Reprinted from:

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

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VOLUME 3
CARBON (cont'd) to CINCHOPHEN

Published by
THE INTERSCIENCE ENCYCLOPEDIA, INC. • NEW YORK

Chlorinated Diphenyls and Related Compounds.

The Aroclors (trade-mark) are chemically inert materials prepared by the chlorination of diphenyl (biphenyl) or terphenyl or more complex polyphenyls, usually without separation of the chlorinated products into individual compounds. The form and appearance vary from mobile oily liquids to fine white crystals and hard noncrystalline resins.

Because of the many forms and properties, these products have found applications in many diverse fields as in electrical insulation, nonflammable hydraulic mediums, lubricants for use at high temperatures and pressures, and also as constituents of adhesives, plastics, lacquers, paints, and varnishes.

Commercial manufacture of the first members of the Aroclor series was started in 1929, and the other Aroclors were developed soon afterwards.

Physical and Chemical Properties

Since Aroclors are chemically inert except under drastic conditions, they are of interest chiefly because of their physical properties (3). All Aroclors are insoluble in

TABLE I. General Properties of Some Aroclors.

Material	Form and color	d^{25}_{25} or n^{25}_{D}	Distillation range,[a] °C.	Flash point,[b] °C.	Flame point,[b] °C.	Pour point,[c] °C.	Softening point,[d] °C.	n^{25}_{D}	Viscosity,[e] sec. At 37.8°C.	Viscosity,[e] sec. At 98.9°C.
Aroclor 1221	Colorless mobile oil	1.177–1.187	275–320	141–150	176	Crystals at 1°C.	—	1.617–1.618	40–42	30–31
Aroclor 1232	Almost colorless mobile oil	1.262–1.272	290–325	152–154	238	−35.5	—	1.620–1.622	47–50	31–32
Aroclor 1242	Almost colorless mobile oil	1.378–1.388	325–360	176–180	334	−19.0	—	1.627–1.629	80–93	34–35
Aroclor 1248	Yellow-tinted mobile oil	1.447–1.457	340–375	193–196	None	−7	—	1.630–1.631	185–240	36–37
Aroclor 1254	Light yellow viscous oil	1.538–1.548	365–390	None	None	10	—	1.639–1.641	1800–2500	44–48
Aroclor 1260	Soft yellow sticky resin	1.618–1.629	385–420	None	None	31	—	1.647–1.649	—	72–78
Aroclor 1262	Light yellow sticky resin	1.646–1.653	400–430	None	None	37	—	1.6501–1.6517	—	90–103
Aroclor 1268[f]	Opaque yellow brittle resin	1.804–1.811	435–450	None	None	—	—	—	—	—
Aroclor 1270[g]	White crystalline powder	1.944–1.960	450–480	None	None	—	—	—	—	—
Aroclor 4465	Transparent yellow brittle resin	1.712–1.723	230–320,[h]	None	None	—	60–66	1.664–1.667	—	90–150 (at 130°C.)
Aroclor 5442	Transparent yellow sticky resin	1.432–1.447	215–300,[h]	247	> 350	46	45–50	—	—	300–400
Aroclor 5460	Yellow transparent resin	1.740–1.745	280–335,[h]	None	None	—	100–105.5	1.660–1.665	—	—
Aroclor 2565	Brown-black opaque resin	1.724–1.740	—	None	None	—	66–72		—	—

[a] A.S.T.M. D90-30. [b] Cleveland open cup. [c] A.S.T.M. D97-47. [d] A.S.T.M. 28-42T. [e] Saybolt Universal, A.S.T.M. D88-44. [f] Hold point on solidification, 135–160°C. [g] Hold point on solidification, 249–300°C.

water, but the oils and resins are readily soluble in most of the common organic solvents and drying oils. The hard crystalline materials are in general less soluble than the oils and resins. The Aroclors are permanently thermoplastic and may be repeatedly melted and cooled without undergoing condensation or permanent hardening. Most of the common metals and alloys have excellent resistance to the Aroclors even at elevated temperatures. However, copper and some of the copper alloys are affected to a limited extent, and show penetration rates between 0.0014 and 0.014 in. per year. Many plastic materials of construction are attacked by the Aroclors.

The general properties of the more important grades of the Aroclors are shown in Table I, and Table II shows the electrical properties of those Aroclors that have found application in the electrical field.

TABLE II. Electrical Properties of Some Aroclors.

Property	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 3442
Dielectric constant at 100 °C. and 1000 cycles[a]	4.6	4.9	4.6	4.1–4.3	3.6–3.8	4.9
Resistivity, ohm-cm., at 100 °C. and 500 volts d.c.	—	—	Above 500×10^9	Above 500×10^9	Above 500×10^9	Above 500×10^9
Dielectric strength,[b] kv.	—	—	—	Above 35	Above 35	—
Power factor, % at 100 °C. and 1000 cycles	—	—	Below 0.1	Below 0.1	Below 0.1	Below 0.1

[a] A.S.T.M. D150–47T. [b] A.S.T.M. D149–44 using a 0.100-in. gap.

Manufacture

The pure compounds formed by the chlorination of diphenyl, terphenyl, or the more complex polyphenyls are crystalline solids, some of which have very high melting points (11). However, mixtures containing a number of such compounds are either liquids or noncrystalline resins. Chlorination of aromatic hydrocarbons to various levels not only gives several isomers of the same chlorine content but also gives appreciable proportions of the isomers of compounds of higher and lower chlorine contents (17,23). At any given level of chlorine content, batch chlorination gives the highest proportion of compounds corresponding in composition to the average chlorine content, while single-stage continuous chlorination gives the lowest proportion of such compounds. As the number of stages is increased, multistage continuous chlorination gives compositions approaching those given by batch chlorination. The proportion of the various isomers and of compounds of higher and lower chlorine contents than the average is also influenced by such factors as temperature, quantity and kind of catalyst employed, degree and type of agitation, and rate of admission of the chlorine.

