KIRK-OTHMER

N. J. De Lollis, *Adhesives, Adherends, Adhesion,* Krieger Publishing Co., Melbourne, Fla., 1980.

A. Pizzi, ed., *Wood Adhesives: Chemistry and Technology,* Marcel Dekker, New York, 1983.

W. C. Wake, ed., *Adhesion and the Formulation of Adhesives,* Elsevier Publishing Co., New York, 1982.

S. Wu, *Polymer Interface and Adhesion,* Marcel Dekker, New York, 1982. A basic textbook covering surface effects on polymer adhesion.

K. W. Allen, ed., *Adhesion,* Vols. 1–14, Elsevier Science Publishers Ltd., Barking, UK, Latest volume is 1990. An annual volume containing recently presented research results.

ALPHONSUS V. POCIUS
The 3M Company

ADIPIC ACID

Adipic acid, hexanedioic acid, 1,4-butanedicarboxylic acid, mol wt 146.14, $HOOCCH_2CH_2CH_2CH_2COOH$ [*124-04-9*], is a white crystalline solid with a melting point of about 152°C. Little of this dicarboxylic acid occurs naturally, but it is produced on a very large scale at several locations around the world. The majority of this material is used in the manufacture of nylon-6,6 polyamide [*32131-17-2*], which is prepared by reaction with 1,6-hexanediamine [*124-09-4*]. W. H. Carothers' research team at the Du Pont Company discovered nylon in the early 1930s (1), and the fiftieth anniversary of its commercial introduction was celebrated in 1989. Growth has been strong and steady during this period, resulting in an adipic acid demand of nearly two billion metric tons per year worldwide in 1989. The large scale availability, coupled with the high purity demanded by the polyamide process, has led to the discovery of a wide variety of applications for the acid.

Chemical and Physical Properties

Adipic acid is a colorless, odorless, sour tasting crystalline solid. Its fundamental chemical and physical properties are listed in Table 1. Further information may be obtained by referring to studies of infrared and Raman spectroscopy of adipic acid crystals (11,12), ultraviolet spectra of solutions (13), and specialized thermodynamic properties (14,4). Solubility and solution properties are described in Table 2. The crystal morphology is monoclinic prisms strongly influenced by impurities (21). Both process parameters (22) and additives (21) profoundly affect

---

Table 1. Phy

Property
molecular fo
molecular w
melting poin
specific grav
coefficient o
vapor densit
vapor press
solid at
18.5
32.7
47.0
liquid a
205.5
216.5
244.5
265.0
specific hea
heat of fusi
entropy of
heat of vap
melt viscos
heat of con

[a]To convert
[b]To convert

crystal m
cant proc
various s
containin
on twent
ties of ad

Chemica

Adipic ac
cation, a
Because
cant pol
Est
class of a

unique reaction, in which a mixture of adipic acid and adiponitrile [*111-69-3*] are heated together, producing an equilibrium mixture containing significant amounts of 5-cyanopentanoic acid [*5264-33-5*]. This material is a precursor to caprolactam [*105-60-2*] and may be isolated from the reaction mixture by a number of methods, including esterification and hydrogenation (41).

Manufacture and Processing

Several general reviews of adipic acid manufacturing processes have been published since it became of commercial importance in the 1940s (42–46), including a very thorough report based on patent studies (47). Adipic acid historically has been manufactured predominantly from cyclohexane [*110-82-7*] and, to a lesser extent, phenol [*108-95-2*]. During the 1970s and 1980s, however, much research has been directed to alternative feedstocks, especially butadiene [*106-99-0*] and cyclohexene [*110-83-8*], as dictated by shifts in hydrocarbon markets. All current industrial processes use nitric acid [*7697-37-2*] in the final oxidation stage. Growing concern with air quality may exert further pressure for alternative routes as manufacturers seek to avoid NO_x abatement costs, a necessary part of processes that use nitric acid.

