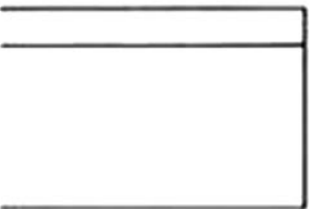


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ers, and road or rail tankers. Steel is a suitable material for construction of containers.

For information on storage and handling, see Section 8.1.5.

Freight classifications are given in Table 49.

8.2.6. Uses

Isomeric mixtures of the monochlorotoluenes are hydrolyzed to cresol on a considerable scale. Chlorotoluenes are also used as solvents in reactions and to dissolve special products, e.g., dyes.

2-Chlorotoluene. 2-Chlorotoluene is a starting material in the production of 2-chlorobenzyl chloride, 2-chlorobenzaldehyde, 2-chlorobenzotrichloride, 2-chlorobenzoyl chloride and 2-chlorobenzoic acid, which are precursors for dyes, pharmaceuticals, optical brighteners, fungicides, and products of other types. 2-Chlorotoluene is also used in the production of dichlorotoluenes (chlorination), 3-chlorotoluene (isomerization), and *o*-chlorobenzonitrile (ammonoxidation).

4-Chlorotoluene. 4-Chlorotoluene is used mainly to produce *p*-chlorobenzotrifluoride, from which is obtained *p*-chlorobenzotrifluoride, an important precursor of herbicides (e.g., trifluralin: α, α, α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine). Other side-chain-chlorinated products or their derivatives are 4-chlorobenzyl chloride (for pharmaceuticals, rice herbicides, and pyrethrin insecticides), 4-chlorobenzaldehyde (for dyes and pharmaceuticals), 4-chlorobenzoyl chloride (for pharmaceuticals and peroxides), and 4-chlorobenzoic acid (for dyes). 4-Chlorotoluene is also a starting material in the synthesis of 2,4- and 3,4-dichlorotoluene and of 4-chlorobenzonitrile.

2,4-Dichlorotoluene. 2,4-Dichlorotoluene is used via its side-chain-chlorinated intermediates to produce fungicides, dyes, pharmaceuticals, preservatives, and peroxides (curing agents for silicones and polyesters).

2,6-Dichlorotoluene. 2,6-Dichlorotoluene is used to produce 2,6-dichlorobenzaldehyde, a dye precursor, and 2,6-dichlorobenzonitrile, a herbicide.

3,4-Dichlorotoluene. 3,4-Dichlorotoluene is used in small amounts in the pro-

duction of 3,4-dichlorobenzyl chloride, 3,4-dichlorobenzaldehyde, 3,4-dichlorobenzotrifluoride, and 3,4-dichlorobenzoic acid, from which disinfectants, crop protection products, and dyes are produced.

2,3,6-Trichlorotoluene. 2,3,6-Trichlorotoluene is used on a small scale, together with 2,4,5-trichlorotoluene, to produce 2,3,6-trichlorobenzoic acid, a herbicide precursor.

Producers of chlorinated toluenes are: Bayer AG (FRG); Enichem (Italy); Hodogaya Chemicals Co. Ltd. (Japan); Hoechst AG (FRG); Ihara Chemical Ind., Ltd. (Japan); Occidental Chemical Co., Ltd. (USA).

8.3. Chlorinated Biphenyls

NewsomeNote: PCBs

Industrial use of the polychlorinated biphenyls first began in 1929 in the USA [880, 881]. The outstanding properties of these compounds, such as their high chemical and thermal stability, high dielectric constant, and the fact that they form only incombustible gases in an electric arc, made them appear ideally suited for use as insulating and cooling fluids for transformers and as dielectric impregnants for capacitors.

In subsequent years many other applications were found as well (see Section 8.3.5), particularly for isomeric mixtures containing two to six atoms of chlorine per mole of biphenyl.

In the mid-1960s, improved analytical methods revealed that polychlorinated biphenyls were accumulating in nature as a consequence of their extremely low rates of biological degradation (rates which decrease as the chlorine content rises). The compounds were detected in fresh water in all parts of the world, but also in many animals (e.g., birds, fish, and plankton). In the late 1970s, it was further discovered that at temperatures of 500 to 800 °C in the presence of oxygen, polychlorinated biphenyls can give rise to polychlorinated dibenzofurans and dibenzodioxins, including (although to a much smaller extent) the particularly toxic compound 2,3,7,8-tetrachlorodibenzodioxin [882 – 887].

