

Use and Replaceability of Polychlorinated Biphenyls[†]

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Introduction

On September 1, 1971, an interdepartmental task force was formed to coordinate

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[†]*Ed. Note:* This paper was given at the PCBs Conference reported in Issue number 1, April 1972, but was not ready for publication in that issue. Since it was submitted the Monsanto Company released PCBs production figures for 1960-1971 (Monsanto press release of November 30, 1971). Information in that release further specifies statements in the paper indicated by a #. Figures from the press release are:

the U.S. Government's scientific studies of polychlorinated biphenyl (PCB's). The task force was coordinated by the Office of Science and Technology and the Council on Environmental Quality. Represented on the task force were the following agencies: the Environmental Protection Agency, The Food and Drug Administration, the National Institute of Environmental Health Services, and the Departments of Agriculture, Commerce, Interior and Justice.

On September 13 individual tasks were assigned to participating agencies, and the Commerce Department was asked to critically

PRODUCTION AND SALES
POLYCHLORINATED BIPHENYLS (PCB)
MONSANTO INDUSTRIAL CHEMICALS COMPANY -
(SHORT TONS)

<u>YEAR</u>	<u>U.S. PRODUCTION</u>	<u>DOMESTIC SALES</u>		<u>U.S. EXPORT SALES</u>
		Electrical ^a Insulating Liquids Uses	All ^b Other Uses	All Uses
1971 (Est)	20236	14417	4401	4938
1970	42527	20268	16263	6826
1969	38194	18564	15034	5312
1968	41427	20568	11990	5616
1967	37655	20387	10846	4062
1966	32925	18897	10642	3426
1965	30240	16203	9695	2117
1964	25417	13769	8666	2048
1963	22367	11448	7618	1824
1962	20986	11683	7339	1809
1961	20333	11108	7661	2076
1960	20786	12444	5163	1827

^a Closed Systems — Transformers and Capacitors

^b Including Heat-transfer Systems, Hydraulics/Lubricants, Plasticizers

explore the question of the utility and replaceability of PCB's. Dr. Robert W. Cairns, Deputy Assistant Secretary of Commerce for Science and Technology requested NBS to assist him in this task.

This study has included consideration of the uses and replaceability of PCB's in the following areas.

1. Dielectric fluids for capacitors and transformers.
2. Industrial fluids for hydraulic, gas turbine and vacuum pump uses.
3. Heat transfer fluids.
4. Plasticizers and miscellaneous uses.

This report is the result of that study. It is a collation of technical information gathered from published literature, special reports, patent reports, and personal conversation with officials of industrial and utility companies. Such trade information as was used has come from sources other than the manufacturer.

The report was prepared through the efforts of several research scientists in the Polymers Division at NBS. These people do not work in the area of commercial applications and the collection and reporting of this information represents a significant departure from their usual responsibilities. This, together with time limitations, limited the amount of information which could be located and included and increased the need for qualifications and stated uncertainties in the report. Original sources were referenced where possible.

The discussion of each of the use categories listed above includes:

1. The physical properties required for the application.
2. Advantages and disadvantages of PCB's.
3. Possibility of replacing PCB's with other materials.

Dielectric Fluids

Dielectric (electrically insulating) liquids are important to the electrical industry for filling agents or impregnants in transformers, capacitors, and other devices. Besides their

electrical functions, the liquids may also be used for cooling and arc quenching functions. Detailed discussions of dielectric fluid applications are available (1-4).

Capacitors

Properties required of capacitor fluids: Generally, industrially important capacitors use liquid impregnated cellulose paper as a dielectric. The required properties of the liquid are:

1. Non-flammability (important for preventing fires, particularly in indoor use).
2. Dielectric constant matching that of paper. A good match reduces electric field inhomogeneities, increases dielectric strength and lifetime and allows decrease in capacitor size.
3. Low dissipation factor (reduces energy loss and destructive heating in a capacitor).
4. High dielectric strength (prevents breakdown and allows decrease in capacitor size).
5. High chemical stability (increases capacitor lifetime and stabilizes its performance).
6. Low vapor pressure (increases physical stability).
7. Inert decomposition products in an electric arc (prevents explosion or corrosion following breakdown).
8. Low toxicity of the material and its decomposition products.
9. Low cost.

Advantages and disadvantages of PCB in capacitors: The PCB capacitor liquids, commonly called askarels, are mixtures of chlorinated biphenyls and chlorinated benzenes. Several standard mixtures are specified by ASTM (5). The askarel capacitor liquids and their decomposition products are non-flammable. Thus their use in capacitors greatly reduces fire and explosion hazards. This characteristic permits economies where safety codes require fire-proof enclosures for capacitors containing flammable liquids.

Table 1. Typical Properties of Liquids

	Uninhib- ited transf. oil	Mineral Oil Capac- itor oil	Pipe cable oil	Heavy cable oil	Polybutenes Pipe cable liquid	Paper impregnant	Capac- itor liquid	Askarels				
Viscosity, SUS 25°C 37.8°C 99-100°C	58.2 ^a	103 ^a 38 ^a	763 ^a 60 ^a	2365 ^a 101 ^a	1,200 ^a 83 ^a	8,000 ^a 176 ^a	300,000 ^a 2,200 ^a	40-42 31-32	44-51 31-32	82-92 34-35	185-240 36-37	1800-2500 44-48
Viscosity, cs. 25°C 37.8°C 99-100°C	9.79	21 3.5	10	21	154 ^b 0.011 ^c	180 ^b 0.011 ^c	252 ^b 0.011 ^c	4.5 <1.8	6.9 <1.8	17.2 2.5	45.3 3.2	46.4 6.14
Flashpoint open cup, °C	146 ^b	154.4 ^b	196.1 ^b	2433 ^b	154 ^b	180 ^b	252 ^b	146.1 ^b	153.3 ^b	182.2 ^b	192.8 ^b	None
Acidity, mgm KOH/gm Pour point, °C	-45.6 ^c	-45.6 ^c	-26.1 ^c	-17.8 ^c	-34 ^c	-22 ^c	1.7 ^c	0.010 max 1.7 ^c	0.010 max -35.5	0.010 max -19.0	0.010 max -7.0	0.010 max 10.0
Specific gravity, 15.6°C 25°C	0.898 ^d	0.907 ^d	0.928 ^d	0.928 ^d	0.862 ^d	0.870 ^d	0.905 ^d	1.18	1.28	1.38	1.45	1.54
Coef. of expan. cc/cc/°C	0.00063				0.00078	0.00076		0.00071	0.00073	0.00068	0.00079	0.00068
Thermal conduc. (gm-cal/sec)(cm ²)(°C/cm) (BTU/hr)(ft ²)(°F)	0.00031 ^m 0.076 ⁿ	0.00031 ^m 0.076 ⁿ	0.00030 ^m 0.072 ⁿ	0.00030 ^m 0.072 ⁿ			0.062 ^l	0.067	0.063	0.058	0.057	0.054
Boiling point at 760 mm, °C								275.0	290.0	325.0	340.0	365.0
Volatility, weight loss												
Dielectric strength, kv./1" (0.254 cm)	32.5 ^e	>30 ^e	>30 ^e	>30 ^e	>35 ^{e*}	>35 ^{e*}	>35	>35	>35	>35	>35	35
Dielectric constant, 60 Hz 10 ³ Hz 25°C 10 ⁶ Hz					2.14 ^q	2.16 ^q	2.22 ^q	4.5	5.7	5.8	5.5	5.0
Dissipation factor, 60 Hz 10 ³ Hz 200°C 10 ⁶ Hz	0.001 ^f	0.001 ^f		0.001 ^f	0.0005 ^f	0.0005 ^f	0.0005 ^f	0.001	0.001	0.001	0.001	0.001
Volume resistivity, ohm-cm					>1x10 ¹¹ ^g	>1x10 ¹² ^g	>1x10 ¹² ^g	>5x10	>5x10	>5x10	>5x10	>5x10

