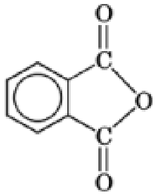
Kirk-Othmer Encyclopedia of Chemical Technology.

PHTHALIC ACIDS AND OTHER BENZENEPOLYCARBOXYLIC ACIDS

This article discusses the benzenepolycarboxylic acids, their anhydrides, and their esters. Table 1 includes IUPAC nomenclature, common names, and CAS Registry Numbers for the benzenepolycarboxylic acids. These acids and anhydrides are highly stable. The carboxylic acid groups provide from two to six sites for reaction for a wide variety of products, mostly polymers and plasticizers.

Phthalic anhydride **(1)** is the commercial form of phthalic acid **(2)**. The worldwide production capacity for the anhydride was ca 3.5×10^6 metric tons in 1993, and it was used in the manufacture of plasticizers (qv), unsaturated polyesters, and alkyd resins (qv) (see Polyesters, unsaturated). Sales of terephthalic acid **(3)** and its dimethyl ester are by far the largest of any of the benzenepolycarboxylic acids; 14.3×10^6 t were produced in 1993. This is 80% of the total tonnage of all commercial forms of the benzenepolycarboxylic acids. Terephthalic acid is used almost exclusively for the manufacture of poly(ethylene terephthalate), which then is formed into textiles, films, containers, and molded articles. Isophthalic acid **(4)** and trimellitic anhydride **(5)** are commercial products, but their worldwide production capacities are an order of magnitude smaller than for terephthalic acid and its dimethyl ester. Isophthalic acid is used primarily in the production of unsaturated polyesters and as a comonomer in saturated polyesters. Trimellitic anhydride is used mainly to make esters for high performance poly(vinyl chloride) plasticizers. Trimesic acid **(6)**, pyromellitic dianhydride **(7)**, and hemimellitic acid **(8)** have specialized commercial applications. The rest of the benzenepolycarboxylic acids are not available commercially.



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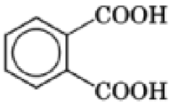

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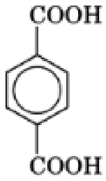

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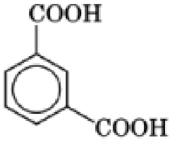

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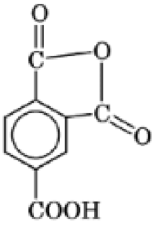

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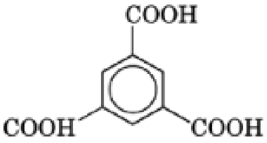

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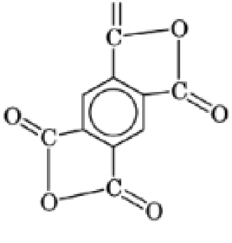

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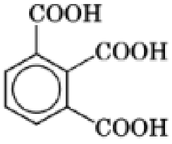
Table 1. Benzenepolycarboxylic Acids

IUPAC Name	Common name	CAS Registry Number	Formula weight
1,2-benzenedicarboxylic acid	phthalic acid	[88-99-3]	166.14
1,3-benzenedicarboxylic acid	isophthalic acid	[121-91-5]	166.14
1,4-benzenedicarboxylic acid	terephthalic acid	[100-21-0]	166.14
1,2,3-benzenetricarboxylic acid	hemimellitic acid	[569-51-7]	210.15
1,2,4-benzenetricarboxylic acid	trimellitic acid	[528-44-9]	210.15
1,3,5-benzenetricarboxylic acid	trimesic acid	[554-95-0]	210.15
1,2,3,4-benzenetetracarboxylic acid	mellophanic acid	[476-73-3]	254.16
1,2,3,5-benzenetetracarboxylic acid	prehnitic acid	[479-47-0]	254.16
1,2,4,5-benzenetetracarboxylic acid	pyromellitic acid	[89-05-4]	254.16
benzenepentacarboxylic acid		[1585-40-6]	298.17
benzenehexacarboxylic acid	mellitic acid	[517-60-2]	342.18



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1. Physical Properties

The physical properties of the acids, the most important anhydrides, and the full methyl esters are summarized in Tables 2, 3, and4. Detailed lists of physical properties for phthalic acid and its anhydride, terephthalic acid and dimethyl terephthalate, isophthalic acid, trimellitic acid and its anhydride, and pyromellitic acid and its dianhydride/ are provided under the sections describing these compounds.

2. Chemical Properties

The chemistry of benzenecarboxylic acids generally is the same as that of other carboxylic acids, which can be converted into esters, salts, acid chlorides, and anhydrides. Each carboxyl group can react separately, so that compounds in which carboxyl groups are converted into different derivatives can be prepared. Because there are aromatic hydrogens available in most of these acids, they also undergo reactions characteristic of the benzene nucleus. Some of the anhydrides have characteristic reactions.

2.1. Reactions of the Carboxyl Groups

Carboxyl groups in the ortho position spontaneously form a strainless five-membered ring when heated to give anhydrides as shown for **(8)**. Salts and esters (4) are readily formed as shown for **(4)** and **(5)**, respectively.

Table 2. Physical Properties of Benzenepolycarboxylic Acids

			Dissociation constants in aqueous solution, 25°C				[a]	Solubility, g/100 g water		Reference[b]		
Common name	Formula weight	Melting point, °C	pK_1	pK_2	pK_3	pK_4	ΔH_f° at 25°C kJ/mol	at 25°C	at 100°C	(1)	(2)	(3)
phthalic	166.14	211[c]	2.95	5.41			−782	0.7	19.0	H 791	04526	5:2740
isophthalic	166.14	384	3.62	4.60			−803	0.012	0.32	H 832	04527	3:1925
terephthalic	166.14	402[d]	3.54	4.46			−816	0.0017	0.033	H 841	04528	5:2949
hemimellitic[e]	210.15	197[c]	2.80	4.20	4.87		−1160	v sol	v sol	H 976	05571	1:331
trimellitic	210.15	238[c]	2.52	3.84	5.20		−1179	2.1	60	H 977	05572	1:331
trimesic	210.15	380	2.12	3.89	4.70		−1190	0.24	6.4	H 978	05573	1:332
mellophanic	254.16	241[c]	2.06	3.25	4.73	6.21	−1562	sol	v sol	H 977	05529	1:331
prehnitic	254.16	238	2.38	3.51	4.44	5.81	−1549			H 977	05530	1:331
pyromellitic	254.16	282	1.92	2.87	4.49	5.63	−1571	1.5	>30	H 977	05531	1:331
benzenepentacarboxylic[f]	298.17	228	1.80	2.73	3.97	5.25	−1930	sol	v sol	H 1006	05158	1:329
mellitic[g]	342.18	288[c]	1.40	2.19	3.31	4.78	−2299	sol	v sol	H 1008	04874	4:2067

[a] To convert J to cal, divide by 4.184.

[b] For Ref. 1, the letter and number refer to the section and paragraph; for Ref. 2, each compound is numbered; for Ref. 3, the numbers refer to the volume and page.

[c] Decomposes at mp.

[d] Sublimes.

[e] Hemimellitic acid usually is handled as the dihydrate; formula $\mathrm{wt} = 246.18$, $\mathrm{mp} = 191^\circ\mathrm{C}$, decomposes.

[f] $\mathrm{p}K_5 = 6.46$.

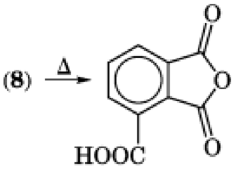
[g] $\mathrm{p}K_5 = 5.89$; $\mathrm{p}K_6 = 6.96$.

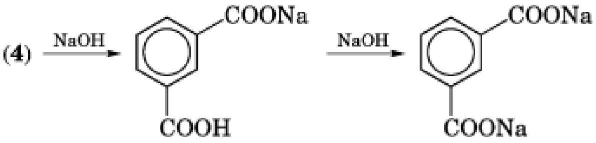
Table 3. Physical Properties of Anhydrides of the Benzenepolycarboxylic Acids

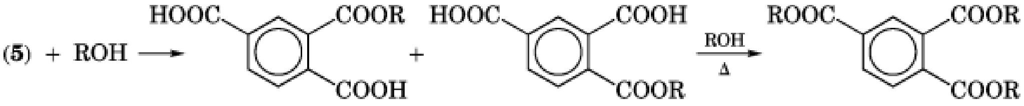
Common name	CAS Registry Number	Formula weight	Mp, °C	Bp, °C
phthalic anhydride	[85-44-9]	148.12	131	284.5
hemimellitic anhydride	[3786-39-8]	192.14	196	
trimellitic anhydride	[552-30-7]	192.14	168	390
mellophanic dianhydride	[4435-60-3]	218.13	198	
pyromellitic dianhydride	[89-32-7]	218.13	285	390
benzene-1,2,4,5-tetracarboxylic dianhydride-3-carboxylic acid	[59025-58-0]	262.14		
mellitic trianhydride	[4253-24-1]	288.14	320 dec	

Table 4. Melting Points of the Full Methyl Esters of Benzenepolycarboxylic Acids

Common name	CAS Registry Number	Formula weight	Mp, °C
dimethyl phthalate	[131-11-3]	194.19	0–2
dimethyl isophthalate	[1459-93-4]	194.19	67
dimethyl terephthalate	[120-61-6]	194.19	141
trimethyl hemimellitate	[2672-57-3]	252.23	102
trimethyl trimellitate	[2459-10-1]	252.23	−13
trimethyl trimesate	[2672-58-4]	252.23	146
tetramethyl mellophanate	[3451-02-3]	310.27	133
tetramethyl prehnitate	[3034-97-7]	310.27	112
tetramethyl pyromellitate	[635-10-9]	310.27	143 dec
pentamethyl benzenepentacarboxylate	[3327-06-8]	368.30	148
hexamethyl mellitate	[6237-59-8]	426.34	188



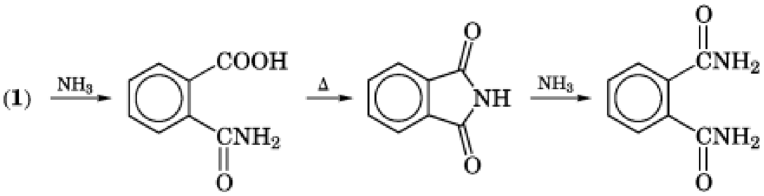




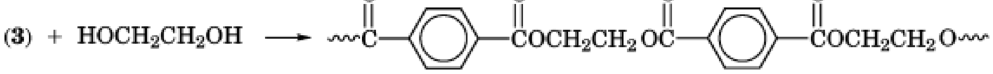
Because each carboxyl group reacts at a different rate with alcohol, a mixed diester or triester can be prepared if the reactions of the acid with ROH and R′OH are carried out sequentially.

Acid chlorides can be formed by reaction with thionyl chloride:

The carboxylic acids react with ammonia and with primary amines in a similar manner:

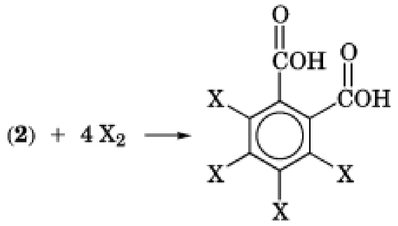


Condensation polymerization also occurs and essentially is the sole reason for the commercial existence of terephthalic acid:

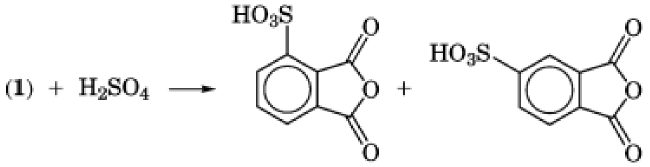


2.2. Reactions of the Benzene Ring

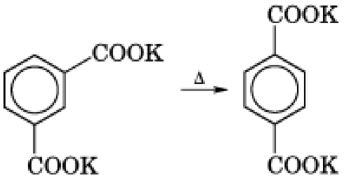
The benzene rings of the benzenepolycarboxylic acids undergo halogenation:



and sulfonation:



When mixed phthalic acids are converted to their dipotassium salts, they can be thermally or catalytically rearranged to the para isomer. This rearrangement is known as the Henkel reaction:



2.3. Other Reactions

Phthalic anhydride **(1)** undergoes condensation to form anthraquinone derivatives:

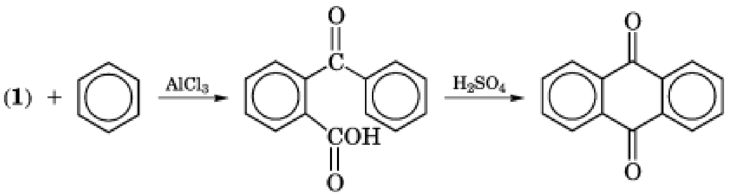
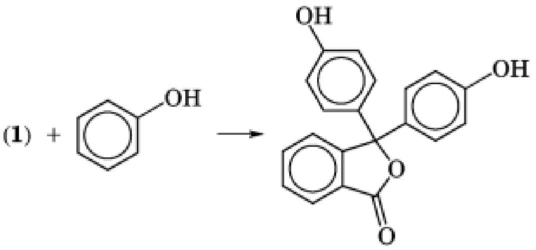


Table 5. Physical Constants of Phthalic Acid and Phthalic Anhydride

Property	Phthalic acid	Phthalic anhydride
mp, °C	211 dec	131
bp, °C		284.5 sub
triple point, °C		131
heat of vaporization at 131°C, kJ/mol[a]		65.3
specific gravity at 4°C	1.593	1.527
specific heat, J/(kg·K)[a]		
at 300°C	1138	1009
200°C	800	763
90°C	433	422
heat of combustion at 25°C, kJ/mol[a]	−3224	−3259
heat of formation at 25°C, kJ/mol[a]	−784	−460
heat of sublimation at 131°C, kJ/mol[a]		88.70
heat of fusion at 131°C, kJ/mol[a]		22.93

[a] To convert J to cal, divide by 4.184.

Also, **(1)** undergoes condensation with phenol to form phenolphthalein:



Phthalic anhydride reacts with urea and metal diacetates to form metal phthalocyanines (qv).

3. Phthalic Acid and Phthalic Anhydride

The first of the benzene polycarboxylic acids to become a commercial product was phthalic acid, mostly in the form of the anhydride. The anhydride is obtained by the catalytic vapor-phase air oxidation of *o*-xylene or naphthalene. The IUPAC name of phthalic anhydride is 1,3-isobenzofurandione [85-44-9].

3.1. Physical and Chemical Properties

Tables 5, 6, and 7 list some of the physical and chemical properties of phthalic acid and its anhydride.

3.2. Manufacture and Processing

Until World War II, phthalic acid and, later, phthalic anhydride, were manufactured primarily by liquid-phase oxidation of suitable feedstocks. The favored method was BASF's oxidation of naphthalene [91-20-3] by sulfuric acid in the presence of mercury salts to form the anhydride. This process was patented in 1896. During World War I, a process to make phthalic anhydride by the oxidation of naphthalene in the vapor phase over a

Table 6. Physical Properties of Liquid Phthalic Anhydride

Temperature, °C	Vapor presure, kPa[a]	Density, g/cm^3	Viscosity, mPas(= cP)
132°C	0.8		1.19
135°C	0.9	1.215	
140°C	1.2	1.208	
160°C	2.7	1.188	
180°C	5.5	1.166	
197°C	10	1.278	0.94
200°C	10.7	1.145	
220°C		1.131	0.55
240°C		1.103	
284.5°C	101		

[a] To convert kPa to mm Hg, multiply by 7.5.

