

CHAPTER V

POLYCHLORINATED BIPHENYLS

PRODUCTION AND USE

MONS 008974

V. Production and Use

Polychlorinated Biphenyls

Introduction

Polychlorinated biphenyls (PCBs) constitute a large group of compounds which are characterized by the partial or complete chlorination of the biphenyl molecule.

This report covers the production and use of four groups of polychlorinated biphenyls with the trade name Aroclor. Each group contains a certain percentage of chlorine along with the biphenyl molecule. Their designations are Aroclor 1242, 1016, 1254 and 1221 containing 42%, 41%, 54%, and 21% chlorine respectively.

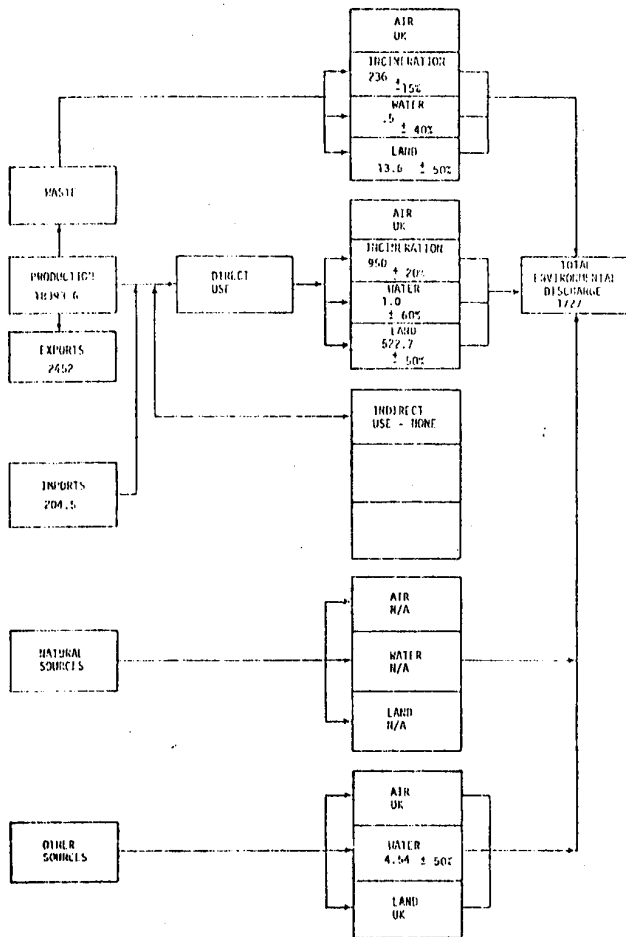
Summary

An overall material balance for PCBs with estimates of reliability of data provided by EPA is shown in Figure 1 for 1974(5).

The total amount of land destined wastes from manufacturers and producers, 536 Kkg, represents a small fraction of the total PCBs entering landfills and dumps yearly (5). The estimated yearly rate of PCBs entering land disposal sites is 5,454 kkg primarily due to the disposal of capacitors (5).

The data on industrial discharges to water and sewers is based on information supplied by industry.

Very little has been done to control air emissions of PCBs in U.S. industrial facilities.(2) It has been assumed by industry that the low vapor pressure of PCBs will result in very little air contamination. Therefore, data is not available for the entire industry on volumes and concentrations of air pollution resulting from manufacturing processes. It is known, however, that considerable air pollution may result from



N/A - NOT APPLICABLE
UK - UNITED KINGDOM

Figure 1. Overall Material Balance with Estimates of Reliability of Values
in kg (5)

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paper incineration, foundries where imported casting waxes are heated to high temperatures, and in some manufacturing processes (2).

The distribution of PCB wastes in water, incineration, and land are shown in Table 1 for 1974 (5). There is no collective data for the industry on air emissions. Incineration data as mentioned before is included instead of air emissions data.

Media distribution of wastewater volumes is shown in Figure 2. Average wastewater flow data was collected from five transformer industries. (5) The average of these waste flows was taken to be the average flow for the rest of the industry. This value may be quite over estimated (+ 40%) since two of the industries are considered to be the largest.

For the capacitor industry, wastewater data from 14 companies was available. (5) The average daily wastewater discharge for the entire industry was estimated the same as in the transformer industry (i.e., the average daily flow for 14 plants was extrapolated to 19 plants).

The location of producers and users of PCBs are shown in Figure 3 (3).

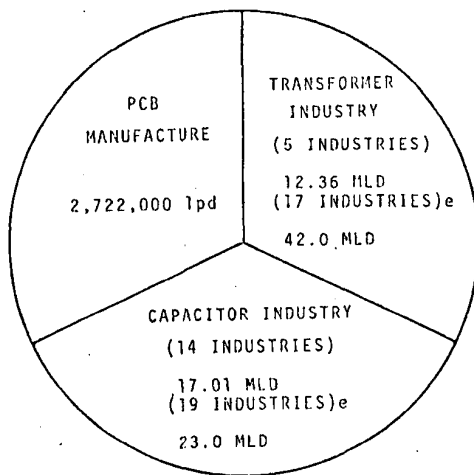
Production

Annual production of polychlorinated biphenyls from 1930 to 1975 in the U.S. has been estimated to be 636,346 Kkg (5). In 1974, the production in the U.S. was 18,393 Kkg (5). Figure 4 lists the quantity of PCBs sold, exported, imported, and kept in stock during 1974.

