



AN INDIRECT AROCLOR HEATER for UNIT CHEMICAL OPERATIONS

Monsanto Technical Bulletin No. O-130

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Monsanto Chemical Company, Organic Chemicals Division, St. Louis 1, Mo.

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*Aroclor** 1248 (chlorinated biphenyl) is an ideal nonflammable liquid phase heat-transfer medium for temperatures up to 600° F.

This bulletin contains a magazine reprint which describes the physical properties of *Aroclor* 1248 and illustrates the design and operation of heaters that have been used successfully by Monsanto plants for many years. The units described are gas fired and the capacities are in the range of 200,000 to 400,000 B.t.u. per hour.

Larger commercial installations using *Aroclor* 1248 have capacities ranging up to 2,000,000 B.t.u. per hour. Also small electrically heated stationary and portable units with capacities around 40,000 B.t.u. per hour are in service.

Although the magazine reprint contained first appeared in 1949, the basic information is still valid. Since that time Monsanto has developed a considerable amount of engineering data on heat transfer applications of *Aroclor* 1248. Those interested in such information are invited to correspond with the Organic Chemicals Division of Monsanto.

Monsanto does not manufacture heat-transfer equipment using *Aroclor* fluids. It supplies only the *Aroclor* 1248 needed. Several leading manufacturers of heating equipment are in a position to build or offer *Aroclor* heating units to meet specific requirements.

*Reg. U.S. Pat. Off.

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An Indirect Aroclor Heater for Unit Chemical Operations

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The characteristics of Aroclor 1248 indicate that it is an ideal liquid phase heat-exchange medium for temperatures up to 300° C. This article discusses its properties and illustrates the design and operation of heaters that have been used successfully by Monsanto plants during the past seven years.

IN CERTAIN manufacturing processes of the Monsanto Chemical Company, it was necessary to employ a noncombustible heat-transfer medium at pressures of 30 pounds per square inch or less and temperatures up to 300° C. The following general properties of a heat-exchange medium were required:

- Freedom from fire hazards.
- Viscosities to permit pumping at room temperatures.
- Boiling point sufficiently above 300° C. to assure a liquid condition at all times.
- Stability against heat, with enough safety factor to accommodate accidental overheating.
- Controllable vaporization losses.
- Freedom from corrosive action against valves, piping, tank jackets, etc., made of cast iron and steels, bronze, and stainless steel.
- Freedom from toxicity hazard.

Aroclor, chlorinated biphenyl (registered in U. S. Patent Office), was selected. The pertinent physical characteristics relative to its use as a heat-transfer medium are given in Table I.

FREEDOM FROM FIRE HAZARDS

FLASH POINT. Limitations of this test for the prediction of the fire hazard of relatively nonvolatile organic fluids have been recognized by the American Society for Testing Materials committee (3, 4).

FIRE POINT is a more significant measurement. The Underwriters' Laboratories (10) state that fire tests more truly reflect the (lack of) fire hazard of Aroclor.

SPONTANEOUS IGNITION TEMPERATURE. The combustion-resisting qualities of Aroclor 1248 are indicated by its high spontaneous ignition temperature of 704° C. (1299° F.) determined by Sullivan, Wolfe, and Zisman (9), using the convenient apparatus described by Sortman, Beatty, and Heron (8).

Under conditions of industrial use the spontaneous ignition temperature will be determined by factors including the nature of the hot surface, the amount of liquid impinging on it, the volume of enclosed space, and the ventilation.

An accidental failure in a heating system demonstrated the nonflammability of Aroclor 1248 and its freedom from the hazard of fire propagation. An operator's failure to start the circulation of the heat-transfer medium when the gas heater was on resulted in excessive coil temperatures and caused the lower coil to soften and sag into the fire chamber. A weld ruptured and Aroclor 1248 poured into the red-hot fire chamber in contact with the flame. Dense smoke arose from the heater but there was no external fire. After the gas flame was cut off, the smoking stopped.