Table 7. Solubilities of Phthalic Acid and Phthalic Anhydride[a]

Solvent	Phthalic acid	Phthalic anhydride
water		
at 25°C	0.7	0.6
at 100°C	19.0	16.5
at 150°C	200	147
ethanol at 18°C	11.7	
diethyl ether at 15°C	0.7	
carbon disulfide at 20°C		0.7
formic acid (95 wt %) at 20°C		4.7
pyridine at 20–25°C		80
acetic acid (glacial) at 100°C	12.0	

[a] g/100 g solvent.

vanadium and molybdenum oxide catalyst was developed in the United States (5). Essentially the same process was developed independently in Germany, with U.S. patents being granted in 1930 and 1934 (6, 7).

Naphthalene (qv) from coal tar continued to be the feedstock of choice in both the United States and Germany until the late 1950s, when a shortage of naphthalene coupled with the availability of xylenes from a burgeoning petrochemical industry forced many companies to use *o*-xylene [95-47-6] (8). Air oxidation of 90% pure *o*-xylene to phthalic anhydride was commercialized in 1946 (9, 10). An advantage of *o*-xylene is the theoretical yield to phthalic anhydride of 1.395 kg/kg. With naphthalene, two of the ten carbon atoms are lost to carbon oxide formation and at most a 1.157-kg/kg yield is possible. Although both are suitable feedstocks, *o*-xylene is overwhelmingly favored. Coal-tar naphthalene is used in some cases, eg, where it is readily available from coke operations in steel mills (see Steel). Naphthalene can be produced by hydrodealkylation of substituted naphthalenes from refinery operations (8), but no refinery-produced napthalene is used as feedstock. Alkylnaphthalenes can be converted directly to phthalic anhydride, but at low yields (11, 12).

3.2.1. Fixed-Bed Vapor-Phase Oxidation of o-Xylene

Well in excess of 90% of the phthalic anhydride produced is obtained by oxidizing *o*-xylene in the vapor phase over a fixed bed of catalyst. In the 1960s, there were two types of fixed-bed processes, low temperature/low space velocity, and high temperature/high space velocity. Catalyst development resulted in higher allowable space velocities for the low temperature case while high yields were maintained. Consequently, use of the low temperature process which runs at $<400°C$ has predominated. Processes of this type are operated by companies listed in Table 9 as well as BASF, Alusuisse, Huels, BP Chemical, and Bayer. A typical flow sheet

Table 8. Estimated World Capacities for Phthalic Anhydride, 10^3 t

	Year		
Location	1976	1988	1993
North America	440	560	455
Western Europe	610	860	950
Far East	280	760	1090
Eastern Europe/Mid-East	200	750	660
South America	35	305	350
Total	*1565*	*3235*	*3505*

Table 9. U.S. Capacities for Phthalic Anhydride, 10^3 t

	Year	
Company	1980	1993
Exxon	59	118
Aristech	91	104
Stepan	91	79
Koppers	147	79
Sterling	0	75
BASF	68	0
Monsanto	118	0
Chevron	23	0
Allied	18	0
Total	*615*	*455*

is shown in Figure 1. A commercially viable plant must operate at high selectivity of at least 75 mol % with a feed *o*-xylene concentration of 60 g/m^3 (13). This concentration is above the lower explosion limit of 43 g/m^3 (14). The catalyst should last at least three years (13).

Some reactors are designed specifically to withstand an explosion (14). The multitube fixed-bed reactors typically have ca 2.5-cm inside-diameter tubes, and heat from the highly exothermic oxidation reaction is removed by a circulating molten salt. This salt is a eutectic mixture of sodium and potassium nitrate and nitrite. Care must be taken in reactor design and operation because fires can result if the salt comes in contact with organic materials at the reactor operating temperature (15). Reactors containing over 20,000 tubes with a 45,000-ton annual production capacity have been constructed.

The catalyst combines two essential ingredients found in earlier catalysts, vanadium oxide and titanium dioxide, which are coated on an inert, nonporous carrier in a layer 0.02- to 2.0-mm thick (13, 16). Other elements such as phosphorus are also used. Ring-shaped supports are used instead of spherical supports to give longer catalyst life, less pressure drop though the reactor, and higher yields (17, 18). Half rings are even better and allow more catalyst to be loaded (18).

There are thermal gradients along the catalyst tube, and a temperature maximum or hot spot develops which tends to place limits in the feed rate owing to possible catalyst damage and to decrease the yield. Various methods are used to reduce this hot spot, including two or more catalysts in series to limit the reaction initially. This use of catalysts could be higher rubidium or potassium concentrations in the first bed, with higher phosphorus levels in the second (19). Different phosphorus levels may also be used (20). Placing varying concentrations of inert packing along the tube length is also possible (18, 21, 22). Another method is to have two temperature zones, the first zone being cooler than the second (23).

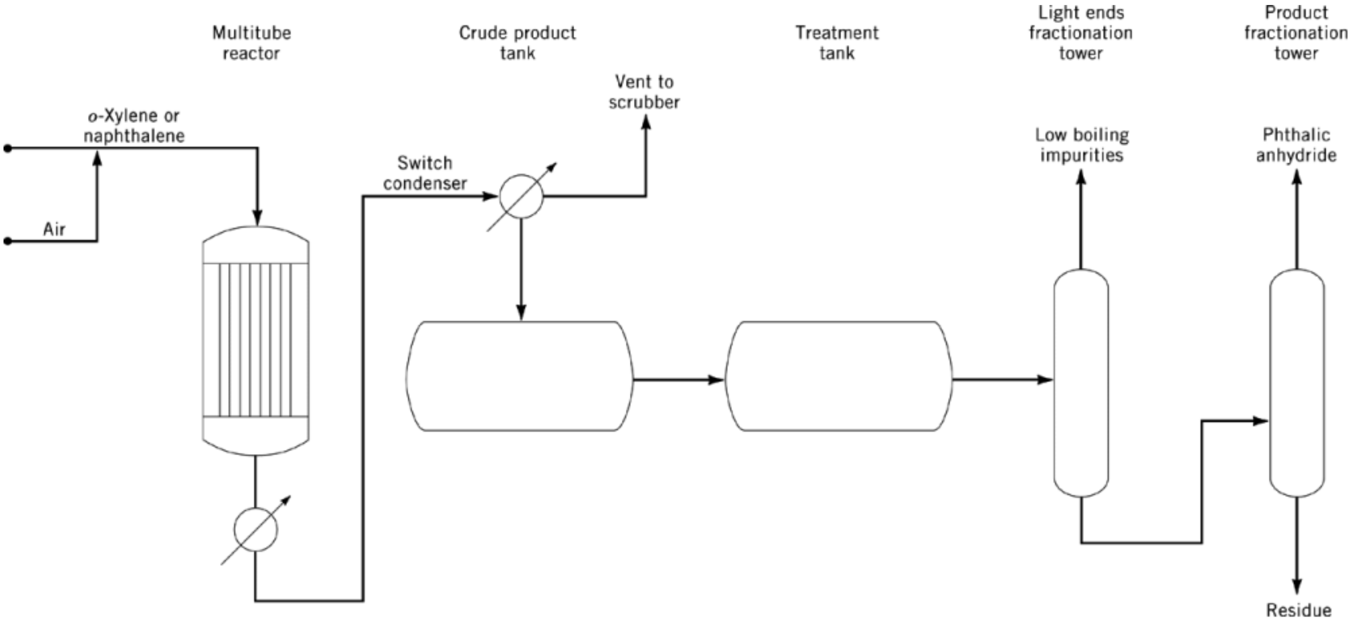


Fig. 1. A typical fixed-bed process for phthalic anhydride.

3.2.2. Fixed-Bed Vapor-Phase Oxidation of Naphthalene

A silica gel or silicon carbide support is used for catalyst involved in the oxidation of naphthalene. The typical naphthalene oxidation catalyst is a mixture of vanadium oxide and alkali metal sulfate on the silica support. Some changes, such as the introduction of feed vaporizers, are needed to handle a naphthalene feed (14), but otherwise the equipment is the same.

3.2.3. Fluidized-Bed Vapor-Phase Oxidation

Fluidized-bed reactors were developed for oxidation of napthalene to phthalic anhydride and started operation in 1945 (24). In the 1990s, there are very few napthalene-feed fluidized-bed plants that are operational, located in the Far East only, and even there possibly only one. There are none using *o*-xylene. The silica gel catalyst support used in the fluidized bed interferes with the oxidation of *o*-xylene (25). Conversely, the titanium dioxide support used in *o*-xylene oxidation does not stand up well in the reactor. As with all fluidized-bed processes, catalyst attrition must be considered and minimized. Commercial plants use a low activity catalyst on silica gel at 340–385°C operating temperature. In spite of the seemingly low activity and temperature, all the naphalene is converted in the bed, although not necessarily to phthalic anhydride (25). The intense mixing in fluidized beds offers several advantages, as illustrated by the complete oxidation noted above. It also minimizes problems of flammability, especially with coal-tar naphthalenes, which may contain pyrophoric substances (26). The agitated catalyst particles quickly dissipate heat, and some catalyst fines in the reactor effluent further prevent buildup of potentially dangerous substances. The capacity of one fluidized-bed process can be adjusted by the operating pressure, which, in turn, changes the time in which the feedstock is in contact with the catalyst (27).

3.2.4. Liquid-Phase Oxidation of o-Xylene

A commercial plant which oxidized *o*-xylene in the liquid phase using acetic acid solvent and a cobalt/manganese/bromine catalyst system was operated in France starting about 1965 but was shut down in the late 1970s. This type of process is described in the section on terephthalic acid. The reaction produces phthalic acid, which is then dehydrated to the anhydride. Yields from this process are high; the yield to phthalic anhydride is at least 90 mol % vs 80 mol % or less for vapor-phase oxidation. Capital costs are high owing to the metallurgy required.

3.2.5. Phthalic Anhydride Recovery and Purification

The accepted method of recovering phthalic anhydride from vapor-phase oxidation processes is first to recover some of the heat of oxidation, eg, by using the reactor effluent to generate steam. Then the vapors are passed through automatically cycled switch condensers where up to 99.5% of the phthalic anhydride solidifies on cooled, finned tubes. Maintaining the condenser temperature above the 131°C phthalic anhydride melting point results in unacceptable product losses. Choice of temperature is critical, because only about 1 vol % of the reactor effluent is phthalic anhydride, 8 vol % water (13). Water condensation must be avoided to prevent formation of the acid from the anhydride. At a preset time, the switch condenser in use is taken off line and another one started. The off-line condenser is then charged with hot oil to melt the anhydride into a storage tank (28). In fluidized-bed processes, the phthalic anhydride concentration is high enough to first condense some 50% of it as a liquid before going to the switch condensers (24). Vent gases from the switch condensers contain maleic anhydride, citraconic acid, and benzoic acid as well as phthalic anhydride. The gas can be scrubbed with water or incinerated, either thermally or catalytically (23), before being released into the atmosphere. The water used to scrub the gases contains these mixed acids, and maleic anhydride can be recovered (29). However, the economics prohibit recovery in view of the high cost of capital equipment vs the small amount of maleic anhydride obtained.

The crude phthalic anhydride is subjected to a thermal pretreatment or heat soak at atmospheric pressure to complete dehydration of traces of phthalic acid and to convert color bodies to higher boiling compounds that can be removed by distillation. The addition of chemicals during the heat soak promotes condensation reactions and shortens the time required for them. Use of potassium hydroxide and sodium nitrate, carbonate, bicarbonate, sulfate, or borate has been patented (30). Purification is by continuous vacuum distillation, as shown by two columns in Figure 1. The most troublesome impurity is phthalide (1(3)-isobenzofuranone), which is structurally similar to phthalic anhydride. Reactor and recovery conditions must be carefully chosen to minimize phthalide contamination (31). Phthalide [87-41-2] is also reduced by adding potassium hydroxide during the heat soak (30).

3.3. Production, Storage, and Shipment

All U.S. producers have at least a 75,000-t annual capacity. There are some small plants and small producers in Europe with less than 20,000-t capacity. These are gradually being shut down, and any new plant would have to be large in order to reach economies of scale in the present market (ca 1995), which is highly competitive.

Storage and shipment are preferably molten. Insulated and heated tanks are used, as are insulated rail tank cars and tank trucks. In the United States, rail tank cars can hold about 84 t, and trucks about 20 t. The molten form can be handled and pumped in bulk form, and as a result is priced lower than the solid. Solid phthalic anhydride is available as flake in 1-t and 0.5-t super sacks, and 22.7-kg multiwall bags.

3.4. Economic Aspects

The estimated world production of phthalic anhydride was 2.7×10^6 t in 1993 (32), well below the 3.5×10^6-t capacity. As seen in Table 8, production has shifted strongly from the developed to the developing areas of the world since the mid-1970s, especially to the Far East. Western Europe includes everything except the former Soviet Union. Eastern Europe/Mid-East then includes the former Soviet Union as well as Pakistan and India,

Table 10. Specifications for Phthalic Anhydride

Property	Specification[a]	Test method
freezing point, °C	130.9[b]	cryoscopy
molten color		
initial, at 250°C, APHA	20	colorimetry
stability, 2 h at 250°C, APHA	60	colorimetry
phthalic anhydride, %	99.7*b*	gas chromatography
phthalic acid, %	0.2	titration
maleic acid, %	0.05	gas chromatography
naphthoquinone, %	0.0002	gas chromatography

[a] Values are maximum unless otherwise noted.
[b] Minimum.

a region which has also experienced high growth. Closing of many old, small, and environmentally less clean plants is expected to continue in the late 1990s.

U.S. capacity is 455 × 10^3 t among five producers, as shown in Table 9 (33). All U.S. producers use *o*-xylene as a feedstock, although Koppers can switch to coal-tar naphthalene. Europe has 20 producers operating 25 plants, 18 of which use *o*-xylene. Demand growth in North America has averaged less than 3% annually since 1981. Prices in 1992 were \$0.77–0.95/kg for molten, and \$0.82–1.01/kg for flake (33).

3.5. Specifications and Standards

Typical specifications for phthalic anhydride are given in Table 10. All specifications are measures of purity. Solidification point is a sensitive indicator of absolute purity, and is a key specification. Another key specification is molten color stability, which is the color after being held at 250°C for two hours. This test ensures acceptable color after shipment in molten form and detects the presence of impurities that can cause discoloration at elevated temperatures. Phthalic acid level is a monitor of how well moisture has been excluded during storage and shipment.

3.6. Analytical and Test Methods

Measurement of the solidification point using a highly sensitive thermometer and of APHA color by comparison of molten samples to APHA standards is straightforward. Specific impurities are measured by gas chromatography. A nonaqueous titration is used to determine phthalic acid content.

3.7. Health and Safety Factors

Phthalic anhydride is a severe irritant to the eyes, respiratory tract, and skin, especially to moist tissue (34–36). The solid may burn skin tissue if it is in contact with it for a significant amount of time. Repeated exposure may result in asthma, irritation of mucous membranes, and diseases of the respiratory tract and digestive organs (37, 38). Contact with skin or the eyes should be followed immediately by washing with large quantities of water. Goggles, a face shield, and heavy leather gauntlets should be worn by workers handling phthalic anhydride. Phthalic anhydride and phthalic acid are toxic, though not strongly so; the LD_{50} by oral ingestion for rats is 4 g/kg for the anhydride and 7.9 g/kg for the acid (39).

