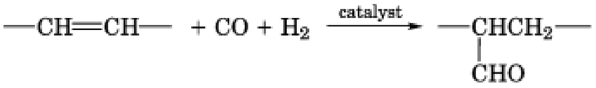
This acid is commercially available from Nippon Mining Company (Tokyo, Japan). It is made by a fermentation process (76). Several years ago, Emery Group, Henkel Corp. (Cincinnati, Ohio) produced brassylic acid via ozonization of erucic acid primarily for captive use in making dimethyl brassylate and ethylene brassylate. A pilot-scale preparation based on ozonization of erucic acid has been described in which brassylic acid yields of 72–82% were obtained in purities of 92–95%. Recrystallization from toluene gave purities of 99% (77).

4.8. C-19 Dicarboxylic Acids

The C-19 dicarboxylic acids are generally mixtures of isomers formed by the reaction of carbon monoxide on oleic acid. Since the reaction produces a mixture of isomers, no single chemical name can be used to describe them. Names that have been used include 2-nonyldecanedioic acid, 2-octylundecanedioic acid, 1,8-(9)-heptadecanedicarboxylic acid, and 9-(10)-carboxystearic acid. The name 9-(10)-carboxystearic acid can be used correctly if the product is made with no double bond isomerization (rhodium triphenylphosphine catalyst system).

There are currently no commercial producers of C-19 dicarboxylic acids. During the 1970s BASF and Union Camp Corporation offered developmental products, but they were never commercialized (78). The Northern Regional Research Laboratory (NRRL) carried out extensive studies on preparing C-19 dicarboxylic acids via hydroformylation using both cobalt catalyst and rhodium complexes as catalysts (78). In addition, the NRRL developed a simplified method to prepare 9-(10)-carboxystearic acid in high yields using a palladium catalyst (79).

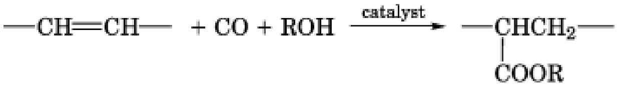
C-19 dicarboxylic acid can be made from oleic acid or derivatives and carbon monoxide by hydroformylation, hydrocarboxylation, or carbonylation. In hydroformylation, ie, the Oxo reaction or Roelen reaction, the catalyst is usually cobalt carbonyl or a rhodium complex (see Oxo process). When using a cobalt catalyst a mixture of isomeric C-19 compounds results due to isomerization of the double bond prior to carbon monoxide addition (80).



$$-\mathrm{CH{=}CH}- \; + \mathrm{CO} + \mathrm{H_2} \xrightarrow{\text{catalyst}} -\underset{\displaystyle\mathrm{CHO}}{\mathrm{CH}}\mathrm{CH_2}-$$

Hydroformylation catalyzed by rhodium triphenylphospine results in only the 9 and 10 isomers in approximately equal amounts (79). A study of recycling the rhodium catalyst and a cost estimate for a batch process have been made (81).

In hydrocarboxylation, the Reppe reaction, the catalyst can be nickel or cobalt carbonyl or a palladium complex where $R = H$ or alkyl.



$$-\mathrm{CH{=}CH}- \; + \mathrm{CO} + \mathrm{ROH} \xrightarrow{\text{catalyst}} -\underset{\displaystyle\mathrm{COOR}}{\mathrm{CH}}\mathrm{CH_2}-$$

The nickel or cobalt catalyst causes isomerization of the double bond resulting in a mixture of C-19 isomers. The palladium complex catalyst produces only the 9-(10)-carboxystearic acid. The advantage of the hydrocarboxylation over the hydroformylation reaction is it produces the carboxylic acids in a single step and obviates the oxidation of the aldehydes produced by hydroformylation.

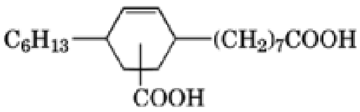
Carbonylation, or the Koch reaction, can be represented by the same equation as for hydrocarboxylation. The catalyst is H_2SO_4. A mixture of C-19 dicarboxylic acids results due to extensive isomerization of the double bond. Methyl-branched isomers are formed by rearrangement of the intermediate carbonium ions. Reaction of oleic acid with carbon monoxide at 4.6 MPa (45 atm) using 97% sulfuric acid gives an 83% yield of the C-19 dicarboxylic acid (82). Further optimization of the reaction has been reported along with physical data of the various C-19 dibasic acids produced. The mixture of C-19 acids was found to contain approximately 25% secondary carboxyl and 75% tertiary carboxyl groups. As expected, the tertiary carboxyl was found to be very difficult to esterify (80, 83).