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SPRAY FLAMMABILITY. When a tube ruptures in a liquid heat-transfer system under high pressure, a spray or mist forms. The possible fire hazard under these conditions requires considerations not covered by the foregoing discussions relative to the material in the liquid form. In their comprehensive study of flammability of the higher boiling liquids and their mists, Sullivan, Wolfe, and Zisman (9) determined the spray flammability limit of numerous materials in accordance with the percentage of oxygen required for combustion. This value was then correlated with the results of incendiary firing tests of the fluids conducted at the Naval Proving Ground, Dahlgren, Va. The oxygen requirement for Aroclor 1248 combustion in the spray flammability limit studies was found to be 64%. Fluids requiring over 45 to 50% oxygen in the spray test failed to cause a fire in the incendiary test. These results establish the nonflammable and noncombustible qualities of Aroclor 1248.

VISCOSITY CONSIDERATIONS

COLD FLOW. For most inside installations centrifugal pumps will handle Aroclor at reduced rates without preheating. Experience confirms this. Outside installations have been started at 0° C. by heating the pump and feed line until circulation through

TABLE I. PHYSICAL PROPERTIES OF AROCLOR 1248

Appearance	Practically colorless mobile liquid	
	° C.	(° F.)
Absolute density, g./ml.	1.44	30 (86)
	1.41	60 (140)
	1.37	100 (212)
	1.27	200 (392)
	1.17	300 (572)
Absolute viscosity, centipoises	112	30 (86)
	17.5	60 (140)
	4.2	100 (212)
	0.99	200 (392)
	0.47	300 (572)
Thermal conductivity, B.t.u./hour/sq. foot/° F./foot.	0.0613	30 (86)
	0.0698	60 (140)
	0.0800	100 (212)
Distillation range, A.S.T.M. D-20, ° C.	340-375	
Flash point, Cleveland open cup, A.S.T.M. D 92-45, ° C.	193-196	
Fire point, Cleveland open cup, A.S.T.M. D 92-45	None	
Pour point, A.S.T.M. D-7, ° C.	-7	
Coefficient of expansion, ml./ml./° C. (25-65° C.)	0.000702	
Specific volume, ml./g.	0.696	30 (86)
	0.709	60 (140)
	0.728	100 (212)
	0.787	200 (392)
	0.860	300 (572)
Specific heat, cal./g./° C.	0.283	50 (122)
	0.297	100 (212)
	0.326	200 (392)
	0.355	300 (572)
Vapor pressure, mm. Hg	0.00037	37.8 (100)
	0.16	100 (212)
	2.9	150 (302)
	18.0	200 (392)
	360.0	300 (572)

TABLE II. STABILITY OF AROCLOR 1248 HEATED FOR 30 HOURS

Temperature, ° C.	Mg. of HCl per Gram of Aroclor
280	0.079
300	0.186
310	0.199
320	0.222
330	0.248

TABLE III. STABILITY OF AROCLOR 1248 CONTINUOUSLY HEATED AT 280° AND 330° C.

Hours	Mg. of HCl per Gram of Aroclor	
	280° C.	330° C.
30	0.079	0.248
60	0.116	0.510
90	0.169	0.923
120	0.194	1.141
150	0.261	1.362

TABLE IV. GAS ANALYSIS OF AROCLOR 1248 HEATED 4 HOURS AT 260° C. AND 210 POUNDS PER SQUARE INCH PRESSURE

Gas	%
Carbon dioxide	None
Carbon monoxide	None
Oxygen (derived from air)	20.2
Methane	0.2
Hydrogen chloride	None
Chlorine	None
Acidity (% by weight HCl)	
Prior to exposure	0.0075
After exposure	0.0075

the heater had been effected so that the system could operate normally.

BOILING POINT

Operating experience has shown that the boiling point of Aroclor 1248 (340° C. at 760 mm.) is enough above the 300° C. operating limit to prevent trouble from this cause. At the maximum operating temperature the vapor pressure is less than 0.5 atmosphere.

HEAT STABILITY

In order to establish a maximum practical operating temperature, the stability of the material when heated to elevated temperatures in the presence of iron was noted. A slow stream of nitrogen was passed over the hot Aroclor to sweep the decomposition products into a caustic trap. The amount of acidic material was determined and calculated as hydrochloric acid. The results given in Table II indicate the stability of Aroclor 1248 when individual samples were heated for 30 hours at the given temperatures. The decomposition is very low at temperatures up to 300° C.

The stability of Aroclor 1248 in contact with iron continuously heated at 280° and 330° C. is indicated by Table III. These test results indicate that Aroclor 1248 in contact with iron can be used satisfactorily at temperatures up to 300° C.

