one described, the curves obtained will doubtless show different slopes and under some conditions may assume quite different shapes. However, if they provide data indicating the general trend of effects for any given combination in which phenol resinoid is included as the principal variable, they will have served the purpose for which the method was designed, and it is hoped may lead to a more complete understanding of the various factors involved.

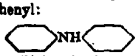
Physical Characteristics and Commercial Possibilities of Chlorinated Diphenyl[1,2]

Chester H. Penning

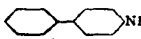
COMMERCIAL RESEARCH DEPARTMENT, SWANN RESEARCH, INC., ANNISTON, ALA.

The physical properties of 2- and 4-chlorodiphenyl and their eutectic mixture are given, together with the physical characteristics of reproducible mixtures of more highly chlorinated isomers, which vary in consistency from that of a light mobile oil through a thick sirupy stage to a solid resinous or crystalline state. This is followed by a discussion of the commercial possibilities suggested by the properties of the compounds, including use in varnish and lacquer, waterproofing, fireproofing, electrical insulation, etc.

FOLLOWING the announcement of the successful production of diphenyl in commercial quantities at a reasonable price, the manufacturer of this new chemical was deluged with suggestions for the synthesis of new compounds using diphenyl as a base, and with requests for quotations on various diphenyl derivatives. Many of these showed a lack of understanding of the nature of a true diphenyl compound, so that it is considered worth while, before discussing these products, to mention briefly the system used in naming them. Most of the so-called "diphenyl" compounds now on the market do not contain the true diphenyl grouping. This may be illustrated by structural diagrams showing, for example, the well-known compound diphenylamine and the corresponding true diphenyl compound, aminodiphenyl:



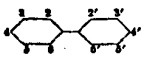
Diphenylamine



Aminodiphenyl

The true diphenyl compound contains two phenyl (C_6H_5) groups directly connected to each other, while the di-phenyl compounds contain two phenyl groups not directly connected.

In designating the positions of various substituted radicals in true diphenyl compounds, numbering begins at the linkage, as shown:



When technical diphenyl (98.5 per cent) is chlorinated under certain conditions of control, as previously described by Jenkins, McCullough, and Booth (*1*), a mixture of the 2- and 4-monochloro isomers is first obtained. The pure 2-chlorodiphenyl is a white crystalline product (monoclinic prisms) melting at 32.2° C. and boiling at 273.7° C., while the 4-chloro derivative crystallizes as flat orthorhombic plates melting at 77.2° C. and boiling at 291.2° C. A eutectic mixture of the two, containing 3 parts of 2-chlorodiphenyl and 1 part of 4-chlorodiphenyl, melts at 14° C. and boils at 278° to 205° C. This mixture, being liquid through a wide temperature range, exhibits marked solvent properties, and is itself soluble in or miscible with a large number of organic liquids. It has a specific gravity at 25°/25° C. of 1.1567; its viscosity is 30 seconds Saybolt at 210° F. (99° C.); it has a flash point of 127–129° C. and a fire point 50 degrees higher.

The monochlorodiphenyl mixture first obtained contains about 19 per cent by weight of chlorine, and is a liquid having practically the viscosity of water. As chlorination proceeds the visible effect of the higher chlorine content is an increase in viscosity. This increase is gradual up to 40 per cent chlorine and then very rapid, as shown in Figure 1. A series of products is thus obtained which varies in consistency from that of a light mobile oil through a thick sirupy stage to a solid resinous or crystalline state. These products are being marketed under the trade name "Aroclor." The Aroclors are not in all cases pure chemical compounds; their peculiar physical properties are probably due in large part to the fact that they are mixtures of various isomers. By careful control of the chlorination and subsequent operations these mixtures can readily be duplicated both physically and chemically.

Table I shows how some of the other physical properties vary with the degree of chlorination. Aroclors 1219, 1242, 1254, 1262, and 1268, representing increasing percentages of chlorine, are taken for comparison. The color changes from water-white to a light amber. The melting and boiling points rise, as does, of course, the specific gravity. The flash point is raised, also the fire point; Aroclors 1262 and 1268 will not take fire below their boiling points.