In the meantime, all but a few of the well-known producers (see Section 8.3.5) discontinued the production of chlorinated biphenyls. Moreover, in many countries the production, sale, and use of polychlorinated biphenyls have

Table 49. Freight classification

GGVE/GGVS and RID/ADR		IMDG Code and IATA-DGR			US-DOT
class	number	class	UN No.	pack. group	
2- and 4-Chlorotoluene	3	3.3	2238	III	UN 1993 Flammable liquid
2,3-Dichlorotoluene	3			not restricted	
2,4-Dichlorotoluene	3			not restricted	
2,6-Dichlorotoluene	3			not restricted	
3,4-Dichlorotoluene	3			not restricted	

been restricted or entirely prohibited by legislation.

For many years, *o*-, *m*- and *p*-terphenyl mixtures were chlorinated and then used as plasticizers, flame retardants, and fillers in thermoplastic pattern and holding waxes. This application likewise has been substantially discontinued [888], particularly in view of the persistent nature of the compounds in question and their accumulation in the environment. Possible toxicological hazards are either unknown or have not been adequately investigated (Table 50).

Table 50. MAK and TLV values of chlorinated biphenyls

	MAK (FRG) mg/m ³	TLV (USA) mg/m ³
Chlorinated biphenyls (42 % Cl)	1 III B	1
Chlorinated biphenyls (54 % Cl)	0.5 III B	0.5

NewsomeNote: These are maximum daily exposure levels.

In view of the above, this article is devoted primarily to a review of recent patents covering methods for the disposal of polychlorinated biphenyls. For information regarding the production of these compounds and their specific physical and chemical properties, attention is directed to earlier surveys [882, 889, 890].

8.3.1. Physical and Chemical Properties

There are 209 possible chlorinated biphenyls. The mono- and dichlorobiphenyls [27323-18-8], [25512-42-9] are colorless crystalline compounds (the melting points of the pure isomers lie between 18 and 149 °C). When burned in air, they give rise to soot and hydrogen chloride.

The most important products are mixtures whose principal components are trichlorobiphenyl [25323-68-6], tetrachlorobiphenyl [26914-33-0], pentachlorobiphenyl [25429-29-2], or

hexachlorobiphenyl [26601-64-9]. Such mixtures are liquid to viscous (pour points increase with chlorine content from -22 to +18 °C), and they are fire-resistant. Further chlorination gives soft to brittle thermoplastic waxes.

Chlorinated biphenyls are soluble in many organic solvents, particularly when heated, but are soluble in water only in the ppm range. Although they are chemically very stable, including to oxygen of the air, they can be hydrolyzed to oxybiphenyls under extreme conditions, e.g., with sodium hydroxide solution at 300–400 °C and under high pressure. Toxic polychlorodibenzofurans may be formed under these conditions.

The fact that the compounds may eliminate hydrogen chloride to a small extent at a high temperature explains why hydrogen chloride acceptors are often added to transformer fluids based on polychlorinated biphenyls.

The excellent electrical property data of polychlorinated biphenyls, such as high dielectric constant, low power factor, high resistivity, favorable dielectric loss factor, and high dielectric strength, have already been mentioned.

8.3.2. Disposal

Many products containing chlorinated biphenyls are still in use throughout the world, particularly in transformers, rectifiers, and capacitors with long service lives. Industry and national governments are now faced with the need to dispose of these products without causing additional pollution of the environment. Appropriate official regulations exist in many countries [888, 891–902].

Attention is drawn in the following survey to patents concerned with the removal of polychlorinated biphenyls from electrical devices and

with the disposal of these compounds. It is impossible to say which of the processes have actually reached maturity and which are already being used.

According to the present state of knowledge, polychlorinated biphenyls can be destroyed harmlessly by combustion at temperatures above 1000 °C and a residence time of 2 s, e.g., in a rotary burner equipped with a scrubbing tower for hydrogen chloride [888, 902 – 904]. Regulations in the Federal Republic of Germany specify a temperature of 1200 °C, a residence time of 0.2 s, and a residual oxygen content in the combustion gas of 6 % [897].

Removal of polychlorinated biphenyls from silicone- and hydrocarbon-based transformer fluids and heat transfer media is accomplished through the formation of a separable fraction rich in polychlorinated biphenyls [905], treatment with polyalkylene glycol and alkali metal hydroxide [906, 907], treatment with sodium naphthalenide [908], or heating with a sodium dispersion to 75 °C [909].

Polychlorinated biphenyls are removed from impregnated electrical parts by irradiation with microwaves, which causes gasification of the compounds [910], or by dry distillation at 500–1000 °C followed by addition of oxygen [911].