Table 1. Media Distribution of Waste in 1974 in kkg With Estimates of Reliability of Values

	Amount Disposed or lost	Estimated Reliability of Values
PCBs Disposal to Land (assume PCBs to be 30% of total solid wastes)		
From PCBs manufacture	13.6	± 50%
From capacitor industry	218	± 50%
From transformer industry	123	± 50%
From investment casting	182	± 30%
Incineration of Scrap PCBs		
From PCBs manufacture	236	520 ^{100%} ± 15% ✓
From capacitor industry	659	± 20%
From transformer industry	291	± 20%
Industrial Discharges to Water and Sewers (as PCBs)		
From PCBs manufacture	.5*	2-3 ^{100%} Day ± 40% probable high
From capacitor industry	.95*	± 60% but to low
From transformer industry	.045*	± 60% are needed
Spills during Transport	4.54	± 50% never had spill

* Developed from data supplied by industry. Most analyses for PCBs concentrations in industrial wastewaters are probably not more accurate than ± 50 per cent.



e - ESTIMATED

Figure 2. Media Distribution Wastewater Volumes

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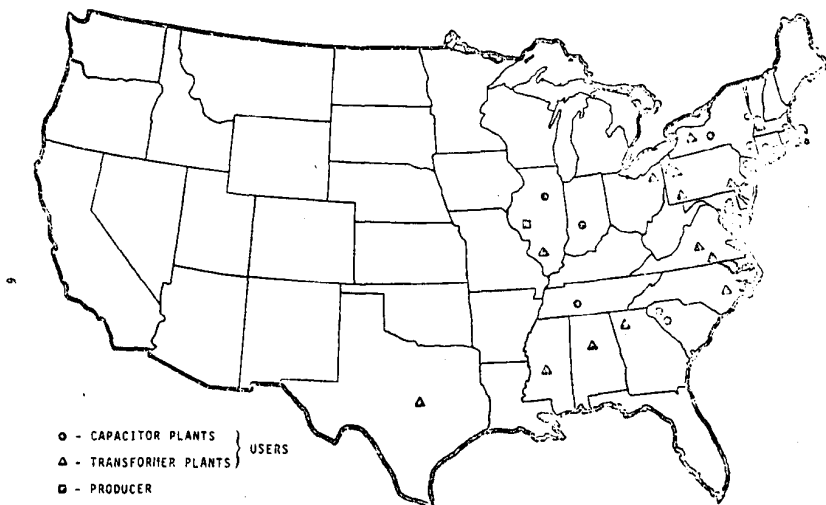


Figure 3 Location of Producers and Users of PCBs

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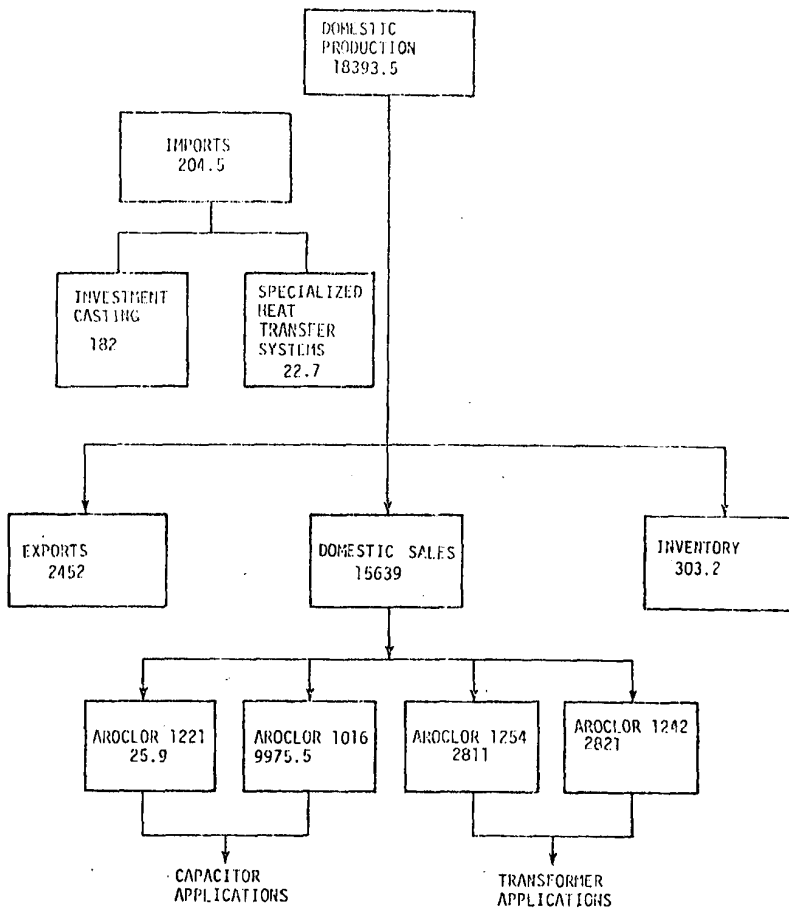


Figure 4. U.S. PCB Market - 1974(5) in kkg

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The sole producer of PCBs in the U.S. is Monsanto, located in Sauget, Illinois. At the end of this year, PCBs will no longer be produced in the United States by this company.

Monsanto, however, expects a small steady growth of usage of PCBs over the next few years (3).

Production Processes

There are two main steps used in the production of PCBs; (3)

1. Biphenyl is chlorinated with anhydrous chlorine in the presence of ferric chloride to produce crude PCB.
2. The crude PCB is distilled to obtain the finished product.

Figure 5 shows the steps involved in the production of PCBs (3).

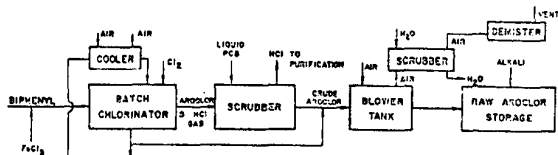
There are four PCB products manufactured called Aroclors 1242, 1016, 1254, and 1221. Their manufacture is dependent on the amount of chlorine, biphenyl and catalyst.

