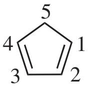
CYCLOPENTADIENE AND DICYCLOPENTADIENE

1. Introduction

Cyclopentadiene [542-92-7] (CPD), C_5H_6, (**1**) and its more stable dimer, dicyclopentadiene [77-73-6] (DCPD), $C_{10}H_{12}$ (**2**) are are the major constituents of hydrocarbon resins, cyclic olefin polymers, and a host of specialty chemicals.



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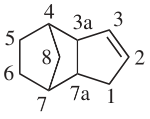


(**2**)

They can be transformed into many chemical intermediates used in the production of pharmaceuticals, pesticides, perfumes, flame retardants, and antioxidants. Because of their wide industrial uses, their chemistry has been extensively investigated and documented. Numerous reviews (1–12) have been published on the subject. The production processes and industrial uses of CPD and DCPD are summarized in Ref. 13. In additional to the classical organic reactions, CPD forms organic metallic complexes, ferrocene, with transition metals (14). Some of these complexes have been established as excellent olefin polymerization catalysts. Several reviews have been published on this rapid growing field (15–19).

2. Physical Properties

The physical properties of CPD and DCPD are given in Table 1. DCPD, 3*a*,4,7,7*a*-tetrahydo-4,7-methano-1*H*-indene, can exist in two stereoisomers, the endo and

Table 1. **Physical Properties of Cyclopentadiene and Dicyclopentadiene**

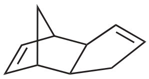
Physical properties	Cyclopentadiene	Dicyclopentadiene
molecular weight	66.1	132.2
bp, 101.3 kPa,[a] °C	40.0	170
mp, °C	−97.2	32
physical form	colorless liquid	colorless solid
odor	sweet terpenic	camphoraceous
d_4^{20}	0.8021	
d_4^{35}		0.9302
n_D^{20}	1.4440	1.5105
n_D^{35}		1.5050
heat of combustion, kJ/mol[b]	2929	5767
heat of vaporization, kJ/mol[d]	28.9	38.5
heat of fusion, kJ/mol[b]	8.0	2.1
specific heat, kJ/(kgK)[b]	1.7	1.7
heat of cracking, kJ/mol[b]		102.9
spontaneous ignition temp, °C		
in oxygen	510	510
in air	640	2.43
dielectric constant at 40°C		2.43
ionization energy, eV	8.5	8.8

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

[b] To convert kJ to kcal, divide by 4.184.

exo forms. Because commercially available DCPD is mostly the endo isomer, the properties in Table 1 are pertinent to those of the endo isomer. Spectroscopical information on CPD and DCPD can be found in the following references: Mass spectrum, ref. 20; nmr spectrum, ref. 21; infrared, ultraviolet and Raman spectra ref. 2.

(endo DCPD)



(exo DCPD)

DCPD decomposes rapidly at its normal boiling point to two molecules of cyclopentadiene. Purification of DCPD by distillation must be conducted under vacuum conditions. Figure 1 depicts the lowering of the boiling point as a function of pressure. The dimer is the form in which CPD is sold commercially.

3. Chemical Reactions

Cyclopentadiene is very reactive. In addition to the vast number of reactions one expects from a conjugated double bond structures which include Diels–Alder addition, hydrogenation, halogen addition, etc, the highly acidic methylene group promotes a number of condensation reactions. On the other hand, DCPD behaves like non-conjugated dienes, with the exception that the double bond in

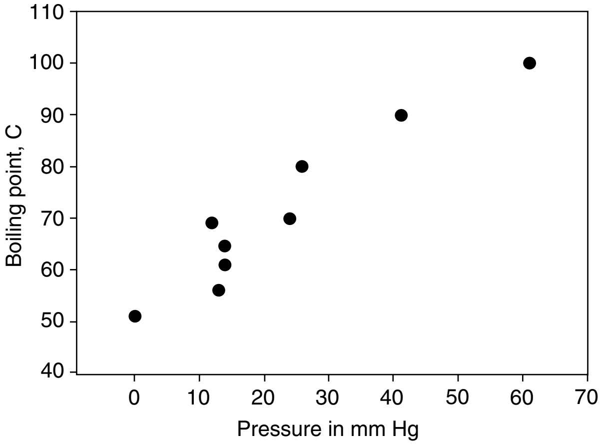
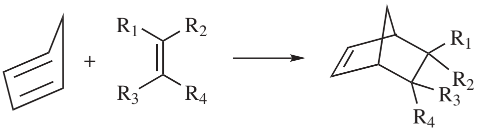


Fig. 1. Boiling point of dicyclopentadiene as a function of pressure.

the bicycloheptene ring is more reactive than that in the five-member ring because of the bond angle strain in the bicycloheptene ring.

