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MANUFACTURING PROCESS - POLYCHLORINATED BIPHENYLS (PCBs)

Process Description

Monsanto, the sole domestic manufacturer of PCBs, manufactures this chemical in their Sauget, Illinois plant. The basic raw material is biphenyl which is manufactured from pure benzene in another Monsanto plant. The PCB manufacturing operation is conducted in two steps. First biphenyl is chlorinated with anhydrous chlorine in presence of ferric chloride to produce crude PCBs and then the crude PCBs are distilled to obtain the finished product. A schematic flow diagram of this process is given in Figure 1.

The reaction section consists of 6 reactors (3 batch and 3 cascade). Currently Monsanto manufactures four different types of Aroclors (1242, 1016, 1254 and 1221). For the manufacture of any given product, the chlorinator is charged with proper quantities of biphenyl and catalyst and heated beyond the melting point of biphenyl. The flow of vaporized chlorine is then started and the charge is circulated with a pump. Throughout the chlorination, the temperature is kept above the melting point of the mixture, but below 150°C to avoid excessive sublimation and plugging of the line discharging the hydrogen chloride produced by the chlorination. The reaction pressure is maintained near atmospheric. The degree of chlorination is principally determined by the time of contact of biphenyl with anhydrous chlorine. The contact time varies from 12 to 36 hours for the manufacture of different Aroclor types. The degree of chlorination is measured by the specific gravity of the mixture or the fall and ring softening point when the product is viscous.

The vapors from the chlorinator (HCl containing PCBs) are scrubbed with liquid Aroclor and the gaseous HCl is sent to another plant at the Sauget complex for purification. The crude product is held at an elevated temperature and blown with dry air for several hours, after which it is sent to the raw Aroclor storage tank where a few tenths of 1 percent of alkali is stirred with the material to react with any remaining hydrogen chloride or ferric chloride. The air from the blower tank is scrubbed with water and vented to the atmosphere through a demister.

The raw Aroclor is subsequently batch distilled under reduced pressure to remove the color, and the traces of hydrogen chloride and ferric chloride. The methods of purification are different for the different types of end products.

Figure 1A - Preparation of Crude Chlorinated Biphenyls
Monsanto Krummrich Plant

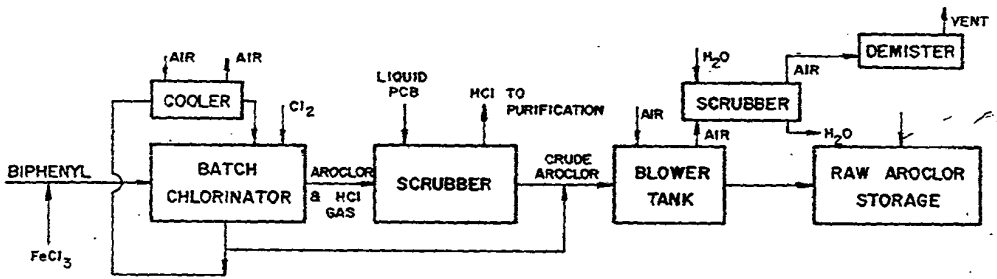
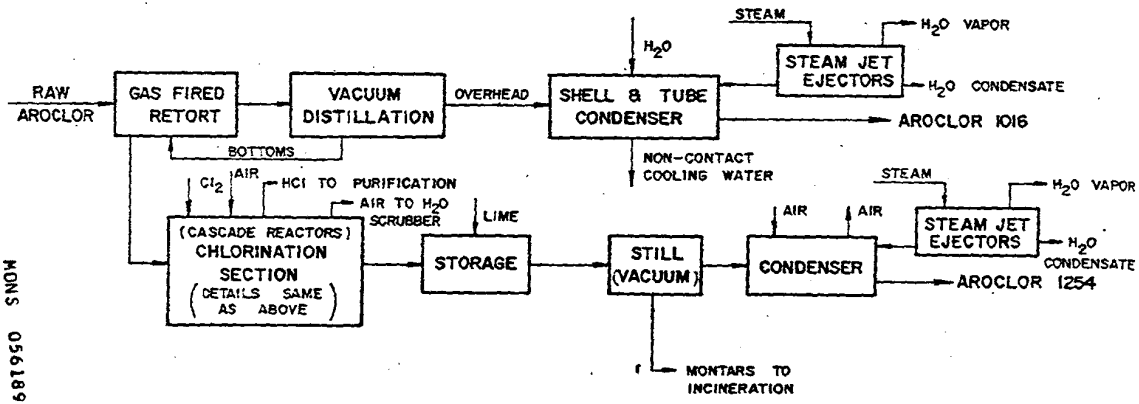


Figure 1B - Distillation of Crude Products
Monsanto Krummrich Plant



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Raw Aroclor 1254, 1242 and 1221, each are distilled in stills under reduced pressure, achieved via steam jet ejectors, the condensate from the still is the finished product while the bottoms are the Montars which are drummed and sent to incineration.

