

DRAFT

CHLORINATED BIPHENYL AND RELATED COMPOUNDS

Biphenyl (diphenyl), terphenyls, higher polyphenyls, or mixtures of these compounds, can be chlorinated to give a wide range of products which have outstanding chemical and thermal stabilities. Individual isomers which range from liquids to high melting crystalline solids have been prepared by various synthetic routes. However, direct chlorination of the hydrocarbons results in mixtures of isomers which have quite different physical properties. Certain of these mixtures were widely used in the United States in a range of commercial applications until the early 1970's and the polychlorinated biphenyls (PCBs) continued to be used in transformers and capacitors until late 1977. Domestic U.S. production was stopped October 1977 because the tendency of these products to resist biodegradation causes them to persist and accumulate in the environment. Governmental actions have resulted in the control of the use, disposal and production or the complete ban of the PCBs in nearly all world areas. Polychlorinated biphenyls were also made commercially in the United Kingdom and Japan. In 1978, they are still produced in Germany, Italy, France and Russia.

Registered trademarks used commercially by the producers of chlorinated biphenyls or polyphenyls are Aroclor (Monsanto Company, U.S.A.), Clophen (I.G. Farben Industry A.G., Germany),

Fenclor (Caffaro Italy), Kanechlor (Kanefaguchi Chemical Co., Japan), Pyralene (Prodelec, France) and Sovtol (Russia). Because of the unique properties of the PCBs, they were formulated into a number of commercial products which were sold under a variety of trade names. The term PCB is commonly used as an abbreviation for polychlorinated biphenyl.

History, Background, Current Status

The chemical structure of the polychlorinated biphenyls has been known for nearly 100 years. Commercial production was initiated in the United States in 1929 in response to the electrical industry's need for an improved dielectric insulating fluid which would also provide increased fire resistant benefits when used in transformers and capacitors.

Mineral oil, the product normally used at this time for these applications, has stability and flammability problems that made it potentially hazardous. Power surges in electrical equipment can cause arcs and a sustained high energy arc can ignite the oil. The unique properties of the PCBs - inertness, fire resistance and the ability to act as dielectric insulators (non-conductors of direct electric current) - made them ideally suited for those applications where high voltage arcing could occur and result in fires and/or explosions, damage to equipment and hazards to people.

As the unique properties of the polychlorinated biphenyls became more fully understood, many additional uses were found. In addition, the chlorinated terphenyls and higher polyphenyls found specific applications. The fire resistant nature of this class of compounds combined with outstanding thermal stability made them excellent choices as hydraulic and heat transfer fluids alone or in formulations. They were also found to improve the water-proofing characteristics of surface coatings and offered many advantages to the manufacturer of carbonless copy paper, printing inks, plasticizers, special adhesives, lubricating additives, vacuum pump fluids, etc.

These are just a few of the many applications developed for this truly unique class of chemicals. The sales of PCBs in the United States reached a maximum level of approximately 80M lbs. per year by 1970.

In the late 1960's there were initial signs of potential PCB accumulation in the environment.

A Swedish biologist identified for the first time PCBs as interference peaks in DDT determinations in the bodies of fish. Analytical methods had to be developed to separate the PCBs from other chlorinated hydrocarbons, like DDT, that were known to be present in the environment and then techniques had to be developed to enable researchers to identify the chemicals in very small amounts (parts per billion).

When scientific investigations first confirmed the presence of PCBs in the environment in the United States in 1970 and long before information regarding the potential impact of this contamination was determined, Monsanto as the sole U.S. manufacturer voluntarily began a program to terminate sales of PCBs to so-called "open" applications which were defined as those which could likely result in losses to the environment. Major applications affected by this withdrawal were in carbonless paper, fire resistant hydraulic fluids, heat transfer fluids and plasticizers. These restrictions resulted in the reduction of the use of PCBs to approximately half of its previous level.