3.1. Diels–Alder Addition. In Diels–Alder addition, the conjugated double bonds of CPD react with the π bond of a dienophile, a compound containing ethylenic or acetylenic unsaturation. The ethylenic or acetylenic group is added across the 1,4 position of the CPD,



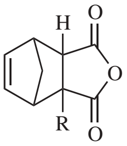
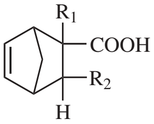
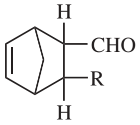
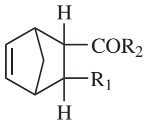
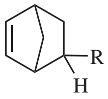
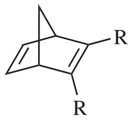
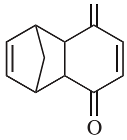
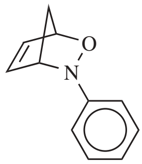
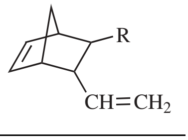
(**1**)

resulting in a bicyclo[2.2.1]heptene derivative, a cyclohexene derivative with a bridged methylene group. Because of Diels–Alder reactions, many multicyclic compounds can be synthesized with CPD as the building blocks. Examples of these reactions, which are highly exothermic (71–75 kJ/mol), are shown in Table 2.

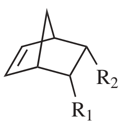
Both CPD and DCPD can be used in the reactions. However for the latter, the reaction needs to be carried out at temperatures above 175°C in order for the DCPD to dissociate rapidly to the CPD monomer. The rate of the reaction is strongly affected by other substituents of the dienophile. For instance, the reaction between CPD and maleic anhydride occurs spontaneously whereas that between CPD and ethylene requires elevated temperatures and very high pressure. A long floppy chain on the dienophile is also a strong inhibitor of the reaction (22).

Diels–Alder addition is stereochemically specific (22). There is a strong tendency of most substituents of the dienophile to orient in the endo configuration in

Table 2. **Diels–Alder Adducts from Cyclopentadiene**

Dienophile	Structure of adduct
Dibasic acids and derivatives maleic anhydride, $R = H$ chloromaleic anhydride, $R = Cl$	
Monobasic acids crotonic acid, $R_1 = H$; $R_2 = CH_3$ methacrylic acid, $R_1 = CH_3$; $R_2 = H$	
Aldehydes acrolein, $R = H$ crotonaldehyde, $R = CH_3$	
Ketones methyl propenyl ketone (3-penten-2-one), $R_1 = CH_3$; $R_2 = CH_3$ methyl vinyl ketone (3-buten-2-one), $R_1 = H$; $R_2 = CH_3$	
Vinyl compounds ethylene, $R = H$ styrene, $R = C_6H_5$ vinyl acetate, $R = CH_3COO$	
Acetylenes acetylene, $R = H$ acetylenedicarbonitrile, $R = CN$	
Quinones *p*-benzoquinone	
Nitroso compounds nitrosobenzene	
Conjugated diolefins 1,3-butadiene, $R = H$	

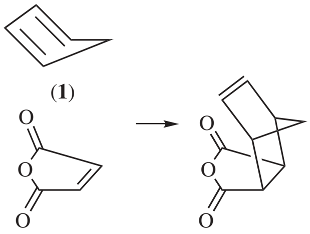
the bicycloheptene derivative formed from CPD.



Endo

Exo

With maleic anhydride as the dienophile, the reaction leads exclusively to the endo form (23) of the nadic anhydride, *endo-cis*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride [129-64-6] (**3**).

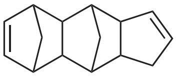


(**1**)

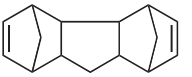
(**3**)

3.2. Polymerization.

Cyclopentadiene dimerizes spontaneously and exothermally at ambient temperature to endo DCPD via the Diels–Alder addition mechanism, in which one of the CPD molecule acts as the dienophile. At temperatures above 100°C, CPD polymerizes thermally to trimers, tetramers, and higher oligomers. Since either one of the nonconjugated double bonds in an oligomer can participate in the Diels-Alder addition to the CPD to form a higher oligomer, the higher oligomers can have several structural isomers. For instance, two trimers, 3*a*,4,4*a*,5,8,8*a*,9,9*a*-octahydro-4,9:5,8-dimethanobenz-1*H*-[*f*]indene, [7158-25-0] (**4**) and 1,4,4*a*,4*b*,5,8,8*a*,9*a*-octahydro-1,4:5,8-dimethano-1*H*-fluorene [35184-08-8] (**5**), are formed in the ratio 87:13 by the addition of CPD to DCPD (24).