Typical Properties of Liquids—continued

	(C ₄ F ₉) ₄ N	Fluorocarbons *n=1/5-5	C ₈ F ₁₈ O	Silicones			Dielectric Grade Castor Oil	Glyceryl Tri- Acetoxy- Stearate	Organic Esters Butyl Stearate Butyl Sebacate		Butyl Naphth- enate	Tetra Hydro- furfuryl Oleate	Ethylene Glycol	Silicate Ester Base Fluid
Viscosity, SUS, 25°C 37.8°C 99-100°C		-/35		360 137.9	720	180			48	46		61		
Viscosity, CS, 25°C 37.8°C 99-100°C	2.59 1.80 0.48	-/2.7 -/0.88	0.82 0.64 0.30	10.5 80 29	200 160 58	500 400 148	500 160 98		7	6		10		12.2 3.95
Flashpoint, open cup, °C				>30	>315	>325	291		167.8	175.0		203.9	118	187.8
Acidity, mgm KOH/gm Pour point °C	-50.0	-154/-84	-100.0	-90	-55	-52.7	-50.0	-23	4.4	21.7	-10.0	-17.8		<-59.5
Specific gravity, 15°C/15°C 25°C	1.89 1.88	1.57/1.82 1.54/1.79	1.79 1.77	0.940	0.970	0.971	0.973	0.959	0.995				1.1154	0.887
Coef. of expan. cc/cc/°C	.0012	.00084/.00036	.0016	0.00095	.00097	.00097	0.00097	0.00066	0.00066				0.00062	.000563
Thermal conduc. (gm-cal/sec)(cm ²)(°C/cm) (BTU/hr)(ft ²)(°F)(ft)	0.049	0.070/0.049	0.081	0.00034	0.086	0.00037	0.087	0.103	0.103				.00063	.000327 0.080
Boiling point at 760 mm, °C	177.8	40.8/224.2	102.2										196-200	>371.1
Volatility, weight loss				31% ^h	10% ^h	<20% ^h								
Dielec. strength, kv./1" (0.254cm)	35 min	29/50	36 min	35 ⁱ	35	35			3.74 ^u	3.57 ^u	3.3	4.4	3.1	4.3
Dielectric constant, 60 Hz 10 ³ Hz 10 ⁶ Hz	1.90 1.89 1.90	3.02/2.45 3.02/2.45	1.86 1.84 1.87	2.7 ^u 2.7 ^u	2.75 2.75	2.75 2.75	2.75 2.75						4.1	2.85
Dissipation factor, 60 Hz 10 ³ Hz 10 ⁶ Hz	<0.0005 ^u <0.0005 <0.0005	<0.00006 <0.00006 <0.00006	<0.0005 ^u <0.00006 <0.00006	.00015 ^u 0.00001 ^u 0.00001 ^u	<0.0001 <0.0001 0.00005	<0.0001 <0.0001 0.00005	0.06 ^u 0.0097 ^u 0.00013	0.01 0.01 0.00015	0.01 0.01 0.00015	0.018 0.019 0.00039				0.0042
Volume resistivity ohm-cm	3x10 ¹⁴	>4x10 ¹⁴	6x10 ¹⁴	1x10 ¹⁴	>1x10 ¹⁴	>1x10 ¹⁴	>1x10 ¹⁴	3x10 ¹⁴	6.3x10 ¹³	5x10 ¹²	1x10 ¹²	<1x10 ¹¹		9x10 ¹⁰

P(CFCF₃O)₄CHFCF₃CF₄

^a ASTM D446
^b ASTM D92
^c ASTM D97
^d ASTM D1250

^e ASTM D877. Suitability of D877 for high viscosity oils such as cable oils and polybutenes listed in table has not been determined.

^f ASTM D924
^g ASTM D974
^h Weight loss in a 15 mg sample in a 50 ml beaker at 150° for 24 hrs.

ⁱ ASTM D664
^j ASTM D1189
^k Weight loss after 48 hrs. at 200°C 100°F

^u 0°C
^v -8°C
^w ASTM D287
^x ASTM D257

^y 23°C
^z 80°C
^{aa} 100°C
^{ab} 10 Hz
^{ac} Hz unknown
^{ad} ASTM D149
^{ae} ASTM D150

Askarels have no true flash point.

The dielectric constant of the askarels is high compared to other common dielectric liquids. Doubling the dielectric constant of the dielectric allows a reduction by half in the area of the capacitor electrodes, and a significant saving in the cost of construction and installation. The dielectric constant of askarels closely matches that of the capacitor paper.

The askarels are adequate with regard to dissipation factor and dielectric strength and have good chemical stability and low vapor

pressure. The breakdown products, in particular HCl, have the advantage of being non-flammable, but are highly corrosive. This dictates the use of special corrosion resistant materials inside the capacitors.

The major disadvantage of the askarels is their suspected toxicity. In ordinary capacitor usage the askarels are used in closed systems to prevent contamination from moisture. This practice also prevents the askarels from reaching the environment. However, when electrical failure occurs, sealed capacitors can leak and are ordinarily discarded.

Replaceability of PCB in capacitors: Capacitors can be made dry or with gas dielectrics. These have inferior electrical strength and, for comparable performance, such a capacitor must be made much larger in size.

The major disadvantage of alternative capacitor liquids is their flammability. When comparing flash point data, as in Table 1, askarel flash points comparable to those of other capacitor liquids are sometimes listed. ASTM states that these are not true flash points but are pseudo-flash points which differ noticeably from the flash obtained on combustible materials and is not indicative of a fire hazard (5). The requirement of non-flammability for most capacitor uses is critical and capacitors with flammable liquids are forbidden in many cases by the National Electrical Code (6). In other cases replacement of askarel capacitors with flammable capacitors requires use of fireproof installations (6).

The fluorocarbons are one group of non-flammable liquids which are used for some dielectric applications (1). The ones listed in Table 1 have low dielectric constants and could not directly replace askarels without increasing capacitor size. The fluorocarbons have low toxicity but the decomposition products may be toxic (1). They are generally more volatile than askarels and are considerably more expensive. The fluorocarbons are a possible replacement for PCB liquids for capacitor use but we know of no fluorocarbon liquid presently available and acceptable for this purpose.

Besides the problem of flammability, possible PCB replacement liquids generally lack either a sufficiently high dielectric constant to keep capacitor size down or a sufficiently high dielectric strength. For example (Table 1) the silicones have the disadvantage of a low dielectric constant whereas the organic esters often have poor dielectric strength. Some silicones deteriorate rapidly under electric arcing (7).

The acceptance of a PCB substitute is a complex process involving not only users but also various regulatory groups. In most of the electrical industry, regulation is non-

governmental and the primary regulatory influence comes from Underwriters Laboratories, who test products and decide on their suitability (8). In addition, control over electrical materials is exercised through companies which insure against fire, utilities which supply electrical power and building codes.

Extent of capacitor use: Presently, almost all industrial capacitors contain PCB's. In 1968, 95% of the U.S. production of capacitor liquids (2.46 million gallons) were PCB's (9). Two important types of capacitors are phase correction capacitors on power lines and ballast capacitors for fluorescent lighting. Non-ballast industrial capacitors produced in 1967 had a value of \$112 million (10), and fluorescent lamp ballast capacitors produced that year numbered 21.7 million units with a value of \$15.5 million (10). In 1970 there were 50.9 million ballast units produced with a value of \$163 million (11). These ballast units are in extensive use inside buildings where non-flammability is important.

Phase correction capacitors are necessary on power circuits to correct for the inductive loading of much electrical power equipment. The amount of phase correction capacitance is ordinarily specified in kilovolt amperes of reactive current or kvars. Most power capacitors are rated at from 1/2 to 25 kvars so that the number of capacitors is very roughly the kvar value divided by 10 (12). As examples of the extent of power capacitor use, TVA has 2-1/4 million kvars (13), and a power company serving suburban New Jersey has 3.6 million kvars on their power lines with 1/2 million kvars on order (14). The value of these capacitors is roughly \$5 per kvar (14). More than 20 million kvars of power capacitors were produced in 1970 (16).

The procurement lag for these capacitors is presently 1-1/2 to 3 years and time estimates for redesigning new systems range from 3 to 10 years according to power company representatives to ASTM Committee D-27 (14, 15). Extensive redesigning is generally anticipated if distribution capacitors were required to use presently available non-PCB liquids. Askarel

capacitors have been developed to the point that failures are considered negligible (13, 15).

Several private sources reported extensive efforts to find replacements for PCB capacitor fluids, but none reported having a good substitute.

Transformers

Properties required of transformer fluids:

Most power transformers contain a liquid to electrically insulate and remove heat from the core and windings. The properties required of these liquids are:

1. Non-flammability (required for indoor use and desirable in remote location use).
2. High dielectric strength (prevents breakdown and allows transformer size reduction).
3. Low viscosity (promotes convective heat transfer).
4. High chemical stability (allows higher temperature operation and reduces degradation of the transformer).
5. Compatibility with other materials.
6. Inert decomposition products (reduces fire danger and damage to other materials following breakdown).
7. Low toxicity of the liquid and its decomposition products.
8. Low cost.