At the same time, because of the lack of replacement products in the electrical power distribution industry, arrangements were made to continue to supply the PCBs in "closed" or "sealed" systems such as transformers and capacitors. It was felt that this would restrict entry into the environment until satisfactory replacements could be developed for these critical electrical applications.

The steps taken did reduce the amount of potential environmental contamination by the PCBs. However, because of the extremely slow biodegradation rates and the development of improved analytical techniques, PCBs were found in many places as researchers in industry, universities, research institutes and government laboratories intensified their efforts to identify, remove and determine the long term effects of these materials.

By late 1976, it was apparent that replacement products were becoming available to the electrical industry and Monsanto made arrangements to completely withdraw from the manufacture of the PCBs. Concurrently governmental actions had resulted in restrictions on the use and application of the PCBs and the Toxic Substances Act contained provisions for discontinuance of their use and eventual disposal.

Physical and Chemical Properties

The properties of the individual chlorinated biphenyl isomers vary widely and a number of reviews on their preparation, chemistry and properties have been published. (ref.) Because the polychloro polyphenyls can no longer be used commercially, the reader is referred to the literature for detailed information. This section reviews in very general terms some of the basic properties which made the products so useful.

The individual isomers of the chlorobiphenyls vary from liquids to waxes to crystalline solids. However, in the commercial process, mixed isomers are produced which result in products having properties quite different, particularly in crystallinity and liquid range compared to the individual isomers.

Chlorinated biphenyls are considered to be generally inert. However, they will react with certain materials under high temperature conditions. For example, sodium hydroxide under extreme conditions can yield phenolic materials.

The chlorinated biphenyls are insoluble in water, glycerol and glycols. However, they are soluble in most of the common organic solvents. The chlorinated biphenyl materials are quite resistant to oxidation. They are permanently thermoplastic in the higher chlorinated levels and are considered extremely fire resistant. Generally they are compatible with most metals making them extremely useful in energy transfer type applications. However, under elevated temperatures, the chlorine could react with metal to give corrosion. Similar phenomena made them useful as extreme pressure additives to lubricants.

Electrical properties of the polychlorinated biphenyls are extremely good showing reasonably high dielectric constants with high volume resistivities and dielectric strengths and low

power factors.

Manufacture

Individual isomers of the chlorinated polyphenyls are described in the literature and are generally made by methods other than direct chlorination. Isolation of individual isomers from the complex mixtures obtained by direct chlorination is difficult.

Direct chlorination of aromatic hydrocarbons gives not only isomers of the same chlorine content but also appreciable amounts of the isomers of compounds of higher and lower chlorine contents. Proportion of the various isomers and compounds of higher and lower chlorine contents is influenced by factors such as temperature, quantity and kind of catalyst employed, degree and type of agitation and rate of chlorine addition to the reaction mass. After the chlorination is complete, the product is generally treated with a neutralizing agent to destroy the catalyst and the crude product distilled to give the finished mixture of isomers. Such processes were operated commercially to give wide ranges of products.

Uses

An extremely wide range of uses were developed for the polychlorinated polyphenyls before they were removed from the market. The largest application was in the electrical industry for which they were originally developed. Since this use continued

after most other applications were stopped and because of the long life of capacitors and transformers, the ultimate disposal of PCBs from such uses must be controlled. Guidelines for such controls and ultimate disposal have been developed by both the electrical industry and the Government and are available in written documents (cite references).

Some of the most important uses of PCBs were as follows:

As a dielectric medium in transformers, either alone or in blends with other materials such as trichlorobenzene; as the dielectric impregnating medium in capacitors; as plasticizers; as ingredients in lacquers, paints and varnishes and adhesives; as water proofing compounds in various types of coatings; as lubricants or lubricant additives under extreme conditions; as heat transfer fluids; as fire resistant hydraulic fluids; as vacuum pump fluids; and as air compressor lubricants. Their success in such diverse applications was due to their unique blend of fire resistance, thermal and oxidative stability, electrical characteristics, solvency, inertness and liquid range.