Destruction of polychlorinated biphenyls has been reported to be possible by the following methods: treatment with sodium naphthalenide in the presence of metallic sodium [912]; treatment at 145 °C with a dehalogenating reagent prepared from an alkali metal, polyethylene glycol, and oxygen [913]; reaction with sulfur in the vapor phase [914]; adsorption on paramagnetic or ferromagnetic material and subsequent irradiation with microwaves in the presence of oxygen [915]; and irradiation with light in aqueous solution in the presence of a catalyst [916].

Thermal decomposition of polychlorinated biphenyls occurs by pyrolysis under oxidative conditions (oxygen-enriched air) on molten alkali carbonates at 900–980 °C [917]; by use of a plasma burner at 3000–4000 °C [918]; by dissolution in kerosene, followed by combustion in air and introduction of the combustion gases into a special decomposition furnace [919]; or by evaporation with hydrogen as a carrier gas, followed by combustion in oxygen [920].

8.3.3. Analysis

The analytical methods most frequently used for detecting chlorinated biphenyls are capillary column gas chromatography coupled with mass spectrometry in the MID (Multiple Ion Detection) mode and capillary column gas chromatography with ECD (Electron Capture Detector). These methods are suitable for solution of even the most difficult problems. Clean-up steps are necessary when complex matrices are concerned, such as preliminary separation by column chromatography.

HPLC (High Pressure Liquid Chromatography) and infrared spectroscopy are applicable to a limited extent.

Summary polychlorinated biphenyl determinations are also possible, though not usual. These require either exhaustive chlorination and measurement of the decachlorobiphenyl content or else dechlorination and subsequent measurement of the biphenyl content.

For literature references on the subject of analysis, see [902, 921 – 927].

8.3.4. Storage and Transportation

At a normal temperature the commercially used polychlorinated biphenyls are liquid to viscous mixtures with a comparatively low vapor pressure (trichlorobiphenyl 6.5×10^{-5} kPa at 20 °C). Steel and aluminum are suitable as container materials. The storage and shipping of these compounds are subject to a variety of national regulations. Since these compounds accumulate in the environment they must be handled so that release cannot occur.

Exposure of polychlorinated biphenyls to fire may result in the formation of toxic chlorinated dibenzofurans and dibenzodioxins [882 – 887] and in the evolution of hydrogen chloride.

Classification of polychlorinated biphenyls are:

GGVE/GGVS and RID/ADR: Class 6.1, Number 23

IMDG-Code and IATA-DGR: Class 9, UN Number 2315, Packaging group II

US D.O.T.: ORM.E, UN Number 2315

8.3.5. Uses

Use of these compounds has fallen drastically [928] as a result of the extensive discontinuation of their production, voluntary renunciation of their application, and national restrictions. No details were available concerning products in which polychlorinated biphenyls are still used, nor concerning the scale of such use. The following list of important fields of application should be regarded as retrospective:

Cooling and insulating fluids for transformers
Dielectric impregnating agents for capacitors
Flame-retardant additives for resins and plastics used in the electrical industry

Alkali- and acid-resistant plasticizers for lacquers, plastics, adhesives, fillers and sealing compositions

Formulations for paints and printing inks

Water-repellent additives for surface coatings

Dye carriers for pressure-sensitive copying paper

Additives for thermally-stable lubricants and gear oils

Incombustible hydraulic fluids (particularly suitable for use in locations to which access is difficult, e.g., in mines)

Heat transfer fluids of high heat stability

Inert sealing fluids for vacuum pumps

Dust control agents for road construction

Mono- and dichlorobiphenyls have been used on a small scale as precursors for the corresponding oxybiphenyls.

Some registered trademarks are listed in Table 51. Most of the listed producers have discontinued production.

Table 51. Trade names of chlorinated biphenyls

Apirolio	Caffaro, Italy
Aroclor	Monsanto, USA, UK
Clophen	Bayer AG, FRG
Delor	Chemco, Czechoslovakia
Fenclor	Caffaro, Italy
Inerteen	Westinghouse, USA
Kanechlor	Kanegafuchi Chem. Co., Japan
Pyralene	Prodelec, France
Pyranol	Monsanto, UK
Pyroclor	Monsanto, USA
Sovtol	USSR

8.4. Chlorinated Naphthalenes

The first industrial applications of chlorinated naphthalenes took place at the beginning of the 20th century [929]. The compounds were used most extensively in the 1930s to 1950s, especially in cable and capacitor production, prompted by their dielectric, water-repellent, and flame-retardant properties.