Batch chlorination has been found most suitable for the manufacture of the Aroclors (22,24). The chlorinators are cylindrical steel towers 3 ft. in diameter and 18 ft. high, which are equipped with chlorine distributors at the bottom and with coils for heating and cooling the material undergoing reaction. Pumps provide agitation by

circulating the charge. The lower half of the chlorinators is filled with iron turnings, which have been burned free of oil and moisture. In German practice, the chlorinators are agitated 10,000-liter lead-lined vessels, and ferric chloride is used as the catalyst instead of iron turnings. Fifteen kilograms of ferric chloride is used for each charge of 6000 kilograms (13).

Raw Materials. The raw material used depends on the grade of Aroclor to be produced; anhydrous chlorine is used as the chlorinating agent in all cases. In general it can be said that diphenyl alone gives liquid or soft sticky noncrystalline Aroclors up to a chlorine content of 60%, low-melting resinous Aroclors between 60% and 65% chlorine content, and partly crystalline or crystalline Aroclors of much higher melting points at chlorine contents above 65% (23). In the case of products that are solid at ordinary temperatures, the higher the proportion of terphenyls or more complex polyphenyls in the mixture before chlorination, the higher the softening point and the less the crystallising tendency of the chlorinated product after distillation. For those Aroclors that are solid or partly crystalline at room temperature, the higher the chlorine content, the higher the softening point and the greater the tendency of the material to crystallise (24).

Preparation of Crude Aroclors. For the manufacture of any given grade of Aroclor, the chlorinator is charged with the proper raw material or mixture of raw materials to give the desired product, and in an amount sufficient to cover the catalyst bed and to permit circulation. Then the flow of vaporised chlorine is started and the charge is circulated with the pump. Throughout the chlorination, the temperature is kept well above the melting point of the mixture, but below 150 °C., to avoid excessive sublimation and plugging of the line discharging the hydrogen chloride produced by the chlorination. Samples are withdrawn for examination from time to time until the desired chlorine content has been reached. At the lower chlorine contents, specific-gravity determinations are used to determine the composition. After the product has become too viscous or has reached too high a melting point for convenient determination of the specific gravity with a hydrometer at temperatures below 100 °C., the degree of chlorination is determined by measuring the hold point in temperature as the material crystallises, or by the ball-and-ring softening-point test (8). The time required for chlorination is 12–36 hr., depending upon the chlorine content of the product. The anhydrous hydrogen chloride, which is evolved during the chlorinations, is absorbed in water in equipment of conventional design.

Distillation of Crude Products. Although the crude products find some applications, for most purposes further purification is necessary to remove the color and the traces of hydrogen chloride and ferric chloride (13,23,24). The methods of purification are somewhat different for the different types of Aroclors. The high-melting solid products are distilled in retorts at atmospheric pressure and the distillate is flaked on chilled rolls. The liquid and resinous Aroclors are held at an elevated temperature and blown with dried air for several hours. Then a few tenths of one per cent of lime or sodium hydroxide is stirred with the material to react with any remaining hydrogen chloride or ferric chloride. This is followed by batch distillation. Complete distillation and mixing of the distillate is necessary in order to obtain uniform material of the desired composition.

If increased electrical resistivity is desired, the material is stirred at an elevated

temperature with a few tenths of a per cent of well-dried fuller's earth and then filtered through paper (13,26).

Containers and Shipping

The liquid Aroclors are packed and shipped in galvanized steel drums or in tank cars constructed of nonrusting metals such as aluminum or tin-coated metal. The resinous Aroclors are packed and shipped in open-top galvanized steel drums. The high-melting solid Aroclors are packed and shipped in wooden barrels. The railroad shipping classification is Resin Synthetic *N.O.I.B.N.*

Health and Safety Factors

The conventional safeguards must be taken to protect personnel from the poisonous effects of chlorine. Experimental work on animals has indicated that prolonged exposure to Aroclor vapor evolved at high temperature or repeated oral ingestion of Aroclor will lead to systemic toxic effects. Repeated bodily contact with liquid Aroclors may lead to an acne-form skin eruption. In the manufacture or use of Aroclors, untoward effects on personnel are prevented by draft ventilation to control the vapors evolved at high temperatures, together with the use of suitable garments to prevent extensive and repeated bodily contact with the liquid products (3).

Uses

Electrical Applications. All of the uses of the Aroclors depend on their chemical stability and their physical properties, which may be varied to suit the specific application. One very important use is as dielectric mediums in such applications as oils for transformers and as impregnants for capacitors and condensers (10,11,12,15,18,21,25). Aroclors, used either alone or in blends with other materials such as trichlorobenzene, meet the need for a nonflammable dielectric liquid with a high resistivity, a high dielectric strength, and a relatively high dielectric constant in relation to a very low power factor. The fact that the dielectric constant is higher than that of hydrocarbon oils and is more nearly equal to that of the solid insulation materials, such as paper, results in a reduction of electrical strains. By substituting Aroclors, or mixtures of Aroclors with trichlorobenzene, for hydrocarbon oils, it has been possible to redesign equipment with a great reduction in size for the same capacity and voltage. At the same time the fire hazards have been eliminated.

Other important electrical applications for Aroclors are as impregnants for cotton or asbestos-fiber insulation (22), as constituents of asphalt-base wire-impregnating compounds, and as plasticizers in wire-coating compounds, particularly those containing neoprene, rubber, or combinations of polyvinyl chloride, ethyl cellulose, and polyvinyl butyral (30–33). Also, Aroclors are employed as sealing mediums for electrical insulators and as impregnants for carbon radio resistors to reduce the influence of moisture.