Since adipic acid has been produced in commercial quantities for almost 50 years, it is not surprising that many variations and improvements have been made to the basic cyclohexane process. In general, however, the commercially important processes still employ two major reaction stages. The first reaction stage is the production of the intermediates cyclohexanone [*108-94-1*] and cyclohexanol [*108-93-0*], usually abbreviated as KA, KA oil, ol-one, or anone-anol. The KA (ketone, alcohol), after separation from unreacted cyclohexane (which is recycled) and reaction by-products, is then converted to adipic acid by oxidation with nitric acid. An important alternative to this use of KA is its use as an intermediate in the manufacture of caprolactam, the monomer for production of nylon-6 [*25038-54-4*]. The latter use of KA predominates by a substantial margin on a worldwide basis, but not in the United States.

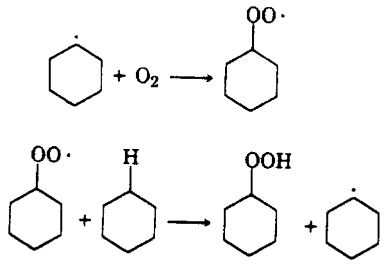
PREPARATION OF KA BY OXIDATION OF CYCLOHEXANE

There are three main variations to the basic cyclohexane oxidation process pioneered by Du Pont in the 1940s. The first, which can be termed metal-catalyzed oxidation, is the oldest process still in use and forms the base for the other two. It employs a cyclohexane-soluble catalyst, usually cobalt naphthenate [*61789-51-3*] or cobalt octoate [*136-52-7*], and moderate temperatures (150–175°C) and pressures (800–1200 kPa = 115–175 psi). Air is fed to each of a series of stirred tank reactors or to a column reactor which contains numerous reaction stages, along with cyclohexane. The catalyst, at 0.3–3 ppm based on cyclohexane feed, is usually premixed by injection into the feed stream, though it is not uncommon to divide the catalyst stream into many separate additions to each of the series reactors. The conversion of cyclohexane to oxidized products is 3–8 mol %, which is quite low compared to most important industrial processes. There are claims of commercial processes operating as low as 1 mol % conversion (48), which translates to 99% of the feed material being recovered and recycled to the oxidation reactors. Low conversion is the major factor in achieving high selectivities to ketone (K) and alcohol (A) (and to cyclohexylhydroperoxide [*766-07-4*] discussed below). This is so because the intermediates of interest (K, A, and cyclohexylhydroperoxide) are all much more easily oxidized than is cyclohexane (49,50). Selectivities vary inversely and linearly with conversion, ranging from around 90 mol % at 1–2 mol % conversion to 65–70 mol % at 8 mol % conversion. Table 6 illustrates the range of reaction conditions to be found in the patent literature.

Because the process operates at such low conversion of cyclohexane per pass through the oxidation reactors, large quantities of unreacted cyclohexane must be recovered by distillation of the oxidizer effluent. This, and the increase in energy prices in the 1970s, has resulted in considerable attention being given to the energy conservation schemes employed in recovering the cyclohexane. Examples of techniques used in energy conservation are process–process heat interchange, high efficiency packed distillation columns, and use of the "pinch-point" technique in designing recovery steps. Contacting the final crude KA oil with water or solutions of caustic soda, or both, for removal of mono- and dibasic acid impurities also can be considered an energy conservation technique since this treatment can eliminate the final steam stripper often used to purify the crude KA oil.

Regardless of the techniques used to purify the KA oil, several waste streams are generated during the overall oxidation–separation processes and must be disposed of. The spent oxidation gas stream must be scrubbed to remove residual cyclohexane, but afterwards will still contain CO, CO_2, and volatile hydrocarbons (especially propane, butane, and pentane). This gas stream is either burned and the energy recovered, or it is catalytically abated. There are usually several aqueous waste streams arising from both water generated by the oxidation reactions and wash water. The principal hydrocarbon constituents of these aqueous wastes are the C_1–C_6 mono- and dibasic acids, but also present are butanol [*71-36-3*], pentanol [*71-41-0*], ϵ-hydroxycaproic acid [*1191-25-9*] , and various lactones and diols (71,72). The spent caustic streams contain similar components in addition to the caustic values. These streams can be burned for recovery of sodium carbonate or sold directly as a by-product for use in the paper industry. The most concentrated waste stream is one often called still bottoms, heavy ends, or nonvolatile residue. It comes from the final distillation column in which the KA oil is steam-stripped overhead. The tails stream from this column contains most of the nonvolatile by-products, as well as metals and residues from the catalysts and from corrosion. Both the metals and acid content may be high enough to dictate that this stream be classified as a hazardous waste. It usually is burned and the energy used to generate steam (73). Much effort has gone into recovering valuable materials from it over the years, including adipic acid, which may be present in as much as 3–4% of the cyclohexane oxidized (74). It has potential as a feedstock in the production of monobasic acids, polyester polyols, butanediol, and maleic acid (75,76). The frequency of fugitive emissions from cyclohexane oxidation plants has been reviewed (77).