The National Board of Fire Underwriters (10) reported that "decomposition of the product [Aroclor 1248] was not appreciable at temperatures below 400° C., but became increasingly apparent at higher temperatures."

Their workers analyzed the decomposition products of Aroclor 1248 heated in the presence of hot iron at 459° C. and also heated in an iron cylinder

at 340° C. fitted with an internal gas burner so that the gas flame impinged directly on the surface of the Aroclor. Analysis of the gases produced under these conditions included 0.6% carbon monoxide, 0.17% oxygen (derived from the air), 0.99% hydrogen chloride, 2.1% combustible gas calculated as methane, 0.002% chlorine, and no phosgene.

The same workers studied the stability of Aroclor when heated for 4 hours in an iron pipe at 260° C. under an internal pressure of 210 pounds per square inch, resulting from the introduction of compressed air. Following this treatment and cooling, the gases removed from the system were analyzed. The acidity of the Aroclor was determined prior to and after exposure to these conditions.

The results given in Table IV reflect an extremely small amount of decomposition under conditions similar to those selected for the practical use of Aroclor 1248 as a heat-transfer medium.

In actual practice using the type of heating unit described below there has been no evidence of hydrochloric acid effect and no carbon deposits have been noted in the heater, pipes, or valves. The heaters have been operated successfully with combustion gases at approximately 600° C. in contact with the coils.

At one time, a spiral coil type of heater was built and through faulty design a burner tunnel was located 1.5 inches from the 2-inch steel pipe coil. The radiation from the white-hot refractory tunnel and the direct impingement of the flame on the pipe caused the pipe to glow a dark red for a space of about 2 inches. This unit was operated almost 3 months before a circulation stoppage occurred. When the line was opened lumps of carbon were found to have come loose and moved forward to lodge in the globe valves. The lumps measured about 1 × 2.5 cm. and one face was formed to fit the pipe curvature. No hydrochloric acid effect was noted and the system was put back into operation after the burner location was changed.

CONTROLLABLE VAPORIZATION LOSSES

The heating systems in which Aroclor 1248 is used are sealed except for the expansion tank, which has a loose cover or a vent pipe. Because this tank is separated from the stream by a substantial length of pipe, the temperature in the tank remains low.

In the light of the relatively low vapor pressure values for Aroclor 1248 (7), and as it is unlikely that the expansion tank will ever reach even the 1-mm. state (130° C.), there should not be a measurable loss of Aroclor from the system. Actual experience bears out this contention.

OTHER LOSSES. Although Aroclor darkens on use, its characteristics remain the same and replacement has not been found necessary after 7 years of continuous use. Accidental leaks or spills constitute the only observed losses.

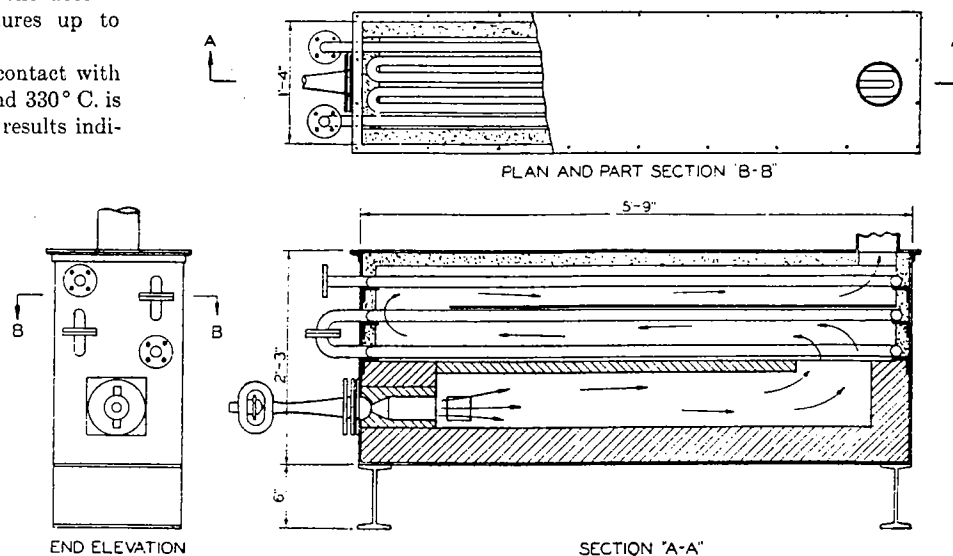


Figure 1. Heater

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TABLE V. RESISTANCE OF STRUCTURAL MATERIALS TO AROCLOR 1248

Metals	At 25° C.	At 125° C.	Metals	At 25° C.	At 125° C.
Aluminum	R	R	Zinc	RR	R
Copper	RR	D	Mild steel	RR	R
Magnesium	RR	R	Phosphor bronze	R	D
Nickel	RR	R	Red brass	D	RR
Silver	R	R	Stainless steel	RR	RR
Tin	R	R	Yellow brass	R	Re