4.9. C-20 Dicarboxylic Acids

These acids have been prepared from cyclohexanone via conversion to cyclohexanone peroxide followed by decomposition by ferrous ions in the presence of butadiene (84–87). Okamura Oil Mill (Japan) produces a series of commercial acids based on a modification of this reaction. For example, Okamura's modifications of the reaction results in the following composition of the reaction product: C-16 (linear) 4–9%, C-16 (branched) 2–4%, C-20 (linear) 35–52%, and C-20 (branched) 30–40%. Unsaturated methyl esters are first formed that are hydrogenated and then hydrolyzed to obtain the mixed acids. Relatively pure fractions of C-16 and C-20, both linear and branched, are obtained after solvent crystallization and fractionation (88).

4.10. C-21 Dicarboxylic Acids

C-21 dicarboxylic acids are a mixture of predominately 5-(6)-carboxy-4-hexyl-2-cyclohexene-1-octanoic acid, 5-isomer [42763-47-3] and 6-isomer [42763-46-2]. C-21 dicarboxylic acids were first described at the Northern Regional Research Laboratory in Peoria, Illinois (89).



C-21 dicarboxylic acids are produced by Westvaco Corporation in Charleston, South Carolina in multimillion kg quantities. The process involves reaction of tall oil fatty acids (TOFA) (containing about 50% oleic acid and 50% linoleic acid) with acrylic acid [79-10-7] and iodine at 220–250°C for about 2 hours (90). A yield of C-21 as high as 42% was reported. The function of the iodine is apparently to conjugate the double bond in linoleic acid, after which the acrylic acid adds via a Diels-Alder type reaction to form the cyclic reaction product. Other catalysts have been described and include clay (91), palladium, and sulfur dioxide (92). After the reaction is complete, the unreacted oleic acid is removed by distillation, and the crude C-21 diacid can be further purified by thin film distillation or molecular distillation.

A 22 carbon atom adduct has been prepared in a similar reaction to that described above by replacing the acrylic acid with methacrylic acid. Somewhat lower yields are obtained when using methacrylic acid [79-41-4] vs acrylic acid (93).

5. Dicarboxylic Acids via Microorganisms

During the 1980s a number of patents were issued describing the preparation of dicarboxylic acids or esters using microorganisms. The α, ω-n-alkanedioic acids that have been prepared generally have 5–25 carbons. One of the first methods described the preparation of dimethyl 1,16-hexadecanedioate using a nutrient solution, *n*-hexadecyl bromide, and certain strains of *Torulopsis* (94). Other methods have been described to give dibasic acid of 8–22 carbons using *n*-alkanes or *n*-alcohols and various organisms (95–98). One particular yeast converts C12–18 *n*-alkanes not only to dicarboxylic acids but also to 3-hydroxydicarboxylic acids as well (99). The unsaturated dicarboxylic acid itaconic acid (2-methylenebutanedioic acid [97-65-4] is produced by fermentation (100). Finally, unsaturated dibasic acids having 14–22 carbons have been prepared from the corresponding unsaturated fatty acids and certain microorganisms. For example, 9-*trans*-octadecenedioic acid has been prepared from elaidic acid; 6,9-octadecadienedioic acid from linoleic acid, and 5-docosenedioic acid from erucic acid (101).

6. Derivatives and Uses

Diacids, owing to their ready incorporation into polymers, are components in a wide variety of materials (100, 102, 103). The diacids are important industrial intermediates for the manufacture of diesters, polyesters, and polyamides. These derivatives find application as plasticizing agents, lubricants, heat transfer fluids, dielectric fluids, fibers, copolymers, inks and coatings resins, surfactants, fungicides, insecticides, hot-melt coatings, and adhesives. Of the higher diacids, azelaic, sebacic, and dodecanoic find the greatest application. Derivatives of glutaric and C-21 diacids also enjoy significant commercial applications.

6.1. Diesters

Many of the diester derivatives are commercially important. The diesters are important plasticizers, polymer intermediates, and synthetic lubricants. The diesters of azelaic and sebacic acids are useful as monomeric plasticizing agents; these perform well at low temperatures and are less water-soluble and less volatile than are diesters of adipic acid. Azelate diesters, eg, di-*n*-hexyl, di(2-ethylhexyl), and dibutyl, are useful plasticizing agents for poly(vinyl chloride), synthetic rubbers, nitrocellulose, and other derivatized celluloses (104). The di-hexyl azelates and dibutyl sebacate are sanctioned by the U.S. Food and Drug Administration for use in poly(vinyl chloride) films and in other plastics with direct contact to food. The di(2-ethylhexyl) and dibenzyl sebacates are also valuable plasticizers. Monomeric plasticizers have also been prepared from other diacids, notably dodecanedioic, brassylic, and 8-ethylhexadecanedioic (88), but these have not enjoyed the commercialization of the sebacic and azelaic diesters.