Plastics, Lacquers, Paints, and Varnishes. The Aroclors are compatible with most of the common plastic materials and resins and are soluble in paint and varnish oils (3). In combination with asphalt, ethyl cellulose, chlorinated rubber, Pliolite S-5, or other plastic materials, they are used extensively in protective coatings for wood, metal, and concrete (3,5,6,20,23). In combination with tricresyl phosphate or dioctyl phthalate they are coplasticisers for polyvinyl chloride compositions (4).

In paints and varnishes the hard resinous Aroclors are used to impart increased hardness to the films, and the softer resins are used to give flexibility. The role of the Aroclor is similar to that of the oil, except for the fact that it does not oxidise and lose its flexibility on aging. In nitrocellulose lacquers, Aroclors are employed either alone or in combination with other plasticizers and resins to impart increased weather resistance, luster, adhesion, and decreased burning rate (3,9,14,16). The hard, white, crystalline Aroclors of high melting point are useful as pigments with the various plastics (29).

Adhesives. The resinous Aroclors are used in synthetic adhesive compositions in combination with such base materials as polyvinyl acetate, ethyl cellulose, chlorinated rubber, polyvinyl butyral, isoprene–styrene copolymer, and polyisobutylene.

Lubricants. Aroclors 1248 and 1254 find application as lubricants under extreme conditions such as highly oxidising conditions, high temperatures, extreme pressures, or submerged locations. The use of Aroclor as the internal lubricant for high-pressure air compressors eliminates the explosion hazards in this operation (1,2). The materials are used also as noncombustible lubricants for regulating the steam valves on high-pressure turbines, and in rolling aluminum sheets. Mixtures with other oils to form heavier-than-water lubricants are used in submerged locations, such as bridge rollers. Lubricants for extreme pressures are made by adding up to 15% of Aroclor to petroleum hydrocarbon oils.

The liquid Aroclors are employed as nonflammable *hydraulic mediums* for transmission of pressure or volume variations. One such application is in die-casting operations with aluminum or zinc alloys, where the Aroclors replace hydrocarbon oils. The advantages are absence of fire hazards when lines break, and the fact that condensed water does not settle in the storage tanks and cause corrosion of the equipment. Another use is as the expansion medium in thermostats. Aroclors 1242, 1248, and 1254 have been found to give excellent service as circulating *liquid heat-transfer mediums* for temperatures up to 325°C. Good circulation and well-designed heating systems are necessary to prevent local overheating (3).

Carnauba wax may be extended by blending it with Aroclors in combination with ceresin and paraffin (7,19). Satisfactory *waxes and polishes* are prepared without the use of carnauba wax by blending ouricury (licuri) wax with Aroclors, ceresin, and paraffin. Aroclors are ingredients of many *fire-resistant compositions.* Fire-retarding paints usually contain antimony oxide or barium sulfate in addition to the Aroclor. In making fireproof fiberboard, emulsified Aroclors are added to the fiber stock (27). Modifying waxes are added to the Aroclor in the preparation of textile-coating materials.

Miscellaneous Applications. In addition to the uses listed above, Aroclors are ingredients of some sealing compounds for use with wood or canvas to give protection against moisture, mildew, or attacks of organisms. Some calking compounds and powdered metal pastes contain Aroclors. Some soil-poison and wood-preserving compositions contain Aroclors as an active ingredient.

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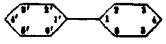
VOLUME 5
DI- to
EXPLOSIONS

Published by
THE INTERSCIENCE ENCYCLOPEDIA, INC. • NEW YORK

DIPHENYL AND TERPHENYLS

Of the series of phenyl derivatives of benzene, the most important are the lowest members of the series. Phenylbenzene (I) is usually called diphenyl but is better called biphenyl in accordance with the I.U.C. rule for using the prefix "bi" to denote the doubling of a radical or compound (see *Nomenclature*). The 3 diphenylbenzenes, *p*-, *m*-, and *o*- (II, III, and IV), are called terphenyls or triphenyls. Quaterphenyls and higher polyphenyls are also known.

(I)   (II)

(III)   (IV)

Stereoisomerism has been observed with certain derivatives of diphenyl (2,2',6,6'- and even some 2,2'-derivatives) and is attributed to restricted rotation of the bond between the 2 phenyl groups as a result of the presence of substituents in the ortho positions (1).

Diphenyl

Diphenyl (biphenyl (I.U.C., *C.A.*), phenylbenzene), $C_6H_5C_6H_5$, formula weight 154.20, is a white or slightly yellow crystalline solid, which gives plates or monoclinic prismatic crystals when crystallised from a solvent. It was first reported in 1862 by Fittig, who prepared it by the action of metallic sodium on bromobenzene. Berthelot prepared it in 1867 by essentially the same process that is used commercially today. In 1875, Büchner found diphenyl in high-boiling fractions from coal-tar distillation. It is used chiefly as a heat-transfer medium and as the raw material for chlorinated diphenyls.

Physical and Chemical Properties. M.p. 69.2°C. (4), f.p. (commercial product) 68.5–69.4°C., b.p. 255.2 ± 0.2°C., d_4^{20} 1.041, d_4^{75} 0.991, crit. temp. 528°C., crit. pressure 31,400 mm. Hg, crit. density 0.343 gram/cu.cm. (5), flash point 106°C., fire point 124°C.

