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CHLORINATED BIPHENYL AND RELATED COMPOUNDS

Biphenyl (diphenyl), terphenyls, higher polyphenyls, or mixtures of these compounds can be chlorinated to give products which have outstanding chemical and thermal stabilities. Individual isomers, which range from liquids to high-melting crystalline solids, are of little commercial importance whereas the mixed chlorinated components have considerable commercial significance.

Registered trademarks for some commercial brands of chlorinated biphenyls in the United States are the following: Aroclor (Monsanto Company), Chlorextol (Allis-Chalmers Manufacturing Company), Dykanol (Cornell-Dubilier Division, Federal Pacific Electric Company), Inerteen (Westinghouse Electric Corporation), Noflamol (Wagner Electric Corporation), Pyranol (General Electric Company), and Therminol (Monsanto Company). Some other registered trademarks or trade names for commercial chlorinated biphenyls found throughout the world are the following: Clophen (I. G. Farbenindustrie A.G., Germany), Fenclor (Caffaro, Italy), Kannechlor (Kanegafuchi Chemical Co., Japan), Pyralene (Prodelec, France), and Sovol (Russia).

Commercial manufacture of the Aroclor brand of chlorinated biphenyls was started in 1929. These products vary from mobile oily liquids to white crystalline solids and hard noncrystalline resins. Because of the many forms and properties, they have found applications in many diverse fields—in electrical insulation, fire-resistant heat-transfer and hydraulic fluids, lubricants for use at high temperatures and pressures, sealant and expansion media, and as constituents in elastomers, adhesives, paints, lacquers, varnishes, pigments, and waxes.

Physical and Chemical Properties

The physical properties of individual chlorobiphenyl isomers vary widely as may be seen in Table 1. Mixed isomers as produced in a commercial product have physical properties which are quite different from those of the individual isomers. This is particularly true for the solidification point.

Chlorinated biphenyls, in general, are considered to be inert materials. However, they will react with certain reagents when treated under rather rigorous conditions. For example, chlorobiphenyls will react with sodium hydroxide at elevated temperatures to yield phenolic materials (28).

Mixtures of chlorinated biphenyls, such as those found in commercial products, will not react with acids, alkalies, or water under normal to moderately rigorous conditions (29). They are insoluble in water, glycerol, and the glycols. The oils and

resins are readily soluble in most of the common organic solvents, but most of the hard crystalline members are less soluble than the liquids or softer resins. The chlorinated biphenyl mixtures are nondrying even when exposed to air in thin films. They are permanently thermoplastic and except for the lower chlorinated members are nonflammable. The resins will adhere strongly to smooth surfaces such as glass, metal, varnished or lacquered surfaces. Most of the common metals and alloys

Table 1. Physical Properties of Chlorobiphenyls

Compound	Melting point, °C	Boiling point, °C (mm Hg)	Bibliography reference s
2-chlorobiphenyl	34	267–268; 154 (12)	(1–3)
3-chlorobiphenyl	80	284–285	(4,5)
4-chlorobiphenyl	75.5; 76; 74	125 (14)	(2,6,7)
2,2′-dichlorobiphenyl	59; 61–62		(8,9)
3,3′-dichlorobiphenyl	23, 29	322–324, 320–326	(9–12)
4,4′-dichlorobiphenyl	148	315–319	(2,9,12)
3,5-dichlorobiphenyl	36	166 (10)	(13,14)
2,5-dichlorobiphenyl		171 (15); 182 (30)	(14,15)
3,4-dichlorobiphenyl	46; 49–50	195–200 (15)	(16,17)
2,3-dichlorobiphenyl		172 (30)	(15)
2,4′ dichlorobiphenyl	44		(15,18)
2,4,5-trichlorobiphenyl	78–79		(19)
2,3,5-trichlorobiphenyl	41		(13)
2,4,4′-trichlorobiphenyl	55–56		(9,20)
2,5,4′-trichlorobiphenyl	67		(21)
3,5,4′-trichlorobiphenyl	88		(13)
3,4,2′-trichlorobiphenyl	65–66		(22)
3,5,2′-trichlorobiphenyl	58		(13)
3,4,3′,4′-tetrachlorobiphenyl	172	230 (50)	(11,23)
3,4,2′,5′-tetrachlorobiphenyl	103		(21)
2,6,2′,6′-tetrachlorobiphenyl	198		(23)
2,5,3′,5′-tetrachlorobiphenyl	162		(23)
2,4,2′,4′-tetrachlorobiphenyl	83		(12,24)
2,5,2′,5′-tetrachlorobiphenyl	84–85		(25)
2,4,5,3′,4′-pentachlorobiphenyl	179	195–220 (10)	(19,26)
3,4,5,3′,4′,5′-hexachlorobiphenyl	198		(23)
2,4,6,2′,4′,6′-hexachlorobiphenyl	111.5–112		(12,27)
2,3,4,5,2′,4′,5′-heptachlorobiphenyl		240–280 (20)	(19)
2,3,5,6,2′,3′,5′,6′-octachlorobiphenyl	161		(23)
2,3,4,5,6,2′,3′,4′,5′,6′-decachlorobiphenyl	310		(23)