(**4**)



(**5**)

In contrast to DCPD, higher thermal oligomers are crystalline compounds with little odor. The yields of the oligomers at various temperatures and contact times are shown in Table 3.

In addition to thermal polymerization, CPD can be polymerized rapidly at low temperatures with the aid of Lewis acid catalysts (25). The catalysts most often uses in the industry are $AlCl_3$ and BF_3 although $AlBr_3$, $TiCl_4$, $SnCl_4$ as well as alkyl aluminum chlorides are all known to be effective catalysts.

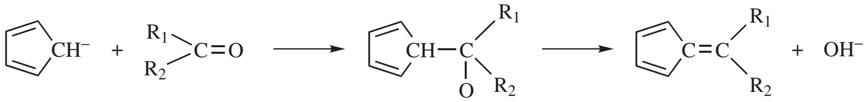
3.3. Condensation Involving the Methylene Group.

Because of the resonance stabilization of the π-electron system, the cyclopentadienyl anion

Table 3. **Yield of Cyclopentadiene Oligomers at Various Temperatures and Contact Times, wt%**

Oligomer	150–160°C 14 h	170–180°C 22 h	200°C 90 h
tricyclopentadiene	40	50	25
tetracyclopentadiene	10	30	45
pentacyclopentadiene	2	5	10
unreacted DCPD	50	10	5

forms readily from CPD after the dissociation of the acidic methylene proton. Under alkaline conditions, CPD undergoes condensation reaction with carbonyl compounds, such as ketones and aldehydes, yielding a family of highly colored fulvene derivatives (26).



The color of the fulvenes increases with the size of R_1 and R_2 (2). The dimethylfulvene is bright yellow whereas fulvenes with aromatic substitutents are blood-red. The aldehyde condensation products are also strongly colored. Because they resinify easily, it is difficult to separate them in the pure form.

Fulvenes can be hydrogenated to the corresponding alkylated cyclopentanes in the presence of nickel or palladium catalysts. Therefore, the condensation reaction provides a convenient route for the synthesis of alkylated cyclopentanes from CPD.

Cyclopentadiene reacts with alkaline oxides and hydroxides forming the alkaline cyclopentadienyl salts. Alkaline hydroxides supported on high surface materials such as kieselguhr and alumina are good absorbents for trace amounts of cyclopentadiene contaminant in other hydrocarbons (27).

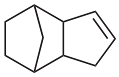
3.4. Hydrogenation.

Cyclopentadiene can be hydrogenated stepwise through cyclopentene to cyclopentane in the presence of hydrogen and noblemetal catalysts such as palladium (2). The heats of reaction at 82°C are as follows (28)

$$C_5H_6 + H_2 \longrightarrow C_5H_8 \qquad 99.2\,\text{kJ/mole}\ (22.2\,\text{kcal/mol})$$

$$C_5H_6 + 2\,H_2 \longrightarrow C_5H_{10} \qquad 212.8\,\text{kJ/mole}\ (50.9\,\text{kcal/mol})$$

Similarly DCPD is hydrogenated first to the dihydro derivative and then to the tetrahydro DCPD (29). The heat of hydrogenation of the double bond of the bicycloheptene ring is 139 kJ/mol (32.2 kcal/mol), whereas that of the five-member ring is 110 kJ/mol (26.2 kcal/mol) (30). Therefore the former double bond is more reactive and is the first to be hydrogenated, yielding the 3*a*,4,5,6,7,7*a*-hexahydro-4,7-methanoindene (**6**), one of the two possible structural isomers of the dihydro DCPD.



(6)

Oligomers of CPD can also be hydrogenated. The endo isomers of the hydrogenated products are waxlike solids. Physical properties of the hydrogenated oligomers can be found in refs. 30–32. Hydrocarbon resins produced by polymerization of CPD are hydrogenated to improve their color, light stability and adhesive properties. Colorless resins obtained this way are used for demanding applications such as adhesives for transparent pressure-sensitive tape.

Hydrogenation of CPD and DCPD with noble metal catalysts tends to produce a mixture of dihydro and tetrahydro derivatives. If only the dihydro derivatives are to be produced, selective hydrogenation catalysts must be used. Hydrogenation catalysts designed for the conversions of conjugated diolefins like 1,3-butadiene or isoprene to the olefins have been used for this service. These catalysts are mostly palladium metal modified with one or more promoters (33).