Diphenyl is one of the most thermally stable of known organic compounds. Chemically it resembles benzene and can be chlorinated, nitrated, sulfonated, and hydrogenated. Diphenyl compounds analogous to benzene compounds may usually be made by the same or slight modifications of procedures used for benzene.

Manufacture. Diphenyl had little commercial value before 1925–1930, when the

first large-scale manufacture was successful. All commercial diphenyl is produced entirely by the thermal dehydrogenation of benzene. Diphenyl can also be obtained by the reduction of benzenediazonium chloride, $C_6H_5N_2Cl$ (see Vol. 5, p. 43), and as a main product or by-product in the well-known Grignard reactions (*q.v.*) using phenyl magnesium halides.

For the commercial production, benzene vapor at 1–2 atm. pressure is heated to 700–850°C., the time of exposure to the higher temperatures being of the order of one second. Under these conditions from 10 to 15% of the benzene is converted in one pass through the reactor to diphenyl, higher homologs, tars, and carbon. The yields depend upon conversion. At 10% conversion the yield of diphenyl is approximately 0.85 lb. and that of the terphenyls and quaterphenyls is 0.07 lb. per pound of benzene consumed. At 15% conversion the yield of diphenyl is 0.80 ib. and that of terphenyl, etc., is 0.12 lb. The mechanical loss of benzene is 0.02–0.04 lb. per pound of benzene consumed.

The product from the reactor is condensed, the benzene distilled off and recycled to the reactor, and the diphenyl purified by vacuum distillation. Benzene in the non-condensable gas (mostly hydrogen) vented from the primary condensers is recovered either by compressing and cooling or by using activated-charcoal adsorbers. The recycled benzene is very pure, as the nitrogen, sulfur, and aliphatic compounds are decomposed at the temperature of the reactor. The process as outlined above is simple and gives good yields from a cheap raw material. However, the tendency of benzene to decompose at temperatures above 650°C. to give carbon and heavy tar deposits on the heat-exchange surfaces of the reactor has presented a serious problem. Practically all of the patents covering the manufacture of diphenyl have been proposed as solutions of this problem.

Heat is best supplied to the reactor usually as electric heat at temperatures above 650°C. through noncatalytic surfaces. Fuel-fired furnaces have not been satisfactory because the usual high-temperature alloys employed in them contain iron and nickel, which are active catalysts for promoting the formation of carbon from benzene. Furthermore, alloys that are relatively inert for benzene pyrolysis are unsatisfactory for direct-fired furnaces because they do not resist scaling from furnace gases.

A carbon-tube furnace designed so the vapors pass both inside and outside of the tubes while the tubes act as resistors is used by Williams (25,31). The benzene vapors enter the carbon-tube section at 650°C. after being preheated by the reactor-product vapors in a conventional metal tubular heat exchanger. In the carbon-tube reactor (tubes 1 in. O.D., 0.75 in. I.D.) apparent overall heat-transfer coefficients of 100 B.t.u./(sq.ft.)(hr.)(°F.) are obtained, at a mass velocity through the tube of 7 lb./(sq.ft.)(sec.). In this reactor the temperature of the benzene vapor approaches within 10°C. the temperature of the carbon tubes. Alternating current at 40–60 volts is used to heat the carbon tubes. Williams (30) has been able to improve the operation of this unit by adding to the benzene stream 0.1% sulfur as a volatile sulfur compound such as hydrogen sulfide, carbon disulfide, or sulfur dioxide. The addition of sulfur reduces the deposition of carbon in both the carbon-tube furnace and in the preheater. Carothers' reactor is similar except that solid metallic resistors (Nichrome) are used to supply heat above 650°C. (19). He emphasizes the importance of high vapor velocity at the heating elements and gives 1.24 seconds as the maximum time in the reaction zone. The I. G. Farbenindustrie diphenyl plant at Leverkusen used copper-tube reactors heated by external electrical resistance elements to produce 27,000 lb. diphenyl per

month (6). Lowdermilk and Turnecock (9) and a BIOS Report (3) state that two batch units were installed, one producing 22,000 lb. per month and the other 80,000 lb. per month. A third, to produce 150,000 lb. per month, was under construction. The reactor was a copper-alloy tube containing 3% manganese electrically heated by its own resistance. Operating at 790–810°C., these reactor coils had a life of eighteen months. All-copper coils lasted only a few days in this type of reactor.

These units were batch units in which a kettle was loaded with benzene and the vapors were circulated through the system by boiling the benzene in the kettle. The vapors were circulated for eight hours, then the batch was transferred to a still. Thiophene-free benzene was used in this copper equipment.

A number of attempts have been made to reduce catalytic activity of ferrous surfaces so that conventional fuel-fired furnaces can be used. Among the suggestions that have been made are coating the walls with antimony pentasulfide, zinc sulfide, iron sulfide, or cobalt sulfide (15,29); nitriding the iron surface by treatment with ammonia (34); and forming a carbide surface on the iron tube (38). In any of the processes using solid surfaces to supply heat to the reactor it is essential that surface temperatures be kept as low as possible, by using low-heat flux through the surfaces and maintaining high gas-film heat-transfer coefficients at the surface. While the reactor is at cracking temperature, steady flow conditions must be maintained at all times.

The use of solid heat-exchange surfaces in contact with benzene vapors has been avoided altogether by bubbling the vapors through an inert liquid bath maintained at 750–850°C. Lead has been suggested as a suitable bath material (12,16,23,24). These lead-bath reactors were probably the first successful commercial reactors. The construction and operation of a laboratory apparatus with a lead-bath reactor has been described (7). One and one-half to three volumes of liquid benzene per hour per volume of lead was used, and by operating at higher pressure, 125 p.s.i., increased conversion, capacity, and yields could be obtained. The use of an inert inorganic salt bath, particularly a mixture of sodium and calcium chlorides, has also been suggested (21). Heating benzene vapors through surfaces can be avoided by mixing benzene vapors at 650°C. with sufficient steam superheated to 950–1150°C. to produce a mixture at 750–850°C. (26) in a reaction and mixing chamber coated with a layer of magnetic iron oxide. This process differs from all the others in that the benzene losses to terphenyl, etc., are very low, and also in that phenol is produced as a by-product.