There are explosion hazards with phthalic anhydride, both as a dust or vapor in air and as a reactant. Table 11 presents explosion hazards resulting from phthalic anhydride dust or vapor (40, 41). Preventative safeguards in handling solid phthalic anhydride have been reported (15). Water, carbon dioxide, dry chemical,

Table 11. Flammability and Explosivity of Phthalic Anhydride

Property	Value
Dust cloud	
explosibility index	>10
ignition sensitivity	13.8
ignition temperature, °C	650
minimum igniting energy, J[a]	0.015
minimum explosive concentration, g/L	0.015
relative flammability, % inert	
by furnace ignition	>90
by spark ignition	90
limiting oxygen concentration, %	
by furnace ignition	11
by spark ignition	14
explosive severity	1.6
dust concentration, g/L	
0.1 g/L dust concentration	269
0.5 g/L dust concentration	496
maximum pressure, kPa[b]	
rate of pressure rise, 10^3 kPa/s[b]	
6.9, average	9.7
9.0, max	29.0
Molten liquid	
flash point, °C	
open cup	165
closed cup	151
autoignition temperature, °C	584
Vapor	
explosive limits in air at 140–285°C, vol %	
lower	1.7
upper	10.5

[a] To convert J to cal, divide by 4.184.
[b] To convert kPa to psi, multiply by 0.145.

or foam may be used to extinguish the burning anhydride. Mixtures of phthalic anhydride with copper oxide, sodium nitrite, or nitric acid plus sulfuric acid above 80°C explode or react violently (39).

3.8. Uses

Phthalic anhydride is used mainly in plasticizers, unsaturated polyesters, and alkyd resins (qv). Phthalic plasticizers consume 54% of the phthalic anhydride in the United States (33). The plasticizers (qv) are used mainly with poly(vinyl chloride) to produce flexible sheet such as wallpaper and upholstery fabric from normally rigid polymers. The plasticizers are of two types: diesters of the same monohydric alcohol such as dibutyl phthalate, or mixed esters of two monohydric alcohols. The largest-volume plasticizer is di(2-ethylhexyl) phthalate [117-81-7] which is known commercially as dioctyl phthalate (DOP) and is the base to which other plasticizers are compared. The important phthalic acid esters and their physical properties are listed in Table 12. The demand for phthalic acid in plasticizers is naturally tied to the growth of the flexible poly(vinyl chloride) market which is large and has been growing steadily.

The second largest use at 21% is for unsaturated polyester resins, which are the products of polycondensation reactions between molar equivalents of certain dicarboxylic acids or their anhydrides and glycols. One component, usually the diacid or anhydride, must be unsaturated. A vinyl monomer, usually styrene, is a

Table 12. Properties of Phthalic Acid Esters

Ester	CAS Registry Number	Mp, °C	Bp, °C	Specific gravity/°C
dimethyl phthalate	[131-11-3]	0–2	282	1.192/20°C
diethyl phthalate	[84-66-2]	−4	296	1.118/20°C
diallyl phthalate	[131-17-9]	65	156–175[a]	1.120/20°C
dibutyl phthalate	[84-74-2]	−40	340	1.042/25°C
butyl cyclohexyl phthalate	[84-64-0]		189–222[b]	1.076/25°C
diamyl phthalate	[131-18-0]	< − 55	342	1.022/25°C
butyl benzyl phthalate	[85-68-7]		370	1.111/25°C
dicyclohexyl phthalate	[84-61-1]	58–65	212–218[b]	1.148/20°C
butyl octyl phthalate	[84-78-6]	< − 50	225[b]	0.993/25°C
butyl decyl phthalate	[89-19-0]	−50	220[b]	0.991/25°C
di(*n*-octyl) phthalate	[117-84-0]	−25	220–248[a]	0.978/20°C
diisooctyl phthalate	[27554-26-3]	< − 50	228–239[b]	0.986/20°C
di(2-ethylhexyl) phthalate	[117-81-7]	−46	231[b]	0.986/20°C
n-octyl *n*-decyl phthalate	[119-07-3]	−28	250[b]	0.970/25°C
isooctyl isodecyl phthalate	[42343-35-1]	−48	235–248[a]	0.967/25°C
diisodecyl phthalate	[19269-67-1]	−48	255[b]	0.961/25°C

[a] At 533 Pa (4.0 mm Hg).

[b] At 666 Pa (5.0 mm Hg).

diluent which later serves to fully cross-link the unsaturated portion of the polycondensate when a catalyst, usually a peroxide, is added. The diacids or anhydrides are usually phthalic anhydride, isophthalic acid, and maleic anhydride. Maleic anhydride provides the unsaturated bonds. The exact composition is adjusted to obtain the required performance. Resins based on phthalic anhydride are used in boat hulls, tubs and spas, construction, and synthetic marble surfaces. In most cases, the resins contain mineral or glass fibers that provide the required structural strength. The market for the resins tends to be cyclical because products made from them sell far better in good economic times (see Polyesters, unsaturated).

The manufacture of alkyd resins (qv), which are obtained by the reactions of polybasic acids or anhydrides, polyhydric alcohols, and fatty oils and acids, consumes about 17% of the phthalic anhydride demand. While materials such as maleic anhydride, isophthalic acid, and fumaric acid can also be used, phthalic anhydride is the most important. The resin provides a binder for coatings that are applied for either protection or decoration. Air quality concerns have put alkyd resins under pressure from water-based coatings which do not emit organic vapors upon drying.

3.9. Derivatives

The remaining uses are better considered as derivatives of phthalic anhydride and consume less than 10% of the demand, but they provide a diverse group of products. Anthraquinone(qv), a starting reagent for a number of dye intermediates, is manufactured by heating phthalic acid and benzene with sulfuric acid as a catalyst. Use of chlorobenzene instead of benzene results in 2-chloroanthraquinone, a dye. Examples of dyes derived from phthalic anhydride are phthalocyanine blues, quinoline yellow, and anthracene brown (see Dyes and dye intermediates). Another use for phthalic anhydride is in the production of isatoic anhydride [118-48-9], a raw material used in the production of saccharin. Tetrachloro- and tetrabromophthalic anhydrides are manufactured by the reaction of phthalic anhydride with chlorine and bromine, respectively, at high temperatures. The halogenated forms impart fire resistance to polyester resins, polyurethane foams, and surface coatings. Phenolphthalein [77-09-8] is the condensation product of phthalic anhydride and phenol in the presence of a dehydrating agent, and is a pH indicator and laxative. Pesticides and anthranilic acid [118-92-3] can be made from phthalimide which is in turn produced from phthalic anhydride.

Table 13. Physical Constants of Terephthalic Acid and Dimethyl Terephthalate

Property	Terephthalic acid	Dimethyl terephthalate
mp, °C	427[a]	140.65
bp, °C		284
triple point, °C	427	140.65
heat of fusion, kJ/mol[b]		31.6
heat of vaporization, kJ/mol[b]		57.3
cryoscopic constant, mol %/°C		2.28
specific gravity at 25°C	1.522	1.283
specific heat, J/(kg·K)[b]	1202	1400[c]
sublimation point, °C	404	
heat of combustion at 25°C, kJ/mol[b]	−3198	−4685
heat of formation at 25°C, kJ/mol[b]	−816	−711
heat of sublimation, kJ/mol[b]	142	88.4

[a] Sealed tube.

[b] To convert J to cal, divide by 4.184.

[c] At 50°C.

Table 14. Vapor Pressures of Terephthalic Acid[a] and Dimethyl Terephthalate[b]

Temperature, °C		
Terephthalic acid	Dimethyl terephthalate	Pressure, kPa[c]
303°C	148°C	1.3
353°C	210°C	13.3
370°C	233°C	26.7
387°C	258°C	53.3
404°C	284°C	101.3

[a] Solid.

[b] Liquid.

[c] To convert kPa to mm Hg, multiply by 7.5.

4. Terephthalic Acid and Dimethyl Terephthalate

Purified terephthalic acid and dimethyl terephthalate are used as raw materials for the production of saturated polyesters. During 1993, the combined worldwide production of purified terephthalic acid plus dimethyl terephthalate exceeded 14×10^6 t (42), which is 80% of the total benzenepolycarboxylic acid production. Terephthalic acid is also produced in technical or crude grades which are not pure enough for manufacture of poly(ethylene terephthalate). In almost all cases, the technical-grade material is immediately converted to purified terephthalic acid or dimethyl terephthalate, which together are the articles of commerce.

4.1. Physical and Chemical Properties

Tables 13, 14, 15, 16, and 17 contain the more important physical and some chemical properties of terephthalic acid and dimethyl terephthalate.

4.2. Manufacture and Processing

Terephthalic acid and dimethyl terephthalate did not become large-volume industrial chemicals until after World War II. Imperial Chemical Industries in the United Kingdom in 1949 and Du Pont in the United States

Table 15. Physical Properties of Liquid and Vapor Dimethyl Terephthalate

	Temperature, °C		
Property	150°C	200°C	250°C
Liquid			
density, g/cm^3	1.068	1.022	0.976
viscosity, mPa·s(= c P)	0.965	0.595	0.405
specific heat, J/(kg·K)[a]	1921	2030	
Vapor			
viscosity, mPa·s(= cP)	0.0086	0.0096	0.0107
specific heat, J/(kg·K)*a*	1290	1390	1500

[a] To convert J/(kg·K) to cal/(g·°C), divide by 4184.

Table 16. Solubilities of Terephthalic Acid[a]

	Temperature, °C				
Solvent	25°C	120°C	160°C	200°C	240
in water	0.0017	0.07	0.37	1.8	8.5
in glacial acetic acid	0.013	0.17	0.50	1.5	4.3
in methanol	0.1	2.1	2.9	15.0	
in dimethylformamide	6.7				
in dimethyl sulfoxide	19.0				

[a] g/100 g solvent.

Table 17. Solubilities of Dimethyl Terephthalate[a]

Solvent	At 25°C	At 60°C	At bp of solvent, (bp, °C)
in ethylene glycol	0.8		
in diethylene glycol			400 245°C
in methanol	1.0	5.7	
in carbon tetrachloride	1.5	3.6	25 77°C
in ethyl ether	1.6		
in acetone			25 56°C
in methyl ethyl ketone	1.6	12.5	
in benzene	2.0	14.0	
in ethyl acetate	3.5	16.0	
in butyl acetate			400 120°C
in toluene	4.3	10.4	>100 111°C
in ethylenediamine			25 117°C
in dioxane	7.5	28.5	
in chloroform	10.0	23.0	

[a] g/100 g solvent.

in 1953 commercialized fibers made from poly(ethylene terephthalate). Dimethyl terephthalate and ethylene glycol were the comonomers used by both companies (see Fibers, polyester).

Initial production of the dimethyl terephthalate started with the oxidation of *p*-xylene to terephthalic acid using nitric acid; both companies reportedly used similar technology (43–45). Versions of the nitric acid oxidation process, which has been abandoned commercially, involved the use of air in the initial oxidation step to reduce the consumption of nitric acid (44, 46, 47). The terephthalic acid was then esterified with methanol to produce dimethyl terephthalate, which could be purified by distillation to the necessary degree (48).

p- Xylene [106-42-3] is still the only feedstock used for either product. However, purified terephthalic acid has replaced dimethyl terephthalate as the leading terephthalate source for poly(ethylene terephthalate). About 75% of poly(ethylene terephthalate) production worldwide is based on the purified acid, and this percentage is increasing as virtually no new dimethyl terephthalate capacity is being built. Terephthalic acid offers distinct cost and product quality advantages to the manufacturer of poly(ethylene terephthalate). This has led to its use in almost all new polymer plants. Specifically, polyester processes that are based on dimethyl terephthalate must have equipment for recovery of methanol, which is the by-product of the transesterification with ethylene glycol. Use of the pure acid produces water as a by-product of direct esterification. In addition, terephthalic acid provides a higher yield of polyester per kilogram of starting feedstock. While excess ethylene glycol is needed in both processes, the percentage of excess needed is much smaller using terephthalic acid, so less in the way of recovery and recycle process equipment is required. The need for transesterification catalysts with dimethyl terephthalate introduces metals into the polyester which can cause undesirable side reactions (49, 50).

Purified terephthalic acid became commercially available from Amoco Chemical Co. in 1965, by which time a considerable polyester industry based on dimethyl terephthalate had already developed. The Amoco process involves purification of crude terephthalic acid by a separate step to attain the high product purity required for polyester manufacture. The Amoco technology is the most-used worldwide, but other processes have been developed and are operating commercially.

4.3. Technical-Grade Terephthalic Acid

All technical-grade terephthalic acid is produced by catalytic, liquid-phase air oxidation of *p*-xylene. Several processes have been developed, but they all use acetic acid as a solvent and a multivalent heavy metal or metals as catalysts. Cobalt is always used. In the most popular process, cobalt and manganese are the multivalent heavy-metal catalysts and bromine is the renewable source for free radicals (51, 52). This catalyst system is used in about 70% of the *p*-xylene oxidations, and the percentage is increasing as new plants almost invariably employ it. Process conditions are highly corrosive owing to the acetic acid and bromine, and titanium must be used in contact with some parts of the process.

Figure 2 is a typical flow sheet for the process using technology originally developed and licensed by Amoco and Mitsui Petrochemical. Acetic acid, air, *p*-xylene, and catalyst are fed continuously into an oxidation reactor that is maintained at 175–225°C and 1500–3000 kPa ($\sim 15-30$ atm). Air is added in amounts in excess of stoichiometric requirements to minimize formation of by-products. The oxidation is exothermic to the extent of 2×10^8 J/kg of *p*-xylene reacted, and this heat is removed by allowing the acetic acid solvent to boil. The vapor is condensed and refluxed to the reactor, and this sets the temperature–pressure relationship. The condensing vapor is used to generate steam, which is employed as a heat source in other parts of the process. Two moles of water are formed per mole of *p*-xylene reacted. The residence time is 30 min–2 h depending on the process. More than 98% of the *p*-xylene is converted and the yield to terephthalic acid is at least 95 mol % in modern plants. Further, this is on a once-through basis. The near exclusive selection of this technology for all new capacity follows from these yield and conversion values.

The effluent from the reactor is a slurry of terephthalic acid because it dissolves to a limited extent in almost all solvents, including the acetic acid–water solvent used here. This slurry passes through a surge vessel that operates at a lower pressure than the reactor. More terephthalic acid crystallizes and the slurry is then ready to be processed at close to atmospheric conditions. The terephthalic acid crystals are recovered by filtration, washed, dried, and conveyed to storage, from which they are in turn fed to the purification step.

This is called a technical or crude grade of terephthalic acid, but the purity is typically greater than 99%. It is not, however, pure enough for the poly(ethylene terephthalate) made from it to reach the required degree of polymerization. The main impurity is 4-formylbenzoic acid [619-66-9], which is incompletely oxidized *p*-xylene and is monofunctional with regard to esterification. 4-Formylbenzoic acid is usually referred to as 4-carboxybenzaldehyde (4-CBA) in the industry.