High Peroxide Process. An alternative to maximizing selectivity to KA in the cyclohexane oxidation step is a process which seeks to maximize cyclohexylhydroperoxide, also called P or CHHP. This peroxide is one of the first intermediates produced in the oxidation of cyclohexane. It is produced when a cyclohexyl radical reacts with an oxygen molecule (78) to form the cyclohexylhydroperoxy radical. This radical can extract a hydrogen atom from a cyclohexane molecule, to produce CHHP and another cyclohexyl radical, which extends the free-radical reaction chain.



The peroxide can be converted to KA easily, and in high yield, in a number of ways; thus maximization of CHHP, at high yield, gives a process with high yield to KA. Techniques employed to produce high CHHP yield include drastically cutting or eliminating metal catalysts in the oxidation step, minimizing cyclohexane conversion, passivating reactor walls, lowering reaction temperature (to as low as 140°C), adding water to the reaction mix to extract acid catalysts from the cyclohexane phase, and adding metal-chelating agents to the reaction mix. Optimization of this process can produce CHHP in a proportion as high as 75% of the reaction products (59). The CHHP then can be converted to KA by any of the following methods: decomposing it with homogeneous or heterogeneous catalysts from the group Co, Cr, Mo, V, Cu, or Ru; dehydrating it by treatment with caustic soda (which preferentially gives K); or hydrogenating it (which preferentially gives A). KA is separated from the reaction mixture in a manner similar to the conventional process. It may be possible, however, to avoid a final steam distillation of the KA overhead if the tails stream from the distillation train is sufficiently clean. This could result from a high yield process that employs thorough water and caustic washing. Figure 1 illustrates schematically the high peroxide process practiced by Stamicarbon (60).

Borate-Promoted Oxidation. Another alternative to the basic cyclohexane oxidation process is one which maximizes only the yield of A. This process uses boric acid as an additive to the cyclohexane stream as both a promoter and an esterifying agent for the A that is produced. Metaboric acid [*10043-35-3*] is fed to the first series oxidizer as a slurry in cyclohexane to give a molar ratio of boron:cyclohexane of around 1.5:100. No other metal catalyst is used. Esterifying the A effectively shields it from overoxidation and thus allows the attainment of very high yields (ca 90%) (65). The ratio A:K in the final product can exceed 10:1. The process was developed in the mid-1960s by a number of companies, including Halcon/Scientific Design (79,80), Institute Francais Petrole (68,81), and Stamicarbon (82). The process was licensed and commercialized by several companies in the decade following its development, including Monsanto, ICI, and Bayer. The major drawback to the process is the need to hydrolyze the borate ester in order to recover A. This is an energy-intensive step and can be quite a mechanical nuisance because of the requirement for handling boric acid solids. Without careful attention to energy conservation and engineering, the savings that accrue from the high yield can be more than offset. The process does, because of its high yield, offer advantages in waste minimization and product purity. It does, however, introduce boron into the waste streams.

Other Routes to KA. Phenol [*108-95-2*] may be hydrogenated to KA in very high yield, typically 97–99% (83). Depending on catalyst selection and operating conditions, the ratio of K to A in the product can be varied over a large range. If the product is to be further oxidized with nitric acid to make adipic acid, then A would be the preferred choice since its reaction with nitric acid results in lower consumption of nitric than does K. If caprolactam is to be produced, then the process would be designed to produce relatively more K, since this is the starting material for the production of caprolactam. Because of the high yield to KA the purification is relatively simple, consisting mainly of removing the small amount of unreacted phenol via ion exchange (84). Economics in recent years has dictated against this process because of the relatively high cost of phenol compared to cyclohexane. Typical reaction conditions are 140°C and 400 kPa (58 psi) using a heterogeneous nickel on silica catalyst (83).