When compared to other well-known dehydrogenation or cracking reactions, the benzene–diphenyl reaction is relatively insensitive to catalysts. No catalyst reported to date lowers the reaction temperature, and the data available do not permit an evaluation of the effect of a catalyst on the ultimate recycle yield of diphenyl from benzene. The high yield (up to 85%) of the uncatalysed thermal reaction does not leave a wide margin for improvement. However, increased conversion at the usual reaction temperatures has been demonstrated. Up to 200% increased conversion (from 10 to 30%) per pass has been claimed by adding to the benzene vapors 0.1–1% of a volatile aliphatic compound containing at least one oxygen atom (36). Suggested materials are alcohols, ethers, or ketones. Surface catalysts recommended are magnesium, aluminum, or copper silicates (28), fire clay (18), and lustrous carbon on which either magnesium, tungsten, or aluminum oxide singly or in combination has been deposited (13,14,17,32). A pumice catalyst has been used with a mixture of benzene and steam at 700°C. and 60 p.s.i.g. (20).

Benzene can be converted to diphenyl in an electric glow discharge at low temperatures (38). Diphenyl is also produced as a by-product from the manufacture of phenol by the direct air oxidation of benzene carried out in a special reactor designed to reduce to a minimum surface catalytic effects (41).

In 1949, the price of diphenyl was 15¢ per pound with benzene at 22¢ per gallon. If a very large demand develops, it seems quite possible that large plants using some of the recently developed equipment and techniques, such as moving-bed pebble heat exchangers or the direct oxidation of benzene to phenol and diphenyl, might permit lower prices.

Uses. Diphenyl-impregnated paper wrappers for citrus fruits are used to reduce storage and handling losses (10,11,39). Diphenyl is used either alone or mixed with phenyl ether (diphenyl oxide), $(C_6H_5)_2O$, as a low-pressure, high-temperature heat-transfer medium (see *Heat transfer*).

Derivatives. Of the derivatives of diphenyl the *chlorinated diphenyls* are probably the most important commercially (see Vol. 3, pp. 826–32). The 2- and 4-*mononitro* and -*monoamino* derivatives are prepared from diphenyl in the same manner as nitrobenzene (*q.v.*) and aniline (*q.v.*), respectively, are made from benzene (8,22,27): 2-nitrodiphenyl, m.p. 37.2°C., f.p. 36.9°C., b_{20} 201.0–201.3°C., sp.gr. 1.44; 4-nitrodiphenyl, m.p. 113.7°C., f.p. 113.8°C., b_{20} 223.7–224.1°C.; 2-aminodiphenyl, m.p. 49.3°C., f.p. 48.7°C., b_{20} 182°C.; 4-aminodiphenyl, m.p. 54.1°C., f.p. 52.6°C., b_{20} 211.0–211.2°C. The 4,4'-diamino derivative, $NH_2C_6H_4C_6H_4NH_2$, called benzidine, is an important dye intermediate (see *Benzidine and related diaminodiphenyls*, Vol. 2, p. 443). *4-Hydroxydiphenyl* (*p*-phenylphenol) (m.p. 164–165°C., b.p. 305–308°C.) may be made by the conventional phenol process through sulfonation and caustic fusion (40), by substituting diphenyl for benzene. The *p*-phenylphenol–formaldehyde condensation product is used as a lacquer resin. The *sulfonated* and *alkylated* derivatives of diphenyl are useful as wetting agents (35,37). For *hydrogenated* derivatives see p. 151.

Terphenyls

The three isomeric terphenyls (diphenylbenzenes, phenyldiphenyls, triphenyls, Santowaxes), $C_6H_5C_6H_4C_6H_5$, formula weight 230.29, occur in the form of white crystalline solids when pure. The commercial grades are light yellow.

Although *m*- and *p*-terphenyl were prepared by synthesis and were also separated from tars and from the residues from diphenyl preparation by earlier workers, there was no extensive study of their properties until 1927, when Bachmann and Clarke prepared pure samples of the three isomers and determined their melting and boiling points (43). A few years later the materials became available as by-products from the manufacture of diphenyl on a commercial scale. The principal uses of the terphenyls as such are based on their stability and high boiling points.

Physical and Chemical Properties. Table I gives the physical properties of the pure terphenyls (43,50,51). Table II gives the physical properties of the commercial grades. The solubility of the commercial grades in various solvents is given in Table III and the compatibility with various waxes and resins in Table IV (48,49). All of the isomers exhibit unusual stability toward heat. They are also stable in the presence of boiling 10% sodium hydroxide or boiling 10% sulfuric acid.

The terphenyls undergo the usual organic reactions of aromatic hydrocarbons and can be chlorinated, nitrated, sulfonated, and hydrogenated. Extensive studies on the preparation and reactions of *o*-terphenyl have been made and a number of derivatives

TABLE I. Physical Properties of Pure Terphenyls.

	M.p., °C.	B.p., °C.	Crystal form	Solubility
o-Terphenyl	57	332	Prisms	Somewhat soluble in cold methanol; readily soluble in benzene, acetone, and chloroform
m-Terphenyl	87	365	Needles	Slightly soluble in hot alcohol; soluble in benzene, ether, and acetic acid
p-Terphenyl	213	376	Monoclinic prisms	Slightly soluble in boiling benzene or boiling ether; almost insoluble in boiling alcohol

TABLE II. Physical Properties of Commercial-Grade Terphenyls.