The distillation section for the 1016 product consists of a gas fired retort and a vacuum distillation tower. The latter is used to allow the separation of the higher chlorinated, less biodegradable compounds from the relatively lower chlorinated and more biodegradable ones. The raw Aroclor (42% chlorinated material) is fed into the reboiler. The vacuum in the tower is maintained at about 100 mm Hg via steam jet ejectors. The steam is partially condensed and the condensate is discharged into the plant discharge sump. The first cut from this tower is recycled back to the retort. At a preset overhead temperature the 1016 product is collected and sent to the product storage. The high boiling residue from the tower is sent to a subsequent chlorination cycle and the resulting raw Aroclor is distilled in a still. The overhead from this still is the finished product. The bottoms from this tower are the Montars, which are sent to incineration.

For special orders, in order to increase electrical resistivity, the Aroclors are stirred, at an elevated temperature, with a few tenths of 1% of well-dried fuller's earth and then filtered through paper.

All Aroclors are stored at 150°F. Steam coils are used on the storage tanks for heating these tanks.

Plant Water Usage

On the average, the PCB plant uses a maximum of 388,800 gallons of water and a maximum of 120,000 lbs of steam, daily. Water is used for non-contact cooling purposes in shell and tube condensers, in a water scrubber, for floor washings, for showers and in eye baths. Steam is used in the steam jet ejectors and for steam tracing purposes. The plant uses municipal water and purchased steam.

The process water from this facility consists of the liquor from their scrubber and the steam condensates which are discharged in one of the two sumps in the manufacturing area.

Additionally, 273,600 gallons of water is used in the incinerator, daily for quenching the hot gases from the fire box. The resulting weak muriatic acid in the quench pot is used in the venturi scrubber and in the packed tower.

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The type and quantities of water used and discharged at this plant are summarized below.

Water Balance

- Manufacturing Plant

	Quantities, GPD	
Process Water	Used	Discharged
in water scrubber	14,400	14,400
showers, eye bath	7,200	7,200
misc. floor wash downs	7,200	7,200
condensate from steam jet ejectors	--	14,400
Non contact cooling water	360,000	360,000
Condensate from steam tracers	--	28,800
Total	388,800	432,000

- Incinerator

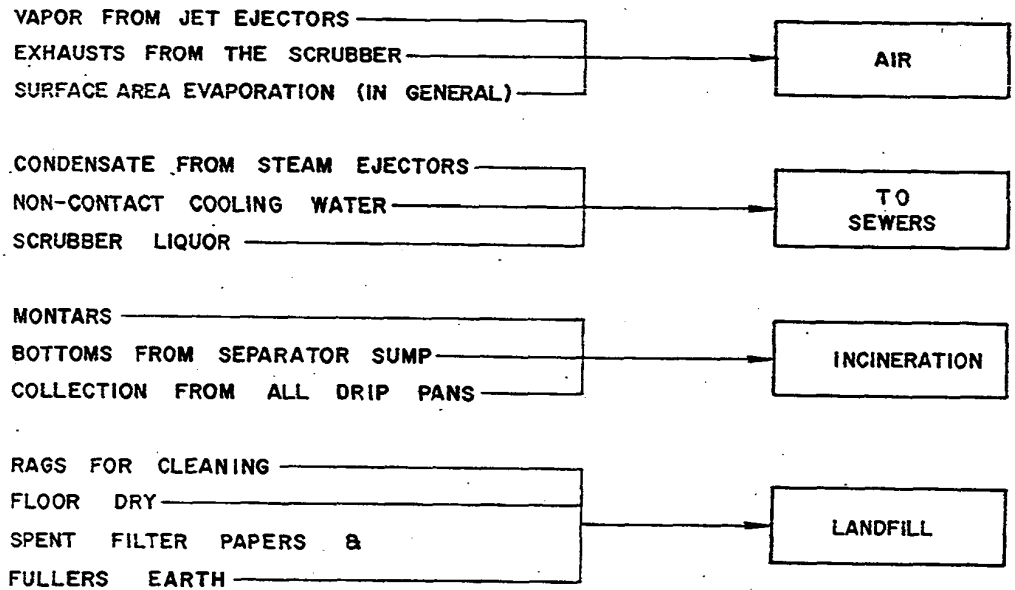
water used for hot gas quenching	273,600	273,600
water phase from the sump	--	14,400
Total	273,600	288,000

Raw Wastes

The raw wastes from the manufacturing area consist of the liquor from the scrubber, the condensate from the steam jet ejectors, water used for showers and eye baths, miscellaneous floor wash downs and waste oil collected in drip pans and drums. The composition and the quantities of the individual waste stream are not monitored. All waste streams generated in the manufacturing area are directed into the sumps in this area. The waste oil collected in the drip pans are emptied into 55 gallon drums and sent to incineration.