In order to produce PCBs, a chlorinator is first charged with the proper quantity of biphenyl and catalyst and is then heated beyond the melting point of biphenyl. Vaporized chlorine is then circulated through the chamber by means of a pump. The contact time in this chamber varies from 12-36 hours depending on the intended chlorine content of the finished product.

The crude product is held at elevated temperatures and blown with dry air for several hours, after which it is sent to a raw Aroclor storage tank where a few tenths of 1% alkali is stirred with the material to react with any remaining hydrogen chloride or ferric chloride. The raw Aroclor is then batch distilled under reduced pressure by steam jet ejectors to remove color, and traces of

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PREPARATION OF CRUDE CHLORINATED BIPHENYLS-MONSANTO KRUMMRICH PLANT



DISTILLATION OF CRUDE PRODUCTS-MONSANTO KRUMMRICH PLANT

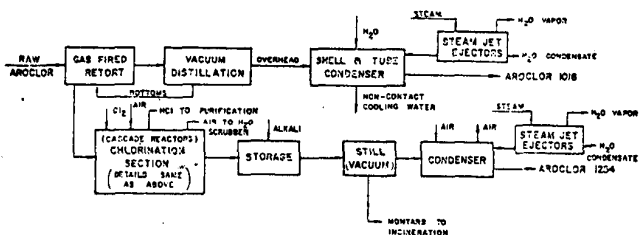


Figure 5. Process for Production of PCBs (3)

hydrogen chloride and ferric chloride. The condensate from the distillation process is the final product. The "bottoms" are called montars which are drummed and sent to incineration.

The vapors that arise in the chlorination are scrubbed with liquid Aroclor and the gaseous HCl is sent to a purification process. The air from the blowers used to dry the crude product is scrubbed with water and vented to the atmosphere.

The aforementioned process is used to produce Aroclor 1254, 1242 and 1221.

In the production of Aroclor 1016, the distillation process is carried out in a gas fired retort and vacuum distillation tower. The first cut from the tower is recycled back to the retort. The overhead from the tower is the finished product. The bottoms are the montars which are sent to incineration.

Production Process Wastes

Those wastes generated in the manufacturing process include liquid from the scrubbers, condensate from steam jet ejectors, water used in drip pans and drums, and the montars (bottom cut from stills). In the incineration process, the sources of wastewaters are the venturi scrubber liquid and the water phase from the separator sump in the incineration area.

Typical quantities of water used and discharged from the plant are shown in Figure 6 (3).

Both the process wastes and incinerator wastes are directed to the sewer. The total wastewater volumes and concentration of PCBs from these sources are shown in Table 2 (3).

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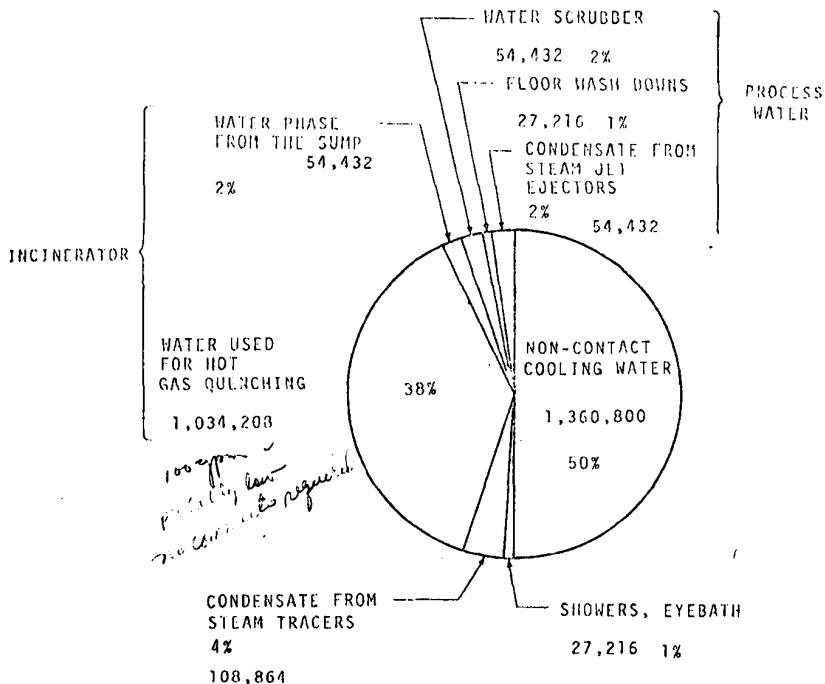


Figure 6. Volume of Wastewater Discharged - 1pd (3)

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Table 2 (3)
Wastewater Discharge from Monsanto Plant

	Manufacturing Process	Incineration
flow, lpd	1,663,000	1,089,000
PCBs, ppm	.75	.15
PCBs, Kg/day	1.23	16
Total discharge =	2,722,000 lpd	

*✓ because
the PCB's
should be
2.16 or less*

The discharge of all wastes to the air, sewers, incineration, and landfills are enumerated in Figure 7 (5). Figure 8 lists the various sources of wastes and their destination in the environment (3).