Property	*o*-Terphenyl[a] (Santowax O)	*m*-Terphenyl[b] (Santowax M)	*p*-Terphenyl[a] (Santowax P)	Mixed isomeric terphenyls (Santowax R)
Melting range, °C.	50–55	75–85	200–215	60–145
Distillation range, °C. (A.S.T.M. D20–30)	330–341	368–378	381–388	364–418
Vapor pressure, mm. Hg				
At 100°C.	0.3	—	—	—
At 150°C.	3.7	1.3	0.3	1.3
At 200°C.	25.0	9.8	5.5	9.8
At 250°C.	110.0	48.0	35.0	48.0
At 300°C.	380.0	180.0	130.0	180.0
At 350°C.	990.0	500.0	390.0	500.0
At 380°C.	1600.0	870.0	680.0	870.0
Density at 25°C.	1.14	1.164	1.236	1.153
Flash point, °C.	171	207	207	191
Flame point, °C.	198	229	238	238
Dielectric constant at 100°C. and 1000 cycles	2.54	2.62	—	2.58
Resistivity at 100°C., ohm-cm.	8200×10^9	2600×10^9	30×10^{9c}	$140{,}000 \times 10^9$

[a] Contains some *m*-terphenyl.
[b] Contains some *o*- and *p*-terphenyls.
[c] At 250°C.

TABLE III. Solubility of Commercial-Grade Terphenyls in Various Solvents.

Solvent	Grams of terphenyl per 100 ml. of solvent					
	o-Terphenyl		*m*-Terphenyl		*p*-Terphenyl	
	At 25°C.	At 50°C.	At 25°C.	At 70°C.	At 25°C.	At 75°C.
3A alcohol	6	23	1	7	0.01	0.2
Benzene	308	540	30	380	0.9	5.9
Stoddard solvent	—	—	3	62	0.2	1.1
Trichlorobenzene	315	520	30	245	0.8	6.6
Turpentine	250	540	4.5	86	0.2	1.2

prepared (42). When concentrated solutions in benzene were refluxed for a short time with a very little aluminum chloride, up to 94% of the *o*-terphenyl was converted to *m*-terphenyl. Longer times of reaction and the use of higher aluminum chloride concentrations resulted in the conversion of as much as 84% to *p*-terphenyl.

More attention has been given to the study of *p*-terphenyl than to the other isomers and it has been prepared by ten methods (46,55). Nitro, amino, halo, hydroxy, methyl, and hydrogenated derivatives have been prepared and their properties determined.

TABLE IV. Properties of Commercial-Grade Terphenyl Compatible in Mixture with Various Waxes and Resins.

Wax or resin	*o*-Terphenyl, %	*m*-Terphenyl, %	*p*-Terphenyl, %
Paraffin	90	<2	—
Carnauba	—	75	—
Candelilla	—	25	—
Paradene No. 1	—	—	5
Beeswax	50	—	—
Japan wax	—	10	—
Opal wax	10	25	—
Shellac	—	10	—
Manila resin	—	10	—
Ester gum	—	10	—

The terphenyls may be cyclohexylated by reaction with cyclohexene, cyclohexyl chloride, or cyclohexanol in the presence of aluminum chloride or other alkylation catalysts (54). When mixed isomers are used, the product is a waxy solid which is useful as a plasticizer. It distills at 285–310°C. at 5 mm. pressure and congeals at about 110°C.

A solution of sodium in liquid ammonia reacts with *p*-terphenyl to give dihydro-terphenyl, m.p. 70°C. (47). Many hydrogenated derivatives of *p*-terphenyl have been prepared by reaction with hydrogen under pressure in the presence of nickel or some other hydrogenation catalyst (45,58). When vapors of terphenyls are mixed with hydrogen and heated to 650–850°C., benzene and diphenyl are formed (56). Best results are obtained by using four or five moles of hydrogen per mole of terphenyl.

Manufacture. The high-boiling by-products from the manufacture of diphenyl give the only commercial source of raw materials for the preparation of terphenyls. At the present time this source is adequate, and if the future demand for terphenyls should increase, it can be met by raising the temperature at which diphenyl is prepared, with the resultant formation of a higher proportion of terphenyls.

After the separation of the diphenyl, the high-boiling by-products contain approximately 8.0% *o*-terphenyl, 49.0% *m*-terphenyl, 23.0% *p*-terphenyl, and 20.0% triphenylene (9,10-benzophenanthrene), quaterphenyls, etc. If mixed terphenyl isomers are desired, the high-boiling material is melted and charged to a still constructed of steel. Distillation is carried out at a low reflux ratio using a 12-plate column. During the distillation the pressure is 100 mm. Hg at the top of the column and approximately 125 mm. Hg in the boiler. The distillate is condensed, and the resultant liquid is either flaked on chilled rolls or solidified and crushed. This procedure gives substantially complete removal of the triphenylene, quaterphenyls, and other residues.

If separation of the isomers is desired, the operation is much more difficult since *o*-terphenyl and *m*-terphenyl are difficult to separate by fractional distillation because of the small proportion of *o*-terphenyl present, and *m*-terphenyl and *p*-terphenyl cannot be separated by fractionation in a column of any practical height. The distillation is carried out by using a reflux ratio of 10:1 or higher to give an *o*-terphenyl-rich fraction

containing less than 60% of *o*-terphenyl together with *m*-terphenyl. This is followed by an intermediate fraction and then by a fraction containing only *m*-terphenyl and *p*-terphenyl. The *o*-terphenyl fraction is enriched by redistillation to give a product containing in excess of 90% *o*-terphenyl. The intermediate fraction and the residue from the redistillation of the *o*-terphenyl fraction are recycled. The final separation of *m*-terphenyl and *p*-terphenyl is effected by centrifuging at a temperature slightly above the melting point of *m*-terphenyl. Similarly, centrifuging at a temperature slightly above the melting point of *o*-terphenyl results in further separation of *m*-terphenyl from the *o*-terphenyl.