The dioctyl, didecyl, and di-(tridecyl) esters of azelaic, sebacic, dodecanedioic, and brassylic acids serve as synthetic lubricants that offer some advantages over petroleum-based lubricants. The dihexyl and dioctyl esters of 8-ethylhexadecanedioic acid also are useful lubricants (88). The viscosity/temperature relationships, low viscosity rise upon oxidation, high flash points, low peroxide value, good additive response, low coking characteristics, and overall excellent lubricity make these diesters desirable for demanding engine and equipment environments (104).

Other applications for the diesters of the diacids are known. Du Pont's Di-basic Ester (DBE) is an effective industrial cleaning solvent and paint stripper. DBE is marketed as an environmentally superior substitute to the chlorinated solvents (105).

6.2. Polyesters

Azelaic and sebacic acids are commonly used for polyester applications. Typical glycols that react with the diacids to give polyesters include 1,2-propylene glycol, 1,3-butylene glycol, and 1,4 butanediol. Aliphatic polyesters, unsaturated polyesters, and copolyesters find application in fibers, films, casting and potting resins, lubricants, resins, adhesives, and laminates. The plasticizers offer greater resistance to solvents, lower volatility, and less migration, but are generally less effective and have poorer low temperature flex characteristics than those of the corresponding aliphatic monomerics. Polyester properties may be tuned by judicious choice of monofunctional additive, either carboxylic acid or alcohol. Diacid-based polyester fibers and films exhibit excellent low temperature flexibility and high tensile strength. The alkyd resins (qv) derived from sebacic and azelaic acids impart flexibility and are used as plasticizers (106).

6.3. Polyamides

The production of aliphatic polyamides, or nylons, consumes a large portion of the total production of the diacids. These polyamides find application in apparel and carpet fibers, engineering plastics, nylon copolymers for monofilament, wire-coating, and molding resin applications. An interesting potential application for nylon-5,7, prepared from pimelic acid and 1,5-pentanediamine, is as a conducting polymer (107). The polyamide produced from suberic acid and 1,4-cyclohexanebis(methylamine) has an exceptionally high melting point (295°C) that enables high melt processing temperatures to be employed without concurrent thermal decomposition; it has properties well-suited for fiber, film, and molding plastic applications (108). The 6,9, 6,10, and 6,12 nylons, derived from azelaic, sebacic, and dodecanedioic acids respectively, find application in engineering plastics, bristles, and fibers. These nylons are more moisture-resistant than is the adipic based nylon-6,6. The alicyclic nylon, Du Pont's Quiana, derived from dodecanedioic acid and bis(4-aminocyclohexyl)methane, was introduced as a replacement for silk in 1968 (109). A recent patent describes the incorporation of dodecanedioic acid into nylon-6,6 to improve the fibers' dyeability (110). Brassylic acid based nylons 13, 6,13, and 13,13 are very moisture resistant. Azelaic and sebacic acids find application in dimer acid based polyamides and contribute to higher tensile strength and higher melting point resins.

6.4. Other Polymeric Derivatives

Hydroxyl-terminated polyesters, derived from reaction of azelaic, sebacic, or dodecanedioic acids with glycols, may be used in polyurethanes. These polymers offer several advantages over adipic acid based materials, including excellent low-temperature properties, water resistance, tear strength, and good elongation. These polymers may be utilized in specialty films, fabric coatings, and Spandex fibers (104). The same diacids may be used as modifiers in poly(ethylene terephthalate)/glycol copolyesters to contribute improved flexibility, melting point, and dyeability. Azelaic, sebacic, dodecanedioic, and brassylic acids may be used in copolyetheresteramides (111). Two patents describe additional applications for the C-9–C-40 diacids for the preparation of polyester carbonates (112), and the copolymerization of epoxides and carbon dioxide by reaction of either glutaric or adipic acids with zinc oxide (113).

6.5. Miscellaneous Derivatives

Pimelic acid is used as an intermediate in some pharmaceuticals and in aroma chemicals; ethylene brassylate is a synthetic musk (114). Salts of the diacids have shown utility as surfactants and as corrosion inhibitors. The alkaline, ammonium, or organoamine salts of glutaric acid (115) or C-5–C-16 diacids (116) are useful as noncorrosive components for antifreeze formulations, as are methylene azelaic acid and its alkali metal salt (117). Salts derived from C-21 diacids are used primarily as surfactants and find application in detergents, fabric softeners, metal working fluids, and lubricants (118). The salts of the unsaturated C-20 diacid also exhibit anticorrosion properties, and the sodium salts of the branched C-20 diacids have the ability to complex heavy metals from dilute aqueous solutions (88).

7. Economic Aspects

The prices and mode of shipment for the various commercial grades of diacids are provided in Table 4. The price of adipic acid is included for comparison. In addition to these diacids, undecanedioic, brassylic, tetradecanedioic, hexadecanedioic, docosanedioic, and tetracosanedioic acids are available, expensive, and in limited quantity from research chemical supply houses.