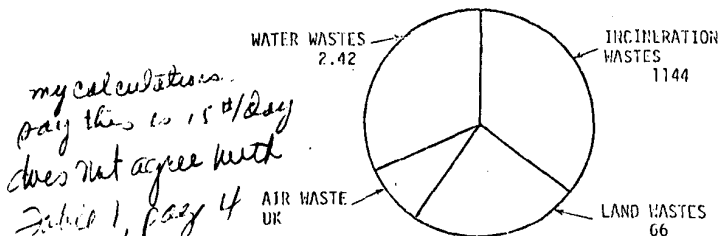


Figure 7. 1974 Media Distribution of Wastes for Producer in kkg

Uses

The major uses of PCBs are in the manufacture of capacitors and transformers. Imported PCBs are used in the investment casting industry and for heat transfer fluids. The end usage of PCBs in 1974 is shown in Figure 9.

*> increase for this plant
Nuclear report was 2-3 #/day, 2.5 15*

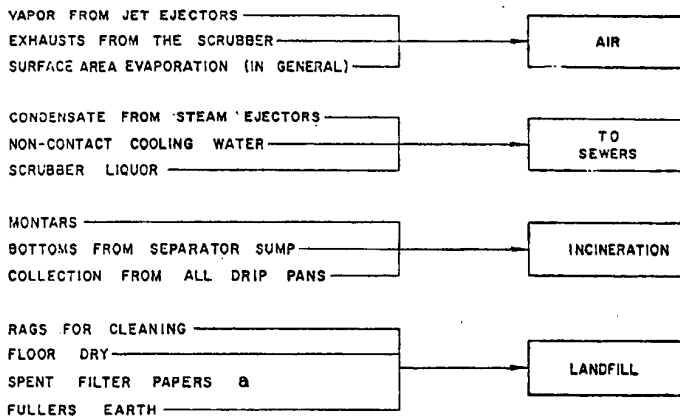


Figure 8. Non-Product PCB Discharges at Monsanto's Krummrich Plant

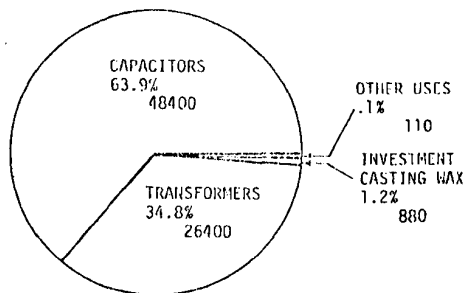


Figure 9. End Use of PCBs (5) in Kkg

The total industrial usage of PCBs in 1974 was 15,659 Kkg. (5).

A summary of the production and uses of PCBs over 1972-1975 is given in Figure 10 (5).

There are 37 user plants in the United States - 19 capacitor plants and 18 transformer plants. Their locations are listed in Tables 3 and 4 (3).

Capacitor Industry

In the capacitor industry, the usage of PCBs is split roughly evenly between the production of large and small capacitors. Approximately 95% of the capacitors manufactured in the U.S. contain PCBs (7). Generalized flow diagrams for the manufacture of large and small capacitors are shown in Figures 11 and 12 (3). The processes involved in the manufacture of capacitors include: filling (under vacuum), sealing, deoiling, and testing.

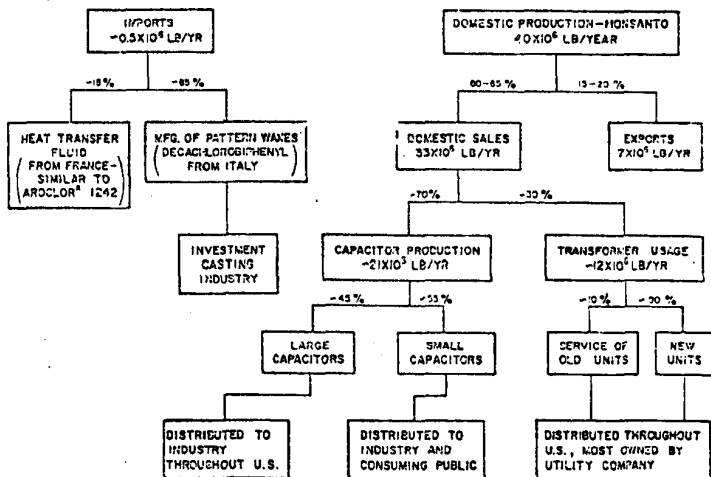


Figure 10. U.S. Production and Usage of PCBs Summary Over 1972-75

Table 3
U.S. Capacitor Manufacturing Industry Using PCBs

<u>Company Name</u> <u>(in order of PCBs usage)</u>	<u>Location of the Plant</u>
General Electric Company	Hudson Falls, N.Y. Ft. Edward, N.Y.
Westinghouse Electric Corp.	Bloomington, Ind.
Aerovox	New Bedford, Mass.
Universal Manufacturing Corp.	Bridgeport, Conn. Totowa, N.J.
Cornell Dubilier	New Bedford, Mass.
P.R. Mallory & Co., Inc.	Waynesboro, Tenn.
Sangamo Electric Co.	Pickens, S. Carolina
Sprague Electric Co.	North Adams, Mass.
Electric Utility Co.	LaSalle, Ill.
Capacitor Specialists Inc.	Escondido, Calif.
JARD Corp.	Bennington, Vt.
York Electronics	Brooklyn, N.Y.
McGraw-Edison	Greenwood, S. Carolina
RF Interonics	Bayshore, L.I., N.Y.
Axel Electronic, Inc.	Jamaica, N.Y.
Tobe Deutschmann Labs.	Canton, Mass.
Cine-Chrome Lab, Inc.	Palo Alto, Calif.