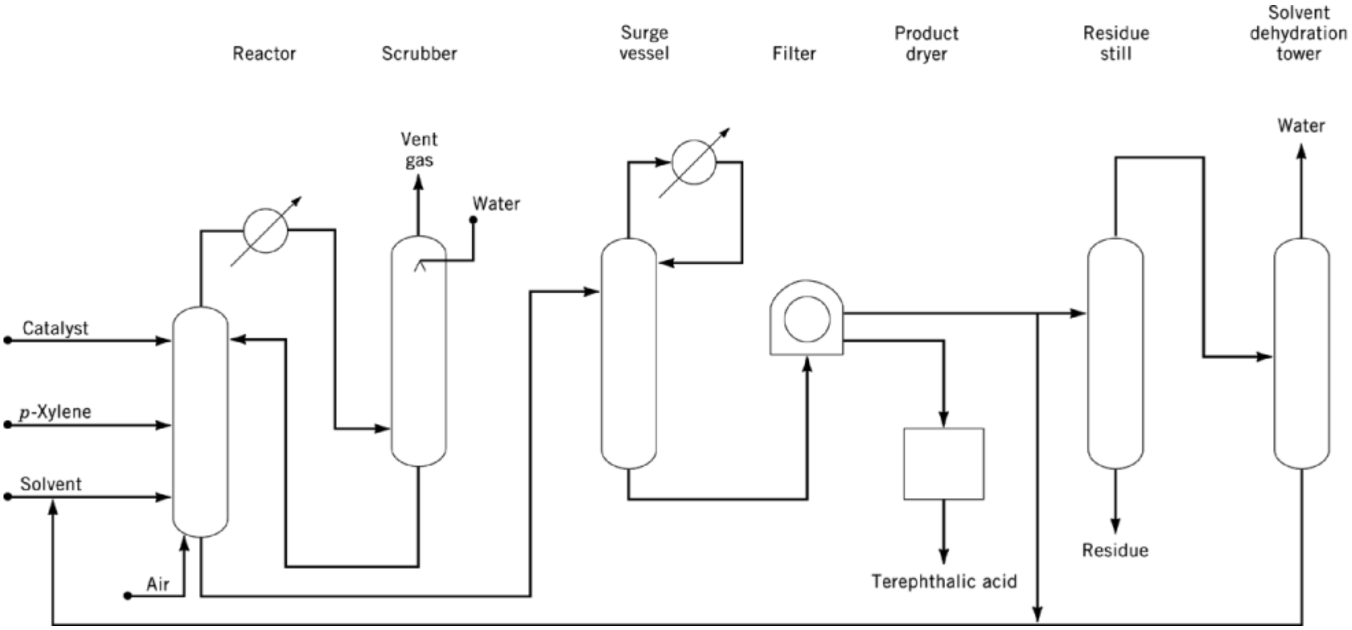


Fig. 2. Terephthalic acid production by catalytic, liquid-phase air oxidation of *p*-xylene.

Water formed in the reaction as well as some undesirable by-products must be removed from the acetic acid solvent. Therefore, mother liquor from the filter is purified in a residue still to remove heavies, and in a dehydration tower to remove water. The purified acetic acid from the bottom of the dehydration tower is recycled to the reactor. The water overhead is sent to waste treatment, and the residue still bottoms can be processed for catalyst recovery. Alternatively, some mother liquor from the filter can be recycled directly to the reactor.

Cleanup of waste streams from the process has been highly developed and is widely practiced commercially. The nitrogen and unused oxygen from the oxidation reactor are scrubbed to recover and reuse valuable components. The gas can then pass to a catalytic oxidation step, followed by a second scrubber to remove trace components and thereby meet the most demanding environmental requirements (53). Wastewater is treated by aerobic oxidation with specially acclimated bacteria, again in order to meet any environmental requirements. Alternatively, an anaerobic wastewater treatment process has been developed and commercially installed which produces much less waste sludge, requires less energy, and in addition produces methane, which can be burned for energy recovery (54).

Acetaldehyde can be used as an oxidation-promoter in place of bromine. The absence of bromine means that titanium metallurgy is not required. Eastman Chemical Co. has used such a process, with cobalt as the only catalyst metal. In that process, acetaldehyde is converted to acetic acid at the rate of 0.55–1.1 kg/kg of terephthalic acid produced. The acetic acid is recycled as the solvent and can be isolated as a by-product. Reaction temperatures can be low, 120–140°C, and residence times tend to be high, with values of two hours or more (55). Recovery of dry terephthalic acid follows steps similar to those in the Amoco process. Eastman has abandoned this process in favor of a bromine promoter (56). Another oxidation promoter which has been used is paraldehyde (57), employed by Toray Industries. This leads to the coproduction of acetic acid. 2-Butanone has been used by Mobil Chemical Co. (58).

4.3.1. Henkel Rearrangement of Benzoic Acid and Phthalic Anhydride

Henkel technology is based on the conversion of benzenecarboxylic acids to their potassium salts. The salts are rearranged in the presence of carbon dioxide and a catalyst such as cadmium or zinc oxide to form dipotassium terephthalate, which is converted to terephthalic acid (59–61). Henkel technology is obsolete and is no longer practiced, but it was once commercialized by Teijin Hercules Chemical Co. and Kawasaki Kasei Chemicals Ltd. Both processes followed a route starting with oxidation of napthalene to phthalic anhydride. In the Teijin process, the phthalic anhydride was converted sequentially to monopotassium and then dipotassium *o*-phthalate by aqueous recycle of monopotassium and dipotassium terephthalate (62). The dipotassium *o*-phthalate was recovered and isomerized in carbon dioxide at a pressure of 1000–5000 kPa ($\sim 10 - 50$ atm) and at 350–450°C. The product dipotassium terephthalate was dissolved in water and recycled as noted above. Production of monopotassium *o*-phthalate released terephthalic acid, which was filtered, dried, and stored (63, 64).

Mitsubishi Chemical Industries, Ltd. practiced a Henkel II technology starting with toluene to produce benzoic acid. Reaction of benzoic acid with potassium hydroxide resulted in potassium benzoate, which was subjected to a disproportionation reaction to produce dipotassium terephthalate and benzene. Dipotassium terephthalate reacted with sulfuric acid, and the resulting terephthalic acid was recovered by filtration and drying (65, 66). Here, dipotassium sulfate was the by-product.

4.3.2. Polymer-Grade Dimethyl Terephthalate

4.3.2.1. Hercules/Dynamit Nobel Process. On a worldwide basis, the Hercules Inc./Dynamit Nobel AG process is the dominant technology for the production of dimethyl terephthalate; the chemistry was patented in the 1950s (67–69). Modifications in commercial practice have occurred over the years, with several variations being practiced commercially (70–72). The reaction to dimethyl terephthalate involves four steps, which alternate between liquid-phase oxidation and liquid-phase esterification. Two reactors are used. First, *p*-xylene is oxidized with air to *p*-toluic acid in the oxidation reactor, and the contents are then sent to the second reactor for esterification with methanol to methyl *p*-toluate. The toluate is isolated by distillation and returned to the first reactor where it is further oxidized to monomethyl terephthalate, which is then esterified in the second reactor to dimethyl terephthalate.

Figure 3 is a flow diagram which gives an example of the commercial practice of the Dynamit Nobel process (73). *p*-Xylene, air, and catalyst are fed continuously to the oxidation reactor where they are joined with recycle methyl *p*-toluate. Typically, the catalyst is a cobalt salt, but cobalt and manganese are also used in combination. Titanium or other expensive metallurgy is not required because bromine and acetic acid are not used. The oxidation reactor is maintained at 140–180°C and 500–800 kPa (5–8 atm). The heat of reaction is removed by vaporization of water and excess *p*-xylene; these are condensed, water is separated, and *p*-xylene is returned continuously (72, 74). Cooling coils can also be used (70).

The oxidation reactor effluent and methanol are sent to the esterification reactor, which operates at up to 250°C and a pressure sufficient to maintain the liquid phase. This latter is about 2500 kPa (25 atm). The oxidation products are converted to methyl *p*-toluate and dimethyl terephthalate without a catalyst. Excess methanol is supplied, and steam and vaporized methanol are removed and enter a methanol recovery column. The esterification products flow to a crude ester column, which separates the toluate from the terephthalate. The overhead stream of methyl *p*-toluate is returned to the oxidation reactor, and the bottoms stream of dimethyl terephthalate goes to a primary distillation. The distillate is dissolved in methanol, crystallized, and solid dimethyl terephthalate is recovered. The dimethyl terephthalate can then be either recrystallized or distilled to yield the highly pure material needed for the polyesterification reaction.

The overall yield of the process is at least 87 mol %, and 2.3 mol of methanol per mole of final product are needed, an excess of 15% over the 2.0 theoretical amount. The methanol can be recycled from the manufacture

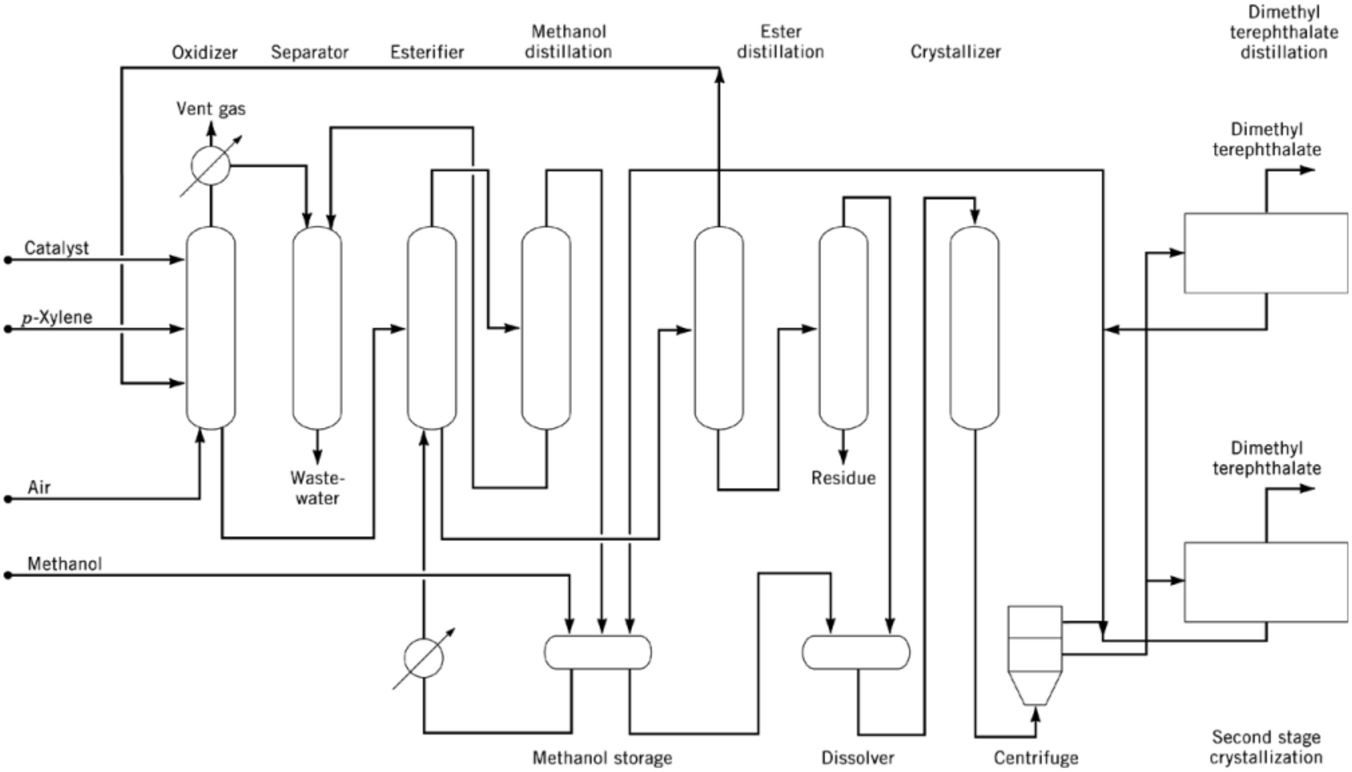


Fig. 3. The Dynamit Nobel process for dimethyl terephthalate (73).(Courtesy of Gulf Publishing Co.)

of poly(ethylene terephthalate). Reported utilities consumptions per kilogram of product are 1.2 kg of 1400-kPa steam, 420 kJ of boiler fuel, and 0.5kW·h of electricity (72).

4.3.3. Esterification of Terephthalic Acid

Esterification of terephthalic acid is also used to produce dimethyl terephthalate commercially, although the amount made by this process has declined. Imperial Chemical Industries, Eastman Kodak, Amoco, Toray, Mitsubishi, and Mitsui Petrochemical have all developed processes. Esterification (qv) generally uses a large excess of methanol in a liquid process at 250–300°C. The reaction proceeds rapidly without a catalyst, but metal catalysts such as zinc, molybdenum, antimony, and tin can be used. Conversion to dimethyl terephthalate is limited by equilibrium, but yields of 96% have been reported (75, 76).

The crude dimethyl terephthalate is recovered and purified by distillation in most processes. Although distillation (qv) is generally a powerful separation technique, the mode of production of the terephthalic acid determines its impurity content, which in turn may make purification by distillation difficult. Processes resulting in the alteration of the impurities by catalytic treatment have been developed so that distillation can perform the necessary purification.

4.3.4. Polymer-Grade Terephthalic Acid

The processes described earlier for production of terephthalic acid do not yield products pure enough for use as raw materials in the production of polyester. However, polymer-grade terephthalic acid is produced through the use of a separate purification process. It is also produced by modifying the liquid-phase oxidation of

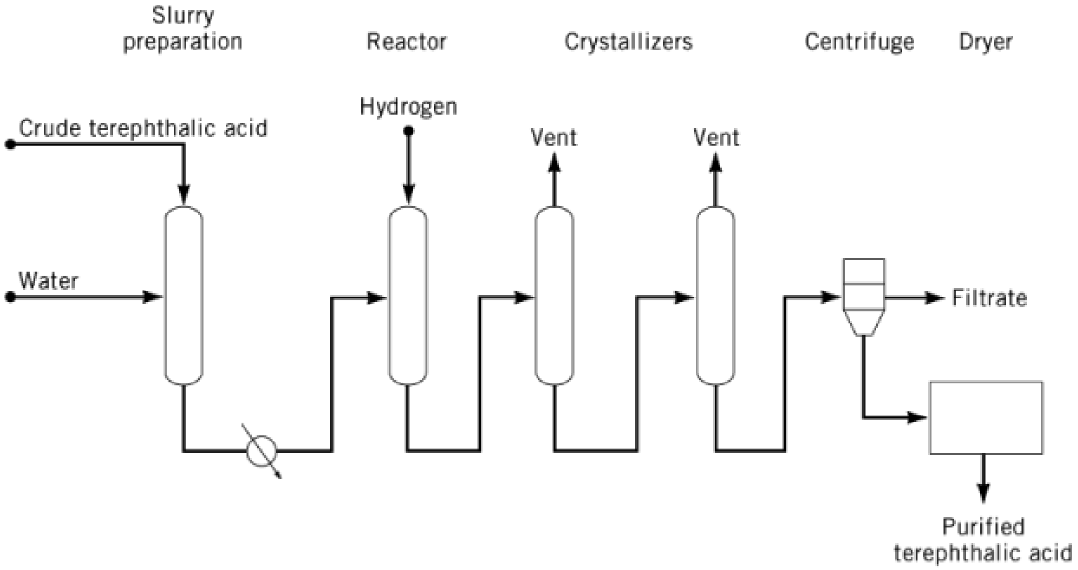


Fig. 4. The Amoco purification process for polymer-grade terephthalic acid.

p-xylene, and it can also be made by modifying the Henkel process. Most polymer-grade terephthalic acid made by modifying the liquid-phase oxidation process is used captively by the producing company or an affiliate, but some is sold on the open market. Polymer-grade terephthalic acid is also produced by hydrolyzing purified dimethyl terephthalate. Here too, though, the producing company also makes poly(ethylene terephthalate) and uses most of it captively.

4.3.5. Amoco Purification Process

The Amoco process is used to purify terephthalic acid produced by the bromine-promoted air oxidation of *p*-xylene. The main impurity in the oxidation product is 4-formylbenzoic acid] [619-66-9] and the Amoco process removes this to less than 25 ppm. Metals and colored organic impurities are also almost completely removed by the purification.