Azelaic acid is available from Henkel's Emery Group in two grades; E1110 and E1144 are 80% and 90% azelaic acid, respectively. Union Camp Corporation offers three grades of sebacic acid: purified, CP, and nylon grades. The nylon grade is >95% sebacic acid with low ash content and low color. Oakamura Oil Mill Ltd.'s C-20 diacids are each unique products. ULB-20 is a mixture of straight-chain and branched unsaturated acids. SL-20 is 85–90% eicosanedioic acid. SB-20 is 80–90% 8-ethyloctadecanedioic acid. Westvaco's C-21 Diacid is offered in two grades. Diacid 1550 is darker in color and lower in acid value than Diacid 1575,with diacid contents of 88% and >97% respectively.

Table 4. Dicarboxylic Acid Prices, \$ / kg

Acid	Grade	Mode of shipment	1979	1991
adipic	resin grade	bags or hopper cars	0.91	1.43
pimelic			132	575
suberic			65	103
azelaic	E1110	multiwall	1.85	3.48
	E1144	bags		3.74
sebacic	purified	multiwall	3.48	4.49
	CP	bags or		4.51
	nylon	super-sacks		4.51
dodecanedioic		multiwall bags	2.65	4.36
eicosanedioic (C_{20} diacids)	ULB-20	steel drums		8.79
	SB20	steel drums		9.66
	SL20	poly-lined paper bags		12.41
C_{21} diacids	D1550	lined steel		1.54
	D1575	drums or tank trunks		3.74

Table 5. Acute Toxicities of Diacids and Derivatives

	Oral LD_{50}, mg/kg		Dermal LD_{50}, mg/kg	
Compound	Species	Dose	Species	Dose
glutaric	mouse	6000[a]		
dimethyl glutarate	rat	8191[b]	rabbit	>2250[b]
pimelic	rat	7000[c]		
azelaic	rat	>10000[d]	rat	>10000[d]
dihexyl azelate	rat	16000[e]		
sebacic	mouse	6000[f]		
diethyl sebacate	rat	14500[g]	guinea pig	7320[g]
dodecanedioic	rat	17000[h,i]	rabbit	>6000[i]
Diacid 1550 (C21)	rat	6176[j]		

[a] Ref. 119, p. 1478.
[b] Ref. 120.
[c] Ref. 121, p. 4937.
[d] Ref. 122.
[e] Ref. 119, p. 334.
[f] Ref. 119, p. 2338.
[g] Ref. 121, p. 2337.
[h] Average lethal dose.
[i] Ref. 123.
[j] Ref. 119.

8. Health and Safety Factors

The acute oral toxicities of the diacids and some common derivatives are provided in Table 5. In general, the higher diacids are essentially nontoxic. There are no indications that the dicarboxylic acids detailed here are carcinogenic or teratogenic in animals or humans. It is generally recognized that these diacids are ocular irritants and that the inhalation of the dust of these diacids is irritating to the mucous membranes and the respiratory tract.

The water solubility of glutaric acid fosters its toxicity. Glutaric acid is a known nephrotoxin. Renal failure has been documented in rabbits administered sodium glutarate subcutaneously (124). Dibasic ester (Du Pont), which contains primarily dimethyl glutarate, has low acute toxicity by inhalation and by ingestion, and is moderately toxic via dermal absorption. The acid is both a dermal and ocular irritant of humans. The ester is a severe skin irritant and may cause a rash in humans (120).

The sodium salts of suberic and azelaic acids are mildly nephrotoxic to rabbits when administered subcutaneously (125). Azelaic acid is both a dermal and ocular irritant, and is a sensitizing agent to guinea pigs (122). Interestingly, neither dermal absorption or irritation are reported for guinea pigs exposed to pimelic acid (121). Sebacic and dodecanedioic acids are not dermal irritants, but are mild ocular irritants. Long-term exposure in white rats to sebacic acid has produced irritation of the respiratory tract and alteration of kidney and liver functions (126).

Of the higher diacids, the alicyclic, unsaturated Diacid 1550 (the Westvaco C-21 diacid) is significantly water soluble and is moderately irritating both dermally and ocularly. The corresponding dipotassium salt, Diacid H-240, is substantially more irritating (127).

8.1. Environmental Effects

In general, the higher diacids do not pose substantial environmental risk; however, releases of significant quantities into surface or ground waters may be reportable under the Clean Water Act. The low biotoxicity of the higher diacids results, in part, from their limited water solubility. Glutaric acid is significantly more water soluble than the other diacids described herein, and the aquatic biotoxicity of glutaric acid and dimethyl glutarate is established. This acid is toxic to both protozoa and fish, and its dimethyl ester is toxic to both aquatic invertebrates and to fish (128, 129). Westvaco's Diacid 1550 (C-21) is relatively more water soluble than the higher, linear diacids, and this diacid is mildly toxic to aquatic invertebrates, fish, and algae (130).