have excellent resistance to the chlorinated biphenyls even at elevated temperatures. However, copper and some copper alloys are affected to a limited extent and show penetration rates between 0.0014 and 0.014 in./yr. Many plastic materials of construction are attacked by chlorinated biphenyls. In addition to high resistance to thermal degradation, they also have many interesting electrical properties.

The general properties of the more important members of the Aroclor brand of chlorinated biphenyl products are shown in Table 2 and the electrical properties are shown in Table 3.

Table 2. General Properties of Some Aroclors

Material	Form and color	Specific gravity	Distillation range,[a] °C (corr)	Flash point,[b] °C	Fire point,[c] °C	Pour point,[d] °C	Softening point,[e] °C	n_D^{20}	Viscosity,[f] sec 37.8°C	Viscosity,[f] sec 98.97°C
Aroclor 1221[g]	colorless, mobile oil	1.182–1.192 (25/15.5°C)	275–320	141–150	176	crystals at 1°C		1.617–1.618	38–41	30–34
Aroclor 1232	almost colorless, mobile oil	1.270–1.280 (25/15.5°C)	290–325	152–154	238	−35.5		1.620–1.622	44–51	31–32
Aroclor 1242	almost colorless, mobile oil	1.381–1.392 (25/15.5°C)	325–366	176–180	none	−19		1.627–1.629	82–92	34–35
Aroclor 1248	yellow-green tinted, mobile oil	1.405–1.415 (65/15.5°C)	340–375	193–196	none	−7		1.630–1.631	185–210	36–37
Aroclor 1254	light yellow, viscous oil	1.495–1.505 (65/15.5°C)	365–390	none	none	10		1.639–1.641	1800–2500	11–18
Aroclor 1260	light yellow, soft, sticky, resin	1.555–1.566 (90/15.5°C)	385–420	none	none	31		1.647–1.649		72–78
Aroclor 1262	light yellow, sticky, clear resin	1.572–1.583 (90/15.5°C)	395–425	none	none	35–38		1.6501–1.6517		86–100
Aroclor 1268	white to off-white powder	1.804–1.811 (25/25°C)	435–450	none	none		150–170[h]			
Aroclor 1270	white crystalline powder	1.944–1.960 (25/25°C)	450–460	none	none		240–300[h]			
Aroclor 4465	transparent, yellow, brittle resin	1.670 (25/25°C)	230–320 (4 mm Hg)	none	none		60–66	1.664–1.667		90–150 (130°C)
Aroclor 5442	yellow, transparent, sticky resin	1.470 (25/25°C)	215–300 (4 mm Hg)	247	>330	46	46–52			300–600
Aroclor 5460	clear, yellow-to-amber, brittle resin	1.670 (25/25°C)	280–335 (5 mm Hg)	none	none		98–105.5	1.664–1.665		
Aroclor 2565	black, opaque, brittle resin	1.734 (25/25°C)		none	none		60–72			

[a] ASTM D-20 (modified). [b] Cleveland open cup. [c] Cleveland open cup; none indicates no fire point up to boiling temperature. [d] ASTM D-97. [e] ASTM E-28. [f] Saybolt Universal, ASTM D-88. [g] Last two digits indicate approximate chlorine content, ie, Aroclor 1221 contains about 21% chlorine. [h] Hokl point on solidification.

Table 3. Electrical Properties of Some Aroclors

Aroclor	Dielectric constant at 1000 cycles[a] 25°C	100°C	Volume resistivity,[b] ft-cm at 100°C, 500 V, dc	Dielectric strength,[c] kV	Power factor,[a] 100°C, 1000 cycles, %
1232	5.7	4.6			
1242	5.8	4.9	above 500×10^9	>35	<0.1
1248	5.6	4.6	above 500×10^9	>35	<0.1
1254	5.0	4.3	above 500×10^9	>35	<0.1
1260	4.3	3.7	above 500×10^9	>35	<0.1
1268	2.5				
5442	3.0	4.9	above 500×10^9		
5454	2.7	4.2			
5460	2.5	3.7			
4465	2.7	3.3			

[a] ASTM D-150-47T.
[b] ASTM D-257-46.
[c] ASTM D-149-44.