Other physical characteristics, not indicated in Table I, may be described briefly. Aroclor 1219 has a very distinctive, though not unpleasant, odor; the other products are practically odorless, and tasteless as well. They have no noticeable action upon the skin; the concentrated vapors are irritating to the nasal passages, and cause violent headaches to certain persons, but aside from this no toxic effects have been noted. All the products are stable on prolonged heating at 150° C. The oils may be distilled at atmospheric pressure without appreciable decomposition and the resins can be distilled under vacuum. Boiling 10 per cent caustic soda solution has no effect upon them.

The Aroclor oils are non-drying; they undergo no appreciable oxidation or hardening on exposure to air. Similarly, the Aroclor resins are apparently permanently thermoplastic. They undergo no further condensation or hardening on repeated melting and cooling, so far as experiments have been carried. They are being produced with softening points between 70° and 75° C., as measured by the A. S. T. M. test for asphalts and pitches; by certain modifications the softening point can be changed considerably.

[1] Received September 15, 1930. Presented before the Division of Industrial and Engineering Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Contribution No. 4 from the Laboratories of Swann Research, Inc., Anniston, Ala.

MONS 096121

The Aroclors are insoluble in water; they are also insoluble in glycerol, and not readily soluble (particularly those of high chlorine content) in the lower alcohols, but they are soluble in a very wide range of other liquids, including practically all of the ordinary organic solvents, solvent mixtures, and mineral and vegetable oils. They in turn dissolve, or are readily miscible, when hot, with such varied substances as sulfur, rubber, asphalt, paraffin, and the natural waxes.

Complete numerical evaluation of the solubilities and other properties of these compounds and mixtures is not available at this time, but is the subject of intensive investigation so that the data may be presented in a subsequent paper. In the meantime the appearance of the new series of compounds on a commercial scale and their contribution to chemical industry justify a preliminary presentation of properties so far determined.

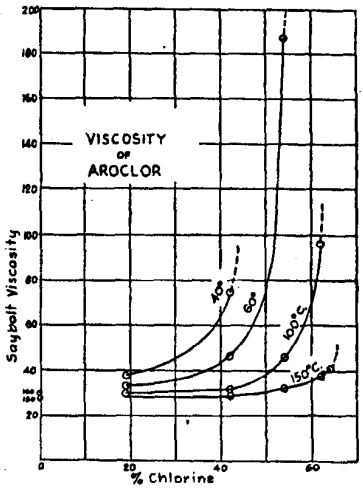
Commercial Applications

Because of their wide range of physical characteristics, the Aroclors are being considered for use in a large number of greatly varied industries. Many of these proposed applications, probably the majority, are likely to result negatively. And it must not be considered strange that those who have already succeeded do not want the details of their work broadcast—at least not until they have had an opportunity to reap some of the rewards of their research work. For this reason nothing may be said of the uses for which certain concerns are now or soon will be consuming the various types in carload lots.

PROTECTIVE COATINGS—The protective-coating industries are greatly interested in Aroclor, and a large amount of work is being done in this line. Quick-drying tung oil varnishes have been made with both the viscous (Aroclor 1254) and the resinous (Aroclor 4465) Aroclors, and the solubility of the viscous products in linseed and tung oils indicates their use as plastic resins or gums for varnishes, especially of the short oil type where failure is due to cracking of a brittle resin present. Aroclor varnishes are resistant to water and alkali and are to some extent flame-resistant. Being light-colored themselves, and in addition appearing to exert a certain bleaching action on oil during processing, the Aroclors produce finished varnishes of very light color.