Advantages and disadvantages of PCBs in transformers:

The PCB transformer liquids, commonly called askarels, are mixtures of chlorinated biphenyls and chlorinated benzenes. Several standard mixtures for transformers (differing from the capacitor askarels) are specified by ASTM (17). These liquids are used to overcome the fire and explosion hazards which are present with transformer oils. For most power transformer applications where occasional explosions and fires do not endanger life and property, mineral oils are still preferred. However, for distribution transformers which are located near congested areas and in buildings askarel and dry-type transformers are required by electrical codes (6). Other advantages of the askarels include

1) their superior chemical stability which eliminates the sludge formation common in mineral oils, 2) a high dielectric strength which reduces electrical failures and 3) suitable viscosity.

The disadvantages of the transformer askarels include 1) a poorer resistance to impulse voltages and production of highly corrosive HCl during arcing, 2) a tendency to damage common insulating solids inside the transformer, 3) probable toxicity and 4) higher cost (about \$1.80 per gallon compared to \$.25 per gallon for mineral oil) (15, 18).

Replaceability of PCBs in transformers:

Askarel transformers cost about 1.3 times as much as oil transformers and dry types cost about 1.5 times as much as oil transformers. Thus most users prefer to use the oil type where possible. This preference for oil transformers accounts for the fact that 96% of transformer liquids in use in 1968 were mineral oil (9). However, fire underwriters will not presently accept the use of oils, silicones and other flammable liquids for indoor transformers. Dry-type transformers can be used indoors but are generally larger in size, require more copper and iron and are somewhat more expensive as shown above. Dry-type transformers could possibly replace askarel transformers in many cases.

We know of no currently available liquid which will replace askarels in existing transformers. Possibly, non-flammable fluorocarbons could be developed as a substitute fluid, similar in important properties to the askarels. Fluorocarbons are currently in use as convective and evaporative dielectric coolants. One main disadvantage of the fluorocarbons is their high volatility and high cost (about 40 times the cost of oil and 6 times the cost of askarels (18).

Extent of transformer use: In 1967, 1.7 million liquid-immersed distribution transformers of 500 kva and smaller valued at \$350 million were produced (10). These include askarel-filled transformers placed under streets to serve 1 - 4 city buildings. These transformers can fail and cause fire

damage if filled with a flammable liquid. An annual report on such failures is compiled by the Edison Electric Institute (19).

Industrial Fluids For Hydraulic, Gas Turbine, and Vacuum Pump Uses:

Hydraulic

Hydraulic fluids are liquids used as force transmitters (20, 21). In general the characteristics of a good hydraulic fluid are (20):

1. High lubricity (lowers heating and increases lifetime of moving components).
2. Stability (increases lifetime of use).
3. Appropriate viscosity and high viscosity index (22-24).
4. Low pour point (necessary for material to flow at low temperatures) (25).
5. Compatibility (prevents interactions with other components, for example, rubber seals).
6. Good heat transfer (reduces local heating and large temperature gradients).
7. High bulk-modulus (important for extreme pressure applications).
8. Low volatility (necessary to prevent malfunctioning due to "vapor lock").
9. Low foaming.
10. Low thermal expansion. Aside from the implication of a more constant volume over a wide temperature range, a low thermal expansion implies a high viscosity index and the constancy of certain other properties with respect to temperature.
11. Good demulsibility.
12. Inhibitor (necessary to prevent oxidation of metals or rusting).
13. Good fire resistance (very important in high temperature environments).
14. Low density (desirable in transportation, particularly airborne applications).
15. Good dielectric properties (reduces arcing or short circuiting should the fluids come in direct contact with electrical components).

16. Non-toxicity (reduces the danger to human beings from rupture of hydraulic equipment or improper disposal and to maintenance personnel during transfer of these fluids).

Since most commercial hydraulic fluid mixtures are proprietary, it is difficult to obtain information with respect to their composition. The results from inquiries with respect to PCB content have been somewhat contradictory. We have no definite knowledge that PCB's are present in commercial hydraulic fluids at this time. Since composition specifications of these fluids are usually not available to the public, PCB content should be established by chemical analysis.

PCB's are useful in hydraulic fluids as lubricating additives in extreme pressure applications (26) and as pour point depressants. Although it is true that the pour point of oils may be lowered by extensive dewaxing, the use of additives is much cheaper. There are other inexpensive additives which are often used for these applications which appear to be adequate. For example, TCP (tricresyl phosphate) is chemically stable as an additive in lubricants, and, although quite toxic, it is more biodegradable than the PCB's.

An important requirement for many applications of hydraulic fluids is good heat and fire resistance (27). Table 2 (28) gives the ignition characteristics for a large number of lubricants; however, in view of the propriety stated earlier, there is no detailed specification of the compositions of those fluids which are given by brand names. PCB's have excellent fire resistance characteristics. The flash and fire points given in the literature for the pentachlorobiphenyls are attributed to the burning of residual contaminants (29). At very high temperatures, however, PCB's with higher chlorine content may emit phosgene (a very toxic gas) in the presence of oxygen. (We have no evidence that high chlorine content PCB's are being used here.)

Aircraft hydraulic fluids are an example of an application where excellent heat and fire resistance are necessary in view of mod-

Table 2. Physical and Other Properties of Lubricating Oils, Engine Oils, and Hydraulic Fluids.

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water = 1)	Flash Point °F	Fire Point °F	Autoignition ² / Temperature °F	Decomposition Temperature °F
		100°F	210°F					
<u>Mineral Oils</u>								
MIL-2190	Mineral Oil	32.2	5.8	0.86	~450	—	665(5)	—
Harmony 44 (Gulf)	Mineral Oil	87.6	9.8	0.88	~460	—	680(5)	—
MLO-5731	Mineral Oil - Naphthenic	—	—	—	—	—	—	640(28)
MLO-7277	Mineral Oil - Naphthenic	—	—	—	—	—	—	725(30)
MLO-60-294	Mineral Oil - Paraffinic, deep dewaxed	14	3.15	0.88	385	430	464(50)	~620(30)
Mobil DTE-103	Mineral Oil	124	8.74 to 10.2	0.92	390	—	700(27)	—
MIL-H-6083B	Mineral Oil	—	—	—	255	—	702, 675(50)	—
MIL-H-5606A	Mineral Oil	—	—	—	—	—	470(50)	—
MIL-O-5606 (Esso Univas J-43)	Mineral Oil	—	—	—	195	225	437(4)	—
					437(2)			—
<u>Glycols and Water Glycols</u>								
Ethylene Glycol	Glycol	8.7	—	—	240	—	856(38)	—
Propylene Glycol	Glycol	19.6	—	—	230	235	835(38)	—
Ethylene Glycol + 50% water	Water-Glycol	2.2	—	—	—	—	903(38)	—
Houghto-Safe 2/1	Water-Glycol	~43	~16(150°F)	1.045	—	—	767(5)	—
Houghto-Safe 5/20	Water-Glycol	43.2	25.1(130°F)	1.075	—	—	—	—
Houghto-Safe 6/20	Water-Glycol	43.2	29.8(150°F)	1.055	—	—	—	—
Nyvac 20 (Mobil)	Water-Glycol and additives	41	—	1.07	—	—	750(51)	—
Irua 902 (Shell)	Water-Oil Emulsion	97.4	51	0.93	—	—	709(51)	—
Ucon 50HB-260	Polyalkylene Glycol	56	—	—	455	500	743(38)	—
Ucon 50HB-280-X	Polyalkylene Glycol	—	—	—	500	600	743(20)	—
Ucon LB-60	Polyalkylene Glycol	10.7	—	—	310	325	653(38)	—
Ucon LB-400-X	Polyalkylene Glycol	—	—	—	—	—	752(20)	—
<u>Phosphate Esters</u>								
Houghto-Safe 1010	Triaryl Phosphate Ester	18.2	3.9	1.20	505	670	>1200(51)	—
Houghto-Safe 1055	Triaryl Phosphate Ester	13.0	8.0	1.145	505	680	1020, 830(50)	—
Houghto-Safe 1115	Triaryl Phosphate Ester	32.2	4.1	1.165	—	680	>1200(51)	—
Houghto-Safe 1120	Triaryl Phosphate Ester	49.8	5.0	1.15	485	690	1020(5)	—
Houghto-Safe 1130	Triaryl Phosphate Ester	62.8	6.0	1.145	490	680	>1200(51)	—
MIL-H-19457 (Type 1)	Triaryl Phosphate Ester	—	—	—	—	—	1040(19)	—
Tricresyl Phosphate	Triaryl Phosphate Ester	38.3	4.48	1.17	470	—	1110(12)	680(48)
Trioctyl Phosphate	Triaryl Phosphate Ester	—	—	0.926	405	—	545(13)	~380(28)
Trihexyl Phosphate	Trialkyl Phosphate Ester	—	—	—	—	—	549(12)	—
Pydraul AC	Phosphate Ester-Chlorinated	88.8	5.0	1.36	450	745	1148(5)	—
	Hydrocarbon							
Pydraul F-9	Phosphate Ester-Chlorinated	50.9	5.9	1.285	430	675	1100(51)	—
	Hydrocarbon							
Cellulube 220 (Shell S.F.R.)	Phosphate Ester	43.4	4.9	1.145	455	665	1038(5)	—
Pydraul 150 (Monsanto)	Phosphate Ester	30.5	7.9	1.125	380	470	975(51)	—
Skydrol	Phosphate Ester	—	—	—	360	470	>1300(51)	—
<u>Mono- and Dibasic Acid Esters</u>								
Plexol 201	Di-2-hexyl Sebacate	12.7	3.31	0.912	420	450	—	—
Plexol 244	Di-isooctyl Adipate	9.64	2.77	0.926	400	445	712(12)	—
Plexol 273	Di-isodecyl Adipate	14.5	3.56	0.920	425	460	—	—
Plexol 79	Polyester	1,250	108	1.023	540	620	—	—

Table 2—Continued.