A flow diagram of the continuous process is presented in Figure 4 (77, 78). Crude terephthalic acid and water are fed to a mixing tank to form a slurry of at least 15 wt % terephthalic acid. The slurry is pumped to heat exchangers, which raise the slurry temperature sufficiently for the terephthalic acid to dissolve. The solution flows through a hydrogenation reactor that contains a palladium-on-carbon support catalyst. Hydrogen is added to the reactor, where it dissolves in the feed solution. Reactor temperature is held above the partial pressure of steam to maintain a liquid phase. In the reactor, 4-formylbenzoic acid is hydrogenated to *p*-toluic acid, and various colored impurities are hydrogenated to colorless products. The catalyst is highly selective; the loss of terephthalic acid by carboxylic acid reduction or ring hydrogenation is less than 1%. The overall effect of the hydrogenation is conversion of impurities to forms which remain in the mother liquor during the subsequent crystallization step. The terephthalic acid is purified by crystallization in a series of vessels where the pressure and therefore the temperature is sequentially decreased (79). As was noted above, impurities remain in the mother liquor for the most part. The purified terephthalic acid crystals are recovered by centrifugation or filtration, followed by drying of the wet cake. Overall yield of a white, free-flowing powder is greater than 98%.

4.3.6. Modifications of Processes Based on Air Oxidation of p-Xylene

Since the mid-1970s, starting in Japan, several companies have developed oxidation processes to yield relatively pure forms of terephthalic acid without a separate purification. These products, normally called medium purity terephthalic acids, contain 200–300 ppm 4-formylbenzoic acid and trace amounts of acetic acid and thus do not meet normal specifications for the highest purity grades available (80, 81).

Processes for medium purity terephthalic acid have been developed by Mitsubishi, Toray, Maruzen Oil Co., Kuraray Yuka Co., Ltd., and Eastman Chemical, among others. As commercially practiced by Mitsubishi Kasei, the oxidation of *p*-xylene in acetic acid with a cobalt–manganese–bromine catalyst is performed, followed by a further oxidation in a second vessel at a higher temperature of 235–290°C. Addition of more catalyst may also be done (82). The higher temperature and longer residence times afforded by a second reactor allow digestion of crystals with consequent release of some 4-formylbenzoic acid molecules. As the 4-formylbenzoic acid enters the solution, it can be oxidized to terephthalic acid. The more intense oxidation also results in more *p*-xylene and acetic acid being converted to carbon oxides (82). After completion of the reaction, the terephthalic acid crystals are separated by centrifugation or filtration and dried.

Eastman Chemical Co. uses only cobalt and bromine, and lower temperature oxidations are held at 175–230°C (83). Solution of 4-formylbenzoic acid is obtained by using hydroclones to replace the mother liquor from the first oxidation with fresh acetic acid. A residence time of up to 2 h is used in order to allow for sufficient digestion to take place and to reduce the 4-formylbenzoic acid content to 40–270 ppm (83). Recovery of dry terephthalic acid is as described above.

4.3.7. Hydrolysis of Dimethyl Terephthalate

Hoechst Celanese and Formosa Chemical Fibers Corp. produce a polymer-grade terephthalic acid by hydrolysis of high purity dimethyl terephthalate. Hüls-Troisdorf AG licenses a process with this step (70). Hydrolysis occurs at 260–280°C and 4500–5500 kPa (45–55 atm) in a hydrolysis reactor without catalysis. The overhead methanol and water vapor is separated and the methanol is returned to the dimethyl terephthalate section for reuse. The reactor liquid is crystallized, cycloned, washed, and further cooled. Finally, the slurry is centrifuged and dried. The product has less than 25 ppm of 4-formylbenzoic acid and very low levels of other impurities. There may be several hundred parts per million of monomethyl terephthalate, which is incompletely hydrolyzed dimethyl terephthalate.

4.3.8. Production, Storage, and Shipment

Modern terephthalic acid plants usually produce at least 250×10^3 t annually. The relatively low selling price dictates large plants so that economies of scale can be realized, and the huge worldwide demand makes plants of this size commercially viable. Storage of terephthalic acid is in silos, and the preferred method for dimethyl terephthalate storage is molten in insulated and heated tanks. The huge-volume use of these chemicals means that bulk shipment is preferred. Rail hopper cars or hopper trucks for terephthalic acid or insulated rail tank cars or tank trucks for dimethyl terephthalate are used where possible. Further, the high purity requirements make dedicated containers highly desirable to prevent cross-contamination. One-ton bags are used for terephthalic acid and the pellet form of dimethyl terephthalate. For shipment by sea and some by truck, the containerized method is often used. The containers are either 6 or 12 m long (20 or 40 ft), and can be loaded with either 20 one-ton bags or fitted with a one-piece polyethylene liner with 20 t blown directly into the lined container.

4.3.9. Economic Aspects

Terephthalic acid and dimethyl terephthalate are usually sold under long-term contracts. Pricing information is at times published but actual contract prices are not revealed. Price data published in 1992 were $0.60/kg for terephthalic acid and $0.57/kg for dimethyl terephthalate (42). The price is mainly influenced by the price of

Table 18. World Capacities[a] for Terephthalic Acid/Dimethyl Terephthalate, 10^3 t

	Year		
Location	1980	1988	1993
North America	3,950	4,420	4,530
Western Europe	1,740	2,270	2,550
Far East	1,460	3,200	6,210
Eastern Europe/Mid-East	600	640	1,100
South America	170	180	190
Total	*7,920*	*10,710*	*14,580*
TA/DMT ratio	37/63	56/44	72/28

[a] Values are estimated.

Table 19. United States Capacities for Terephthalic Acid/Dimethyl Terephthalate, 10^3 t

	Year		
Company	1980	1988	1992
Amoco[a]	1250	1450	1540
Du Pont[b]	900	925	880
Eastman[b]	650	670	680
Cape Industries[b]	630	635	635
Total	*3430*	3680	3735

[a] TA only.
[b] TA and DMT.

p-xylene. The price of terephthalic acid is more than dimethyl terephthalate because a kilogram of it produces 17% more polyester. The price of dimethyl terephthalate takes this factor plus a credit for the methanol generated during polyester production into consideration.

Capacity figures for terephthalate feedstocks are given in Tables 18 and 19 (42, 84, 85). Healthy growth has characterized the terephthalate market since its inception after World War II, and this growth is projected to continue. Based on announced capacity expansions, most of the growth will occur for purified terephthalic acid (TA), with dimethyl terephthalate (DMT) capacity remaining essentially flat or declining as some dimethyl terephthalate plants are converted to produce medium-purity terephthalic acid. The medium-purity component will gain slightly. Terephthalic acid output and dimethyl terephthalate output were equal in 1985, but terephthalic acid will contribute over 80% of the total after the year 2000. Also seen in Table 18 is the rapid expansion of capacity in the Far East, where much of the world's garment sewing is concentrated. This expansion will continue. As in the phthalic anhydride tables, Eastern Europe/Mid-East includes areas ranging from the former Soviet Union to as far east as India.

U.S. capacities, given in Table 19, show considerable stability both as to the producers and the amount produced. There have been no entrances or exits from the producer list since the 1970s. Amoco is totally a merchant supplier, whereas the other producers are poly(ethylene terephthalate) producers who exclusively or mostly satisfy their own requirements.

Amoco Chemical is the principal producer of terephthalic acid, with 18% of the world capacity in 1992. Joint ventures of Amoco add another 19%. Other significant producers of polymer-grade terephthalic acid are Imperial Chemical Industries, Mitsubishi Kasei, and Mitsui Petrochemical with 9, 8, and 5%, respectively. Several producers of poly(ethylene terephthalate) have back integrated by licensing polymer-grade terephthalic acid technology. Medium purity terephthalic acid is mainly produced by Mitsubishi Kasei and Eastman and their licensees. Dimethyl terephthalate is primarily produced by Hoechst in Europe and Hoechst-Celanese,

Table 20. Specifications for Polymer-Grade Terephthalic Acid

Property	Specification	Test method
acid number, mg KOH/g	675 ± 2	titration
ash, ppm	15 max	combustion
total significant metals,[a] ppm	9 max	atomic absorption or inductively coupled plasma
4-formylbenzoic acid, ppm	25 max	liquid chromatograph
p-toluic acid, ppm	125 ± 45	capillary electrophoresis
moisture, wt %	0.2 max	Karl Fischer
5% dimethylformamide soln color, APHA	10 max	colorimetry

[a] Mo, Cr, Ni, Co, Fe, Ti, and Mn.

Table 21. Specifications for Dimethyl Terephthalate

Property	Specification	Test method
freezing point, °C	140.62 min	cryoscopy
molten color, APHA	25 max	colorimetry
color stability, 4 h at 175°C, APHA	25 max	colorimetry
aldehyde ester, ppm	30 max	gas chromatography
acid number, mg KOH/g	0.03 max	nonaqueous titration

Eastman, and Du Pont in the United States. Eastman and Du Pont have converted some dimethyl terephthalate capacity to a polymer-grade terephthalic acid. There are several small, older plants, primarily in Europe. Hoechst-Celanese and Formosa Chemical Fiber hydrolyze some dimethyl terephthalate to polymer-grade terephthalic acid.

4.3.10. Specifications and Standards

Polymer-grade terephthalic acid must conform to strict standards of purity because of the demanding nature of the polyesterification process. There are no industry-wide standards which can be considered international or official, but all polymer-grade terephthalic acid generally conforms to specifications and has typical analyses, as given in Table 20. There is some movement to express specifications as a target and range to ensure product consistency, as opposed to allowing, for example, any value below a certain maximum.

Polymer-grade terephthalic acid is over 99.9 wt % pure, exclusive of some residual water which has a specification. With this degree of purity, impurity contents are usually given instead of total purity. A purity measurement is acid number, which refers to the milligrams of potassium hydroxide needed to titrate 1 g of terephthalic acid, and is theoretically 675.5.

Equally strict purity requirements apply to dimethyl terephthalate, as shown in Table 21. Freezing point is a sensitive measure of purity and can be measured to at least 0.01°C. This is used for dimethyl terephthalate but not for terephthalic acid, which does not melt at atmospheric pressure. Because dimethyl terephthalate is preferentially handled in a hot, molten form, color stability and acid number are important. These reflect product resistance to oxidation, discoloration, and thermal degradation. Acid number is a measure of the residual unesterified carboxylic acid groups.

4.4. Analytical and Test Methods

The acid number of terephthalic acid discussed above is a titration of a sample dissolved in pyridine, using a sodium or potassium hydroxide titrant. However, specifications on certain impurities are so strict that this test cannot, as a practical matter, be failed. Its use has been discontinued by some manufacturers.

Ash in terephthalic acid refers to the residue left after combustion of the sample. Ash consists of oxides of trace metals, which are determined individually by atomic absorption or inductively coupled plasma. A Karl Fischer titration is specific for the water content.

4-Formylbenzoic acid and *p*-toluic acid are determined by high performance liquid chromatography or capillary electrophoresis. Gas chromatography can be used for the aldehyde ester content of dimethyl terephthalate, this being the counterpart of 4-formylbenzoic acid in terephthalic acid.

Terephthalic acid is pure white, and molten dimethyl terephthalate is colorless. Impurities or degradation products can be yellow or brown, so the darkness of either a solution of terephthalic acid in dimethylformamide or molten dimethyl terephthalate can be compared to APHA color standards.

4.5. Health and Safety Factors

Terephthalic acid has a low order of toxicity. Inhalation by rats for 6 h/d, 5 d/wk for 4 wk produced no fatalities at a dust exposure level of 25 mg/m^3. The mean acute oral toxicity for rats is over 18 g/kg (86), and for mice over 6 g/kg (87). When terephthalic acid was fed as 3% of the diet to rats, urinary calculi formed in 90 d, some of which led to cancer. High doses of terephthalic acid lead to formation of calcium terephthalate at levels exceeding its solubility in urine. This insoluble material leads to the calculi and provides a threshold below which cancer is not observed (88). Normal precautions used in handling industrial chemicals should be observed with terephthalic acid. If ventilation is inadequate, a toxic-dust respirator should be used to avoid prolonged exposure.

Dimethyl terephthalate also shows low toxicity. Inhalation by rats of dust for 4 h/d for 58 d showed no toxicological effects at levels up to 86 mg/m^3 (89). Mean acute oral toxicity here was reported as over 6 g/kg for rats (90). Urinary calculi were also formed when dimethyl terephthalate was added at 3% to the diet of rats. As in the case of terephthalic acid, a toxic-dust respirator should be worn when ventilation is inadequate.

Molten dimethyl terephthalate burns if ignited. Dimethyl terephthalate vapor and dust, and terephthalic acid dust form explosive mixtures with air. The flammability limits for terephthalic acid and dimethyl terephthalate are given in Table 22. Dimethyl terephthalate is classified as a severe relative explosive hazard by the U.S. Bureau of Mines. Relative to phthalic anhydride, dimethyl terephthalate has a lower ignition sensitivity and a higher explosive severity (41, 42, 91). Fires can be extinguished with dry chemical, carbon dioxide, water or water fog, or foam. When dimethyl terephthalate is near flames, it may melt, flow, and contribute to the spreading of the fire.

4.6. Uses

Essentially all polymer-grade terephthalic acid and dimethyl terephthalate are used to make saturated polyesters, the great majority being poly(ethylene terephthalate). Poly(ethylene terephthalate) is employed to make fiber and is the largest-volume synthetic fiber in the world. Fiber use makes up 73% of worldwide poly(ethylene terephthalate) production (92). It is used for woven and knitted fabrics for clothing, draperies, upholstery, and carpeting. In clothing applications, it is usually blended with other fibers, primarily cotton (qv). Applications for high strength polyester continuous fibers are reinforcing cord for tires, V-belts, conveyor belts, and hoses (see Fibers, polyester).

Polyester film consumes 7% of production. When coated with a chemical emulsion, it is used as x-ray and microfilm; when coated with a magnetic emulsion, it is used for audio and video tapes; and when coated with an adhesive, it is used for wrapping and sealing tapes (see Films and sheeting).

The fastest growing application for poly(ethylene terephthalate) is in packaging, especially bottles. It currently accounts for 15% of production. U.S. FDA approval of polyester bottles has made it the polymer of choice for beverage and food applications. Polyester bottles have almost displaced glass carbonated beverage

Table 22. Flammability and Explosivity of Terephthalic Acid and Dimethyl Terephthalate

Property	Terephthalic acid	Dimethyl terephthalate
Dust cloud		
explosibility index	6.9	>10
ignition sensitivity	3	5.9
ignition temperature, °C	680	570
minimum igniting energy, J[a]	0.020	0.020
minimum explosive concentration, g/L	0.050	0.030
relative flammability, % inert		
by furnace ignition		>90
by spark ignition	80	>90
limiting oxygen concentration, %		
by furnace ignition at 850°C		12
by spark ignition	15	6
explosive severity	2.3	5.8
maximum pressure at concentration/L, kPa[b]		
0.1 g/L	227	372
0.5 g/L	503	634
1.0 g/L	579	641
2.0 g/L	531	724
average pressure rise at concentration, g/L, 10^3 kPa/s[b]		
0.1 g/L	3.4	15
0.5 g/L	12	21
1.0 g/L	9.6	13
2.0 g/L	4.1	11
maximum pressure rise at concentration, g/L, 10^3 kPa/s[b]		
0.1 g/L	14	62
0.5 g/L	41	83
1.0 g/L	26	41
2.0 g/L	8.3	34
Molten liquid		
flash point, Cleveland open cup, °C		146–147
fire point, Cleveland open cup, °C		155

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to psi, multiply by 0.145.

bottles due to their clarity, light weight, and shatter-resistant properties. Applications in food packaging are expanding rapidly for the same reasons (see Polyesters, thermoplastic).

Small amounts of polymer-grade terephthalic acid and dimethyl terephthalate are used as polymer raw materials for a variety of applications, eg, adhesives and coatings. They are also used to make high performance polymers or engineering resins. Poly(ethylene terephthalate) is itself an engineering resin, although one more widely used is poly(butylene) terephthalate, formed by reaction with 1,4-butanediol as the comonomer. 1,4-Cyclohexanedimethanol can be the comonomer. Terephthalic acid can also be the diacid in specialty nylons (see Polyamides). Specialty fibers, including certain high modulus aramid fibers, are made from terephthalic acid–dimethyl terephthalate derivatives.