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Table 4
U.S. Transformer Manufacturing Industry Using PCBs

<u>Company Name</u>	<u>Location of the Plant</u>
Westinghouse Electric Corp.	South Boston, Va. Sharon, Pa.
General Electric Company	Rome, Ga. Pittsfield, Mass.
Research-Cottrell	Finderne, N.J.
Niagara Transformer Corp.	Buffalo, N.Y.
Standard Transformer Co.	Warren, Ohio Medford, Oregon
Helena Corp.	Helena, Alabama
Hevi-Duty Electric	Goldsboro, N.C.
Kuhlman Electric Co.	Crystal Springs, Miss.
Electro Engineering Works	San Leandro, Calif.
Envirotech Buell	Lebanon, Pa.
R.E. Uptegraff Mfg. Co.	Scottsdale, Pa.
H.K. Porter	Belmont, Calif. Lynchburg, Va.
Van Tran Electric Co.	Vandalia, Ill. Waco, Texas

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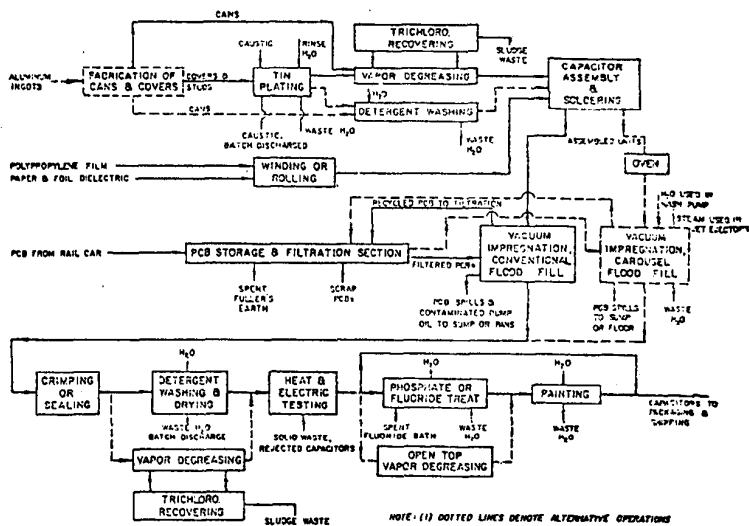


Figure 11. Generalized Flow Diagram for the Manufacturing of Small Capacitors

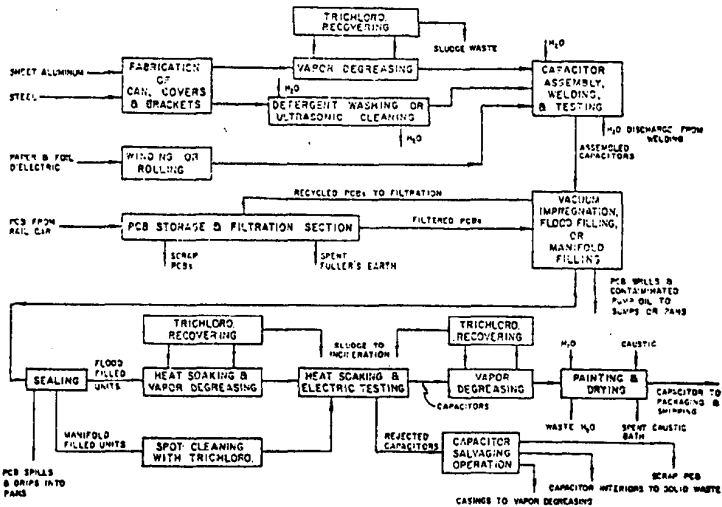


Figure 12. Generalized Flow Diagram for the Manufacturing of Large Capacitors

Sources of wastewater in the manufacturing process consist of scrap PCBs collected in pumps, drums and drip pans, contaminated vacuum pump oils, fractionator bottoms from trichloroethylene recovery, caustic bath (some plants), spent detergent wash and rinse water from capacitor or component cleaning operations, steam condensate from jet ejectors, seal water used in vacuum pumps, water used in phosphatizing and fluoride baths, water spray used in the paint booths, boiler blow downs and cooling tower blow down.

Solid wastes consist of scrap capacitors or capacitor interiors, floor dry and rags and newspapers used for cleaning spills, spent fuller's earth and other filtering media used for PCBs filtration and waterless cleaners used at some plants for hand cleaning purposes.

The effluent from these plants range from 9,450 - 4,762,800 lpd (3). The PCB content ranges from .0005 - 1.08 Kg/day on the average (3).

The quantities and characteristics of the individual process wastes for the industry are not available. Their nature is highly variable due to the variety of housekeeping practices provided in each plant. In many cases, process wastes are segregated, recycled or treated, and discharged to rivers or sewers. Typical treatment processes include oil/water separation, lagooning, aeration, filtration and carbon adsorption, and incineration (5).

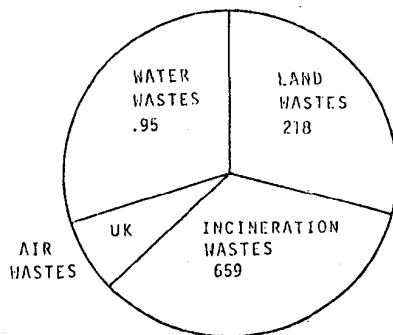
Typical flow rates and PCB concentrations from capacitor plants are given in Table 5 (3). Figure 13 shows the distribution of wastes in the environment for 1974 (5).