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water = 1)	Flash Point °F	Fire Point °F	Autoignition ^{2/} Temperature °F	Decomposition Temperature °F
		100°F	210°F					
		Mono- and Dibasic Acid Esters (Cont.)						
MIL-L-7808 (0-60-18, Esso 4040)	Sebacate-adipate Diester	12.1	3.1	—	437	460	728, 486(7)	490(26)
MIL-L-7808 (H-1026)	Di-2-ethylhexyl Sebacate	12.58	3.3	—	—	—	755(50)	575(15)
MIL-L-9236B (0-60-7, TP-653B)	Trimethylol Propane Ester	15.1	3.4	—	430	475	738, 491(7)	~650(24)
MIL-L-9236 (0-60-27)	Trimethylol Propane Ester	14.8	3.45	—	435	485	—	—
MIL-L-9236 (0-60-23)	Trimethylol Propane Ester	15.99	3.62	—	470	525	—	—
MIL-L-9236 (0-61-17)	Trimethylol Propane Ester	15.78	3.59	—	490	535	—	—
MIL-L-9236B	Trimethylol Propane Ester	16	3.2	0.97	425	510	>800(51)	~650(24)
MLO-54-581 (Texaco, TL-2456)	Diester	—	—	—	435	475	734(2)	—
TP 653B (Hey, Newport)	Trimethylol Propane Ester	—	—	~0.97	—	—	705, 507(50)	—
P/O (Esso 4275)	Polyester	—	8.04	0.951	510	—	711, 500(50)	748(30)
MLO-60-50	Trimethylol Propane Ester	—	—	—	—	—	—	748(30)
Trimethylolpropane Triphenylphosphonate	Trimethylol Propane Ester	—	—	—	—	—	—	606(26)
Silanes								
MLO-54-408C	Tetra Dodecyl Silane	34.58	6.37	—	555	625	775(17)	658(15)
MLO-56-280	Diphenyl di-n-dodecyl Silane	37.2	6.2	—	530	580	690(17)	>680(15)
MLO-56-578	Octadecyl trioctyl Silane	27.5	5.76	—	520	590	790(17)	—
MLO-56-582	Octadecyl tridecyl Silane	33.9	6.8	—	545	595	750(17)	—
MLO-56-610	Dodecyl tridecyl Silane	26.4	5.6	—	535	575	750(17)	—
MLO-56-611	Didodecyl dioctyl Silane	23.1	5.0	—	520	565	750(17)	—
MLO-57-9	Tetra undecyl Silane	29.26	6.11	—	545	600	760(17)	—
Silicates and Silicones								
Tetra (2-ethylhexyl) Silicate	Ethyl hexyl Silicate	—	—	—	—	—	—	638(28)
Orsil B.F. 1	(2-ethylhexyl) Silicate	—	—	—	—	—	~570(12)	—
Oronite 8200	Silicate Ester	31.75	11.14	—	385	440	716(2)	—
Oronite 8515	Silicate Ester	24.3	8.11	—	390	450	710(50)	—
MLO-54-645	85% Oronite & 15% Plexol	—	—	—	340	455	716(2)	—
MLO-54-540 (Monsanto OS-45)	Silicate Ester	—	—	—	325	430	703(2)	—
MLO-54-856 (Hollingshead, 72073C)	Silicate Ester	—	—	—	315	440	716(2)	—
Versilube F-50	Silicone	52	16	1.045	550	640	900(51)	>600(51)
Versilube F-44	Silicone	55	17	1.045	550	640	900(51)	>600(51)
Dow Corning 190	Polymethyl Siloxane	22.6	—	—	240	—	860(38)	—
Dow Corning 400	Polymethyl Siloxane	10.9	—	—	255	280	610(38)	—
Dow Corning 500	Polyethyl Siloxane	44.9	—	—	470	—	900(38)	—
Dow Corning 550	Silicone	65 to 87	—	1.065	600	—	740(23)	—
Dow Corning 700	Poly (methyl, phenyl) Siloxane	2.8	—	—	305	325	940(38)	—
Dow Corning 710	Methyl Phenyl Siloxane	220	—	1.112	520	—	—	588(15)
MLO-59-98	50% Methyl Phenyl Siloxane (DC 258) plus 50% TMP Adipate Tetracaproate	61.8	13.5	—	—	—	—	625(30)
Halogenated Silicones and Hydrocarbons								
MLO-53-446 (GE 81406)	Chlorinated Silicone	—	—	—	580	710	786(2)	514(15)
MLO-59-287 (GE F-50)	Chlorophenyl Methyl Silicone	—	—	—	—	—	—	630(30)
Fluorolube F-S	Polytrifluorochloroethylene	5	—	1.86	—	—	~1205(12)	>620(51)
Pydraul A-200	Chlorinated Hydrocarbon	49.8	5.0	1.42	350	680	1200(51)	—

Table 2—Continued.

Fluid	Chemical Class or Compound	Viscosity, cs		Specific Gravity (Water = 1)	Flash Point °F	Fire Point °F	Autoignition ^{2/} Temperature °F	Decomposition Temperature °F
		100°F	210°F					
Halogenated Silicones and Hydrocarbons (Cont.)								
Arachlor-1248	Tetrachlorodiphenyl	43.0	3.2	1.41	380	None	~1185(12)	—
Arachlor-1242	Trichlorodiphenyl	17.7	—	—	350	633	1230(38)	—
Arachlor-1254	Chlorinated Hydrocarbon	—	—	—	—	—	~1085(12)	—
Aromatic Ethers								
OS-124 (Monsanto, 5P4E)	5 Ring Polyphenyl Ether	363	13.1	1.20	550	660	1112(50)	≥830(30)
MCS-293 (Monsanto)	Aromatic Ether	25.2	4.13	1.19	428	518	914(50)	675
MLO-59-692 (Monsanto)	Bis (phenoxyphenoxy) Benzene	—	—	—	—	—	—	942(30)
mm-4P4E	Bis (m-phenoxyphenyl) Ether	60.9	5.98	—	465	—	1095(17)	~835(17)
pp-4P3E	Bis (p-phenoxyphenyl) Ether	2.83(300°F)	1.51(400°F)	—	516	585	1040(17)	~835(15)
mm-5P4E	m-Bis (m-phenoxyphenoxy) Benzene	332	12.7	—	540	660	1050(17)	870(17)
5P4E	Bis (phenoxyphenoxy) Benzene	380	13.4	—	560	660	1130, 1030(7)	870(26)
pppp-6P5E	Bis [p-(p-phenoxyphenoxy) phenyl] Ether	4.20(400°F)	1.55(600°F)	—	635	—	1030(17)	773(15)
Phosphonitrites								
MLO-63-24	Hexaphenyltriphosphonitrite	—	—	—	—	—	—	810(30)
MLO-63-25	Phenoxy base Triphosphonitrite	—	—	—	—	—	—	905(30)
K488 (Olin Matheson)	Tetrameric Octylfluoroamyl Phosphonitritate	—	—	—	—	—	900(19)	—
Miscellaneous Oils								
Lard oil	—	—	—	<1	395	—	833(47)	—
Linseed oil	—	—	—	0.95	435	535	820(47)	—
Lube oil, cylinder	—	—	—	<1	—	535	783(47)	—
Lube oil, light machine	—	—	—	<1	318	370	—	—
Lube oil, spindle	—	—	—	<1	169	200	—	—
Menhaden oil	—	—	—	0.927	435	—	828(47)	—
Mineral seal oil	—	—	—	—	170	255	—	—
Olive oil	—	—	—	0.91	437	—	826(47)	—
Palm oil	—	—	—	0.92	421	—	650(47)	—
Pine oil	—	—	—	0.86	172	175	—	—
Rapeseed oil	—	—	—	0.915	325	550	836(47)	—
Rosin oil	—	—	—	0.98-1.1	266	—	648(47)	—
Soybean oil	—	—	—	0.925	540	—	833(47)	—
Tung oil	—	—	—	0.94	552	—	855(47)	—
Turkey-red oil	—	—	—	—	476	—	833(47)	—
S.A.E. No. 10 lube oil	—	—	—	—	340	380	720(20)	—
S.A.E. No. 60 lube oil	—	—	—	—	480	620	770(20)	—

1/ Autoignition and decomposition temperature data from references cited in parentheses. Viscosity, specific gravity, flash point, and fire point data mainly from vendor's literature.