3.5. Oxidation. Cyclopentadiene reacts spontaneously with oxygen to form a brown, gummy substance that contains a substantial amount of peroxides. Dicyclopentadiene reacts with air slowly, yielding a gummy deposit. The gum formation in DCPD can be inhibited by the addition of 100–200 ppm by weight of antioxidants such as t-butylcatechol and α-naphthol. Vapor-phase catalytic oxidation of CPD over vanadium oxide at 400–525°C yields maleic anhydride, carbon dioxide, and formaldehyde. Dihydroxylcyclopentenes and tetrahydroxylcyclopentane can be prepared by treating CPD with hydrogen peroxide (34–37).

3.6. Halogenation. Halogens and hydrogen halides react readily with the conjugated double bonds of CPD, producing a series of halogenated compounds ranging from the monohalocyclopentene to tetrahalocyclopentane. 3-Chlorocyclopentene is not stable. It decomposes on standing, with resinification and the release of hydrogen chloride.

The halogenated derivatives of cyclopentadiene serve as the starting points for the synthesis of a large number of organic compounds, including amines, alcohols, and thiocyanates. Of all the chloro compounds derived from CPD, only hexachlorocyclopentadiene [77-47-4] has been used in commercial quantities. It is prepared by a liquid phase chlorination of CPD below 50°C (38). Tetrachlorocyclopentane is produced first, by chlorine addition, and is then converted to octachlorocyclopentane by catalytic chlorination over arsenious oxide or phosphorus pentachloride at 175–250°C. Octachlorocyclopentane is then dehydrochlorinated thermally to the hexachlorocyclopentadiene.

Hexachlorocyclopentadiene is the basis for a number of pesticides such as Chlorodane, Aldrin, Dieldrin, and Kepone. The production of some of these materials has been banned in many regions because of their carcinogenic properties and toxicity to wildlife. Hexachlorocyclopentadiene is also the raw material for chlorendic acid, which is used as a flame retardant (39) for unsaturated polyester resins.

3.7. Alkylation. Cyclopentadiene can be multiply alkylated in high yields using alkyl halides, oxo alcohols, and Guerbet alcohols (40,41). The multiply alkylated cyclopentanes obtained by hydrogenation of the diene derivatives have been demonstrated to be useful as synthetic lubricants.

4. Source and Production

Steam crackers for the production of ethylene are the primary source of cyclopentadiene and dicyclopentadiene, although a small amount is still recovered from coal tar distillation. The amount of CPD produced depends on the feedstock to the cracker. The yield from a naphtha cracker is 6 to 8 times of that from a gas cracker, which uses ethane and propane feed mixture.

The cracked gas leaving the furnace section of a steam cracker contains many chemical components. They are separated by a series of fractionation columns. The bottom stream from the debutanizer column, known as the pyrolysis gasoline in the industry, contains the C5 and heavier fraction of the cracked gas. Typically, cyclopentadiene plus dicyclopentadiene constitute 15–25 w% of the pyrolysis gasoline. Because CPD dimerizes readily, it is usually recovered in the form of the DCPD.

There are two ways by which DCPD can be obtained from the pyrolysis gasoline, depending on whether the pyrolysis gasoline is processed immediately after leaving the debutanizer. When the pyrolysis gasoline is processed immediately, the amount of DCPD present is small. The process scheme generally follows that depicted in Figure 2. The C5 fraction of the pyrolysis gasoline is first separated as the overhead of a depentanizer. The C5 stream is heat-soaked in a dimerizer at about 100°C. The CPD in the C5 stream is converted to DCPD. The separation of the low-boiling C5 components from the DCPD is achieved by a

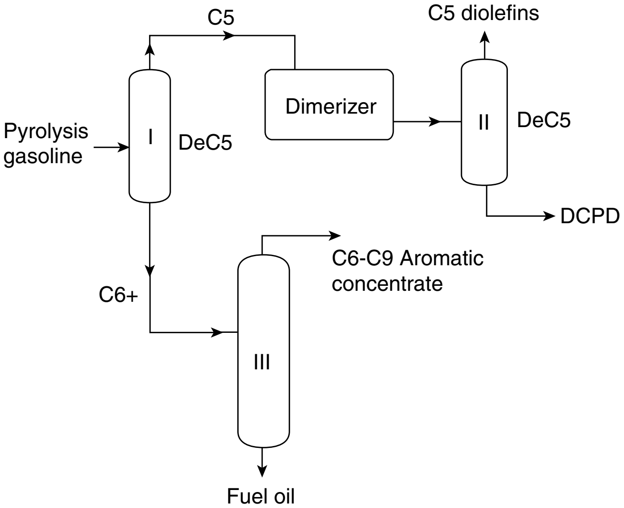


Fig. 2. Process scheme for extracting dicyclopentadiene from pyrolysis gasoline when the gasoline is processed immediately after its production in an ethylene plant.