Table 5
Range of Flow Rates & PCB Concentration in Effluents
From Capacitor Manufacturing Plants

Plant No.	Outfalls	Effluent	Effluent PCB Content		Disposition of effluent
		Flow rate gal/day	lbs/day avg/mo	lbs/day avg/mo	
100	001	800,000	17/55	0.1134/0.1670	River
101	None	9,000	161/161	0.0121/0.0121	Sewer
102	001	807,000	9	0.0605	River
	002	165,000	3.2	0.0044	River
	003	36,000	3.4	0.0010	River
104	Major outfall	1,060,000	21	0.1856	River
	Cooling water & roof drains	100,000	7.8	0.0065	River
	Lab & roof drains	32,000	4.4	0.0011	River
	Compressor cooling water	72,000	3.7	0.0022	River
	Paint strip rinse	50	4800	0.0002	River
105	Major outfall	650,000	370	2.0958	River
	Freon spray paint leakage	1,500 ¹	13,300	0.1664	River
106	None	336,500	26.6	0.075	Sewer
107	None	150,000	1900/4000	2.3769/5.7546	Sewers
108 ²	Cooling water & boiler blowdown	48,000	45/108	0.0180/0.0432	River
	Cooling water	125,000 ²	338/705	0.3636/0.7585	Sewer
	Roof runoff	2,900	1360/2370	0.3290/0.0573	River
	Storm runoff	unknown	3/11	-	River
109	001	100,000	57/63	0.0475/0.0692	River
110	None	2,570	821	0.0176	Sewer
111 ³	None	18,000	8.7	0.0013	Sewer
112 ³	None	10,224	130	0.0110	Sewer
113	001	12,000	14.3	0.0014	River
126	None	500	6200 ³	0.03	Sewer

Notes: (1) Discharged once every 4-5 weeks.
 (2) Contains 10,000 gal sanitary sewage and 8000 gal of surface water infiltration.
 (3) These facilities recycle most of the non-contact cooling water used at the plant. These effluents consist of a small fraction of the cooling water plus their sanitary discharge.

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Figure13. Distribution of Wastes in Environment
for Capacitor Industry in 1974 in kkg

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Transformer Industry

In the transformer industry, PCBs are used in the manufacture of new transformers and in the repair of old transformers. Flow diagrams for the manufacture of transformers are shown in Figures 14, 15, and 16 (3). Only 5% of the transformers manufacture in the U.S. contain PCBs (7). Typical manufacturing operations include a predrying step for removal of moisture from the transformer interiors, several stages of askarel filling and topping, addition of electrical connections and bushings, electrical testing and sealing.

Water is not an essential component of the transformer manufacturing process (3). It is primarily used for non-contact cooling purposes. PCBs, consequently, reach water streams by occasional losses during handling and residuals accumulated around drainage systems from past operations where no precautions were taken in the handling and disposal of PCBs (3).

Wastewater sources include waste askarel collected in sumps or pans at filling stations, contaminated vacuum pump seal oil and contaminated kerosene like petroleum distillate (3). Solid wastes include rags and floor dry used for cleaning purposes and spent clay from Aroclor filtration operations (3).

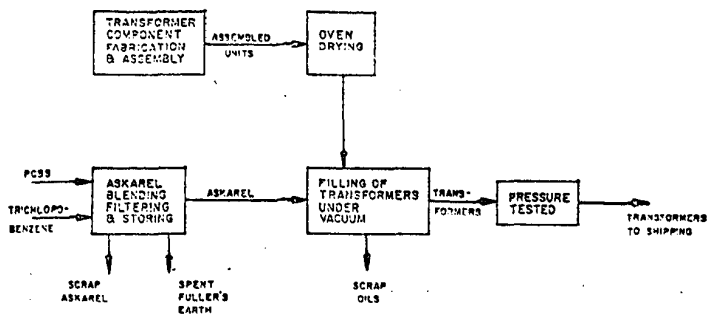


Figure 14. Transformer Filling Operation With Oven Predrying of Assembled Hardware

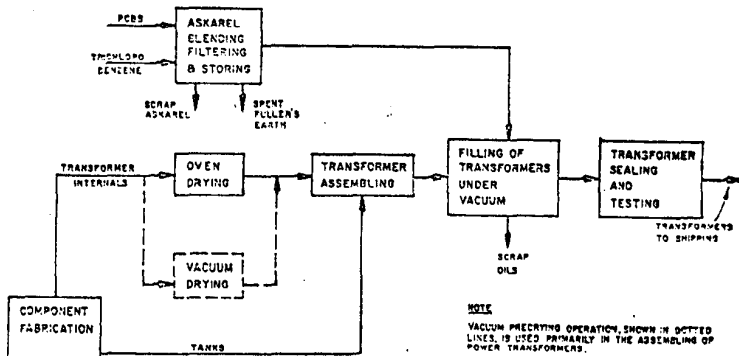


Figure 15. Transformer Filling With Oven or Vacuum Chamber Predrying
of Transformer Internals

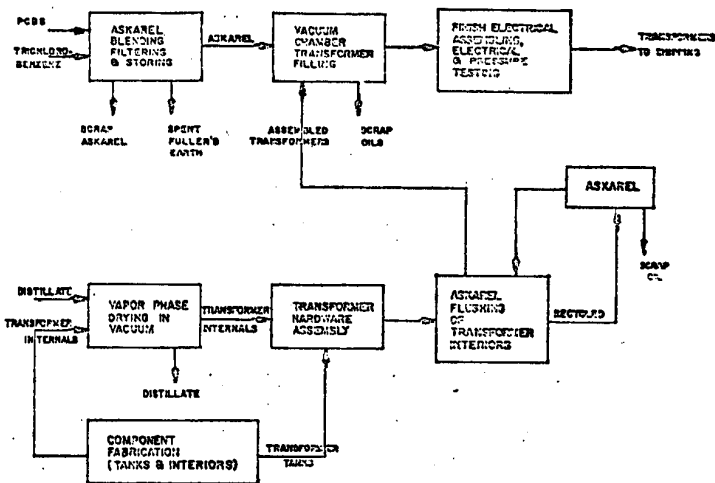


Figure 16. Transformer Filling With Vapor Phase Predrying of Interiors.