2/ Ignition evidenced by visible flame except for underlined values where sudden pressure rise was used. Bureau of Mines data (Refs 2, 4, 5, 7, and 50) were obtained using reaction vessels ≥200 cc. Values listed for other references were determined in reaction vessels ≤125 cc.

erately high operating temperatures and frequent accidents involving ruptured hydraulic components in the proximity of hot metallic surfaces. Also the fiberglass acoustic blankets in the jet engines become soaked with leaking hydraulic fluid within as little as one year of use (30). Fire resistance in phosphate ester type hydraulic fluids has been related to PCB content (31). Phosphate ester hydraulic fluids have been used extensively for commercial aircraft (32). According to one manufacturer, no PCB's are currently being incorporated in these fluids. PCB's have been assumed to be useful as "snuff-ers" in that they tend to extinguish a fire supported by other constituents.

The market value of used phosphate ester type hydraulic fluids is sufficiently high that they are being recycled (33). The recycled products are said to satisfy the same specifications as the uncycled fluids.

Considerable research is being done in connection with fire resistant hydraulic fluids for military aircraft. Some of the hydraulic fluids being tested do not contain PCB additives, but do contain TCP. It is possible that under appropriate processing, PCB's may be replaced by TCP and perhaps certain other additives to obtain satisfactory lubrication.

In naval applications current research includes development of water based hydraulic fluids (34), which would not contain PCB's. The boiling points of these fluids are too low to permit their use in aircraft.

It is possible that PCB's are also used in phosphate ester and other halogenated hydraulic fluids for industrial applications at high temperatures. The requirements here are similar to but not as stringent as those for aircraft hydraulic systems.

Table 3. High-Temperature Lubricant Specifications

	MIL-L-9236 B	MIL-L-27502	DERD 2497
Viscosity, cs at 500°F	—	1.0 min	—
400°F	1.0 min	—	2.0 min
210°F	—	Report	8.5 max
100°F	Report	Report	—
-30°F	—	13,000 max	—
-40°F	—	—	13,000 max
Viscosity stability test temp	-65°F	-30°F	-65°F
Vis change in 3 hr	6% max	6% max	—
Vis after 3 hr, cs	21,000 max	13,000 max	—
Vis after 72 hr, cs	24,000 max	17,000 max	—
Vis at -40°F after 12 hr	—	—	Report
Shear stability at 212°F	—	—	± 2% KV/210°F
Pour point, °F	-75 max	-40 max	—
Flash point, °F	425 min	500 min	500 min
Spontaneous ignition temp, °F	750 min	Report	752 min
Vapor pressure at 500°F, mm Hg	—	5.0 max	—
Evaporation loss test temp	400°F	500°F	392°F
% Loss 6-1/2 hr at 29.9" Hg	15 max	10 max	Report
% Loss 6-1/2 hr at 5.5" Hg	—	Report	—
Specific heat, BTU/lb/°F at 100°F	—	0.35 min	—
Specific heat, BTU/lb/°F at 500°F	—	0.45 min	—
Rubber swell, 72 hr	12-25% at 400°F	12-25% at 500°F	—
Rubber swell, 168 hr	—	—	15-25% at 158°F
Foaming sequence 1-2-3, max vol	100-25-100 ml	100-25-100 ml	100-25-100 ml
Foaming collapse time, max, min	5-3-5	5-3-5	5-3-5
Gear scuff at 165°F % reference	56 min (8 sides)	100 min (8 sides)	—
Gear scuff at test temp, % reference	Report (400°F)	Report (500°F)	100 min (392°F)
Gear fatigue, hr to failure	Report (400°F)	Report (500°F)	(Ref. oil at 230°F)

Gas Turbines

The characteristics of a good gas turbine lubricant are similar to those of hydraulic fluids except for the additional requirement of lubricity at high rates of shear (35). Particular emphasis is placed on heat resistance, high viscosity index, low pour point, and oxidation and foaming resistance. Sample U. S. and U. K. military specifications are given in Table 3 (36). Usually, dibasic acid esters containing appropriate additives meet the above requirements. In the case of the turboprops, the same lubricant is usually used for both the turbine and prop-drive gear.

PCB's seem to be useful as additives in gas turbine lubricants but we have no evidence that PCB's are currently used for this purpose. Research along these lines has been done, and there is some indication that some PCB's have on occasion been added to gas turbine lubricants. The objection to PCB's and other chlorinated hydrocarbons is that they tend to be corrosive at the high temperatures reached in gas turbines. This corrosion is accelerated by decomposition of the PCB's and the formation of hydrochloric acid at high temperatures. The corrosiveness of PCB's is a major deterrent against their use in these lubricants. Since it also has the desirable property of point depressant and antioxidant. TCP also has the desirable property of reacting with metallic surfaces at high temperatures to form a protective coating.

Jet engines are run for approximately 18,000 hours (37) between overhauls. The lubricants are not usually changed during this period; however, the appropriate "oil level" is maintained at frequent intervals. Immediately before engine overhaul the lubricant is drained and discarded. Unlike the hydraulic fluids used in commercial aircraft, there appears to be no general recycling facility for gas turbine lubricants (37). As a result of their increase in acidity and viscosity during use, recycling of gas turbine fluids would demand expensive redistillation and reblending.

Vacuum Pump Applications (22, 23)

Both mechanical and diffusion pump applications require fluids of one highly fractionated component. Accordingly, additives generally are not used. However, PCB's are used in pure form as a diffusion pump oil in commercial applications.

The characteristics (38) of a good diffusion pump fluid are:

1. Relatively high vapor pressure at operating temperatures.
2. Low vapor pressure at room and lower temperatures. (The vapor pressure imposes a lower limit on the ultimate vacuum.)
3. Heat resistance (prevents cracking or molecular degradation at operating temperatures).
4. Narrow vapor pressure range and freedom from contaminants like absorbed gases and liquids with higher vapor pressures. (This requirement often implies the necessity of a narrow fraction.)
5. Oxidation resistance (important because air may enter a diffusion pump during operation either accidentally or through slow leakage).
6. Nonhydroscopic (absorbed water increases pump maintenance and may contaminate the vacuum system).
7. Compatibility (must be compatible with pump and vacuum system components).
8. Stability in the presence of the vapor being pumped.

Some of the pertinent properties of many diffusion pump fluids are given in Table 4 (39). The stability, oxidation resistance, appropriate vapor pressures, and, in particular, the relatively low cost of PCB's make them a desirable choice for many industrial applications. Although the ultimate vacuum using PCB's is limited by their relatively high vapor pressure at low temperatures, their use at high boiler pressures makes possible operation with poor fore vacuums. Hence they are useful as booster pump fluids. In this