Cyclohexene, produced from the partial hydrogenation of benzene [*71-43-2*], also can be used as the feedstock for A manufacture. Such a process involves selective hydrogenation of benzene to cyclohexene, separation of the cyclohexene from unreacted benzene and cyclohexane (produced from over-hydrogenation of the benzene), and hydration of the cyclohexene to A. Asahi has obtained numerous patents on such a process and is in the process of commercialization (85,86). Indicated reaction conditions for the partial hydrogenation are 100–200°C and 1–10 kPa (0.1–1.5 psi) with a Ru or zinc-promoted Ru catalyst (87–90). The hydration reaction uses zeolites as catalyst in a two-phase system. Cyclohexene diffuses into an aqueous phase containing the zeolites and there is hydrated to A. The A then is extracted back into the organic phase. Reaction temperature is 90–150°C and reactor residence time is 30 min (91–94).

ARCO has developed a coproduct process which produces KA along with propylene oxide [*75-56-9*] (95–97). Cyclohexane is oxidized as in the high peroxide process to maximize the quantity of CHHP. The reactor effluent then is concentrated to about 20% CHHP by distilling off unreacted cyclohexane and cosolvent *tert*-butyl alcohol [*75-65-0*]. This concentrate then is contacted with propylene [*115-07-1*] in another reactor in which the propylene is epoxidized with CHHP to form propylene oxide and KA. A molybdenum catalyst is employed. The product ratio is about 2.5 kg of KA per kilogram of propylene oxide.

NITRIC ACID OXIDATION OF CYCLOHEXANOL(ONE)

Although many variations of the cyclohexane oxidation step have been developed or evaluated, technology for conversion of the intermediate ketone–alcohol mixture to adipic acid is fundamentally the same as originally developed by Du Pont in the early 1940s (98,99). This step is accomplished by oxidation with 40–60% nitric acid in the presence of copper and vanadium catalysts. The reaction proceeds at high rate, and is quite exothermic. Yield of adipic acid is 92–96%, the major by-products being the shorter chain dicarboxylic acids, glutaric and succinic acids, and CO_2. Nitric acid is reduced to a combination of NO_2, NO, N_2O, and N_2. Since essentially all commercial adipic acid production arises from nitric acid oxidation, the trace impurities patterns are similar in the products of most manufacturers.

Chemistry. Papers addressing the mechanism of nitric acid oxidation began appearing in the mid 1950s (100). Then, a series of reports beginning in 1962 described the mechanism of the oxidation in considerable detail (101–105). The reaction pathway diagram shown in Figure 2 is based on these and other studies of nitric acid oxidation chemistry. A key intermediate in the reaction sequence is 2-oximinocyclohexanone [*24858-28-4*], , produced via nitrosation of cyclohexanone. Nitrous acid [*7782-77-6*] is produced during the conversion of cyclohexanol to the ketone, and also upon oxidation of aldehyde and alcohol impurities usually accompanying the KA and arising in the cyclohexane oxidation step. The nitric acid oxidation chemistry is controlled by nitrous acid, which is in equilibrium with NO, NO_2, HNO_3, and H_2O in the reacting mixture. Total inhibition of reaction can be achieved by incorporating a small amount of urea [*57-13-6*], which effectively scavenges (106) nitrous acid from the mixture. Further nitration leads to 2-nitro-2-nitrosocyclohexanone [*23195-89-3*], which is converted via hydrolytic cleavage of the ring to 6-nitro-6-hydroximinohexanoic acid (nitrolic acid) [*1069-46-1*]. Of all the intermediates shown in Figure 2, the nitrolic acid is the only one of sufficient stability to be isolable under very mild conditions. It is hydrolyzed to adipic acid in one of the slowest steps in the sequence. Further hydrolysis produces adipic acid. Nitrous oxide (N_2O) is formed by further reaction of the nitrogen-containing products of nitrolic acid hydrolysis. The NO and NO_2 are reabsorbed and converted back to nitric acid, but N_2O cannot be recovered in this manner, and thus is the major nitric acid derived by-product of the process.