One plant does have a PCB related process where water is used in the waste incineration system for quenching hot gases.

No wastewater treatment methods are used in the transformer industry for the removal of PCBs.

Most plants report that their water usage is minimal (3). Data from a few plants is given in Table 6 (3). Figure 17 shows the distribution of wastes in the environment (5).

In the repair of transformers, sources of wastewater include accidental spills, junked transformers, cleaning drums used to transport PCBs, and scrap PCBs disposed of in landfill. It was estimated that the repair industry used 7% of the total usage of PCBs by the transformer manufacturing industry in 1974 (5).

Processes used in maintaining and repairing transformers are shown in Figures 18 and 19 (5).

Investment Casting Industry

The sole supplier of PCB blended waxes is Yates Manufacturing Co. in Chicago, Illinois. PCBs are imported by this company in the form decachlorobiphenyl (deka) at the rate of 136 - 227 Kkg/year (6).

A typical manufacturing process used by this industry is shown in Figure 20 (5). Waste streams are shown in Figure 21 (5).

In the manufacturing process, a wax pattern is made and a ceramic mold is formed on the wax. The wax is melted out, and the mold, after baking in a furnace is ready for use. PCB loss to the atmosphere could be significant during the melting out process and in the furnace.

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Table 6

PCB Concentration in Effluents from Transformer
Manufacturing Plants

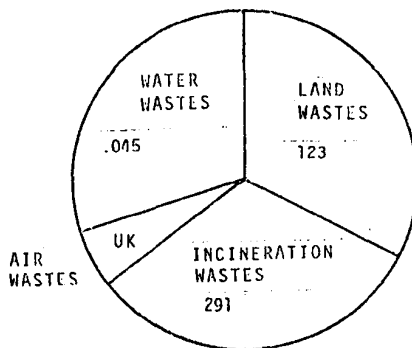
Plant No.	Effluent Flow Rate Gal./Day	Effluent PCB Content		Disposition of Effluent
		ppb Avg./Max	Lb./Day Avg./Max	
103 ⁽¹⁾	1,310,000	4.9/120	0.0535/1.311	River
	550,000	7/75	0.0321/0.344	River
114	50,000	Unknown	Unknown	Sewer
	2,000 ⁽²⁾	Unknown	Unknown	River
115	36,000	<1/2	<0.0003/0.0006	River
	24,000	2/113	0.0004/0.0226	River
	156,000	<1/3	0.0013/0.0039	River
116 ⁽³⁾	257,000	(#1) 3.4/11	0.0071/0.0231	River
	378,720	(#2) 2.1/3.0	0.0066/0.0120	River
	504,000	(#3) 8/19.1	0.0336/0.0603	River
117	13,500	28.6/unknown	0.0032/unknown	Sewer

Notes: (1) This plant has other discharges out of their properties. Discharges listed above are those associated with PCB related operations.

(2) Estimated.

(3) Discharges designated as #1, #2, and #3 are the combined effluents from their power house, and one each from their two manufacturing areas, respectively. According to the plants' Corps of Engineers permit application form, filed in July 1971, this plant has 13 outfalls.

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Figure 17. Distribution of Wastes In the Environment
for Transformer Industry in 1974 in kkg

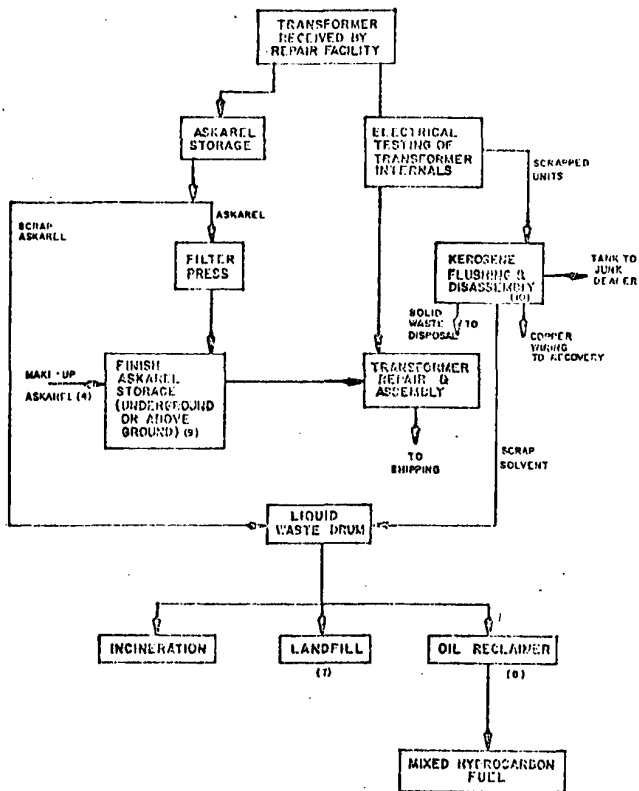


Figure 18. Transformer Repair

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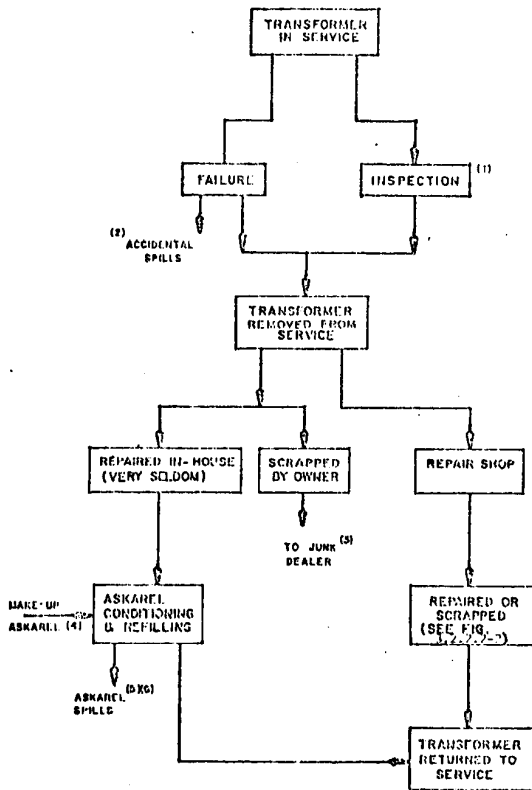