4.7. Derivatives

In general, the esters of terephthalic acid derived from saturated alcohols undergo the same reactions as dimethyl terephthalate. Some physical properties of six of these esters are listed in Table 23. The di-*n*-butyl

Table 23. Properties of terephthalic acid ester and Terephthaloyl Chloride

Ester	CAS Registry Number	Mp, °C	Bp, °C (Pa)[a]	Specific gravity/°C
diethyl terephthalic acid esters	[636-09-9]	43–44	140–142 400 Pa	1.102
di-*n*-propyl tereph-thalic acid esters	[1962-74-9]	25	164–166 530 Pa	1.072
di-*n*-butyl tereph-thalic acid esters	[1962-75-0]	16.6–18.1	181–189 270 Pa	1.045
di(2-ethylhexyl) terephthalic acid esters	[6422-86-2]	−63.5	186–192 13 Pa	0.982
diisooctyl terephthalic acid esters	[4654-26-6]	amorphous solid	189–190 6.7 Pa	0.981
diallyl terephthalic acid esters	[1026-92-2]	−10	140–143 130 Pa	1.138
terephthaloyl chloride terephthalic acid esters	[100-20-9]	78	259	

[a] To convert Pa to mm Hg, divide by 133.3.

Table 24. Physical Constants and Properties of Isophthalic Acid

Property	Value
mp (closed tube), °C	345–348
vapor pressure, kPa[a]	
at 100°C	0.009
125°C	0.08
230°C	0.23
260°C	1.03
290°C	3.98
specific gravity at 4°C	1.53
heat of combustion at 25°C, kJ/mol[b]	−3202
heat of formation at 25°C, kJ/mol[b]	−802
heat of sublimation at 25°C, kJ/mol[b]	106.7

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert J to cal, divide by 4.184.

and di-2-ethylhexyl esters find use as plasticizers (qv). Terephthaloyl chloride, which is prepared by reaction of terephthalic acid and thionyl chloride, is used to prepare derivatives of terephthalic acid.

5. Isophthalic Acid

Like terephthalic acid, isophthalic acid is used as a raw material in the production of polyesters. Much of the isophthalic acid is used for unsaturated polyesters, whereas terephthalic acid is used almost exclusively in saturated (thermoplastic) polyesters. However, a considerable amount of isophthalic acid is used as a minor comonomer in saturated polyesters, where the principal diacid is terephthalic acid. The production volume of isophthalic acid is less than 2% that of terephthalic. Isophthalic acid was formerly produced in technical or crude grades and only a small amount was purified. Now, however, it is all purified to a standard similar to that of terephthalic acid.

5.1. Physical and Chemical Properties

Selected physical and chemical properties of isophthalic acid are shown in Tables 24 and 25.

Table 25. Solubilities of Isophthalic Acid[a]

	Temperature, °C				
Solvent	25°C	50°C	100°C	150°C	200°C
water	0.012	0.035	0.32	2.8	25
acetic acid (glacial)	0.23	0.41	1.3	4.3	11.1
methanol	2.5	4.0			
1-propanol	1.7	2.7	7.0		
dimethylformamide	37				
dimethyl sulfoxide	64				

[a] g/100 g solvent.

5.2. Manufacture and Processing

Isophthalic acid is synthesized commercially by the liquid-phase oxidation of *m*-xylene [108-38-3]. The chemistry of the oxidation is almost identical to that of *p*-xylene oxidation to terephthalic acid, and production facilities can be used interchangeably for these two dicarboxylic acids. However, because isophthalic acid is more soluble than terephthalic acid in reaction solvents as can be seen by comparing data in Tables 16 and 25, crystallization equipment is more important in isophthalic acid facilities.

Vapor phase oxidation of *m*-xylene is not satisfactory. Its vapor pressure, although low, is higher than that of terephthalic acid. However, isophthalic acid remains on the catalyst until it decomposes, resulting in poor or no yield. Summaries of patent literature describing oxidation of *m*-xylene with oxygen-containing gases, with nitric acid, with sulfur compounds, and by other routes are given in Reference 93.

Chevron Chemical Co. began commercial production of isophthalic acid in 1956. The sulfur-based oxidation of *m*-xylene in aqueous ammonia at about 320°C and 7,000–14,000 kPa produced the amide. This amide was then hydrolyzed with sulfuric acid to produce isophthalic acid at about 98% purity. Arco Chemical Co. began production in 1970 using air oxidation in acetic acid catalyzed by a cobalt salt and promoted by acetaldehyde at 100–150°C and 1400–2800 kPa (14–28 atm). The crude isophthalic acid was dissolved and recrystallized to yield a product exceeding 99% purity. The Arco technology was not competitive and the plant was shut down in 1974.

Amoco Chemical Co. used the cobalt–manganese–bromine catalyst system and, in 1958, started isophthalic acid production by oxidizing mixed xylenes and then separating the acids. Acid separation proved difficult, and mixed xylenes were not necessarily in proportion to the market demand for the acids. Feedstock to the oxidation was then switched so that the acid product had the same isomeric content as the xylene feed. Today, only pure *m*-xylene is fed. Formerly, an 85%:15% *m*-xylene–*p*-xylene mix was also used to make a mixed acid of the same proportion, which was sold and used commercially. Figure 2 and the description of the terephthalic acid process also represent the *m*-xylene-to-isophthalic acid process. The surge vessel in Figure 2 is a crystallizer as well as pressure let-down vessel in isophthalic acid production. The reaction is carried out at 170–230°C and 2000–3500 kPa (20–35 atm). As with terephthalic acid, the temperature–pressure relationship is determined by the boiling of the acetic acid/water solvent. This vaporization with reflux of the condensed solvent removes the heat of oxidation. The solubility of isophthalic acid gives a solution or a dilute slurry in the reactor depending on the temperature. The isophthalic acid must therefore be crystallized downstream.

Impurities in isophthalic acid from the oxidation process are analogous to those in terephthalic acid, eg, 3-formylbenzoic acid and *m*-toluic acid. Also present are other impurities such as benzoic acid and residual catalyst metals. All isophthalic acid made by this liquid-phase oxidation is now purified in a process similar to that used for terephthalic acid, as shown in Figure 4. Lower temperatures are used owing to the greater solubility of isophthalic acid vs terephthalic acid.

Table 26. Specifications for Isophthalic Acid

Property	Specification	Test method
isophthalic acid, wt %	99.8 min	polarography
ash, ppm	18 max	combustion
metals,[a] ppm	1–3 max	atomic absorption or inductively coupled plasma
3-formylbenzoic acid, ppm	25 max	polarography
m-toluic acid, ppm	150 max	esterification gas chromatography
moisture, wt %	0.1 max	Karl Fischer

[a] Al, Ca, Cr, Co, Fe, Mn, Mo, Ni, K, Na, and Ti.

Societa Italiana Serie Acetica Sintetica (SISAS) produces isophthalic acid commercially by a proprietary process (94, 95). They have installed purification facilities for hydrogenation and crystallization similar to those used for terephthalic acid.

5.3. Production, Storage, and Shipment

A plant of 50,000-t annual capacity could be considered viable for production of isophthalic acid, although no new plants have been constructed since the early 1980s. Storage of isophthalic acid is in silos. Shipment is in 22.7- and 25-kg bags, 0.5-t and 1-t bags, or hopper trucks. The far lower production quantity of isophthalic acid and its more varied applications vs terephthalic acid mean that high volume rail hopper cars are not used to any extent, and hopper truck shipment is also small.

5.4. Economic Aspects

Isophthalic acid in North America sold for $1.19– $1.32/kg in 1994, depending on the shipment method. The price of *m*-xylene plays a role, although not to the same extent as *p*-xylene in terephthalic acid. The far lower production volumes and smaller plant sizes for isophthalic acid do not give the same economies of scale.

Worldwide capacity available for production of isophthalic acid was about 270×10^3 t in 1994. About 200×10^3 t was actually produced. Amoco Chemical with plants in the United States and Europe is the principal producer, with over 60% of the production, and AGIC, an Amoco–Mitsubishi Gas Chemical joint venture in Japan, and SISAS produce the remainder.

5.5. Specifications and Standards

The specifications for isopthalic acid used by Amoco are given in Table 26. Because the same process is used, the specifications closely parallel those of terephthalic acid. These specifications are more demanding than those used before 1990, when a technical-grade isophthalic acid as produced by the oxidation process was available. Owing to the introduction of a water-based purification process including a recrystallization, impurity limits are much tighter. Purified isophthalic acid is over 99.9 wt % pure, exclusive of some residual water which has a specification. With this degree of purity, impurity contents are usually given instead of total purity.

5.6. Analytical and Test Methods

Ash in isophthalic acid refers to the residue left after combustion of the sample. Ash consists of oxides of trace metals that are determined individually by atomic absorption or inductively coupled plasma. A Karl Fischer titration is specific for the water content.

Table 27. Flammability and Explosivity of Isophthalic Acid

Property	Value
explosibility index	4.0
ignition sensitivity	3.3
ignition temperature, °C	700
minimum igniting energy, J[a]	0.025
minimum explosive concentration, g/L	0.035
limiting oxygen concentration (spark ignition), %	14

[a] To convert J to cal, divide by 4.184.

3-Formylbenzoic acid and *p*-toluic acid can be determined by high performance liquid chromatography. In some cases, polarography is used for 3-formylbenzoic acid and esterification gas chromatography for the *m*-toluic acid content.

Isophthalic acid is pure white, but some impurities can be yellow. A measure of these impurities is obtained by the yellowness, or b-value, of the sample.

5.7. Health and Safety Factors

Isophthalic acid has a low order of toxicity. Inhalation by rats for 4 h at 11.4 g/m^3 showed no toxicity. The LD$_{50}$ level for rats is high at 10.4 g/kg (96). As with terephthalic acid, isophthalic acid was found to form urinary tract calculi in rats in 90 d when it constituted 3% of their diet. This led to some cancer owing to the presence of the calculi. Some mild eye irritation is possible, so eye protection should be worn. Otherwise, normal precautions used in handling industrial chemicals should be observed with isophthalic acid.

Isophthalic acid dust forms explosive mixtures with air at certain concentrations. These concentrations and other information on burning and explosiveness of isophthalic acid dust clouds are given in Table 27 (40, 41). Fires can be extinguished with dry chemical, carbon dioxide, water or water fog, or foam.

5.8. Uses

About 35% of the isophthalic acid is used to prepare unsaturated polyester resins. These are condensation products of isophthalic acid, an unsaturated dibasic acid, most likely maleic anhydride, and a glycol such as propylene glycol. The polymer is dissolved in an inhibited vinyl monomer, usually styrene with a quinone inhibitor. When this viscous liquid is treated with a catalyst, heat or free-radical initiation causes cross-linking and solidification. A range of properties is possible depending on the reactants used and their ratios (97).

Because of higher raw material and manufacturing costs, isopolyesters are more expensive than phthalic anhydride-based polyesters. However, the isopolyesters have higher molecular weights; give improved water, chemical, and weathering resistance; and have higher heat-distortion temperatures. Most isopolyesters are used with glass fiber reinforcement. These include sheet molding compounds, bulk molding compounds, and filament windings. Uses for reinforced isopolyesters include storage tanks and piping, architectural panels for exterior or interior use, automobile body panels, swimming pools and spas, and boat hulls, including some over 45-m long. In particular, isopolyesters show much less blistering in boat hulls, owing to their greater hydrolytic stability. Applications of isopolyesters without reinforcement include gel coats, concrete coatings, and terrazzo glaze coats.

The second application of isophthalic acid, with about 30% of the output, is for alkyd coatings. Isophthalic alkyds are made by reaction of isophthalic acid and other polybasic acids such as trimellitic anhydride, polyhydric alcohols such as glycerol, and usually fatty oils or acids such as tall oil. These resins can be formulated into solvent-based, water-based, or solventless coatings for both commercial and consumer applications. As

Table 28. Properties of Isophthalic Esters and Isophthaloyl Chloride

Ester	CAS Registry Number	Mp, °C	Bp, °C (Pa)[a]	Specific gravity
dimethyl isophthlate	[1459-93-4]	66–68	155–159 1333 Pa	1.194
diethyl isophthlate	[636-53-3]	11.5	302	1.124
diisooctyl isophthlate	[137-89-3]		127–138 53 Pa	0.987
di(2-ethylhexyl) isophthlate	[137-89-3]		241 666 Pa	0.984
diallyl isophthlate	[1087-21-4]		150–152 120 Pa	0.114
diphenyl isophthlate	[744-45-6]	134–138		
isophthaloyl chloride isophthlate	[99-63-8]	43–44	276	1.388

[a] To convert Pa to mm Hg, divide by 133.3.

with isopolyesters, these coatings are more expensive than those made with phthalic anhydride, but they offer faster drying; higher hardness; and better resistance to weathering, marring, and high temperatures.

The third, and fastest growing, area of isophthalic acid use is in other types of polymers, primarily as a minor comonomer with terephthalic acid in saturated polyesters. Over 20% of the isophthalic acid is sold in this application. One rapidly expanding use is in polyester beverage bottles where addition of up to 3% isophthalic acid to the terephthalic acid allows faster production of more complex shapes. In this way, single piece bottles can be made, vs a round-bottomed bottle that needs a separate base cup. Fibers are also modified with isophthalic acid.

Isophthalic acid is also used in formulations for adhesives, inks (qv), wire enamels, and dental materials (qv). Copper isophthalate [10027-31-3] is an ingredient in algicides and fungicides (98).

5.9. Derivatives

Commercially significant derivatives of isophthalic acid are its diesters with saturated alcohols and isophthaloyl chloride. This derivation is similar to that of terephthalic acid. Some properties of these compounds are given in Table 28. Plasticizers form the main use of the diesters, these being the dimethyl, dioctyl, and di(2-ethylhexyl) isophthalates. Diallyl isophthalate is a cross-linking agent for high temperature resistant polybenzimidazoles. Isophthaloyl chloride is used in the manufacture of high temperature-resistant polyamide fibers, films, dyes, and protective coatings.

6. Trimellitic Acid and Trimellitic Anhydride

Of the three benzenetricarboxylic acids, only trimellitic acid as the anhydride is commercially produced in large volume, by liquid-phase air oxidation of either pseudocumene or dimethyl benzaldehyde. The pseudocumene oxidation is another variant of the cobalt–manganese–bromine catalyst in acetic acid solvent as described in the terephthalic acid section. The acid is available as a laboratory chemical (99). The IUPAC name of trimellitic anhydride is 5-isobenzofurancarboxylic acid (1,3-dihydro-1,3-dioxo).

Owing to the dual functional groups of acid and anhydride, trimellitic anhydride imparts performance enhancements to its end-use applications, many of which are similar to those of phthalic anhydride. In many cases, products made from trimellitic anhydride exhibit properties superior to those of phthalic anhydride. For example, trimellitate esters are used as plasticizers for poly(vinyl chloride) where higher permanency is required, especially at high temperatures. Accordingly, they are used for high temperature wire insulation and applications such as automobile interiors which become heated during summer months. Other important uses of trimellitic anhydride are solvent-borne and water-borne coatings, powder coatings, wire enamels used in electric motor and generator windings, alkyd resins, amide–imide polymers, and epoxy curing.