Safety, Health and Environmental

During the long years of use of the PCBs, much work was done to determine their gross toxicity. Exposures to large concentrations were examined extensively in animal studies as well as skin testing. In general, they were found to be relatively innocuous materials with some cases of irritation to the skin reported by specific people. However, these studies did not indicate that the materials were of such a nature that continued use should be stopped.

Prolonged exposure to PCB vapor at high temperature was known to lead to systemic toxic effects. Inhalation studies on animals indicated that the maximum safe concentration of vapor was in the range of 0.5 to 1.0 milligrams of the lower chlorinated biphenyl mixtures per cubic meter of air. Therefore, limits were set as to the maximum allowable concentration per 8 hour working day of 1.0 milligram of the lower chlorinated biphenyl compounds per cubic meter of air and 0.5 milligrams of the more highly chlorinated biphenyl compounds per meter of air. Although the chlorinated biphenyls were not normally skin irritants, their solvent action could remove natural protective oils and fats which led to drying and cracking of the skin.

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All of this information indicated that normal care should be taken in the use of the PCBs but until the incidents cited in the history section, there were no indications that additional precautions were necessary. As noted, with the development of improved analytical techniques, it was found that small amounts of the PCBs did accumulate in the food chain. Since the PCBs' ability to persist in the environment for long times was not known, they were introduced into the environment by open burning or incomplete incineration, by vaporization from paints, coatings and plastics, by direct entry or leakage into sewage and streams, by dumping of waste materials and by various disposal techniques which did not destroy the material. The occurrence of PCBs in

water in extremely low levels (now measurable) has undoubtedly occurred for long periods of time. PCBs being fat soluble are stored in the lipids of animals. They resist metabolic changes and tend to be concentrated in succeeding higher levels in animals higher in the food chain. It was found that the higher the chlorine content of PCBs, the more stable they are to biodegradation. Because of these facts, action was taken first to restrict the fluids to closed applications followed by complete removal from the market and cessation of domestic manufacture.

It should be noted that these steps will not completely remove the chlorinated biphenyls from the environment since they will persist because of low degradation rates. Therefore, it is important that all materials containing PCBs be properly disposed of now and in the future to prevent increasing amounts in the environment. However, since some biodegradation does occur, it can be expected that the concentration will eventually decrease.

The PCBs are destroyed by incineration at high temperatures (greater than 2,000°F.) with long residence time in properly designed incinerators. This service is best provided by firms specializing in such work. Ordinary incinerators used to dispose of organic matter may not be satisfactory for the disposal of PCBs since they may tend to vaporize the product instead of converting them to carbon dioxide, water and hydrogen chloride.

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The other way of disposing of the PCBs is by use of proper land-

fill techniques. Because of the nature of the materials, approved landfills where entry into underground waters or the general environment can be prevented must be used. Government agencies have posted regulations concerning such sites and the EPA should be contacted for approved disposal areas. The major end products which are still in wide use where disposal is important are capacitors and transformers or other electrical equipment containing PCBs. These units can last for periods up to 20 years or more and therefore correct disposal practices should be observed for such equipment.

The amount of PCBs present in environmental materials can be determined using ASTM D3304-74, "Standard Method for Analysis of Environmental Materials for Chlorinated Biphenyls".

Summary

The chlorinated polyphenyls and in particular, the polychlorinated biphenyls or PCBs, are a unique group of chemicals which have extreme stability and fire resistant characteristics but which, for the same reasons, represent a potential environmental hazard. They biodegrade at very slow rates and therefore tend to accumulate in the environment. The long term effects of exposure to small amounts of PCBs and their concentration in animals and in man are the subjects of much research and positive conclusions as to their effects are still being determined (early 1978). However, because of the potential problems and hazards, the compounds are no longer commercially available in the United States and their use and disposal is controlled. This is also

true for Japan and Sweden at the time of this article and it is expected that future restrictions will develop in other world areas.

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