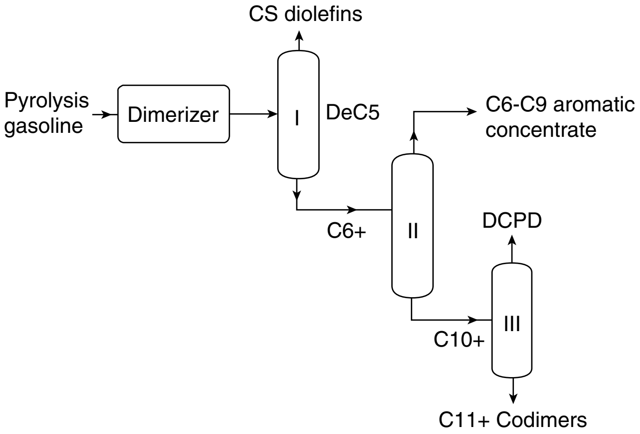


Fig. 3. Process scheme for extracting dicyclopentadiene from pyrolysis gasoline when the gasoline was in storage for an extended period of time after its production in an ethylene plant.

second fractionation in which the DCPD is recovered as the bottom product. The DCPD is mainly in the endo form and has a purity of 82–90%.

If the pyrolysis gasoline is placed in storage before it is processed or if the process is supplemented with purchased pyrolysis gasoline, a significant amount of the CPD in the pyrolysis gasoline is already in the form of DCPD, since cyclopentadiene dimerizes to DCPD at a rate of 9 mol%/h at 35°C. The recovery of the DCPD follows a different process scheme as shown in Figure 3. The pyrolysis gasoline is first heat-soaked in a dimerizer to convert remaining CPD to DCPD. The effluent from the dimerizer is fractionated in one or more columns where the C5–C9 components are separated from the C10 and heavier fraction. (Usually, this fractionation is carried out in two steps: First a CPD-lean C5 stream is produced as the overhead of a depentanizer. The bottom stream of the depentanizer is further processed in a second column which separates the C6–C9 components as the overhead while the C10 and heavier fraction becomes the bottom stream.) The C10 and heavier stream, which contains 50–70% DCPD, is distilled to yield a DCPD overhead product. The purity of the DCPD is 82–95%.

The process in Figure 2 requires less demanding fractionation but it has the disadvantage of leaving in the DCPD all the oligomers produced during the heat-soak step. The process scheme in Figure 3 also has the advantage of flexibility in adjusting the DCPD product to a desirable purity by simply varying the fractionation conditions in the last column.

High-purity DCPD in the range of 98–99% is produced by thermal cracking of the lower-purity DCPD. Pure CPD is separated from the crude DCPD by distillation and is redimerized in controlled conditions to avoid oligomer formation. Unreacted CPD is stripped from the high-purity DCPD by mild fractionation (42).

The annual capacity of DCPD production for all grades in the United States is estimated to be in excess 350 millions pounds in the 1999. The major U.S producers are B. F. Goodrich Company, Equistar Chemicals (a joint venture of Lyondell Petrochemical, Milennium Chemicals, and Occidental Petroleum Company), Exxon Chemical Company, Phillips Petroleum Company, Shell Oil Company, Texmark Chemicals, and Velsicol Chemical Corporation. The major consumptions of DCPD in the United States are in the production of hydrocarbon and unsaturated polyester resins (80%), ethylene–propylene terpolymers (10%), reaction injection molding (5%), and miscellaneous uses (5%). The last includes flame retardants, pesticides, antioxidants, and metallocene catalyst production. The demand for DCPD will grow in a rate of 4% per year in the next several years.

Western Europe and Japan have, respectively, annual DCPD production capacities of 176 and 195 millions pounds, and predicted annual growth rates of 5% and 6% (43). The major producers in Europe are Exxon, EniChem, Dow, and Shell. Nippon Zeon and JSR are the major producers in Japan.