If additional quantities of either *m*-terphenyl or *p*-terphenyl are needed, and other terphenyls are available, the desired material may be prepared by an isomerisation process (57). Any terphenyl or mixture of terphenyls is heated with 1-3% of aluminum chloride for about one hour to form an equilibrium mixture containing 65–70% *m*-terphenyl and 30–35% *p*-terphenyl. If *m*-terphenyl is desired, the reaction product is cooled quickly, by mixing with ice, and the aluminum chloride is removed by treatment with hydrochloric acid and filtration. Then the *m*-terphenyl and *p*-terphenyl are separated. If *p*-terphenyl is desired, the reaction product is cooled to 90–165°C. and held at this temperature while *p*-terphenyl crystallizes. Yields of over 90% of *p*-terphenyl may be obtained in this manner.

Freezing-point or melting-point determinations are the chief criteria of purity for the pure isomers. Fractional distillation is necessary for analysis of the mixed isomers.

The terphenyls are sold as crushed or flaked yellowish-colored solids. They are shipped in wooden barrels or fiber drums and are available in carload lots. The shipping classification is Coal-Tar Resin. In 1949, the approximate price for the mixed isomeric terphenyls was 17¢ per pound in ton lots.

Uses. The terphenyls are useful as heat-storage and heat-transfer agents (52, 53). The vapor pressure does not exceed atmospheric pressure until temperatures above 350°C. are reached. The stability of the terphenyls renders them useful as high-temperature lubricants. They are of value also as constituents of waxes and polishes and as plasticizers for resin-bodied paints.

Derivatives. The chlorinated and hydrogenated derivatives of the terphenyls have found extensive application. For *chlorinated* derivatives, see Vol. 3, p. 826; for *hydrogenated* derivatives, see below.

Hydrogenated Derivatives of Diphenyl and Terphenyls

Diphenyl or terphenyl may be hydrogenated to form a number of derivatives of which three are of commercial importance. *Cyclohexylbenzene* (phenylcyclohexane), $C_6H_{11}C_6H_5$, formula weight 160.25, is formed by hydrogenation of one ring of the diphenyl molecule, and *bicyclohexyl* (dicyclohexyl), $(C_6H_{11})_2$, formula weight 166.30, is formed by complete hydrogenation of diphenyl. A partially hydrogenated mixture of isomeric terphenyls ("HB-40") is the third product of commercial importance.

All of the materials are high-boiling liquids, with freezing points well below normal atmospheric temperatures. The principal uses are as solvents and plasticisers in the plastics, coating, and adhesive fields.

Physical and Chemical Properties. The properties of pure bicyclohexyl, cyclohexylbenzene, and a number of hydrogenated compounds derived from *p*-terphenyl are given in Table V (45,47,59,60). The properties of commercial grades of bicyclo-

TABLE V. Properties of Hydrogenated Derivatives of Diphenyl and *p*-Terphenyl.

Compound	M.p., °C.	B.p., °C.	Density	Refractive index
Bicyclohexyl	3.5–4.0	239.5–240	0.8838^{25}_{4}	1.4800^{25}_{D}
Cyclohexylbenzene	7–8	233–234/735	0.947^{15}	1.5274^{15}_{D}
Dihydro-*p*-terphenyl	70	—	1.022^{25}	—
Tetrahydro-*p*-terphenyl	146–148	—	—	—
Hexahydro-*p*-terphenyl	86	—	—	—
Octahydro-*p*-terphenyl	110	—	—	—
Decahydro-*p*-terphenyl	97–98	225–230/12	—	—
p-Dicyclohexylbenzene	101	—	—	—
Dodecahydro-*p*-terphenyl	86	—	—	—
Stereoisomer[a]	Liquid	144–6.5	—	—
Hexadecahydro-*p*-terphenyl	111–113	190/10	—	—
Octadecahydro-*p*-terphenyl	55–57	—	—	—
Stereoisomer[b]	162	—	—	—

[a] Rearranges on heating with carbon disulfide and aluminum chloride.
[b] Rearrangement could not be effected.

TABLE VI. Properties of Commercial-Grade Products.

Property	Bicyclohexyl	Cyclohexylbenzene	HB-40
Appearance	Clear oily liquid	Clear oily liquid	Clear oily liquid
Odor	—	—	Faint and pleasant
n_D^{25}	1.4790	1.5205	1.5675 ± 0.0075
d_{25}^{25}	0.884	0.935	1.004 ± 0.003
F.p., °C.	2.0	4.8	—
Freezing characteristics	—	—	Few crystals form at 0 to −5°C.
Distillation range, 5–95%, °C.	238–240	239–241	340–396
Flash point, °C.	101	99	174 ± 6
Flame point, °C.	104	104	196 ± 6
Viscosity, Saybolt universal seconds			
At 100°F.	34.2	31.2	144 ± 20
At 210°F.	—	—	39 ± 1
Pour point, °C. (A.S.T.M. D97–39)	—	—	−25 ± 1
Coeff. of expansion, ml./ml./°C.	—	—	0.000741
Dielectric constant			
At 25°C.	—	—	2.5
At 100°C.	—	—	2.4
Dielectric strength at 25°C., kv.	—	—	30
Resistivity at 100°C., ohm-cm.	48×10^{12}	11.4×10^{12}	1×10^{13}
Power factor at 100°C. and 1000 cycles, %	—	—	0.13

hexyl, cyclohexylbenzene, and HB-40 are shown in Table VI (62). The hydrogenated derivatives of diphenyl and terphenyl are not soluble in water, but are soluble in, or miscible with, many organic solvents and oils.