Manufacture

A number of the pure compounds formed by the chlorination of biphenyl, terphenyl, or more complex polyphenyls are crystalline solids, some of which have very high melting points (30). However, mixtures containing a number of such compounds may be 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 portions of the isomers of compounds of higher and lower chlorine contents (31,32). At any level of chlorine content, batch chlorination gives the highest proportion of compounds corresponding in composition to the average chlorine content, whereas 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 obtained 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 factors such as temperature, quantity and kind of catalyst employed, degree and type of agitation, and rate of admission of the chlorine.

A procedure for carrying out a single-stage fluid-bed chlorination is described in the patent literature for polychlorination of biphenyl (33). Continuous liquid chlorination in a multiple-stage unit can also be used. Batch chlorination has been found to be particularly well suited for the manufacture of the various products (32,34).

The chlorinators may be 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 liquid 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 kg of ferric chloride is used for each charge of 6000 kg (35) of biphenyl.

Raw Materials. The raw material used depends on the type of chlorinated material to be produced; anhydrous chlorine is used as the chlorinating agent in all cases. In general, it can be said that biphenyl alone gives liquid or soft, sticky noncrystalline products up to a chlorine content of 60%, low-melting resinous products between 60 and 65% chlorine content, and partly crystalline or crystalline products of much higher melting points at chlorine contents above 65% (32). 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 crystallizing tendency of the chlorinated product after distillation. For those products 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 crystallize (34).

Preparation of Crude Chlorinated Biphenyl. For the manufacture of any given grade of chlorinated biphenyl, the chlorinator is charged with the proper raw material or mixture of raw materials to give the desired product in an amount sufficient to cover the catalyst bed and to permit circulation. Then the flow of vaporized 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 measurements are taken using a hydrometer 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 at temperatures below 100°C, the degree of chlorination is determined by measuring the hold point as the material crystallizes, or by the ball-and-ring softening-point test (36). The time required for chlorination is 12 to 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 (32,34,35). The methods of purification are somewhat different for the different types of end products. The high-melting solid products are difficult to distill. Distillation under reduced pressure is particularly difficult as it is desirable to keep the boiling point above the solidification point. Generally, these products are distilled in gas-fired retorts at atmospheric pressure. The distillate is flaked on chilled rolls. From practical considerations of quality and better overall processing efficiency, the liquid and resinous products are distilled at lower temperatures in more conventional equipment under reduced pressure. The crude liquid and resinous products are held at an elevated temperature and blown with dry air for several hours, after which a few tenths of 1% 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 under reduced pressure. 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 1% of well-dried fuller's earth and then filtered through paper (35,37).

Containers and Shipping

The liquid chlorinated biphenyls 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 products are packed and shipped in open-top galvanized-steel drums, and the high-melting solid products are packed and shipped in bags. The railroad shipping classification is Resin Synthetic NOIBN.

Health and Safety Factors

Prolonged exposure to chlorinated biphenyl vapor evolved at high temperature can lead to systemic toxic effects. Inhalation tests on animals indicate that the maximum safe concentration of vapor is in the range of 0.5 to 1.0 mg of the lower chlorinated biphenyl mixtures per cubic meter of air. The threshold limits (maximum allowable concentration for an eight-hour working day) set by the American Conference of Governmental Industrial Hygienists are 1.0 mg of the lower chlorinated biphenyl compounds (42% chlorine) per cubic meter of air and 0.5 mg of the more highly chlorinated biphenyl compounds (54% chlorine) per cubic meter of air. When chlorinated biphenyl compounds are used at elevated temperatures, engineering controls must be applied, either by the use of closed systems or by effective local mechanical exhaust ventilation together with general workroom exhaust. Although the chlorinated biphenyls are not normally skin irritants, their solvent action can remove natural protective oils and fats, and lead to drying and cracking of the skin. Also, continuous or repeated skin contact with chlorinated biphenyls should be avoided because of the possible occurrence of a condition called "chloracne" (38).

Uses

Electrical Applications. All of the uses of the chlorinated biphenyls 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 fluids for transformers and as impregnants for capacitors and condensers (29, 30,39–44). Chlorinated biphenyls, used either alone or in blends with other materials such as trichlorobenzene, meet the need for a fire-resistant dielectric fluid with a high resistivity, a high dielectric strength, a relatively high dielectric constant, and a very low power factor. By replacing hydrocarbon oil with chlorinated biphenyls or mixtures of chlorinated biphenyls with trichlorobenzene, 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. See also Dielectrics and piezoelectrics; Insulation, electrical.