Table 4. Some Properties of Pumping Fluids

Fluid	Proprietary names	Chemical nature	Molecular weight	Specific gravity (room temp.)	Flash point (°C)	Viscosity (centistokes) at 20°C	Approx. pour point (or freezing point) °C	Approx. boiling point at 1 torr °C	Estimated true vapour pressure (torr)
Apiezon A	As under 'fluid'	Paraffinic hydrocarbons	414	0.872	218	69	-12	190	10 ⁻⁶ (20°C)
Apiezon B	As under 'fluid'	Paraffinic hydrocarbons	468	0.873	235	100	-12	220	5 x 10 ⁻⁸ (20°C)
Apiezon BW	As under 'fluid'	Paraffinic hydrocarbons	472					225	~10 ⁻⁷ (20°C)
Apiezon C	As under 'fluid'	Paraffinic hydrocarbons	574	0.880	265	295	-9.5	255	4 x 10 ⁻⁹ (20°C)
Apiezon G	As under 'fluid'	Paraffinic hydrocarbons	445	0.873	232	86	-12	210	2 x 10 ⁻⁷ (20°C)
Apiezon FW	As under 'fluid'	Paraffinic hydrocarbons	380					165	5 x 10 ⁻⁶ (20°C)
Convcoil 10	As under 'fluid'	Paraffinic hydrocarbons	250	0.91	191	147	-23	150	6.7 x 10 ⁻⁵ (20°C)
Convcoil 20	As under 'fluid'	Paraffinic hydrocarbons	400	0.86	218	120	-8.9	195	2.3 x 10 ⁻⁷ (20°C)
Di-n-butyl phthalate	—	C ₆ H ₄ (COOC ₄ H ₉) ₂	278	1.044	159	19	-71	102	1.5 x 10 ⁻⁷ (20°C)
Di-2-ethyl hexyl phthalate	Octoil	C ₆ H ₄ (COOC ₈ H ₁₇) ₂	391	0.983	196	75	-52	204	10 ⁻⁷ (20°C)
Di-2-ethyl hexyl sebacate	Octoil-S	C ₈ H ₁₆ (COOC ₈ H ₁₇) ₂	427	0.912	209	24	-56	215	10 ⁻⁸ (20°C)
	Narcoil-20								
	Viacoil-20								
	Narcoil-40								
	Viacoil-40								
Di-nonyl phthalate	—	C ₆ H ₄ (COOC ₉ H ₁₉) ₂	419	0.973	215			215	10 ⁻⁷ (20°C)
Tri-cresyl phosphate	—	(CH ₃ C ₆ H ₄) ₃ PO ₄	368	1.17	240	105		219	5 x 10 ⁻⁶ (25°C)
Tri-xylene/yl phosphate	—	[(CH ₃) ₂ C ₆ H ₄] ₃ PO ₄	414	1.14	243	160		245	
Glycerol	—	(CH ₂ OH) ₂ CH(OH)	92	1.26		1180		123	5.6 x 10 ⁻⁵ (15°C)
Mixed chlorinated diphenyls	Aroclor 1248 Convactor 8 Clophen A-40	Approx. C ₁₂ H ₆ Cl ₄	292	1.45	193	400	-7	137	1.5 x 10 ⁻⁴ (20°C)
Mixed chlorinated diphenyls	Aroclor 1254 Edwards Booster fluid A	Approx. C ₁₂ H ₅ Cl ₅	326	1.54	none	~6000	10	150	8 x 10 ⁻⁵ (20°C)
	Narcoil-10								
	Viacoil-10								
	Convactor-12								
	Clophen A-50								
Silicone D.C. or M.S. 702	As under 'fluid'	Methyl polysiloxanes	530	1.071	194	38	-40	173	
Silicone D.C. 703	As under 'fluid'	(CH ₃) ₃ SiO[(CH ₃) ₂ SiO] _n (CH ₃) ₃ Si	570	1.089	227	40	-36	206	10 ⁻⁸ (20°C)
Silicone D.C. or M.S. 704	As under 'fluid'	Tetraphenyl tetramethyl trisiloxane	484	1.086	216	47	-38	223	5 x 10 ⁻¹⁰ (25°C)
Silicone D.C. or M.S. 705	As under 'fluid'	Pentaphenyl trimethyl trisiloxane	546	1.095	243	170	-15	254	
						(25°C)			
Convalex 10 or V.R.T. fluid E	As under 'fluid'	Mixed 5-ring polyphenyl ethers	447	1.198	288	2500	4.5	285	1.3 x 10 ⁻⁸ (25°C)
						(25°C)			
Mercury	—	Hg	200.6	13.6	—	1.15	-38.9	127	1.1 x 10 ⁻³ (20°C)

respect the vapor pressure-temperature properties are closely matched by amyl phthalate.

Except for certain applications where alternative liquids may be incompatible with the vapors being pumped, the advantage of using PCB diffusion pump oils appears to be mostly an economic one. Other fluids may often be preferable though considerably more costly. TCP is used as a commercial diffusion pump fluid and is also inexpensive. Its vapor pressure (40) is lower than that of the PCB's making it less desirable in booster pumps, but in many applications TCP may be a suitable replacement. PCB diffusion pump oils can be decomposed after use by incineration. This service is available mainly for disposal of Askarel transformer fluids containing PCB's.

Heat Transfer Applications

Heat transfer fluids are used to absorb thermal energy from a source and by cooling or changing phase, deliver heat to a place of utilization. The reverse process, using a fluid as a coolant, requires similar fluid properties. Summaries of heat transfer fluids and applications are available (41, 42). The properties required of heat transfer fluids are (41):

1. Suitable density and expansion coefficient.
2. High heat capacity or heat content (increases amount of heat transferred during cooling or phase change).
3. High heat conductivity (increases heat transfer).
4. Low viscosity (necessary for fluid flow through system).
5. Physical stability (will not have unpredictable phase or property changes).
6. Chemical stability (will not degrade, oxidize, etc.).
7. Radiolytic stability (will not suffer damage from radiation if present).
8. Low cost.

9. Low surface tension (reduces fluid flow and heat transfer between fluid and surroundings).
10. Low corrosion (reduces damage to metal parts of the system).
11. Low flammability (reduces fire and explosion danger).
12. Low toxicity.

Electrical properties, refractive index, appearance and odor may be considered for some applications.

Advantages and disadvantages of PCB's as heat transfer fluids:

The main advantage of the PCB's as heat transfer fluids is their fire resistance. This property is of primary importance where there is a possibility that fire from high temperature leakage could endanger life and property. The other advantages of PCB's are low pour points and viscosities and good thermal stability up to 600°F. PCB's are relatively inert and have excellent electrical properties which makes them valuable for cooling transformers. The cost is relatively low. Disadvantages of PCB's include possible toxicity, a tendency to decompose to form highly corrosive HCl, a lower decomposition temperature than some alternate liquids (43) and relatively poor radiation resistance (44).

Replaceability of PCB's as heat transfer fluids:

Increased risk from fire and explosion is a major disadvantage with most PCB replacement fluids. Other non-flammable fluids are 1) fluorocarbons, which have low toxicity, high thermal stability and in spite of high cost are used as convective or evaporative coolants (1), 2) water, which is quite corrosive, has a high temperature limit of 374° C and requires extremely expensive high pressure systems for its use above the atmospheric boiling temperature and 3) molten salts and metals which, because of their resistance to radiation damage, are useful in reactor applications.

Several liquids are more stable at high temperatures than the PCB's. Table 5 (42) shows the decomposition point range of liquids in a variety of chemical classes. Few

Table 5. (42)

Decomposition Point Range (°F)	Chemical Class
Over 800	Unsubstituted Polyaromatic compounds Unsubstituted Polyphenyl ethers Unsubstituted Aromatic amines Unsubstituted Aryl silicates Unsubstituted Aryl silanes Unsubstituted Aryl borates
700-800	Lower alkylaromatic ethers Aromatic phosphates Aromatic sulfones Aromatic ketones Silicones Halo-substituted aromatic ethers Halo-substituted polyphenyls (including PCB's)
600-700	Alkyl borates Alkyl silicates Higher alkylaromatic ethers Highly refined mineral oils Fluorinated esters Neopentylpolyol esters
500-600	Sebacate esters Methyl aryl esters Aliphatic tertiary amides

of these liquids are non-flammable, however, as can be seen from Table 2. The phosphate esters, silanes, and aromatic ethers have high fire points (around 600° F) but they are flammable and it is not clear how high the fire point must be for a fluid to be safe in a high temperature system, especially in the event of leakage into a furnace. The details of specific heat transfer applications are necessary to evaluate the suitability of PCB replacement fluids.

Plasticizer and Miscellaneous Uses

A plasticizer is a material incorporated in a plastic to increase its workability and flexibility (45, 46). The addition of a plasticizer may lower the melt viscosity and flow temperature (increasing the ease with which the plastic can be made to flow), or lower the elastic modulus (making the plastic softer) (46). Plasticizers are generally non-volatile

*Note that the term compatibility has here a meaning very different from that used earlier. In the earlier case, compatibility meant that two materials could coexist *without* either being affected by the other. The present meaning is quite the opposite.

liquids or low-melting solids. A major requirement of a plasticizer is that it have high compatibility* (mixes well to form a homogeneous composition with useful properties) (42) with the material being plasticized. Figures are given in Table 6 for the compatibility of some common plasticizers with some common synthetic thermosetting or thermoplastic resins (45). Other properties which are important when considering plasticizers are specific gravity, refractive index, color, odor, moisture sensitivity, vapor pressure (volatility), boiling range, stability (to light and heat) toxicity and cost (47). Of course the properties of the final plasticized material are of prime importance. Certain plasticizers provide formulations with specific properties such as:

- phthalate esters - general purpose.
- adipates and ozelates - low temperature flexibility.
- highly aromatic esters - fast processing, strain and extraction resistance.
- epoxies - heat stabilization during processing.
- phosphate esters and PCB's - fire retardant materials.