The first experiments with the Aroclor resins as constituents of lacquers indicated that they should be used with a high percentage of plasticizer; otherwise incompatability of nitrocellulose and the resin would be observed. By compounding 100 grams of half-second nitrocellulose with 50 grams of resin and 50 grams of tricresyl phosphate, with balanced solvents of butyl acetate and toluene, a film free from blushing and possessing a very good gloss was obtained. Later it was found that an excess of plasticizer could be avoided if the mixture of cotton, Aroclor, and solvents be cooked at 300° F. under pressure. Experimental work now being conducted indicates that excellent lacquers can be made with the Aroclors when the proper solvents are used.

WATERPROOFING—Because they are not water-soluble and because they have excellent penetrating properties, the Aroclor oils and resins should be useful in waterproofing textiles, paper, wood, wallboard, stone, cement, stucco, and other materials. The Aroclors alone are apparently not suitable for this purpose, but when mixed with other compounds satisfactory results may be obtained.



FLAMEPROOFING—One of the first uses considered for the resins when their non-flammability was discovered was as a fireproofing agent for wood. It was found that a practically fireproof product could be obtained, but at a cost considerably greater than when the common mineral salts, such as ammonium phosphate, are used. The treated wood, however, instead of being brittle and lifeless as is the case with the mineral salt process, gains in strength and is indeed a superior product. This treatment, therefore, has a place in the manufacture of articles made wholly or partly of wood in which the original cost of the wood is small compared with the value of the finished article or where the cost of replacing is high.

The flameproofing of textile fabrics is another possibility.

MOLDING COMPOUNDS—Aroclor has not been successfully incorporated into synthetic resins of the Bakelite type, and because it is permanently thermoplastic one cannot get overly enthusiastic over its possibilities as an ingredient of molding

Table I—Physical Data on Chlorinated Diphenyls

PROPERTY	TECHNICAL DIPHENYL	AROCLOR 1219	AROCLOR 1242	AROCLOR 1254	AROCLOR 1262	AROCLOR 1268	AROCLOR 2565	AROCLOR 4465
Appearance	Very light yellow crystals	Water-white liquid	Water-white liquid	Pale yellow liquid	Light yellow, waxy resin	Pale yellow, hard, crystalline mass	Black resin	Pale amber resin
Melting or softening point	68.6° C.	14° C.	Liquid at 0° C.	Pliable wax at 0° C.	Brittle resin at 0° C.	127–171° C.	78° C.	70° C.
Boiling point or distillation range	255.6°	278–295° C.	320–360° C.	360–400° C.	374–410° C.	395–415° C.	250–360° C. (10 mm.)	240–290° C. (9 mm.)
Specific gravity	1.007	1.1667 (25°/25° C.)	1.38 (65°/65° C.)	1.52 (65°/65° C.)	1.64 (65°/65° C.)	1.8 (65°/65° C.)	1.7 (25°/25° C.)	1.7 (25°/25° C.)
Viscosity, seconds Saybolt at 210° F.		39	36	46	99	Solid	Solid	Solid
Flash point	118–119° C.	127° C.	174–178° C.	210° C.	221° C.	241	230°	232°
Flame point	139–143° C.	176° C.	224° C.	None below boiling	None below boiling	None up to 405° C.	None up to 405° C.	492° C.
Refractive index		1.6125	1.6248	1.6391	1.6493			

MONS 096122

compounds to supplant the phenol-formaldehyde resins. But where it is desired to remelt and recast the compound, Aroclor has the advantage over natural waxes that on heating it is not altered in character by the loss of easily volatile constituents; it remains uniform in composition.

ELECTRICAL INSULATION—The excellent electrical properties of the various types of Aroclor suggest their use in a number of ways in electrical products. The more viscous oils particularly are valuable for their high dielectric constant and resistivity and their low power factor. These insulating properties, together with their flameproofing and waterproofing values, make the Aroclors of great interest to manufacturers of electrical equipment.

ADHESIVES—The tackiness and non-drying qualities of Aroclor 1262 suggest its use in adhesive tape, as an ingredient of rubber cement, and as a cement for laminated glass. For the biologist it may take the place of Canada balsam for mounting microscope slides; the refractive index, however, is high. Some interesting sealing waxes have been made in a variety of colors. It has even been considered for chewing gum, as a substitute for chicle.