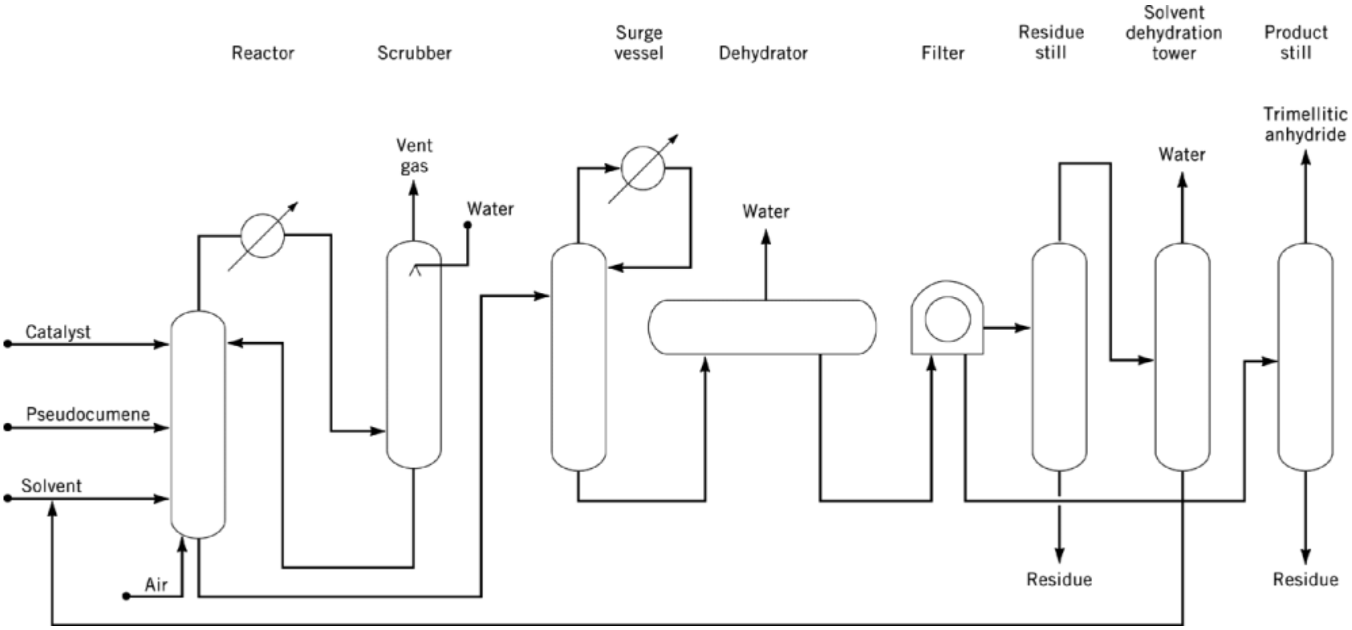


Fig. 5. The Amoco process for trimellitic anhydride.

6.1. Physical and Chemical Properties

Trimellitic acid and trimellitic anhydride are odorless white crystalline solids in their pure form. The acid is reasonably stable up to the melting point, where dehydration to the anhydride occurs. The anhydride reacts with atmopsheric moisture, even at room temperature, to revert to the acid. Physical properties of the acid and its anhydride are listed in Tables **??**–**??**.

6.2. Manufacture and Processing

Trimellitic anhydride has been commercially available only since the early 1960s. In theory, trimellitic acid could be obtained by oxidizing almost any 1,2,4-tri-substituted alkylbenzenes with a suitable oxidizing agent. Either nitric acid oxidation of pseudocumene (1,2,4-trimethylbenzene) [95-63-6] or a combination of liquid-phase air and nitric acid oxidation had been commercially practiced in Japan and in the Federal Republic of Germany in the 1960s. Those operations were discontinued in the early 1970s. A poor yield and the need for extensive purification to remove by-products made the processes uneconomical. Unlike vapor-phase oxidation of *o*-xylene to phthalic anhydride, vapor-phase oxidation of pseudocumene results in a poor trimellitic anhydride yield. A significant product from the vapor-phase oxidation is phthalic anhydride, as a result of an extensive decarboxylation.

Amoco Chemical Co. is the sole U.S. producer of trimellitic anhydride, with a 47,500-t/yr plant in Joliet, Illinois. The Amoco process is the liquid-phase air oxidation of pseudocumene using acetic acid as a solvent and a cobalt–manganese–bromine catalyst system (100–103). The oxidation process is much like that for terephthalic acid or isophthalic acid and is illustrated in Figure 5. Trimellitic acid is recovered from the oxidation reactor effluent by a suitable means, and the acetic acid solvent is sent to the solvent tower to remove the water of reaction and for recycling. Trimellitic acid is thermally dehydrated to form trimellitic anhydride and further purified by fractional distillation to obtain high purity trimellitic anhydride.

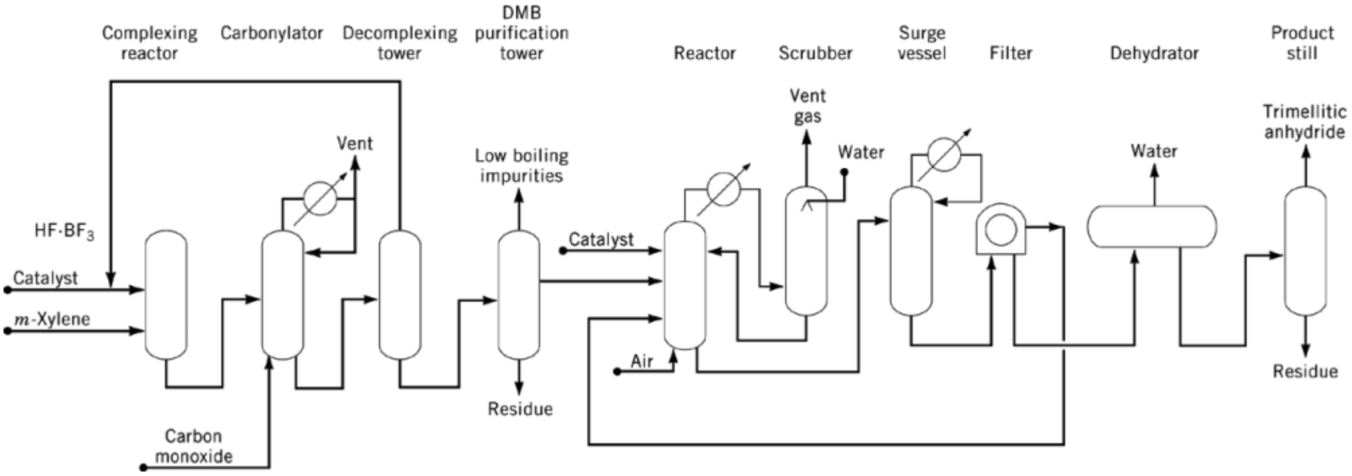


Fig. 6. The Mitsubishi Gas Chemical process for trimellitic anhydride. DMB = dimethylbenzaldehyde.

Mitsubishi Gas Chemical Co. of Japan started the production of trimellitic anhydride at their Mizushima Works in 1986 with a name plate capacity of 15×10^3 t/yr (104, 105). Pyromellitic anhydride is also produced from the same unit on a blocked out basis. Hence, the actual production of trimellitic anhydride is expected to be less than the stated capacity. The Mitsubishi Gas Chemical process for the manufacture of trimellitic anhydride starting from *m*-xylene is shown in Figure 6. *m*-Xylene is first carbonylated with carbon monoxide in the presence of boron trifluoride and hydrogen fluoride to form 2,4-dimethylbenzaldehyde. The 2,4-dimethylbenzaldehyde [15764-16-6] is decomplexed from the acids, purified, and oxidized to trimellitic acid. The air oxidation is carried out in the liquid phase using water as a solvent and manganese bromide as a catalyst along with hydrobromic acid promoter. Trimellitic acid is recovered from the reactor effluent and is subjected to normal dehydration and purification steps to obtain high quality trimellitic anhydride (106–108).

In 1991, Alusuisse Italia announced the construction of a 20×10^3 t/yr trimellitic anhydride unit at Bergamo, Italy (109) and commenced production in late 1994. A European patent application (110) assigned to Alusuisse suggests that the process used is very similar to that of Amoco, that is, pseudocumene is air oxidized in the liquid phase using heavy-metal catalysts and bromine. A number of other companies have shown interest in the production of trimellitic anhydride (111–113).

6.3. Production, Storage, and Shipment

Trimellitic anhydride is produced by Amoco, Mitsubishi Gas Chemical, and Alusuisse as described above. It is available only as flakes (114). It is packaged in 906- and 500-kg bulk fabric bags and 22.6-kg kraft bags for the U.S. domestic use, and in 25-kg kraft bags for export. All bags contain moisture-barrier liners to protect the anhydride from water during storage and shipping.

6.4. Economic Aspects

When trimellitic anhydride was introduced in semicommercial quantities in 1962, it was priced at \$1.19/kg. The price was reduced to \$0.55/kg as it became available in commercial quantities in 1968. The mid-1994 price was quoted as \$2.31/kg from Amoco, fob, the Joliet, Illinois plant. A price history is given in Table 29. Although trimellitic anhydride production and sales figures are not available, the published U.S. Tariff Commission's

Table 29. U.S. Trimellitic Anhydride Prices and Trimellitate Ester Production

Year	Trimellitic anhydride price, \$/kg	Trimellitate ester production, 10^3 t/yr
1975	0.77	7.3
1980	1.47	[a]
1985	1.87	22.1
1990	2.09	23.0
1993	2.31	24.0

[a] Data not available.

Table 30. Specifications for Trimellitic Anhydride

Property	Specification	Test method
physical appearance	white flakes	visual
freezing point, °C	166 min	cryoscopy
anhydride content, wt %	95.5 min	methanolysis
color, ΔE	2.4 max	total color difference

production data for trimellitate esters provides data for the trimellitic anhydride demand trend in the United States, since the largest single use of trimellitic anhydride is for the trimellitate esters (115). These data are given in Table 29.

6.5. Specification, Standards, and Analytical and Test Methods

The sales specifications of trimellitic anhydride from Amoco Chemical Co., the sole U.S. producer, are shown in Table 30. Trimellitic anhydride is a trifunctional, highly reactive aromatic anhydride. The reactivity of the anhydride function is important in many applications in adhesives, coatings, and amide–imide polymers, among many others. Hence, determination of the anhydride content is essential (116). A preferred method and one subject to the least interference from contaminants is achieved by comparing the results of methanolysis and hydrolysis of trimellitic anhydride. In the first step, the anhydride is hydrolyzed with hot water and titrated with standard base. The titration provides a measure of both carboxylic groups in the anhydride configuration, of the free-acid group, and of any free acid in the sample. In the second step, the anhydride is esterified to its half ester with excess absolute methanol and is titrated. This titration provides a measurement of one carboxyl group from the anhydride function, of the free carboxyl group, and of any free acid in the sample. The anhydride content is calculated from the difference between the two titrations.

The freezing point of trimellitic anhydride, the maximum temperature reached during crystallization of a molten sample, is a measure of the product purity. Impurities and trimellitic acid formed by hydrolysis depress the freezing point.

A measure of the color developed by impurities when trimellitate esters are produced can be correlated with the anhydride color measurement. The method measures the color difference in light transmittance between a trimellitic solution and a 3.0 N sodium hydroxide solution as a reference. The difference in light transmittance or ΔE (total color difference) is obtained using a colorimeter.

6.6. Health and Safety Factors

Trimellitic anhydride may cause respiratory irritation and, in some cases, individuals exposed over long periods may become sensitized and experience mild to severe reactions upon subsequent exposure. It should be handled with caution and treated as a toxic agent in the workplace because exposure may result in irritation of the pulmonary tract, eyes, nose, and skin (117), immunological sensitization and, in rare cases, hemolytic anemia and noncardiac pulmonary edema. Allowable and recommended exposure limits have been established by the Occupational Safety and Health Administration for a permissible exposure limit (PEL), the American Conference of Governmental Industrial Hygienists for a threshold limit value (TLV), and Amoco for a ceiling limit are all 0.4 mg/m^3. The PEL and TLV are an 8-h time-weighted average. The mean lethal acute oral dosage in rats is 5.6 g/kg. Handling precautions include effective ventilation and use of respirators, protective clothing, and goggles when exposure to dust is expected.

Hazardous Material Identification System/National Fire Protection Association (HMIS/NFPA) codes for trimellitic anhydride are health, 3; flammability, 1; and reactivity, 1. Flaked or molten trimellitic anhydride will burn if ignited. High dust concentrations in the air from either trimellitic anhydride or acid have a potential for combustion or explosion. High voltage static electricity buildup is possible when handling trimellitic anhydride; therefore, adequate precautions, including bonding and grounding of equipment, as well as use of inert gas purge, should be observed. The vapor from molten trimellitic anhydride forms explosive mixtures with air. Estimated upper flammable limit for trimellitic anhydride in air is 7 vol %, and lower limit, 1 vol %. Other health- and safety-related properties are flash point, 227°C (ASTM D1310); and minimum explosive dust concentration in air, 35 g/m^3 (117, 118).

6.7. Uses

The largest end-use application of trimellitic anhydride is as high performance poly(vinyl chloride) plasticizers in the form of triesters of aliphatic alcohols. The second most important use is in coatings applications; conventional solvent-borne, water-borne, and powder coatings. The third largest market is the use in wire enamels for high temperature performance. These three end uses make up about 95% of total trimellitic anhydride usage. Other minor applications are as epoxy curing agent (119), textile sizing agent (120–122), rubber curing accelerator (123), electrostatic toner binder (124, 125), and a vinyl cross-linking agent as triallyl trimellitate (126).

The trimellitates used as plasticizers for poly(vinyl chloride) are higher molecular weight triesters made with 3 mol of monohydric aliphatic alcohols and 1 mol of trimellitic anhydride. The plasticizer-grade alcohols typically include the range of 7–13 carbon atoms. The trimellitates are approximately 40% higher in molecular weight than the corresponding phthalates owing to the third ester group presence. Accordingly, the trimellitates are significantly less volatile and less water-soluble than the corresponding phthalates, allowing the trimellitates to be used in a variety of special applications requiring high temperature permanency, low temperature flexibility, and low water extractability. A wire and cable insulation capable of withstanding 90–105°C environment, launderable vinyl apparel, refrigerator and freezer gaskets, antifogging automobile upholstery and trim, and the manufacture of floor covering are a few examples. Estimated production of trimellitates by individual type in 1990 (115) is as follows (10^3 t/yr): tri(2-ethylhexyl) trimellitate (TOTM), 10.9; triisononyl trimellitate (TINTM), 10.0; linear C_7–C_9 and C_8–C_{10} trimellitates, 1.8; and tri(*n*-hexyl) and other trimellitates, 0.3.

Growing concerns over solvent costs and atmospheric pollution from solvent-borne coatings necessitate low volatile organic compounds (VOC) formulations, with an ultimate target of zero VOC coatings. The trifunctionality of trimellitic anhydride permits synthesis of many polymers useful in formulating paints and coatings for water-based and conventional solvent-based resins. Particularly interesting are the water-soluble resins that use the third functional group as a solubilizing site. Through a proper selection of polymer ingredients and cross-linking agents, trimellitic anhydride-based resins can be formulated into air-dry, oven-cured, or powder coatings with a wide range of application and performance properties, while minimizing environmental concerns (127–132).

Polymers based on trimellitic anhydride are widely used in premium electromagnetic wire enamels requiring high temperature performance. Several types of trimellitic anhydride-derived polymers are used as wire enamels: poly(amide–imide)s (133), poly(ester–imide)s (134), and poly(amide–imide– ester)s (135).