The raw wastes generated in the incinerator consist of the venturi scrubber liquor and the water phase from the separator sump in the incerator area. The composition of the combined stream is monitored. However, the composition of the individual stream is not known. Non-product PCB discharges are shown in Figure 3.

Figure 3 - Non-Product PCB Discharges at Monsanto's Krummrich Plant



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Waste Water Treatment and Housekeeping

Monsanto reports significant environmental controls at their Krummrich, Sauget plant. Since 1969, they have invested more than 22 man years of work and millions of dollars in this program. The in-house goals have reduced the PCB discharges into water and air to less than one pound per day, each.

A John Zink designed incinerator was erected at Sauget in 1970 to safely dispose of PCBs. A schematic flow diagram of this operation is given in Figure 2. Aroclor is steam atomized and fed into the fire box. Natural gas is used for combustion and the feed is incinerated at temperatures above 2200°F at 5% excess oxygen with a retention time of 2-3 seconds. The gases are quenched with water and the exhausts from the quench pot are passed through a high-energy venturi scrubber, then through a packed column which is irrigated by the weak muriatic acid originating from the quench pot. Exhausts are then vented to atmosphere through a demister. These exhausts as well as the effluent from the incinerator section are monitored.

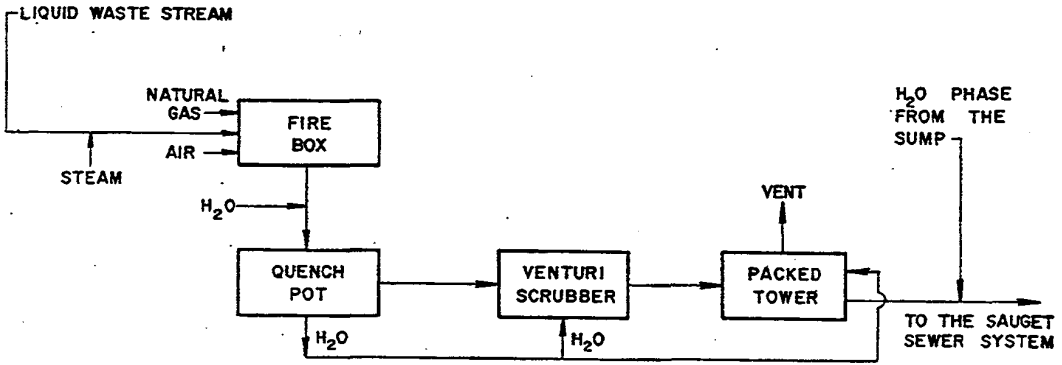
In the incineration area, drainage is directed to trenches and piping which flow into a 10,000 gallon underground concrete basin. The water layer from this basin is pumped continuously, combined with the scrubber liquor, metered, monitored and discharged into the sanitary sewers of the Sauget complex and from there it is sent to the East St. Louis municipal sewers. The organic phase from the sump is periodically pumped into waste storage tanks for incineration.

The incineration unit has a rated design capacity of 10 million pounds per year. However since the start of its operation this unit has achieved a service factor of about 0.6. Monsanto reports that this incinerator can achieve a maximum of 6 million pounds of capacity annually. This unit is plagued with various mechanical problems.

Monsanto uses their incinerator to process both their own wastes and as a service to other industries. The service charge for incineration is an average of 5¢ per lb of material.

The incinerator feed is brought into the plant either by truck, in 55 gallon sealed drums, by tank trucks or by rail. The drums are opened, picked-up by a fork lift and emptied into a concrete pit. The tank truck carrying the waste liquids enters the incinerator area and the liquid waste is then pumped from the truck into the pit. The material in this pit is periodically pumped via a vertical centrifugal pump in one of the four 20,000 gallon, each, incinerator waste feed tanks.

Figure 2 - Process Flow Diagram of the John Zink Incinerator at Monsanto's Krummrich Plant



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The rail truck is brought into a designated area close to the incinerator site. The material from the rail truck is normally pumped into a long term, 500,000 gallon storage tank. The material from this tank is pumped into the incinerator feed tanks located on the incinerator pad, when required.

Drainage is provided along the rail tracks. These drains empty into the 10,000 gallon sump located under the incinerator pad.