MISCELLANEOUS USES—Printing inks, artificial leather, leather finishing, textile finishing—no attempt will be made to complete the list of multitudinous projects on which work is being done with the Aroclors. And when it is considered that these products represent only one of many types of derivatives which may be made from diphenyl, one gets some idea of the enormous field opened by the production of this compound at a reasonable price.

Acknowledgment

The author desires to acknowledge the assistance given him in the determination of the physical constants of the Aroclors by C. R. Durgin and R. N. Foster, of the Chemical Research Department of Swann Research, Inc.

Literature Cited

(1) Jenkins, McCullough, and Booth, IND. ENG. CHEM., 22, 31 (1930).

Some Aspects of Double Refraction and Structure in Rubber[1]

B. W. Rowland

GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Evidence has been presented to show that the micelle in distorted rubber is anisotropic, exhibiting a positive rodlet type of double refraction; that the micelle orients with its long axis in the direction of stretch; and that the micelle orients upon compression as a rodlike structure perpendicular to the direction of compression.

It is proposed that stretch involves an intimate distribution of the soluble viscous hydrocarbon within the gel phase, tending toward an optical homogeneity of the mass and loss of distinction between the two phases.

The double refraction of artificially polymerized isoprene is very similar to that of natural rubber.

Photographs are presented to show the similarity of double refraction in rubber to that of a uniaxial crystal.

EARLY measurements (*1*, *5*) were made to discover a quantitative relationship between double refraction and deformation in rubber, while more recently de Visser (*6*) noted the difficulty of relating calender effect to double refraction, because the anisotropy was found to vanish during the swelling of the material for examination as an optically "mixed body." De Visser believed the sign of the double refraction to be positive, a point of uncertainty in much of the earlier work.

Kroger (*4*) examined the double refraction of a rubber film stretched equally in all directions and concluded that a negative-form double refraction resulted, characteristic of a lamellar structure, in accordance with the Wiener theory (*7*).

Van Geel and Eymers (*3*) examined films of dried latex and found the double refraction to be a function of stress similar to the double refraction of liquid crystals as a function of field strength. These authors concluded that an anisotropic alignment of molecules probably exists in stretched rubber.

Zocher and von Fischer (*8*) studied the double refraction of different types of rubber (including frozen rubber) and as an interpretation of the results have proposed the explanation that stretching and racking express a crystallizable substance within the rubber structure. This substance then crystallizes and forms a discontinuous phase.

The present work includes a number of observations of double refraction of rubber under compression as well as under stretch, and an attempt to interpret the behavior in terms of the Wiener theory of micelle double refraction.

Experimental

According to the Wiener theory (*7*, *2*) there is a possibility that crude rubber, consisting of a viscous phase mixed with a gel phase, whose refractive indices do not differ materially, may be considered as a mixed body having two components of the same refractive index. The double refraction, as noted in rubber, would then originate from an optically anisotropic gel micelle. The measurements given in Table I show that both hydrocarbon phases of crude rubber are optically anisotropic under tension. The measurements were made with a Babinet quartz wedge compensator and read in wave lengths. Samples were all very nearly 0.5 mμ in thickness and were stretched to 50 per cent elongation. The orange and violet lines of the mercury arc were used as monochromatic illumination.

Table I—Double Refraction Measurements of Rubber

TYPE OF RUBBER	λ = 570 mμ	λ = 435 mμ	CHANGE
			Per cent
Diffusion rubber	0.107	0.165	+54
Acetone-extracted whole rubber	0.123	0.214	+74
Benzene-insoluble rubber	0.107	0.258	+140
Polymerized isoprene	0.124	0.237	+91

The data show both of the hydrocarbon phases to be anisotropic upon stretch, at least when examined separately after drying from solution. Difference either in type or size of structure is, however, revealed by the variations noted in double refraction as related to wave length. The double refraction of polymerized isoprene (polymerized by 10 months' heat at 80° C.) is somewhat different from that of rubber, or of the two phases separately.

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

MONS 096123