BIBLIOGRAPHY

"Acids, Dicarboxylic" in *ECT* 1st ed., Vol. 1, pp. 152–157, by C. J. Knuth and P. F. Bruins, Polytechnic Institute of Brooklyn, and R. R. Umbdenstock, Chas. Pfizer and Co., Inc.; in *ECT* 2nd ed., Vol. 1, pp. 240–254, by W. M. Muir, Harris Research Laboratories, Inc.; "Dicarboxylic Acids" in *ECT* 3rd ed., Vol. 7, pp. 614–628, by Paul Morgan, Consultant.

Cited Publications

1. E. H. Pryde and J. C. Cowan in J. K. Stille and T. W. Campbell, eds., *Condensation Monomers*, Wiley-Interscience, New York, 1972, 1–153.
2. J. A. Dean, ed., *Lange's Handbook of Chemistry*, 11th ed., McGraw-Hill Book Co., Inc., New York, 1973.
3. F. Krafft and H. Noerdlinger, *Chem. Ber.* **22**, 816 (1889).
4. L. J. Durham, D. J. McLeod, and J. Cason, *Organic Synthesis Collective Volumes*, Vol. **4**, Wiley, New York, 1963, p. 510.
5. H. Noerdlinger, *Chem. Ber.* **23**, 2356 (1890).
6. J. G. Erickson, *J. Am. Chem. Soc.* **71**, 307 (1949).
7. C. Hell and C. Jordanoff, *Chem. Ber.* **24**, 991 (1891).
8. L. Ruzicka, Pl. A. Plattner, and W. Widmer, *Helv. Chim. Acta.* **25**, 1086 (1942).
9. *Ibid.*, p. 604.
10. D. E. F. Armstead, *Sch. Sci. Rev.* **55**, 416 (1973).
11. R. Hill, ed., *Fibres from Synthetic Polymers*, Elsevier Science Publishing Co., Inc., New York, 1953, pp. 135, 164, 311.
12. P. W. Morgan, *Condensation Polymers by Interfacial and Solutions Methods*, Wiley-Interscience, New York, 1965, pp. 244, 382.
13. P. W. Morgan and S. L. Kwolek, *Macromolecules* **8**, 104 (1975).
14. V. V. Korshak and S. V. Rogozhin, *Izv. Akad. Nauk SSSR Otd. Khim, Nauk.*, 531 (1952).
15. V. V. Korshak and S. V. Rogozhin, *Dokl. Akad. Nauk. SSSR* **76**, 539 (1951).