Table 31. Properties of Trimellitic Acid Esters and the Chlorocarbonyl Anhydride

Ester	CAS Registry Number	Bp, °C (Pa)[a]	Specific gravity
trimethyl trimellitate	[2459-10-1]	194 1600 Pa	
triethyl trimellitate	[14230-18-3]	230 3730 Pa	
tri-*n*-butyl trimellitate	[1726-23-4]	206 133 Pa	1.059
tri-*n*-hexyl trimellitate	[1528-49-0]	243 533 Pa	1.006
triisooctyl (TIOTM) trimellitate	[27251-75-8]	283[b] 333 Pa	0.989
tri(2-ethylhexyl) (TOTM) trimellitate	[3319-31-1]	260[b] 133 Pa	0.989
triisononyl (TINTM) trimellitate	[53894-23-8]		0.979
triisodecyl trimellitate	[36631-30-8]	272 133 Pa	0.969
triallyl trimellitate	[2694-54-4]	109–116 600 Pa	
4-chlorocarbonyl-trimellitic 1,2-anhydride	[1204-28-0]	175[c] 2000 Pa	

[a] To convert Pa to mm Hg, divide by 133.3.

[b] Melting point = $< -40°C$.

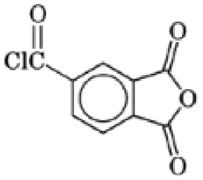
[c] Melting point = $68-69°C$.

Excellent performance characteristics are imparted by trimellitic anhydride-based polymers for wire enamel requirements of flexibility, snap, burnout, scrap resistance, heat shock, and dielectric strength.

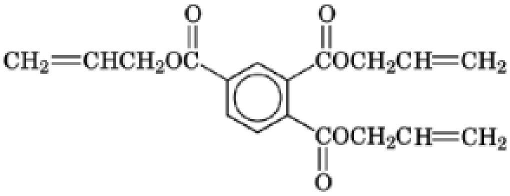
6.8. Derivatives

The dual functionality of trimellitic anhydride makes it possible to react either the anhydride group, the acid group, or both. Derivatives of trimellitic anhydride include ester, acid esters, acid chloride, amides, and amide–imides (136). Trimellitate esters are the most important derivatives, and physical properties of more significant esters are listed in Table 31.

4-Chlorocarbonyltrimellitic acid 1,2-anhydride [1204-28-0] **(9)**, is used in the preparation of esters and amide–imide polymers. Triallyl trimellitate [2694-54-4] **(10)** is used as a cross-linking or co-curing agent for ethylene-derived rubbers and plastics.



(9)



(10)

Table 32. Specifications for Trimesic Acid

Property	Specification	Test method
physical appearance	free flowing powder	
freezing point, °C	374–376	cryoscopy
acid number, mg KOH/g	786 min	titration
organic impurities, wt %	0.5 max	chromatography
volatiles, wt %	0.5 max	ASTM E203
ash, wt %	0.15 max	combustion

7. Trimesic Acid

Trimesic acid is also referred to as 5-carboxyisophthalic acid [554-95-0] trimesinic acid, or trimesitinic acid. It is a small-volume, synthetic chemical and is sold commercially. Traces of trimesic acid as well as other aromatic carboxylic acids with three or more carboxylic acid groups are found in lignite (137), and when various types of coals or coal components such as brown coal, asphaltene, or coal-tar pitch are oxidized.

7.1. Manufacture

The only current U.S. manufacturer of trimesic acid is Amoco Chemical Co. It is produced by oxidation of mesitylene (1,3,5-trimethylbenzene) via the liquid-phase oxidation in acetic acid using the cobalt– manganese–bromine catalyst system (138). This is a variant of the system used to produce terephthalic and isophthalic acids as well as trimellitic anhydride. American Bio-Synthetics Corp. did produce it by batch oxidation of mesitylene with potassium permanganate.

7.2. Economic Aspects

Trimesic acid being a small-volume chemical, availability is in polyethylene-lined fiber drums in 34- and 136-kg quantities. Mesitylene [108-67-8], the raw material, is readily available, and oxidation to trimesic acid presents no problems. The market size is dictated by commercial uses.

7.3. Specifications and Standards

Table 32 lists specifications for trimesic acid as produced by Amoco Chemical (139). Typically, the product is over 98% pure.

7.4. Health and Safety Factors

Trimesic acid is an irritant to the skin, eyes, and respiratory system (140). It is mildly toxic when ingested. The oral LD_{50} in rats has been reported as 8.4 g/kg (141). Trimesic acid is flammable, and precautions similar to those noted for terephthalic acid and isophthalic acid as regards dust clouds and fire extinguishing agents should be followed.

7.5. Uses

The only significant commercial use for trimesic acid is as a cross-linking agent in solid rocket fuels. Other reported uses include cross-linking agents for polymers (142), as the base acid in making triesters as plasticizers

Table 33. Physical Contants of Pyromellitic Acid and Pyromellitic Dianhydride

Property	Pyromellitic acid	Pyromellitic dianhydride
mp, °C	281–284.5	284–286
bp, °C		380–400
vapor pressure, kPa[a]		
at 290°C		8.4
350°C		44
heat of vaporization, kJ/mol[b]		83.4
specific gravity at 20°C		1.680
heat of combustion at 25°C, kJ/mol[b]		−3313
heat of formation at 25°C, kJ/mol[b]	−1571	−907
heat of fusion at 285°C, kJ/mol[b]		15.8

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

(143), as a component of electrostatic toners (144), and as a stationary phase for gas chromatography (145, 146). Trimesic acid is sold as a research chemical (99).

8. Hemimellitic Acid

Hemimellitic acid is not manufactured commercially but is available as a laboratory chemical in a hydrate form (99). Like trimesic acid, it is formed when coal-like materials are oxidized, but can be synthesized in a purer form by oxidizing hemimellitene [562-73-8] (1,2,3-trimethylbenzene) or hemimellitol [526-85-2]. Hemimellitic anhydride can be produced by thermal dehydration of the acid in trichlorobenzene at 261°C (147). Synthesis of hemimellitic acid and anhydride have been described (148). There are no reported uses which are unique to hemimellitic acid.

9. Pyromellitic Acid and Pyromellitic Dianhydride

Pyromellitic acid is a commercial product, and it forms a dianhydride which has specialized commercial applications, primarily as an ingredient in the preparation of high temperature polymers. The IUPAC name of the dianhydride is 1*H*,3*H*-benzo(1,2-*c*:4,5-*c*′)difuran-1,3,5,7-tetrone.

9.1. Physical and Chemical Properties

Tables 33 and 34 contain some of the physical and chemical properties of pyromellitic acid and its anhydride.

9.2. Manufacture and Processing

Pyromellitic acid and its dianhydride can be synthesized by oxidizing durene [95-93-2] (1,2,4,5-tetramethylbenzene). Liquid-phase oxidation using strong oxidants such as nitric acid, chromic acid, or potassium permanganate produces the acid which can be dehydrated to the dianhydride in a separate step. This technology is practiced by Allco Chemical Co., a part of International Specialty Chemicals.

The use of the liquid-phase process in acetic acid with the cobalt– manganese–bromine system as explained in the terephthalic acid section is also possible (149). This process has been used by Amoco Chemical to produce

Table 34. Solubilities of Pyromellitic Acid and Pyromellitic Dianhydride[a]

	Temperature, °C		
Solvent	25°C	50°C	70°C
pyromellitic acid			
water[b]	1.5	5.0	12
ethanol	15	22	30
dimethylformamide		31	
dimethyl sulfoxide[c]			
pyromellitic dianhyhdride			
acetone	7.5	8.5	
dimethylformamide	18	35	72
dimethyl sulfoxide	24	43	80

[a] g/100 g solvent.
[b] 30 g/100 g H_2O at 90°C.
[c] 62 g/100 g DMSO at 100°C.

pyromellitic acid, and facilities remain in place to do so again in the future. As with all liquid-phase oxidations of this type, yields are high. A separate dehydration step would be needed to yield the dianhydride.

Mitsubishi Gas Chemical Co. in Japan produces pyromellitic dianhydride in the same unit used for trimellitic anhydride production (105). This process starts with pseudocumene, which is first carbonylated with carbon monoxide in the presence of boron trifluoride and hydrogen fluoride to form 2,4,5-trimethylbenzaldehyde. The liquid-phase oxidation of the trimethylbenzaldehyde to pyromellitic acid and subsequent processing steps are much the same as described for the Mitsubishi Gas Chemical process in the trimellitic acid section. The production of pyromellitic anhydride is in conjunction with a joint venture agreement with Du Pont.

Vapor-phase catalytic oxidation of durene is a more direct route to the dianhydride. Hüls in Europe apparently uses this route, which eliminates the need for a separate dehydration step and for handling of any oxidants or solvents. Continuous operation is facilitated, corrosion is minimized, and product recovery is simplified. The vapor-phase oxidation of durene is similar to that of *o*-xylene to phthalic anhydride, and phthalic anhydride units can be converted to produce pyromellitic dianhydride. Production of the durene with two anhydride rings and a lower vapor pressure than phthalic anhydride is more difficult, however. In theory, the vapor-phase oxidation does not result in the formation of carboxyl groups that are subsequently dehydrated by the same catalyst. It proceeds through an intramolecular, five-membered ring which oxidizes to 4,5-dimethylphthalic anhydride. This is the presumed intermediate in the production of pyromellitic dianhydride (150). Catalysts specifically noted for durene oxidation contain vanadium, titanium, tin, zirconium, phosphorus, niobium, potassium, cesium, rubidium, tellurium, and antimony (151). Honeycomb supports with titanium and vanadium catalysts are also noted (152).

9.3. Production, Storage, and Shipment

As noted above, Allco Chemical, Amoco Chemical, Mitsubishi Gas Chemical, and Hüls all produce either the acid or the anhydride using different production techniques. The relatively small production volumes of pyromellitic acid and dianhydride results in both storage and shipment in polyethylene-lined fiber drums of 22–136-kg capacity.

9.4. Economic Aspects

Prices for pyromellitic acid were about $14/kg in 1994. The dianhydride sold for about $19–25/kg depending on purity, and prices of the dianhydride ground to a fine 3-μm size were $2/kg higher (153). Production amounts

Table 35. Specifications for Pyromellitic Dianhydride

Property	Specification	Test method
purity, % min	99.5	by difference
organic impurities, wt %	1.5 max	chromatography
color	almost white	visual
mp, °C	282 min	cryoscopy
ash, ppm	400 max	combustion
volatiles, wt %	0.5 max	evaporation
bp[a], °C	397–400	
bp[b], °C	305–310	

[a] At 101.3 kPa = 1 atm·

[b] At 4 kPa = 0.04 atm·

are not released and are dictated by market needs. The use of some multipurpose units to make this product means that the amounts produced are highly variable.

9.5. Specifications and Standards

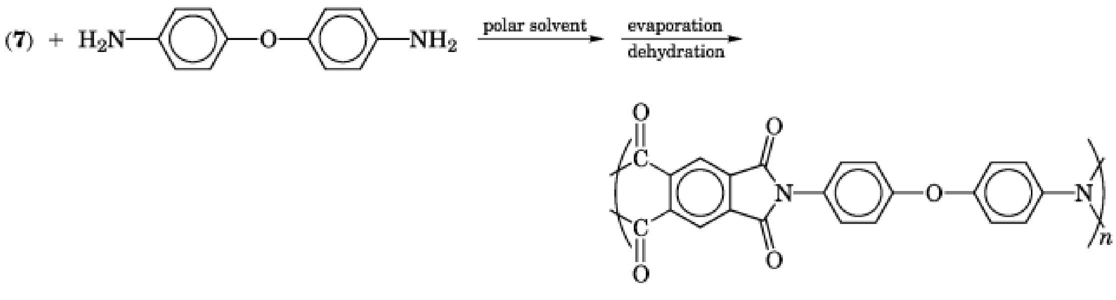
Typical properties of pyromellitic acid are given in Table 35 (154, 155). In many cases, specifications are negotiated between manufacturer and customer based on the needs of the final product.

9.6. Health and Safety Factors

Both pyromellitic acid and its dianhydride irritate skin, eyes, and mucous membranes, and they cause skin sensitization (156). When it comes in contact with moist tissue the dianhydride converts to the acid. Direct contact with should be avoided and protective clothing should be worn in areas where it is used. The LD$_{50}$ for intergastric administration in rats is 2.2–2.6 g/kg (157). In 6-mo experiments, the maximum nontoxic dose was 0.07 mg/kg/d, and it affected the liver, kidney, and reproductive tract. Precautions against fire and dust explosions as explained in the terephthalic acid section should be followed.

9.7. Uses

Pyromellitic dianhydride imparts heat stability in applications where it is used. Its relatively high price limits its use to these applications. The principal commercial use is as a raw material for polyimide resins (see Polyimides). These polypyromellitimides are condensation polymers of the dianhydride and aromatic diamines such as 4,′-oxydianiline:



Du Pont produces this polymer under the trade names of Kapton, Pyralin, Vespel, and Pyre-ML. The trade names refer to polyimides used for film, semiconductor coatings, molding applications, and wire enamel, respectively. They have excellent thermal, electrical, and physical properties.

Because the heat distortion temperature of cured epoxy resins (qv) increases with the functionality of the curing agents, pyromellitic dianhydride is used to cross-link epoxy resins for elevated temperature service. The dianhydride may be added as a dispersion of micropulverized powder in liquid epoxy resin or as a glycol adduct (158). Such epoxies may be used as an insulating layer in printed circuit boards to improve heat resistance (159). Other uses include inhibition of corrosion (160, 161), hot melt traffic paints (162), azo pigments (163), adhesives (164), and photoresist compounds (165).

10. Mellophanic and Prehnitic Acids

Neither mellophanic acid nor prehnitic acid are commercial products, nor are they available as laboratory chemicals. Some references identify the 1,2,3,4-isomer as prehnitic acid, and the 1,2,3,5-isomer as mellophanic acid; this designation relates to the name prehnitene [488-23-3], which is used for 1,2,3,4-tetra-methylbenzene. However, *Chemical Abstracts* identifies the 1,2,3,4-isomer as mellophanic acid and the 1,2,3,5-isomer as prehnitic acid. Both acids could be synthesized by oxidizing the corresponding tetramethylbenzenes. Mellophanic acid has been made by the ring dehydrogenation of 1,2,3,4-cyclohexanetetracarboxylic acid with bromine (165). Prehnitic acid has been synthesized by the cobalt catalyzed carbonylation of Schiff bases (166). These acids are also formed in the oxidation of coal-like materials.

Mellophanic acid and prehnitic acid have few literature references for uses. Possible applications are as a tanning agent in combination with an aluminum salt (167), to give a pearl-like gloss to polyester–polymethacrylate resins (168) or brightness to polypropylene fibers (169), or to increase detergent efficiency (170). Mellophanic dianhydride has a relatively low melting point and good solubility in epoxy resins. It has therefore been considered as a substitute for pyromellitic dianhydride as a cross-linking agent (171).

11. Benzenepentacarboxylic Acid and Mellitic Acid

Neither benzenepentacarboxylic acid nor mellitic acid are manufactured commercially, but synthetic mellitic acid can be purchased as a laboratory chemical (99). Both can be synthesized by oxidizing the corresponding methylbenzenes or other substituted benzenes, and both are present in trace amounts after oxidation of coal or coal-like substances.

Both the acids, their sodium salts, as well as benzenetricarboxylic and benzenetetracarboxylic acids have been considered as substitutes for phosphorus- and nitrogen-containing detergent builders (172). Although satisfactorily biodegradable, these acids are not as effective as other builders and have not been used (173). Other potential uses for mellitic acid are as part of the resin component of sand molds (174), as an additive to anodizing baths for improving finishes on aluminum (175), and as an additive to oral antibacterial preparations for preventing tooth discoloration (176). Both benzenepentacarboxylic acid and mellitic acid have been mentioned as ingredients in bonding agents (177) and dental fillings (178).

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