More recently, most producers of polychlorinated naphthalenes have stopped their production, and output has been reduced drastically in all parts of the world. The reasons for this follow. First, connections have been established between highly chlorinated naphthalenes, especially pentachloronaphthalene and hexachloronaphthalene, and illness. Moreover, because of their high chemical and thermal stability, highly chlorinated naphthalenes are able to accumulate in the environment. Finally, new materials (polyesters and polycarbonate) have been introduced as substitutes for chlorinated naphthalenes in the capacitor and cable industries.

Monochloronaphthalenes, by contrast, are not considered to be problematic with regard to their effects on health and accumulation in the environment [930].

Official regulations relating to chlorinated naphthalenes differ considerably from country to country. In Japan, for example, polychlorinated naphthalenes are prohibited entirely. In the USA they may still be used without restriction, but changes in their production, importation, or use must be reported to the U.S. Environmental Protection Agency (EPA) [931], so that the effects of these changes on the environment may be monitored.

8.4.1. Physical Properties

Naphthalene has 75 chlorinated derivatives. To date, however, only a few have been synthesized and isolated in pure form. Only isomeric mixtures characterized according to their chlorine content are as a general rule commercially available. This situation arises because of the fact that the most important characteristics of the compounds are a function solely of their degree of chlorination, as a result of which there is little demand for the pure compounds. Moreover, precisely because the physical properties of the

available on chronic effects or effects on reproduction caused by chlorinated toluenes.

In *humans*, no cases of poisoning or skin irritation caused by chlorinated toluenes have been reported [1064].

Regulations. *o*-Chlorotoluene TLV 50 ppm

10.2.3. Polychlorinated Biphenyls

Acute Toxicity. The acute toxicity of mixtures of polychlorinated biphenyls (PCB) seems to depend on the chlorine content. Table 64 demonstrates the influence of the chlorine content in mixed isomers of PCBs, in addition to their relatively low acute oral toxicity.

NewsomeNote: LD₅₀ is the median Lethal Dose to kill 50% of a population. Lower numbers are more toxic. **Table 64.** Acute oral toxicity of PCBs [1090]

Chlorine content, wt %	LD ₅₀ (rat, oral), g/kg
21	3.98
32	4.47
42	8.65
48	11.0
62	11.3
68	10.9

The administration of acute or subacute doses results in **liver enlargement**, mainly due to enzyme induction; when the doses were increased, fatty degeneration and central atrophy of the liver occurred. In addition, hyperplasia and hemosiderosis of the **spleen** were also observed [1091, 1092]. Polychlorinated biphenyls are not likely to possess a substantial local irritating potential. Nevertheless, they seem to be **readily absorbed through the skin, exerting such systemic effects as liver damage.**

Chronic Effects. After oral application, severe liver damage (hypertrophy, fatty degeneration, and centrolobular necrosis) is most likely to be observed. The skin is also often affected (hyperplasia, hyperkeratosis, and cystic dilatation) [1069]. Polychlorinated biphenyls can interfere with heme metabolism as shown by an increased porphyrin content of the liver in rats [1069]. Hepatocellular tumors are produced in rats and mice after long-term oral application of PCBs [1066], vol. 20. However, the tumor formation is regarded as a response to tissue damage rather than triggered by a genotoxic mechanism.

The PCBs failed to show positive response in validated *mutagenicity* test systems. The interference of polychlorinated biphenyls with reproduction could be demonstrated in numerous studies with mammals. **The compounds pass through the placental barrier and exhibit embryotoxic effects** [1069].

Absorption, Metabolism, and Excretion. Polychlorinated biphenyls are **readily absorbed from the gastrointestinal tract after ingestion or from the lung after inhalation.** The rates of metabolism and excretion decrease and the storage in body fat increases with increasing chlorine content. The compounds are generally metabolized by selective hydroxylation. In primates, most of the metabolites are excreted as conjugates in the urine, whereas excretion of free metabolites in the feces is the major route in rodents [1093].

Other Effects. Immunosuppressive action of polychlorinated biphenyls in mammals could be evidenced by a decrease in infectious resistance with atrophy of the spleen, cortical thymus atrophy, and dose-dependent decreased in the production of specific antibodies [1063, 1069]. **In hens,** growth retardation, high mortality, and subcutaneous edema could be observed. These findings were accompanied by focal necrosis of the liver, hydroperitoneum, and epicardial as well as lung edema (chicken edema disease) [1063, 1069].

Experience in Humans. **Accidental acute intoxications with PCBs are not reported** [1069]. With workers handling these compounds, acne-form dermatitis was observed, in addition to liver damage with necrosis [1063, 1069].