16. W. Sweeny and J. Zimmerman in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **10**, Wiley-Interscience, New York, 1969, 483–507.
17. R. C. Wilhoit and D. Shiao, *J. Chem. Eng. Data* **9**, 595 (1964).
18. P. E. Verkade, H. Hartman, and J. Coops, *Recl. Trav. Chim. Pays-Bas* **45**, 380 (1926).
19. S. N. Das and D. L. G. Ives, *Proc. Chem. Soc.*, 373 (1961); W. J. Hamer, J. O. Burton, and S. F. Acree, *J. Res. Natl. Bur. Stand.* **24**, 269 (1940).
20. L. S. Darken, *J. Am. Chem. Soc.* **63**, 1007 (1941); G. D. Pinching and R. G. Bates, *J. Res. Natl. Bur. Stand.* **40**, 405 (1948).
21. G. D. Pinching and R. G. Bates, *J. Res. Natl. Bur. Stand.* **45**, 322 and 444 (1950).
22. I. Jones and F. G. Soper, *J. Chem. Soc.*, 133 (1936).
23. B. Adell, *Z. Phys. Chem. (Leipzig)* **185**, 161 (1939).
24. G. Kortum, W. Vogel, and K. Andrussow, *Pure Appl. Chem.* **1**, 190 (1960).
25. G. Bonhomme, *Bull. Soc. Chim. Fr.*, 60 (1968); *Chem. Abstr.* **68**, 117603 (1968); **82**, 72408 (1975).
26. F. L. Breusch and E. Ulusoy, *Fette, Seifen, Anstrichm.* **66**, 739 (1964).
27. *Dibasic Esters*, technical bulletin, Du Pont Chemicals, Wilmington, Del., 1991.
28. C. S. Marvel and W. F. Tuley, in Ref. 4, Vol. 1, rev. ed., 1946, p. 289.
29. T. J. Otterbocher, in Ref. 4, Vol. 1, 2nd ed., 1946, p. 290.
30. G. Paris, L. Berlinguet, and R. Gaudry, in Ref. 4, Vol. 4, 1963, p. 496.
31. J. English Jr. and J. E. Dayan, in Ref. 4, Vol. 4, 1963, p. 499.
32. U.S. Pat. 2,452,741 (Nov. 2, 1948), H. W. Fleming (to Phillips Petroleum Co.).
33. H. R. Snyder, C. A. Brooks, and S. H. Shapino, in Ref. 4, Vol. 2, rev. ed., 1943, p. 531.
34. A. Muller, in Ref. 4, Vol. 2, rev. ed., 1943, p. 535.
35. U.S. Pat. 4,888,443 (Dec. 19, 1989), J. H. Murib and J. H. Katy (to National Distillers and Chemical Corp.).
36. Ref. 1, 56–57.
37. Belgian Pat. 660,522 (Sept. 2, 1965), R. B. Judge, M. F. Levy, and J. H. Quinn (to Wallace and Tiernan).
38. U.S. Pat. 3,219,675 (Nov. 23, 1965), R. Seekerchen (to Columbia Carbon Co.).
39. U.S. Pat. 3,441,604 (Apr. 29, 1969), E. K. Baylis, W. Pickles, and K. D. Sparrow (to Gergy Chemical Corp.).
40. U.S. Pat. 3,280,183 (Oct. 18, 1966), A. Maggiolo (to Wallace and Tiernan, Inc.).
41. W. Reppe and co-workers, *Justus Liebigs Ann. Chem.* **560**, 1 (1948).
42. K. E. Miller and co-workers, *J. Chem. Eng. Data* **9**, 227 (1964).
43. H. Stetter in W. Forest, ed., *Newer Methods of Preparative Organic Chemistry*, Vol. **2**, Academic Press, Inc., New York, 1963, p. 79.
44. U.S. Pat, 2,813,113 (Nov. 12, 1957), C. G. Goebel, A. C. Brown, H. F. Oehlschlaeger, and R. P. Rolfes (to Emery Industries, Inc.).
45. U.S. Pat. 3,402,108 (Sept. 17, 1968), H. F. Ohlschlaeger and H. G. Rodenberg (to Emery Industries, Inc.).
46. U.S. Pat. 2,450,858 (Oct. 5, 1948), J. D. Fitzpatrick and L. D. Meyers (to Emery Industries, Inc.).
47. U.S. Pat. 2,389,191 (Nov. 20, 1945), J. D. Fitzpatrick and L. D. Meyers (to Emery Industries, Inc.).
48. J. W. Hall and W. L. McEwen, in Ref. 4, Vol. 2, 1943, p. 53.
49. E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind. Trans.* **44**, 43T (1925).
50. U.S. Pat. 2,203,680 (June 11, 1940), E. K. Ellingboe (to E. I. du Pont de Nemours & Co., Inc.).
51. U.S. Pat. 2,365,290 (Dec. 19, 1944), F. J. Sprules and R. Griffith (to Napco Chemical Co.).
52. U.S. Pat. 3,021,348 (Feb. 13, 1963), V. P. Kuceski (to C. P. Hall Co.).
53. U.S. Pat. 2,292,950 (Aug. 11, 1942), D. J. Loden and P. L. Salzberg (to E. I. du Pont de Nemours & Co., Inc.).
54. T. M. Patrick and W. S. Emerson, *Ind. Eng. Chem.* **41**, 636 (1949).
55. U.S. Pat. 4,606,863 (Aug. 19, 1986), M. Nakazawa, K. Fujitani, and H. Manomi (to Japan Chemical Co., Ltd.).
56. D. T. Thompson, *Platinum Met. Rev.* **19**, 88 (1975).
57. H. K. Schwitzer in T. H. Applewhite, ed., *World Conference on Oleochemicals into the 21st Century*, American Oil Chemists Society, Champaign, Ill., 1990.
58. D. D. Nanavat, *J. Sci. Ind. Rev.* **35**, 163 (1976).
59. U.S. Pat. 2,731,495 (Jan. 17, 1956), R. S. Emslie (to E. I. du Pont de Nemours & Co., Inc.).
60. U.S. Pat. 2,318,762 (May 11, 1943), G. D. Davis and B. A. Dombrow (to National Oil Products Co.).
61. U.S. Pat. 2,674,608 (Apr. 6, 1954), G. Dupont and O. Kostlitz (to Société Organico).