5. Storage and Handling

Because CPD monomer dimerizes spontaneously at room temperature and a large quantity of heat (75 kJ/mol or 18 kcal/mol) is released in the process, material containing a substantial amount of CPD should not be stored in any sealed container without the provision of removing the heat. The rate constant of the dimerization is $1.2 \times 10^6 \exp(-16.7/RT)$ L/mol s (2). Thus the rate of reaction accelerates rapidly with increasing temperature. Without adequate heat dissipation, runaway dimerization occurs. The resulting high temperature leads to the building up of pressure, which will eventually burst the container. Commercial quantity of CPD is usually produced, stored, and shipped in the form of the stable dimer, DCPD. Because of the high freezing point of DCPD, the material is transported in tank cars, rail cars, or barges equipped with heating elements. The heating of the DCPD must be regulated. Otherwise, excess temperature will lead to the formation of the undesirable oligomers. Exposing DCPD to even a trace amount of oxygen or rust at temperatures in excess of 100°C promotes the formation of peroxides and other oxygenates. The oxygenates degrade the quality of the DCPD because they impact undesirable color to the product. DCPD is usually stabilized with 100–200 ppm of antioxidants such as *tert*-butyl catechol to prevent gum deposit during storage.

Temp. °C	Dimerization rate mol %/h	Temp. °C	Dimerization rate mol %/h
−20	0.05	25	3.5
0	0.5	30	6
10	1	35	9
15	1.5	40	15
20	2.5		

For commercial applications, which require the cyclopentadiene monomer, the CPD is obtained from DCPD by thermal cracking. The process involves distilling the DCPD at its normal boiling point (170°C) under an inert atmosphere. At 170°C, DCPD cracks at a rate of 36%/h. By maintaining the overhead temperature of the column at 41–42°C, the boiling point of CPD, an overhead condensate of pure CPD monomer can be obtained. The thermal cracking and distillation can also be accomplished by heating the DCPD in the presence of a heavy oil at about 250°C. The heavy oil functions as a solvent to minimize fouling due to resinification at high temperature. Another method of producing CPD is by cracking the DCPD in the vapor phase at 350–400°C. At these temperatures, the decomposition of the DCPD is instantaneous. The vapor-phase process has the disadvantage that C10 codimers presented in the DCPD also crack at the high temperatures, producing C5 diolefins such as isoprene and piperylenes. The C5 diolefins makes the purification of the CPD much more difficult. To minimize the cracking of C10 codimers, one needs to maintain the temperature below 250°C (44–46).

Because CPD reacts spontaneously with oxygen to form gummy peroxide-containing products, it must be protected from air if not being used immediately. To minimize dimerization, CPD should be stored at a temperature below −20°C.

6. Health and Safety Factors

DCPD is a toxic substance. By oral administration in rats, the LD_{50} is 353 mg/kg of body weight, and by skin absorption in rabbits, the LD_{50} is 6.72 ml/kg. An atmospheric concentration of 2000 ppm causes death in rats exposed for a period of 4 h. Studies with rats indicate that DCPD has no deleterious effects on the blood and blood-forming organs. Toxicological effects are similar to terpenes rather than to benzene. The TLV and PEL for DCPD are both 5 ppm, as established by ACGIH and OSHA. Chronic exposure causes damages to the liver, kidneys and lungs.

7. Uses of Cyclopentadiene and Dicyclopentadiene

There are two general categories of industrial end uses of cyclopentadiene and dicyclopentadiene: (1) commodity resins and polymers, which include hydrocarbon resins, unsaturated polyester resins, and ethylene propylene diene rubbers (EPDM); (2) specialty polymers and fine chemicals, which include cyclic olefin copolymers, flame retardants, agrochemicals, specialty norbornenes, flavor and fragrance intermediates. Over 90% of the U.S. consumption of CPD and DCPD is in the first category.

7.1. Hydrocarbon Resins.

About 50% of the DCPD produced is used in hydrocarbon resins. Crude DCPD with 60–75% purity is typically used in this application. Other components in the feedstock may consist of codimers of CPD with isoprene, piperylene, and methylcyclopentadiene, and a small amount of the dimers of methylcyclopentadiene. Both DCPD and the codimers are incorporated into the hydrocarbon resins (47,48). Other C5 diolefins can also be added to the process.

The hydrocarbon resins can be produced by a simple thermal polymerization process (49–51) or by Lewis acid catalyzed reaction (52). The thermal process is carried out at a high temperature in the range of 200–280°C and a reactor pressure above 300 psig. At temperatures below 200°C, the Diels–Alder polymers are formed. They are not desirable in most resins because they are insoluble in aromatic solvents. If reaction temperature exceeds 280°C, decomposition of the resins would occur.