About 60–70% of the reaction occurs as in path 1 in Figure 2, the remainder by other pathways. About 20% of the reaction occurs by the vanadium oxidation of 1,2-dioxygenated intermediates (path 2 in Fig. 2). This chemistry has been discussed in detail (104,105). This path is noteworthy since it does not produce the nonrecoverable nitrous oxide. The other reactions shown in Figure 2 occur to varying degrees, depending on either an excess or deficiency of nitrous acid, arising from variations in reaction conditions. These lead to varying yields of the lower dicarboxylic acids. Yield of monobasic and dibasic acid by-products also is a function of the purity of the KA feed. A distinguishing characteristic for several of the commercial processes is the degree to which the intermediate KA is refined, prior to feeding it to nitric acid oxidation.

Process Description. In a typical industrial adipic acid plant, as schematically illustrated in Figure 3, the KA mixture reacts in reactor A with 45–55% nitric acid containing copper (0.1–0.5%) and vanadium (0.02–0.1%) catalyst (107,108). Design of the oxidation reactor for optimum yield and heat removal has been the subject of considerable research and development over the years of use of this process (109). The reaction occurs at 60–90°C and 0.1–0.4 MPa (14–58 psi). It is very exothermic (6280 kJ/kg = 1500 kcal/kg), and can reach an autocatalytic runaway state at temperatures above about 150°C. Control is achieved by limiting the KA feed to a large excess of nitric acid in a stirred tank or circulating loop reactor. Two stages of oxidation are sometimes employed to achieve improved product quality (110). Oxides of nitrogen are removed by bleaching with air in column C, then water is removed by vacuum distillation in column E.

The concentrated stream, nominally adipic acid and lower dibasic acid coproducts in 35–50% HNO_3 (organic-free basis), is then cooled and crystallized (F). Crude adipic acid product is removed via filtration or centrifugation (G), and the mother liquor is returned to the oxidizer. Further refining is required to achieve polymer grade material, usually by recrystallization from water. Residual lower dibasic acids, nitrogen-containing impurities, and metals are removed in this step. Additional purification steps occasionally are employed, including slurry washing, further recrystallization, and charcoal treatment. The bleacher off-gas, containing NO and NO_2, reacts with air and is reabsorbed as nitric acid for reuse (D).

In order to control the concentration of lower dibasic acid by-products in the system, a portion of the mother liquor stream is diverted to a purge treatment process. Following removal of nitric acid by distillation (Fig. 3, K), copper and vanadium catalyst are recovered by ion-exchange treatment (Fig. 3, N). This area of the process has received considerable attention in recent years as companies strive to improve efficiency and reduce waste. Patents have appeared describing addition of SO_2 to improve ion-exchange recovery of vanadium (111), improved separation of glutaric and succinic acids by dehydration and distillation of anhydrides (112), formation of imides (113), improved nitric acid removal prior to dibasic acid recovery (114), and other claims (115).

Because of the highly corrosive nature of the nitric acid streams, adipic acid plants are constructed of stainless steel, or titanium in the more corrosive areas, and thus have high investment costs.

Wastes and Emissions. Nitric acid oxidation may be used to recover value from waste streams generated in the cyclohexane oxidation portion of the process, such as the water wash (116) and nonvolatile residue (76) streams. The nitric acid oxidation step produces three major waste streams: an off-gas containing oxides of nitrogen and CO_2; water containing traces of nitric acid and organics from the water removal column; and a dibasic acid purge stream containing adipic, glutaric, and succinic acids. The off-gas usually is passed through a reducing-flame burner to the atmosphere, or it may be oxidized back to NO_x at 1000–1300°C and recovered as nitric acid, as claimed in a patent (117). The overhead water stream usually is treated (eg, neutralization, biotreatment) and reused or disposed of. The dibasic acid stream usually is either burned or disposed of by deepwell injection or biotreatment. However, as more uses for these acids are discovered, the necessity for their disposal diminishes. The principal emissions of concern from these processes are related to nitric acid, either as the various oxides of nitrogen or as a very dilute solution of the acid itself. The fate of these waste streams varies widely, subject to the usually very complex environmental and regulatory situations at each individual manufacturing site. These issues are now a prime consideration, equal to economics, in the design of chemical processing systems in the petrochemical industry (118).

OTHER ROUTES TO ADIPIC ACID

A number of processes for producing adipic acid without producing the intermediates K and A, and from feedstocks other than cyclohexane and phenol, have been investigated. None has been employed at a commercial scale. A one-step air

(118) CHEM. ENG. SCI. 40, 781-797 (1985)