62. U.S. Pat. 2,734,916 (Feb. 14, 1956), D. S. Bolley and F. C. Naughton (to Baker Castor Oil Co.).
63. U.S. Pats. 2,695,500 and 2,696,501 (Dec. 7, 1954), W. Stein (to Henkle & Cie, GmbH).
64. U.S. Pat. 2,851,491 (Sept. 9, 1958), (to Baker Castor Oil Co.).
65. U.S. Pat. 4,237,317 (Dec. 2, 1980), K. Yamataka, Y. Matsuoka, and T. Isoya (to Asahi Kasei Kogyo Kabushiki Kaisha).
66. U.S. Pat. 4,299,976 (Nov. 10, 1981), (to Atlantic Richfield Co.).
67. R. V. Lindsey, *J. Am. Chem. Soc.* **81**, 2073 (1959).
68. U.S. Pat. 4,377,451 (Mar. 22, 1983), W. J. M. van Tilborg and C. J. Smit (to Shell Oil Co.).
69. C. E. Frank and W. E. Foster, *J. Org. Chem.* **26**, 303 (1961).
70. U.S. Pat. 2,858,337 (Oct. 28, 1958), S. A. Mednisk, R. Wynkoop, and J. Feldman (to National Distillers and Chemical Corp.).
71. Ger. Offen. 1,912,569 (Oct. 2, 1969), J. O. White and D. D. Daves (to E. I. du Pont de Nemours & Co., Inc.).
72. U.S. Pat. 3,280,183 (Oct. 18, 1966), A. Maggiolo (to Wallace and Tiernan, Inc.).
73. T. R. Steadman and J. O. Peterson, *Ind. Eng. Chem.* **50**, 59 (1958).
74. U.S. Pat. 4,733,007 (Mar. 22, 1988), J. Andrade, K. Koehler, and G. Prescher (to Degussa Aktiengesellschaft).
75. U.S. Pat. 5,026,461 (June 25, 1991), D. D. Davis and D. L. Sullivan (to E. I. du Pont de Nemours & Co., Inc.).
76. U.S. Pat. 4,339,536 (July 13, 1982), K. Kato and N. Vemura (to Nippon Mining Co., Ltd.).
77. E. J. Dufek, W. E. Parker, and R. E. Koos, *J. Am. Oil Chem. Soc.* **51**, 351 (1974).
78. E. N. Frankel and E. H. Pryde, *J. Am. Oil Chem. Soc.* **54**, 873A (1977).
79. E. N. Frankel and F. L. Thomas, *J. Am. Oil Chem. Soc.* **50**, 39 (1973).
80. E. T. Roe and D. Swern, *J. Am. Oil Chem. Soc.* **37**, 661 (1960).
81. J. P. Friedrich, G. R. List, and V. E. Sohns, *J. Am. Oil Chem. Soc.* **50**, 455 (1973).
82. H. Koch, *Fette, Seifen, Anstrichm.* **59**, 493 (1957).
83. N. E. Lawson, T. T. Chang, and F. B. Slezak, *J. Am. Oil Chem. Soc.* **54**, 215 (1977).
84. W. Cooper and W. H. T. Davison, *J. Chem. Soc.*, 1380 (1952).
85. U.S. Pat. 2,601,223 (June 24, 1952), M. J. Roedel (to E. I. du Pont de Nemours & Co., Inc.).
86. M. S. Kharasch and W. Nudenberg, *J. Org. Chem.* **19**, 1921 (1954).
87. D. D. Coffman and H. N. Cripps, *J. Am. Chem. Soc.* **80**, 2880 (1958).
88. *Higher Dibasic Acids and Their Derivatives*, technical bulletin, Okamura Oil Mill, Ltd., Osaka, Japan, 1985.
89. J. C. Cowan, W. C. Ault, and H. M. Teeter, *Ind. Eng. Chem.* **38**, 1138 (1946).
90. U.S. Pat. 3,753,968 (Aug. 21, 1973), B. F. Ward (to Westvaco Corp.).
91. U.S. Pat. 4,156,095 (May 22, 1979), A. H. Jevne and G. L. Schwebke (to Henkel Corp.).
92. Ger. Offen. 2,406,401, (1974), B. F. Ward (to Westvaco Corp.).
93. U.S. Pat. 3,899,476 (Aug. 12, 1975), B. F. Ward (to Westvaco Corp.).
94. U.S. Pat. 3,483,083 (Dec. 9, 1969), G. W. Elson, R. Howe, and D. F. Johes (to Imperial Chemical Industries, Ltd.).
95. U.S. Pat. 3,843,466 (Oct. 22, 1974), S. A. Akabori, I. Shiio, and R. Uchio (to Ajinomato Co., Inc.).
96. U.S. Pat. 3,975,234 (Aug. 17, 1976), D. O. Hitzman (to Phillips Petroleum Co.).
97. U.S. Pat. 4,220,720 (Sept. 2, 1980), A. Tooka and S. Uchida (to Bio Research Center Co., Ltd.).
98. U.S. Pat. 4,624,920 (Nov. 25, 1986), S. Inove, Y. Kimura, and S. Adachi (to Eiji Suzuki).
99. U.S. Pat. 4,827,030 (May 2, 1989), F. F. Hill (to Huels Akliengesellschaft).
100. Jpn. Kokai 8,463,190 (1984), Iwata Kagasku Kogyo K. K.; Jpn. Kokai 81,137,893 (1981), Banda Kagaku Kogyo K. K. (to Shizuoka Prefecture); N. Nakagawa and co-workers, *J. Ferment. Technol.* **62**, 201–203 (1984); Jpn. Kokai 8,034,017 (1980) (to Mitsubishi Chemical Industries Co. Ltd.); S. Ikeda, *Hakko Kogaku Kaishi* **60**, 208–210 (1982).
101. U.S. Pat. 4,474,882 (Oct. 2, 1984), E. Kuneshige and T. Morinaga (to Daicel Chemical Industries, Ltd.).
102. E. C. Leonard in E. H. Pryde, ed., *Fatty Acids*, American Oil Chemist's Society, Champaign, Ill., 1979, Chapt. 25.
103. R. W. Johnson in R. W. Johnson and E. Fritz, eds., *Fatty Acids in Industry*, Marcel Dekker, Inc., New York, 1989, Chapt. 13.
104. *Emerox Azelaic Acid and Polymer Intermediates*, technical bulletin, Emery Industries, Cincinnati, Ohio, 1981.
105. *DBE Solvent Applications*, technical bulletin, Du Pont Chemicals, Wilmington, Del., 1991.
106. H. J. Lansen in J. I. Kroschwitz, ed., *Encyclopedia of Plastics and Engineering*, Vol. **1**, 1985, p. 653.
107. G. Froyer and co-workers, *J. Polymer Sci., Polymer Chem. Ed.* **19**, 165–174 (1981).
108. M. T. Watson and G. M. Armstrong, *SPE J.*, **21**, 475 (1965).
109. Ref. 102, p. 15.