HB-40 is miscible at 25°C. with many solvents and oils including methyl abietate (Abalyn), acetone, benzene, carbon tetrachloride, castor oil, ethyl ether, ethyl acetate, linseed oil, mineral oil, solvent naphtha, and turpentine. It dissolves in ethyl alcohol to the extent of only 6% by volume. Table VII shows the solubility of a number of natural and synthetic waxes and resins in HB-40 and Table VIII shows the compatibility with several plastic materials.

TABLE VII. Solubility of Waxes and Resins in HB-40.

Solute	Temperature, °C.	Solubility, g./100 g. HB-40	Solute	Temperature, °C.	Solubility, g./100 g. HB-40
Acrawax C	100	<2.0	Naphthalene	35	30.0
Beeswax	45	2.0	Nonaethylene glycol hexaricinoleate	25	>50.0
Candelilla	46	5.0			
Carnauba	50	2.0	Santowax O	25	>30.0
Montan	56	5.0	Santowax M	25	>10.0
			Santowax P	61	5.0

TABLE VIII. Compatibility of HB-40 with Plastic Materials.

Plastic material	Parts of HB-40 compatible with 100 parts of plastic	Plastic material	Parts of HB-40 compatible with 100 parts of plastic
Butvar, low PVOH (polyvinyl butyral)	50	Formvar, type E (polyvinyl formal)	30
Cellulose nitrate, 20–30 sec., 11% N	10	Polymethyl methacrylate	20
Chlorinated rubber	100*	Polystyrene	100*
Ethyl cellulose (Dow Standard)	100	Vinylite VYNW	30

* Forms a sticky product; may be even more compatible.

Manufacture. Bicyclohexyl and cyclohexylbenzene have been prepared by a number of methods. In 1907, Ipatieff reported that reaction of diphenyl with hydrogen at a pressure of 110–120 atm. and a temperature of 200–250°C., in the presence of nickel compounds, resulted in the formation of bicyclohexyl. Sabatier and Murat formed both bicyclohexyl and cyclohexylbenzene by the reaction of diphenyl with hydrogen in the presence of nickel.

Complete hydrogenation of mixed terphenyl isomers gives a waxy solid, but incomplete hydrogenation may be carried out so as to form a liquid product (HB-40) of high boiling point, low vapor pressure, and unusual solvent properties (58). In the commercial preparation of this liquid, mixed isomeric terphenyls are melted and charged to a stirred steel tank. The spent nickel catalyst from a previous batch is added and the mixture is stirred under a hydrogen atmosphere and at about 200°C. for about two hours. Stirring is stopped, and after the catalyst settles it is drained from the bottom of the tank. Unless the foregoing pretreatment operation with spent catalyst is employed, the quantity of fresh catalyst needed is considerably greater.

Two per cent of fresh nickel catalyst is added and then the terphenyl containing the nickel catalyst in suspension is pumped into a stirred steel autoclave equipped with cooling coils, and is treated with carefully purified hydrogen at 200–250°C. and 300–900 p.s.i. The reaction is exothermic and the heat released is removed by water that is circulated through the cooling coils. The time required for hydrogenation varies between 2 and 8 hours, depending on the purity of the materials.

Samples are withdrawn from the autoclave from time to time and their density is determined. When the density has fallen to 1.004 ± 0.003 at 25/15.6°C., the reaction is considered complete, and the hydrogen in the autoclave is vented until the pressure falls to 25–50 p.s.i. Then the contents of the autoclave are emptied into a separation

tank, and the spent catalyst which settles is separated for use in the pretreatment of a subsequent batch. The supernatant liquid is transferred to a clay treatment tank, where it is agitated for 30 minutes at 100°C., with 0.3% of dried fuller's earth. Then it is filtered, using paper as the filter medium, to give the finished product.

If bicyclohexyl or cyclohexylbenzene is the desired product, diphenyl instead of mixed isomeric terphenyls is used as the starting material in processes similar to the process for HB-40.

The products are packed and shipped in galvanized steel drums or in steel tank cars. The railroad shipping classification for dicyclohexyl and phenylcyclohexane is Chemical N.O.I.B.N., and for HB-40, Pyroxylin Plasticizer.

Health and Safety Factors. As in other processes employing hydrogen under pressure, it is essential that the equipment be designed with adequate safeguards. The explosion disks must vent the hydrogen outside the building in the event of rupture. All equipment must be swept with inert gas before hydrogen is admitted. Also, the spent catalyst is a potential hazard, since on exposure to air, it may develop heat by rapid oxidation and set fire to any combustible materials with which it is in contact. HB-40 itself offers no particular hazards since it has a high flash point and tests have indicated that it is practically nontoxic.

Uses. In the plastics field, the hydrogenated diphenyl and terphenyl derivatives, particularly HB-40, are of interest for use with polystyrene, vinyl resins, ethyl cellulose, and asphalt compounds. HB-40 is of especial value as a constituent of polystyrene-emulsion adhesives and as a softener for rubber-type compounds. It is used as a high-temperature lubricant for chain drives on bakery ovens, because of its lubricity, its nontoxic qualities, and its lack of odor. As a heat-transfer medium, it is used in melting-point baths where temperatures exceeding 300°C. are not desired (61). It is also useful as an actuating medium for thermostatic controls.

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