The maximum dielectric constant of commercial chlorinated biphenyl mixtures at 1000 cycles and 25 °C is approximately 6.0. In recent years, considerable attention has been given to upgrading this property (45–48). Combinations of fractional distillation, chlorination, and isomerization can be used to obtain dielectric constants of 7.0 or slightly above. Direct synthesis of specific trichlorobiphenyl isomers can be utilized to obtain dielectric constants in the order of 10 (49). Improved analytical techniques, primarily capillary gas chromatography (50), have been of great aid in studying the complex chlorobiphenyl mixtures.

Other important electrical applications for the chlorinated biphenyls are as impregnants for cotton or asbestos-fiber insulation (51), 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, ethylcellulose, and polyvinyl butyral (52–55). Also, chlorinated biphenyls are employed as sealing mediums for electrical insulators and as impregnants for carbon resistors to reduce the influence of moisture.

Plastics, Lacquers, Paints, and Varnishes. Chlorinated biphenyls are compatible with most of the common plastic materials and resins, and are soluble in paint and varnish oils (29). In combination with asphalt, ethylcellulose, chlorinated rubber, Pliolite (styrene–butadiene copolymer), or other plastic materials, they are used extensively in protective coatings for wood, metal, and concrete (38,56,57). In combination with dioctyl phthalate, they are coplasticizers for polyvinyl chloride compositions (29,38). See also Coatings, industrial; Paint.

In paints and varnishes the hard resinous chlorinated biphenyls are used to impart increased hardness to the films, and the softer resins are used to give flexibility. The role of these materials is similar to that of the oil, except that they do not oxidize and lose flexibility on ageing. In nitrocellulose lacquers, chlorinated biphenyls are employed either alone or in combination with other plasticizers and resins to impart increased weather resistance, luster, adhesion, and decreased burning rate (57–60). The hard, white, crystalline chlorinated biphenyls of high melting point are useful as pigments with various plastics (61).

Adhesives (qv). The resinous products are used in synthetic adhesive compositions in combination with such base materials as polyvinyl acetate, ethylcellulose, chlorinated rubber, polyvinyl butyral, isoprene–styrene copolymer, and polyisobutylene. Chlorinated biphenyls are used in the preparation of coatings of pressure-rupturable capsules for adhesive tape (62).

Lubricants (qv). Chlorinated biphenyls find application as lubricants under extreme conditions such as highly oxidizing conditions, high temperatures, extreme pressures, or submerged locations. 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 the chlorinated biphenyls to petroleum hydrocarbon oils.

Heat-Transfer Media (qv). Chlorinated biphenyls have been used for some time in indirect heating applications (63). Recently, products of this type sold by Monsanto Company under the registered trademark Therminol have been introduced, which are specifically directed to use as heat-transfer media (64). These fluids are particularly well suited for efficient and safe operation in applications involving flammable materials where uniform temperatures are required and for high-temperature (bulk temperatures of 600°F) indirect heating. Specifically designed units for such applications are required to prevent local overheating.

Miscellaneous Applications. Carnauba wax may be extended by blending with chlorinated biphenyl in combination with ceresin and paraffin (29,65). Satisfactory waxes and polishes are prepared without the use of carnauba wax by blending ouricury (licuri) wax with chlorinated biphenyl, ceresin, and paraffin. Chlorinated biphenyls are ingredients of many fire-resistant compositions. Fire-retarding paints usually contain antimony oxide or barium sulfate in addition to the chlorinated biphenyl. In making fireproof fiberboard, emulsified chlorinated biphenyl is added to the fiber

stock (66). Modifying waxes are added to chlorinated biphenyl in the preparation of textile-coating materials.

In addition to the uses listed above, chlorinated biphenyls are ingredients of some sealing compounds for use with wood or canvas to give protection against moisture, mildew, or attacks of organisms. They are also used in formulating caulking compounds, powdered metal pastes, some soil-poison and wood-preserving compositions, paper transparentizers, and printing inks. Carbonless reproducing paper is made by an encapsulation procedure which uses chlorinated biphenyl as part of the formulation (67) (see Encapsulation).

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CHLORINATED NAPHTHALENES

Laurent, in 1833, observed that waxlike materials resulted from reaction of chlorine with naphthalene in the presence of certain catalysts. These chlorination products were further studied by Fischer in 1878. It was more than twenty years later, however, that Aylsworth discerned their technological potentialities (1).

Chemically and physically, the chlorine derivatives of naphthalene presented investigators with a much more complex problem than the chlorobenzenes. Following Erlenmeyer's establishment of the fused-ring structure of naphthalene in 1866, many years elapsed before many of the theoretically possible chlorination derivatives of the compound were isolated and identified; even today the positions of the substituent chlorine atoms in all isolated tetrachloro- and pentachloronaphthalenes have not been allocated with certainty (see Table 1). Physically, the difficulty of isolating isomers from the mixtures produced by chlorination of naphthalene is such that indirect