In the acid-catalyzed process, crude DCPD is mixed with a Lewis acid such as BF_3 in the presence of an alcohol or ether (53). An aromatic co-solvent may also be used. Temperature control is critical for producing the resin. After reaction, the Lewis acid is removed by a caustic solution and the resin is further washed with water to remove any caustic and catalyst residues. Unreacted DCPD and the co-solvent are removed by steam stripping.

The DCPD concentration and reaction temperatures have strong influence on the properties of the final resins such as the softening point, color, unsaturation, and reactivity. The resin may be hydrotreated to improve the color and thermal stability. The resins are sold in the solid form as flakes or pellets. The main applications of the resins are in adhesives, tackifiers in tires and floor tiles, surface coating and varnishes, and ink. Water-white resins produced by hydrogenation process are used in road-marking paint, hot-melt adhesives with thermoplastic rubber, which can be found in diapers and feminine hygiene products.

7.2. Unsaturated Polyester Resins. Unsaturated polyester resins based on DCPD are produced by reacting glycols, maleic anhydride, and DCPD (12). There are at least four different methods (12,54) in making the DCPD-based polyesters. They are usually two-step batch processes. In one commonly used method, the glycol and maleic anhydride are first allowed to react at a temperature below 150°C, typically around 130°C. Then DCPD is added to the mixture and the reactor temperature is gradually raised to 200°C. After an acid number between 30 and 40 is obtained, the polyester is allowed to cool and is diluted with a mixture of styrene and inhibitors.

DCPD-based polyester resins have several advantages over the conventional polyester resins based on phthalic anhydride. Besides the lower cost of the DCPD, low cost glycols like ethylene glycol can be used instead of the more expensive propylene glycol. Since the DCPD based resins require less styrene than the phthalic anhydride based resin, there is less styrene emission in the production and processing of the DCPD based resins.

The resins are used primarily in the fiber-reinforced form as laminates, castings, and coatings (55,56). Glass fiber is one of the common fillers for the reinforcement. Because of the low viscosity of the resin, the DCPD-based sheet molding compounds can incorporate a greater amount of the low-cost fillers. The low print-through of the fillers makes the DCPD based resins ideal for applications in which aesthetic effects are important. These include marine applications (recreation boats, jet skis), automotive parts, safety helmets, bathroom counter tops, shower stalls, and tubs. In the nonreinforced form, the resins have been used as insulation coating for electrical coils (57,58).

7.3. Elastomers. Ethylene–propylene–diene monomer (EPDM) rubbers is a terpolymer of ethylene, propylene and a nonconjugated diene. The diene provides the double bonds in the polymer for the cross-linking, thus increasing the flexibility of the polymer. Dicyclopentadiene and ethylidene norbornene (ENB), a CPD derivative, are among the most important dienes. Typically, high-purity DCPD in the 94+% range is used. High purity DCPD is also preferred in the synthesis of ENB, which is a two-step process. EPDM rubber has a wide variety of applications, particularly in the automotive industry. It is used in side walls of tires, door and window weatherstripping, cable insulation, radiator and heater hose, and belting.

In the ENB production, DCPD is thermally cracked to CPD, which subsequently reacts, via the Diels–Alder mechanism, with butadiene to form the 5-vinylbicyclo[2.2.1]-hept-2-ene [3048-64-4] (VNB) (7) (59,60). The vinyl double bond is then isomerized in the presence of a selective super-base catalyst such as NaK amide to yield the 5-ethylidenebicyclo[2.2.1]-hept-2-ene [16219-75-3] (ENB) (8) (61–63).

7.4. Cyclic Olefin Copolymers.

Cyclic olefin copolymers (COC) are produced by copolymerization of ethylene with a cyclic olefin monomer such as norbornene, dihydro DCPD, phenyl norbornene, and tetracyclododecene. Ziegler–Natta and metallocene catalysts are used in the polymerization processes. COC resins have excellent transparency, near zero birefringence, low density, low water uptake, and good chemical resistance. The target markets for the polymers are in high-density electronic storage media such as optical disks, high-quality lenses, medical labware, high-performance films, and pharmaceutical blister packaging (64).

Cyclic olefin monomers are derivatives of CPD or DCPD. Norbornene derivatives are produced by the Diels–Alder condensation of an olefin and cyclopentadiene. For instance, 2-norbornene (9) is obtained by reacting excess ethylene with DCPD at a high temperature (>200°C) and pressure (>2900 psia), the condition in which the DCPD is cracked to CPD (65). Reactions of CPD or DCPD at high temperatures with styrene and norbornene yield, respectively, the phenylnorbornene (10) and tetracyclododecene (11).

