Benzotrichloride may be used to prepare benzoic acid (*q.v.*) (8,9). The prominence of benzotrichloride, however, results from its extensive use in the field of dyes. At one time it was used extensively in the production of Malachite Green but has since been replaced to some extent by benzaldehyde. However, the dye industry is still the largest consumer. The dyes produced from benzotrichloride appear in Table III (2).

TABLE III. Dyes Manufactured from Benzotrichloride.

Class of dye	Common name	C.I. No.	Other components
Triphenylmethane	Malachite Green	657	*N,N*-Dimethylaniline
Xanthene	Rosamine	745	*m*-Dimethylaminophenol
Quinoline	Quinoline Red	805	Quinaldine, isoquinoline
Anthraquinone	Alizarin Yellow A	1014	Pyrogallol

Bibliography for Benzyl Chloride, etc.

(1) Beilstein, 4th ed., Vol. V, pp. 292–300; 1st Suppl., Vol. V, pp. 151–52.
(2) *Colour Index*, 1924; Suppl., 1928.
(3) Davey, W., *J. Inst. Petroleum*, **31**, 73–88 (1945).
(4) Ginsburg, A., *et al.*, *Ind. Eng. Chem.*, **38**, 478–85 (1946).
(4a) Huntress, E. H., *Organic Chlorine Compounds*, Wiley, N.Y., 1948, pp. 1160–80, 856–61, 879–83.
(5) Lock, G., *Ber.*, **74B**, 1568–74 (1941).
(5a) Brit. Pat. 310,910 (June 26, 1929), N. Bennett and W. C. Sprent (to Imperial Chemical Industries).
(6) Brit. Pat. 378,866 (Aug. 16, 1932), T. D. Wheeler (to Imperial Chemical Industries).
(7) U.S. Pat. 721,961 (March 3, 1903), L. Marckwald.
(8) U.S. Pat. 1,557,153 (Oct. 13, 1925), A. George (to Mathieson Alkali Works).
(9) U.S. Pat. 1,591,245 (July 6, 1926), F. E. Stockelback (to Mathieson Alkali Works).
(10) U.S. Pat. 2,211,708 (Aug. 20, 1940), D. W. Story and E. W. Fuller (to Socony-Vacuum Oil Co.).
(11) U.S. Pat. 2,221,882 (Nov. 19, 1940), L. T. Rosenberg (to National Oil Products Co.).
(12) U.S. Pat. 2,376,291 (May 15, 1945), F. J. Sowa.
(13) U.S. Pat. 2,383,775 (Aug. 28, 1945), W. E. Craig and W. F. Hester (to Rohm & Haas Co.).

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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	Sp. gr. $\frac{25}{25}$	Distillation range,[a] °C.	Flash point,[b] °C.	Flame point,[b] °C.	Pour point,[c] °C.	Softening point,[d] °C.	n_D^{25}	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	1.894–1.811	435–450	None	None	—	—	—	—	—
Aroclor 1270[g]	White crystalline powder	1.944–1.960	450–460	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[i]	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	—	69–72	—	—	—

[a] A.S.T.M. D20–30. [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. DSS–44. [f] Hold point on solidification, 135–160°C. [g] Hold point on solidification, 240–300°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 5442
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 (23,24). 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 crystallizing 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 crystallize (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 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 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 crystallizes, 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 so id 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 (3,5,6,20,28). In combination with tricresyl phosphate or dioctyl phthalate they are coplasticizers 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 oxidize 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 oxidizing 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.

Bibliography for Chlorinated Diphenyls

(1) Andrews, R. W., and Kipp, E. M., *Am. Machinist*, 88, 107 (1914).
(2) *Aroclor Incombustible Lubricants Used in High-Pressure Compressors* (Technical Bull. P-128), Monsanto Chemical Co., St. Louis, Mo., 1938.
(3) *Aroclors* (Application Data Bull. P-115), Monsanto Chemical Co., St. Louis, Mo.