In 1968, a subacute intoxication of more than 1000 people in Japan by contaminated rice oil was reported (Yusho disease). Initial symptoms were, for instance, **swelling of the eye lids, fatigue, and gastrointestinal disturbances.** Later on, discoloration of the skin and mucous membranes, headache, signs of sensory nerve injury, diarrhea, and jaundice were found. Cases of influence on human fetuses have been attributed to this high PCB exposure [1063, 1069].

Polychlorinated biphenyls **accumulate in fat and adipose tissue.** They have been demonstrated **in human milk.** Because the PCB level was found to be higher in infant blood but lower in umbilical blood in comparison to maternal

blood, the transfer of PCBs via the milk is probably much more important than placental transfer [1063, 1094].

Regulations. The following exposure limits have been established:

Chlorine content 42 %: MAK 0.1 ppm
Chlorine content 54 %: MAK 0.05 ppm

NewsomeNote: These are maximum daily exposure levels.

Polychlorinated biphenyls are considered as possible teratogens [1095] and carcinogens [1069].

10.2.4. Chlorinated Naphthalenes

Monochlorinated naphthalenes are of low to moderate acute toxicity, as shown by their oral LD₅₀ (Table 65). Subacute to subchronic uptake of mixtures of higher chlorinated naphthalenes (predominantly penta- and hexachloronaphthalene) resulted in liver injury [1063]. In general, the toxicity of chlorinated naphthalenes increases with the degree of chlorination [1064]. Chlorinated naphthalenes irritate the rabbit skin [1063]. Ingestion of lubricants containing chloronaphthalenes resulted in injury to farm animals (X disease). Marked hyperkeratosis of the skin, degenerations of the cells in pancreas, liver, and gall bladder, and damage of the renal cortex could be observed. Cattle poisoned with highly chlorinated naphthalenes show a rapid decline in vitamin A plasma levels [1063]. Octachloronaphthalene fed to rats also greatly enhances the loss of vitamin A from the liver [1096]. Mixtures of penta- and hexachloronaphthalenes can produce the so-called chicken edema disease, characterized by hydropericardium and ascites in chickens [1096].

Table 65. Oral LD₅₀s of monochlorinated naphthalenes [1083]

Compound	Species	LD ₅₀ (oral), mg/kg
1-Chloronaphthalene	rats	1540
	mice	1019
2-Chloronaphthalene	rats	2078
	mice	886

1-Chloronaphthalene and 1,2,3,4-tetrachloronaphthalene, when tested for point mutations in the *Salmonella* assay (*Ames test*), exhibited no positive results [1097, 1098]. No data are available on the effects of chlorinated naphthalenes on reproduction.

Metabolism. Chlorinated naphthalenes are readily absorbed. Metabolism occurs by conjugation or via hydroxylation to the respective naphthols or dihydrodiols. The metabolites are excreted with the urine or the feces [1063, 1096].

Effects in Humans. The main health problem arising from use and handling of chlorinated naphthalenes is chloracne, which usually occurs from long-term contact with the compounds or exposure to hot vapors. The penta- and hexachloro derivatives are suggested to have the greatest potential to generate acne [1063].

In accidental intoxications, liver damage occurred independently from chloracne. After loss of appetite, nausea, and edema of the face and hands, abdominal pain and vomiting followed; later on jaundice developed. Autopsy in cases of fatal intoxication revealed yellow atrophy of the liver [1096].

Regulations. The following exposure limits have been established:

Trichloronaphthalene: MAK 5 mg/m³, TLV 5 mg/m³
Tetrachloronaphthalene: TLV 2 mg/m³
Hexachloronaphthalene (skin): TLV 0.2 mg/m³
Pentachloronaphthalene: TLV 0.5 mg/m³
Octachloronaphthalene (skin): TLV 0.1 mg/m³

10.2.5. Benzyl Chloride

The acute oral toxicity (LD₅₀) of benzyl chloride in rats is 1231 mg/kg and in mice 1624 mg/kg [1083]. The subcutaneous LD₅₀ (in rats) of benzyl chloride in oil solution is 1000 mg/kg [1099]. Exposure of rats and mice to benzyl chloride concentrations of 100–1000 mg/m³ for 2 h caused irritation of the mucous membranes and conjunctivitis [1066], vol. 11. Benzyl chloride is a strong skin-sensitizing agent for guinea pigs [1100]. Benzyl chloride acts weakly *mutagenic* in validated test systems [1101, 1102].

Subcutaneous injection of weekly doses of 80 mg/kg for 1 year followed by a post-observation period resulted in local sarcomas with lung