Advantages and disadvantages of PCB's as plasticizers:

PCB's are attractive as plasticizers because of their high compatibility factor. They have been made with a wide range of properties as shown in Table 7 (48). The PCB's are permanently thermoplastic, chemically stable, non-oxidizing, non-corrosive, have excellent solvating powers and are fire resistant (48, 49). They are not normally attacked by acids, alkalines or water. They are insoluble in water, glycerol and glycols and soluble (at the lower chlorine contents) in organic solvents (48).

The main disadvantages of PCB's are their possible toxicity, and relatively high cost.

Adhesives

An adhesive is a substance capable of holding materials together by surface attach-

Table 6. Approximate Maximum Compatibility, phr[†], of Plasticizers with Various Resins

	Phthalates			Adipates			Phosphates			Phthalyl glycolates			Polyesters			Ep-oxides amides			Miscellaneous						
	Dibutyl	Di-2-ethylhexyl	Ditridecyl	Dicyclohexyl	Butyl benzyl	Di-2-ethylhexyl	Ditridecyl	Triphenyl	Tricresyl	2-Ethylhexyl	Tri-2-ethylhexyl	Tributoxy ethyl	Methyl phthalyl ethyl glycolate	Butyl phthalyl glycolate	Sanitizer ^a 405	Sanitizer ^b R-2H	Paraplex G-25	Paraplex G-54	Paraplex G-62	N-Ethyl-o,p-toluene-sulfonamide	o,p-Toluene-sulfonamide	Chlorinated biphenyl	HB-40 ^a	Polyethylene glycol di-2-ethylhexoate	
poly(vinyl chloride)	100	100	100	30	100	100	50	20	100	100	100	60	20	100	100	100	100	100	100	40	1	35	40	100	
poly(vinyl acetate)	100	100	1	50	100	1	1	80	40	50	1	40	100	100	75	100	11	33	1	100	50	50	50	25	
poly(vinylidene chloride)	50	75	25	10	20	75	15	10	20	75	75	50	75	75	10	25				50	20	50	20		
polystyrene	100	100	50	100	20	100	25	20	15	50	100	30	30	30	1	50				20	100	100	100		
ethylcellulose	100	100	100	50	100	100	100	30	70	100	100	50	75	75	10	33	1	<1	100	60	75	75	100	100	
cellulose nitrate	60	100	100	50	100	35	35	75	100	100	100	100	100	100	100	100	100	100	80	50	100	100	100		
cellulose acetate	80	25	1	1	1	10	1	35	15	20	<11	10	100	50	1	1	1	1	90	30	1	1	1	1	
cellulose acetate butyrate	100	100	50	20	100	25	50	50	30	80	>25	25	100	50	100	100	1	100	1	50	25	50	30		
chlorinated rubber	25	100	33	100	20	80	100	50	100	100	100	100	100	80	50	50	100	100	100	50	25	100	100		
high styrene-butadiene copolymer	20	50	50	50	20	50	20	20	50	50	50	50	50	50	15	25			25	25	50	25			
protein-based plastics	20	20	1	1	1	10	1	1	30	25	10	20	40	1	1	1	1		50	40	1	1	1		
shellac	5	1	1	1	1	1	1	1	1	1	1	1	10	30	1	1			40	60	1	1			
acrylic resins	100	70	25	25	25	75	10	1	25	100	100	25	60	70	1	1	1		25	25	10	20	25		
polyamides	1	25	20	10	25	25	25	10	25	25	15	1	20	1	1	1		50	25	25	25	1			
polyesters	5	20	20	15	20	20	1	1	10	20	20	20	5	20	5	10		10	5	25	1	5	1		
epoxy resins	1	25	1	10	25	1	1	10	25	25	25	25	25	25	1	1		50	50	50	1	50	1		
phenolic resins	25	50	25	25	25	50	25	50	50	50	50	50	50	50	15	25		60	50	25	25	25			
alkyd resins	25	70	25	25	25	50	50	25	50	70	70	50	70	70	20	25		25	25	25	15	15			
melamine-formaldehyde resins	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		50	80	1	1	1			
polyurethan	25	25	25	10	25	15	15	10	25	25	25	25	25	25	10	15		20	10	25	15	15			
nitrile and neoprene rubber	100	100	50	33	50	100	20	33	50	55	40	50	50	50	25	50	33		50	50	50	50	50		

^a Trademark Monsanto Co.^b Trademark Union Carbide Corp.^c Trademark Rohm and Haas Co.[†] parts per hundred

Table 7. General Properties of Some Aroclors (PCB)

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	η^{20}_D	Viscosity, ^f sec	
									37.8°C	98.9°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	30-31
Aroclor 1232	almost colorless, mobile oil	1.270-1.280 (25/15.5°C)	200-325	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	185-240	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	44-48
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		249-300 ^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	>350	46	46-52			300-400
Aroclor 5460	clear, yellow-to-am- ber, brittle resin	1.670 (25/25°C)	280-335 (5 mm Hg)	none	none		98-105.5	1.660-1.665		
Aroclor 2565	black, opaque, brittle resin	1.734 (25/25°C)		none	none		66-72			

^aASTM D-20 (modified). ^bCleveland open cup. ^cCleveland open cup; none indicates no fire point up to boiling temperature. ^dASTM D-97. ^eASTM E-28.

^fSaybolt Universal, ASTM D-88. ^gLast two digits indicate approximate chlorine content, ie, Aroclor 1221 contains about 21% chlorine. ^hHold point on solidification.

ment (50-52). The major types of plasticized resin adhesives are emulsion, hot-melt, delayed tack, solution, pressure-sensitive and adhesive primers and coatings. Almost every thermoplastic resin is used individually or in resin blends as a hot melt adhesive. This necessitates a wide range of plasticizers. Of special value are the solid plasticizers. They plasticize the resin while hot and while the bond is being formed, but solidify at lower temperatures to overcome the problem of excessive softness (53). Among those solid plasticizers used are: o,p-toluenesulfonamide, N-cyclohexyl-p-toluenesulfonamide, triphenyl phosphate, and diphenyl phthalates. The more resinous chlorinated polyphenyls would also be included in this category. Hot melt adhesive compositions based on phenolic resins are used in brake linings, clutch faces and grinding wheels. Reactive plasticizers, such as the toluenesulfonamides, are employed because they improve the flow properties by reducing the viscosity of the

phenolic resins (54). They help the resin wet the fillers and abrasives. Chlorinated polyphenyls and aryl phosphates (non-reactive plasticizers) also improve flow properties of phenolic resins prior to curing as well as imparting some flame-proofing characteristics to the compositions. PCB's have also been used in laminating adhesive formulations involving polyurethanes and polycarbonates (55-57) to prepare safety and acoustical glasses. The laminates have improved strength and resistance to delamination over a broad temperature range, and improved sound-absorption and energy dissipation properties.

Polyarylene sulfides, treated with chlorinated biphenyls, are employed to laminate ceramics and metals (58, 59). An ethylene-propylene copolymer blended with PCB has been used in a hot melt adhesive having improved toughness and resistance to oxidative and thermal degradation. It has excellent adhesion to polyethylene films (60).

Similar adhesives, used to bond polyethylene to itself or other plastics, were prepared from styrene, α -methylstyrene or methylmethacrylate (61). Washable wall coverings and upholstering materials, made from films of polyvinyl chloride, are claimed to be improved by the addition of PCB to the adhesive formulation (62). PCB's can also be applied in the preparation of polyvinyl alcohol adhesive compositions which are used to manufacture envelopes (63), in self-adhering films (64), and in preparation of coatings of pressure-rupturable capsules for adhesive tape (65).

Textile Coatings

A textile coating for ironing board covers can be formed from a mixture of chlorinated biphenyl, cellulose acetobutyrate and aluminum metal particles (66). PCB's also can be used as a de-lustering agent for rayons (67, 68). Poly- α -olefins, (i.e. polypropylene) films, when coated with a mixture of PCB's, UV light absorbers, and antioxidants show increased stabilization to oxidative degradation on exposure to sunlight and weathering (69, 70). Polyamide (nylon-type) yarns were found to be flame proofed when treated with PCB (71). Chlorinated biphenyls can also be used as ingredients in some sealing formulations employed to waterproof canvas (48).