110. U.S. Pat. 5,025,087 (June 18, 1991), F. P. Williams (to E. I. du Pont de Nemours & Co., Inc.).
111. U.S. Pat. 4,483,975 (Nov. 20, 1984), E. de Jong, K. H. Hapelt, and H. Knipp (to Plate Bonn Gesellschaft Haftung).
112. U.S. Pat. 5,025,081 (June 18, 1991), L. P. Fontana and P. W. Buckley (to General Electric Co.).
113. U.S. Pat. 5,026,676 (June 25, 1991), S. A. Montika, T. L. Pickering, A. Rokicki, and B. K. Stein (to Air Products and Chemicals, Inc., Arco Chemical Co., and Mitsui Petrochemical Industries, Ltd.).
114. *Chem. Week* **97**, 69 (1965).
115. U.S. Pat. 4,448,702 (May 15, 1984), G. Kaes (to Lang & Co.).
116. U.S. Pat. 4,647,392 (Mar. 3, 1987), J. W. Darden, C. A. Triebel, W. A. Van Neste, and J. P. Maes (to Texaco Inc. S. A. and Texaco Belgium N.V.).
117. U.S. Pat. 4,578,205 (Mar. 25, 1986), E. L. Yeakey, G. P. Speranza, C. A. Triebel, and D. R. McCoy (to Texaco Inc.).
118. *Diacid Surfactants*, technical bulletin, Westvaco Chemical Division, Charleston Heights, S.C.
119. N. I. Sax, *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold Co., New York, 1984.
120. MSDS 00000004, *Dibasic Esters*, Du Pont Chemicals, July 1991.
121. G. D. Clayton and F. E. Clayton, eds., *Patty's Industrial Hygiene and Toxicology*, 3rd ed., John Wiley & Sons, Inc., New York, 1981.
122. Emerox 1144, Quantum Chemical Corp., Jan. 1989.
123. MSDS 00000003, *Dodecanedioic Acid*, DuPont Chemicals, Mar. 6, 1990.
124. W. C. Rose, *J. Pharmacol.* **24**, 147 (1924).
125. W. C. Rose and co-workers, *J. Pharmacol.* **25**, 59 (1925).
126. MSDS 240,104,541, Union Camp Corp., Apr. 1989.
127. *Diacid Surfactants*, technical bulletin, Westvaco Chemical Division, Charleston Heights, S.C.
128. K. Verschuerren, *Handbook of Environmental Data on Organic Compounds*, Van Nostrand Reinhold Co., Inc., New York, 1977, p. 354.
129. MSDS E-77995-3, Du Pont Chemicals, Dec. 1987.
130. *Westvaco Diacid Toxicological and Environmental Testing*, technical bulletin, Westvaco Chemical Division, Charleston Heights, S.C.

ROBERT W. JOHNSON
CHARLES M. POLLOCK
Union Camp Corporation
ROBERT R. CANTRELL
Union University

Related Articles

Phthalic acids and other benzenepolycarboxylic acids; Carboxylic acids