(4) *Aroclors as Co-Plasticizers for Polyvinyl Chloride* (Technical Bull. P-131), Monsanto Chemical Co., St. Louis, Mo., 1948.
(5) *Aroclors as Used in Chlorinated Rubber* (Technical Bull. P-124), Monsanto Chemical Co., St. Louis, Mo., 1948.
(6) *Aroclors as Used in Pliolite S-5* (Technical Bull. P-126), Monsanto Chemical Co., St. Louis, Mo., 1948.
(7) *Aroclors as Used to Extend or Substitute Carnauba Wax* (Technical Bull. P-132), Monsanto Chemical Co., St. Louis, Mo., 1948.
(8) A.S.T.M., *Standards, 1946*, Part III-A, Nonmetallic Materials: D28-42T.
(9) Bowron, H. W., *Paint Technol.*, 2, 25-27 (1937).
(10) Burnham, L. H., and Maunder, S. T., *Gen. Elec. Rev.*, 42, 236-39 (1939).
(11) Clark, F. M., *Trans. Electrochem. Soc.*, 65, 59-71 (1934).
(12) Clark, F. M., *Ind. Eng. Chem.*, 29, 698-702 (1937).
(13) Fay, J. W. J., and Richards, J. H., "Impregnants Used in German Paper Capacitors," *Office Tech. Services Rept.*, PB-75859 (1947); *BIOS Final Rept.*, No. 893.
(14) Gardner, H. A., and Sword, G. G., *Natl. Paint Varnish Lacquer Assoc., Sci. Sec., Circ.*, No. 55, 100-03 (1938).
(15) Jackson, W., *Proc. Roy. Soc.* (*London*), A153, 158-66 (1935).
(16) Jenkins, R. L., and Foster, R. N., *Ind. Eng. Chem.*, 23, 1362-65 (1931).
(17) MacMullin, R. B., *Chem. Eng. Progress*, 44, No. 3, 183-88 (1948).
(18) White, A. H., and Morgan, S. O., *J. Franklin Inst.*, 216, 635-41 (1933).
(19) Wood, G. W., *Mfg. Chemist*, 19, No. 3, 99-101 (1948).
(20) U.S. Pat. 1,812,732 (June 30, 1931), J. H. Young (to H. H. Robertson Co.).
(21) U.S. Pat. 1,836,180 (Dec. 15, 1931), C. R. McCullough and R. L. Jenkins (to Swann Research; reassigned to Monsanto Chemical Co.).
(22) U.S. Pat. 1,863,147 (June 14, 1932), J. H. Young (to H. H. Robertson Co.).
(23) U.S. Pats. 1,892,397; -398 (Dec. 27, 1932), R. L. Jenkins (to Swann Research; reassigned to Monsanto Chemical Co.).
(24) U.S. Pat. 1,892,400 (Dec. 27, 1932), R. L. Jenkins and J. A. Sikarski (to Swann Research; reassigned to Monsanto Chemical Co.).
(25) U.S. Pats. 1,931,373; -455 (Oct. 17, 1933), F. M. Clark (to General Electric Co.).
(26) U.S. Pat. 1,991,302 (March 12, 1935), F. M. Clark (to General Electric Co.).
(27) U.S. Pat. 2,030,653 (Feb. 11, 1936), R. G. Quinn (to International Paper Co.).
(28) U.S. Pat. 2,044,505 (June 16, 1936), W. Koch (to Hercules Powder Co.).
(29) U.S. Pat. 2,077,700 (April 20, 1937), E. Kline (to Du Pont).
(30) U.S. Pat. 2,129,157 (Sept. 6, 1938), E. W. Truefander and W. C. Wilson (to Pyroxylin Products).
(31) U.S. Pat. 2,130,264 (Sept. 13, 1938), F. M. Clark and J. H. Koenig (to General Electric Co.).
(32) U.S. Pat. 2,141,910 (Dec. 27, 1938), W. C. Hayman (to General Electric Co.).
(33) U.S. Pat. 2,158,281 (May 16, 1939), J. G. Ford and C. F. Hill (to Westinghouse Electric and Manufacturing Co.).

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Chlorinated Naphthalenes.

The chlorinated naphthalenes are of interest from both the technical and the purely scientific points of view. They are of considerable importance commercially and find many uses in the chemical, petroleum, electrical, and related fields. On treatment with chlorine, naphthalene (I) forms two types of derivatives. In the absence of a chlorination catalyst, addition takes place across the double bonds, forming such derivatives as naphthalene dichloride (II) and naphthalene tetrachloride (III). In the presence of catalysts such as ferric chloride or iodine, substitution occurs, giving rise to monochloronaphthalenes, mainly 1-chloronaphthalene (IV), as the first step. On further chlorination at higher temperatures, there is next formed a mixture of di-