Surface Coatings

In paints and varnishes, the hard resinous PCB's impart increased hardness to films, and the softer resins give flexibility (48). The role of these materials is similar to the oil, except that they do not oxidize and lose flexibility on aging. In nitrocellulose lacquers, PCB's either alone or in combination with other plasticizers and resins impart increased weatherability, luster, adhesion, and decreased burning rates (48, 72).

Some comparison studies have been made recently on the effects of various plasticizers upon the overall properties of paints and varnishes made from acrylic latexes (73). Films plasticized with tricresyl phosphate

(TCP) had better stability, tensile strength and adhesion than did film plasticized with dibutyl phthalate or PCB (73). For varnishes prepared from polyvinyl chloride formulations, and plasticized with either di-butyl phthalate or PCB, the films plasticized with PCB had better overall properties with or without pigments (TiO_2) (74).

PCB and other plasticizers can be used in combination with poly (organosiloxanes) to prepare film casting solutions. These polymeric films could be employed in electrical coatings, insulating tapes and protective lacquers (75-78).

Plastic vessels, i.e. bottles, manufactured from polyethylene, polyvinyl chloride, polyvinylidene chloride or similar resins coated with an epoxy lacquer (which contains PCB) make the vessels pliant, impervious, and resistant to aromas, acids and alkalis (78).

Paints at atomic energy installations are needed for (a) contaminated areas, (b) tolerance to high energy radiation, and (c) to meet clean condition standards. Paints for (a) should be glossy and smooth and should not transmit contaminants. For this purpose, the vinyl polymers are preferred over epoxy lacquers. The best plasticizers for use in this area are claimed to be the PCB's (79). The extent, if any, of their use in this application is unknown.

The PCB's are usually compatible with epoxy resins, and they give good final hardness and impact resistance equal to the unmodified resin (80). They also aid in the acceptance by the resin of larger amounts of fillers. Epoxy resins in combination with PCB can be used as protective coatings for metals, i.e., encapsulating electrical capacitors (81), for ferrite magnet cores (82) (used in computers), for corrosion resistant resistors (83), for pigmented metal coatings (84, 85) for winter camouflage coatings (86), and for pipes and blocks (87).

Sealants

Sealing and caulking compositions include a wide range of compounds which can be used to seal joints or voids against water and water vapor, air and other gases, dust,

sound, vermin, heat and cold (88). Specialized applications require resistance to certain chemicals or atmospheric environments. PCB's can be used as plasticizers in the formulation of putties from copolymers of ethylene-vinyl acetate or styrene (89). The products are non-hardening, and resistant to moisture and frost and show good weatherability. A non-sticky, non-hardening putty was also prepared from polysulfide mixtures which employs PCB as the plasticizer. This putty gave good bonding to building materials, had good extrudability and shape retention (90). Elastic pavement or concrete sealing compositions, used for traffic markings, were prepared from coal-tar-polysulfide mixtures which are plasticized with PCB (91). A sealant, effective for concrete and asphalt applications, can be formulated from a mixture of polysulfide, chlorinated rubber, polyisocyanate, and plasticized with PCB (92).

Printing

Chlorinated biphenyls have been employed as part of the formulations used to prepare pressure-sensitive record (93, 94) and colored copying papers (95, 96, 102, 103). They have been used to coat papers used in thermographic duplicating processes (97-101) as well as in xerographic transfer processes (104-105). Solvent-free printing on polyolefin plastics can be accomplished by heating a mixture of low molecular weight material, chlorinated biphenyl or terpene resin, and suitable pigments and dyes. Durable prints can be made on the surface of the polyolefin at the time of their thermoplastic shaping (106). Printing plates, hard enough for high quality letterpress printing, and sufficiently flexible for use as flexographic plates, can be prepared from compositions containing a liquid resin such as epoxy, polyester, urethan, acrylic or vinyl with an excess of curing agent and PCB as the plasticizer (107). The extent, if any, of current uses of PCB's in printing applications is unknown.

Fire Retardant and Flame-Proofing Compositions

When PCB's are used as plasticizers, they impart a certain degree of non-flammability to the objects as described previously. However, for increased effectiveness in flame retardant applications, the PCB's can be admixed with various metal oxides. Some flame retardant compositions based upon these mixtures are: polyolefin yarns (108); organopolysiloxane sealants (109); thermoplastic poly (hydroxyethers) (110); fire-proof panels made from starch which can be used for doors, floors, ceilings, and partitions (111); polyamides (112); and in fire-proof fiberboards (113). Rigid polyurethane foams (114-116) and hardboard compositions (117), when treated only with PCB's do not show any significant increase in flame retardant activity.

Miscellaneous Applications

The wide range of chemical and physical properties exhibited by the PCB's (see Tables 6 and 7) make them desirable for an assortment of miscellaneous uses. Some of the more interesting and non-conventional uses are given below.

1. Catalyst carrier for polymerization of olefins (118).
2. Conversion of water-permeable soil to a non-permeable state. Soil is made non-permeable by applying to the soil a composition consisting of an ethoxylene-based resin, polyamide, camphor and PCB as plasticizer. The composition had a density greater than water and it hardened under water. It could be applied to river banks, where it flowed down the bank, and after hardening, prevented penetration of water (soil erosion-retardant) (119).
3. Combined insecticide and bactericide formulations. The composition contains aldrin or dieldrin, naphthalene hydrocarbons, malathion, methoxychlor, lindane, chlordane, terpeneol,

and chlorinated biphenyl as active agents (120).

4. Inhibitors of microbial growth in enamel clay formulations (121).
5. Plastic sound insulating materials for railway cars (122).
6. Plastic (PVC) decorative articles which give the impression of internal scintillation (123).
7. Increasing the density of carbon plates by impregnation with PCB (124).
8. Graphite electrodes with low thermal expansion coefficients and high bending strengths (125).
9. Increasing the coke yield from coal pitch. The coke is very hard, dark, and brilliant (126).
10. As a metal quencher or tempering agent for steel, alloys and glass (127, 128).
11. As an aid to fusion cutting of stacked metallic plates without adherence. The cutting is done with an electric arc or oxy-gas torch (129).

Possible replacement of PCB's in plasticizer and miscellaneous applications:

We find no evidence that PCB's are indispensable to a particular plasticizer or miscellaneous application. In most of the formulations and compositions cited, there were usually alternative plasticizers included in the citation (see Table 6) which did not appear to be detrimental to the application.

Summary

The major value of the PCB liquids is that those with four or more substituted chlorines per molecule are non-flammable as are their decomposition products. Thus they can be used as fluids at temperatures up to 700°F without the danger of explosions and fire. The major disadvantage of the PCB's is their possible toxicity danger. The other comparable class of non-flammable fluids are the fluorocarbons which typically have a lower vapor pressure and lower boiling point than the chlorinated compounds.

PCB's are used in fluids (known as askarels) for electrically insulating and cooling transformers when the transformers are used in or near buildings. Mineral oils are the preferred fluids when fire does not create a hazard. Dry transformers can also be used but are larger and more expensive. Fluorocarbon liquids require a special transformer design. Fluorescent light ballast capacitors and phase correction capacitors utilize the high dielectric constant of the PCB's to effect significant reduction in capacitor size and cost. Few suitable fluids have a comparably high dielectric constant. Flammable fluids are not allowed by insurance companies and building codes in capacitors used in buildings. Replacement of PCB's in capacitors and transformers would require considerable time and money for reengineering, manufacture and application of substitute equipment.

PCB's are useful in hydraulic systems where leakage onto hot metal surfaces could cause a dangerous fire. Hydraulic fluids can also be made with phosphate esters which are toxic and which will burn at high temperatures. Replacement of PCB's in some hydraulic systems could increase loss of life due to fire. Gas turbines require lubrication at high temperatures. PCB's can be used but tend to be corrosive. Phosphate ester lubricants seem better in this respect. Chemical stability is more important for high temperature lubricants than is non-flammability. PCB fluids are useful in diffusion booster pumps to produce moderately high vacuums with relatively poor fore vacuums. Non-flammability is not especially important for diffusion pump liquids, and with a few possible exceptions alternative liquids are available.

Flammable heat transfer fluids present a fire hazard if they leak into a furnace or onto hot surfaces. The use of PCB's can prevent this danger. In some cases water is a suitable substitute at moderately high temperatures. Other heat transfer fluids are commercially available and in use. Replacement of PCB's is satisfactory in some, but may be dangerous in other heat transfer uses.

The PCB's are good plasticizers for use with adhesives, textiles, surface coatings, sealants and copy paper. In some cases the PCB's act as fire retardants. There are no particularly unique properties of PCB's for plasticizer uses, and equally effective alternatives are generally available (e.g. phosphate esters are often used as fire retardants). The extent of current use, if any, in such applications has not been determined.

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