Figure 19. Transformer Maintenance & Servicing

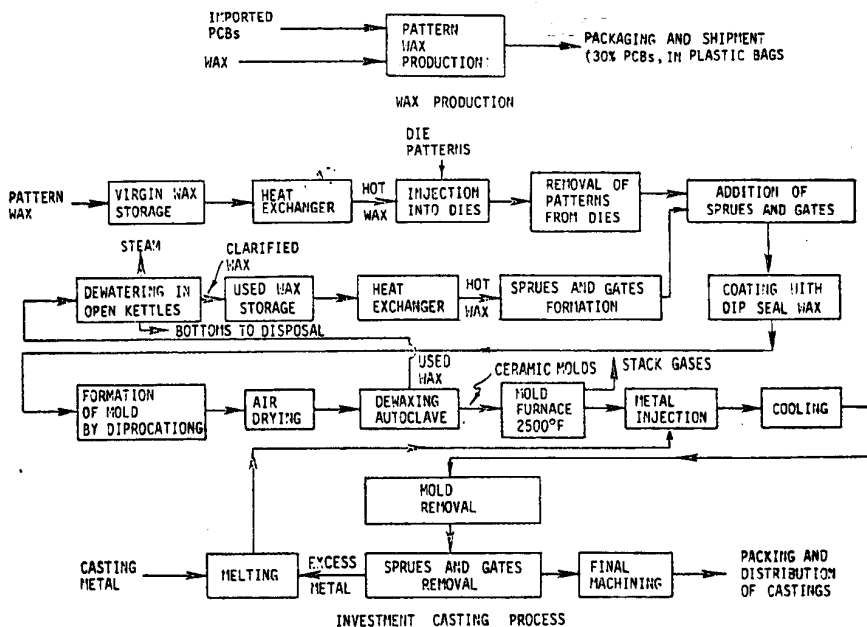


Figure 20. Flow Chart of PCB's Usage in Investment Casting

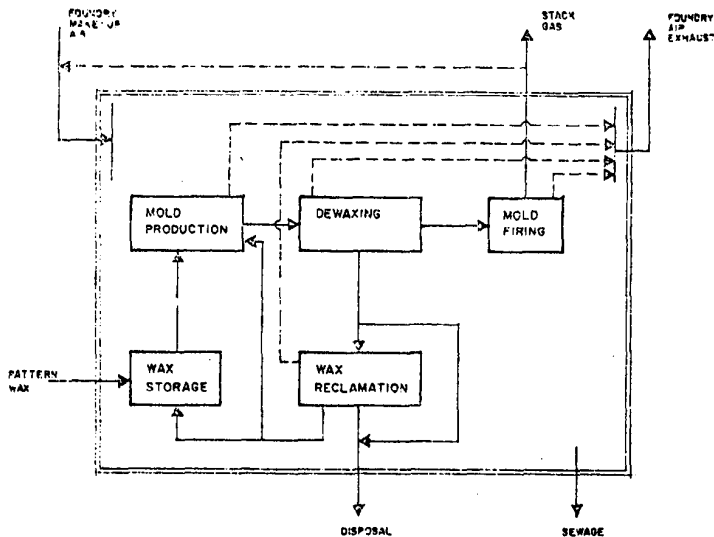


Figure 21. Idealized Flow Chart for an Investment Casting Foundry, Showing Waste Streams

Solid wastes include unreclaimed used wax, bottoms from reclamation, waste spills, and equipment cleanout. These wastes are sent to landfills and were estimated to be 182 Kkg in 1974 (5).

Process water does not appear to be used except possibly for cooling purposes.

Non-Industrial Waste Sources and Quantities

There are no natural sources of PCBs in the environment. Those PCBs found in the environment are a result of previous discharges of the material.

It is believed that much of the PCBs measured in streams and rivers are a result of fallout from the air (2).

Over the past few years studies have been done on various drainage basins in the U.S. Water data indicates PCB levels of .2-3.0, .1-.3, .1-1.6, and .1-.8 Ppm over the years 1971-1974 respectively (1). PCBs measured in bottom sediments over that period of time ranged from 1.2-64.5, 2-30, 5-50, and 2-160 mg/Kg respectively (1).

Inadvertent discharges of PCBs into the environment have been recognized from the following sources: paper recycling facilities where effluent recycle streams were contaminated with PCBs, effluents from plants which were engaged in the manufacture of machinery and mechanical products, chlorination of biphenyls in wastewater treatment plants, discharges from paper mills and aluminum foundries, and runoff from sewage sludges on the land.

It has been estimated that over the period 1930-1975, only 25,000 Kkg ($\pm$ 70%) or 4.4% of the total quantity of PCBs purchased have been destroyed (5). It is believed that 60% of the total purchase or 344,545 Kkg ($\pm$ 20%) are still in service and 250,000 Kkg ($\pm$ 40%) are currently in the environment (5).

References

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