In the manufacturing area, Monsanto has taken a number of significant steps to prevent loss of PCBs to the environment. Drainage is directed to trenches and piping, and then to one of two concrete 3,000-gallon underground settling basins. This insures PCB containment in case of accidental spill or equipment failure. Relief valve lines and atmospheric vents are routed through catch tanks, or are redirected to settling basins.

When small quantities of PCBs are collected in the settling basins of the manufacturing area they are later pumped into 55 gallon drums, and eventually incinerated. The overflow from these sumps is combined with the non-contact cooling water used at the plant, monitored and then discharged into the Sauget complex's sanitary sewer and from there to the East St. Louis municipal system.

PCBs are packed and shipped in galvanized-steel 55 gallon drums, in tank cars or in rail cars. All rail cars are top loaded. In the drum filling area spills are cleaned via rags or floor dry and these materials are drummed and sent to landfill located in the town of Sauget.

In the PCB truck or rail car loading area drainage is directed into a small concrete pit. The material accumulated in this pit is periodically pumped into the basins located in the manufacturing area.

Nitrogen blanketing is provided on storage tanks to eliminate any "breathing" of the tanks and resultant PCB escape.

Mist eliminaters have been installed in vapor lines to eliminate the possibility of PCBs leaving the manufacturing area through these lines.

Finally, underground sewers have been replaced with above-ground sewers, and repaired or combined with others, so that the effluent from the department can be monitored. In addition, this step will prevent any unknown buildup of PCBs in the sewer systems or any contamination of PCBs into other sewers.

A high housekeeping level is maintained in the plant itself. Housekeeping responsibilities which the operators have assumed are as follows:

-- All pumps are checked for leakage on every shift. Drip pans that collect leaks are emptied into scrap PCB drums.
-- All leaks are reported and documented so that corrections can be made and settling basins observed.
-- "Floor Dry" is used to absorb any PCBs that have spilled or leaked. If it becomes necessary to flush PCBs to the settling basin, a minimum amount of water is used.
--Sampling drums and scrap PCB drums are quickly palletized, labeled and transferred to the incineration area.

Treatment Costs

The installed cost of the incinerator system is reported to be $950,000. The annual operation cost of this unit is $600,000 of which $200,000 is for maintenance. This unit employs a crew of five on a 24 hr operating day basis.

Plant Effluents

This plant has no point source discharge from their operation. There is a single discharge from the manufacturing operation (the combined stream of process and non-contact cooling water) to the main sewer system of the Sauget complex and their is a second discharge from the incinerator area to the same sewer system. The composition of these streams as reported by Monsanto are as follows:

	Effluent from the Manufacturing Operation	Effluent from the Incineration area
flow rate, gpd	432,000	288,000
pH		
Alkalinity, mg/l		
BOD, 5-day, mg/l		
Chemical oxygen, mg/l		
TS, mg/l		
TDS, mg/l		
TSS, mg/l		
TVS, mg/l		
Ammonia, mg/l		

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(AN)
Kjeldahl Nitrogen, mg/l
Nitrate AsN, mg/l
Phosphorus Total, mg/l
Color (As P)
Turbidity, mg/l
Total hardness, mg/l
Organic Nitrogen, mg/l
Sulfate, mg/l
Sulfide, mg/l
Chloride, mg/l
Cyanide, µg/l
Fluoride, mg/l
Aluminum - total, µg/l
Boron - total, µg/l
Calcium - total, mg/l
Chromium - total, µg/l
Cobalt, total, µg/l
Copper - total, µg/l
Iron - total, µg/l
Lead - total, µg/l
Magnesium - total, µg/l
Manganese - total, µg/l
Mercury - total, µg/l
Molybdenum - total, µg/l
Nickel - total, µg/l
Potassium - total, mg/l
Silver - total, µg/l
Sodium - total, mg/l
Tin - total, µg/l
Titanium - total, µg/l
Zinc - total, µg/l
Oil & Grease, mg/l
Phenols, µg/l
Surfactants, mg/l
Chlorinated hydrocarbons, mg/l
(except pesticides)
PCBs, µg/liter

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Treatment Facility for the Sauget Complex

Monsanto is in the process of building a solids removal, primary treatment plant for the treatment of the sewer effluent at the Sauget complex. This plant is due to completion in 1976. A secondary treatment plant for this effluent, which will consist of a neutralization operation, is in the planning stage at the present time. This latter project is due for completion in 1978.

Additionally, a regional biological treatment plant is also in the planning and negotiation stage. The completion date of this project is not known. However, Monsanto will have access to this treatment facility and will utilize this plant as a tertiary treatment stage for the sewer discharge from the Sauget complex.

from Leroy given directly to Contos.

.175 ppm process.

.15 ppm incinerator