7.5. Polydicyclopentadiene.

Ultrapure (98+%) DCPD can be polymerized catalytically to form polydicyclopentadiene [25038-78-2], a low-viscosity gel that is dark in color and flows like water. Very intricate moldings with good impact resistance can be obtained after curing the polyDCPD. In reaction injection molding (RIM), polyDCPD is formed by the injection into a mold two equal amounts of DCPD, one part containing a metal catalyst, and the other part containing aluminum alkys activators (66,67). Upon mixing, the catalyst is activated and initiates the metathesis polymerization. The whole process lasts for 30 s to a few minutes. Reviews of the chemistry and properties of polyDCPD have been published (68,69). Companies like Hercules, B. F. Goodrich, Orkem, Shell, Nippon Zeon and Teijin hold many patents on the polyDCPD synthesis, catalysts, modifiers, and applications. The major industrial uses of polyDCPD are in moldings for golf carts, automobile bumpers, housing for the hull and body of recreation water vehicles, and body panels for automobiles.

7.6. Cyclopentene.

High-purity cyclopentene is produced from CPD by selective hydrogenation. The process involves the cracking of DCPD to high-purity CPD followed by the selective saturation of one of the two double bonds of CPD in a fixed-bed reactor containing a palladium-based catalyst. Cyclopentene is used as an intermediate in the production of many specialty chemicals.

7.7. Pesticides. Hexachlorocyclopentadiene, produced by reacting cyclopentadiene with chlorine, is the starting material for a host of insecticides including aldrin, chlorodane, dieldrin, and heptachlor. Because of environmental regulation, most of the DCPD based insecticides are no longer produced and used in the United States.

7.8. Flame Retardants. Chlorendic anhydride [115-27-5] (12), produced by the Diels–Alder condensation of hexachlorocyclopentadiene and maleic anhydride, is used as a flame retardant for unsaturated polyester resins. The anhydride is incorporated in the resins by the esterification reaction with glycols.

Flame-retardant polyester formulation may contain 10–50% of the anhydride, with 30% being typical. They are used primarily in construction including shower systems, lavatories, panels in exterior sidings of office buildings, roof lights, glazing, and door panels. The chlorendic anhydride based resins tend to demand high prices because of their translucency and increased corrosion resistance.

7.9. Specialty Uses and Applications. Numerous reactions of DCPD and higher oligomers have been described in the patent literature. These involve the addition of the reacting chemical at the double bond of the bicycloheptene ring of the DCPD molecule to give such products as secondary alcohols, ethers, esters, and halides. When the reaction is acidcatalyzed at elevated temperatures, the resulting products have the exo configuration even though endo DCPD is used as the starting material. For example, in the presence of sulfuric acid, water adds to DCPD to form the exo secondary alcohol. Dicyclopentadiene alcohol can be used as a component of unsaturated polyester resins, perfumes, and plasticizers. Some dicyclopentadiene esters are also used as perfume components (70). Dicyclopentadiene alcohol, a number of esters, ethers, and glycol adducts have been claimed as coal and ore flotation aids.

Cyclopentadiene oligomers have been formed by vapor deposition of CPD on kaolin to afford a sorbent for removal of oil from water (71). They are also employed as coatings for controlling release rates of fertilizers (72). Thermal addition of sulfur to a mixture of DCPD and CPD oligomers has led to a number of beneficial applications such as waste water oil adsorbent powdery foam (73), plasticized backing for carpets and artificial turfs (74), and in modified sulfur cements for encapsulating low-level radioactive wastes (75).

Cyclopentadiene itself has been used as a feedstock for carbon fiber manufacture (76). It is also a component of supported metallocene–alumoxane polymerization catalysts in the synthesis of polyethylene and polypropylene polymers (77), as a nickel or iron complex in the production of methanol and ethanol from synthesis gas (78), and as Group VIII metal complexes for the production of acetaldehyde from methanol and synthesis gas (79).

Adamantane, tricyclo[3.3.1.1]decane [281-23-2] (15), can be produced by heating tetrahydrodicyclopentadiene [6004-38-2] (14) in the presence of aluminum trichloride (80). It is the base for drugs that control German measles and influenza (80,81).

Other specialty applications of DCPD and CPD derivatives includes dicyclopentadiene dioxide, dicyclopentadiene diepoxide and dicyclopentadiene dicarboxylic acid in surface coatings, and the tetrahydrogenated DCPD and CPD as high energy fuels for racing cars, missiles, and jet S (82,83).

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