RR. Excellent resistance, less than 1.0×10^{-4} cm. per day penetration or 0.00014 inch per year.

R. Good resistance, penetration between 1.0×10^{-4} and 10×10^{-4} cm. per day or between 0.00014 and 0.0014 inch per year.

D. Doubtful resistance, penetration between 10×10^{-4} cm. per day and 100×10^{-4} cm. per day or between 0.0014 and 0.014 inch per year.

e. Following letter indicating resistance, signifies material may be better than indicated if totally immersed, as weight loss is believed to come from oxidation of part of test strip exposed to air.

FREEDOM FROM CORROSIVE ACTION

The resistance of various metals (7) at 25° and 125° C. is given in Table V.

Similar studies made at 325° C. (6) indicate that the penetration, in inches per year, for mild steel is 0.0028; for yellow brass, 0.00047; for copper, 0.00145.

Many years of practical operating experience with Aroclor 1248 as a heat-transfer medium have shown that the material is practically noncorrosive to valves, piping, tank jackets, etc., made of cast iron and steels, bronze, and stainless steel.

FREEDOM FROM TOXICITY HAZARD

Aroclor 1248 is a very stable, unreactive liquid. If the material is spilled on the skin, there are no noticeable ill effects; however, it is well to wash the skin with soap and water after contact.

A skin burn resulting from accidental contact with hot Aroclor should be treated in the normal procedure used for hot oil burns. Aroclor adhering to the burned area need not be removed immediately unless treatment of the burn demands it; in this case soap and water or repeated washings with a vegetable oil (linseed oil) should be used.

The vapors emitted by Aroclor 1248 heated to elevated temperatures are injurious to the liver on prolonged exposure and should not be breathed. Drinker (5) indicated that 0.5 mg. of Aroclor 1248 per cubic meter of air is the maximum safe amount permissible in workrooms.

In commercial heat-transfer installations, the presumption is that the Aroclor is in a closed system free from leaks. Accordingly, there should be no opportunity for workers to come in contact with vapors from the hot heat-transfer medium.

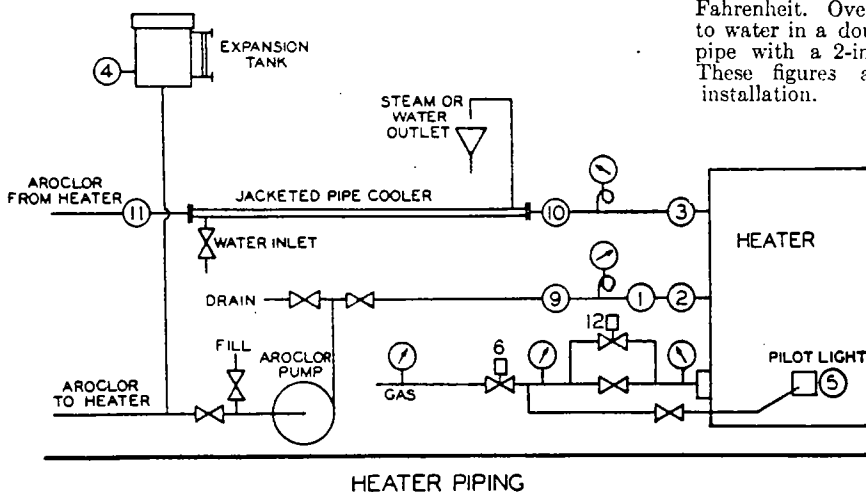


Figure 2. Cooler, Pump, and Expansion Tank

DESIGN AND CONSTRUCTION

HEATING SYSTEM. The heating system required to utilize Aroclor 1248 as the exchange medium includes a heater (Figure 1), cooler, pump, and expansion tank (Figure 2), and control and safety circuits (Figure 3).

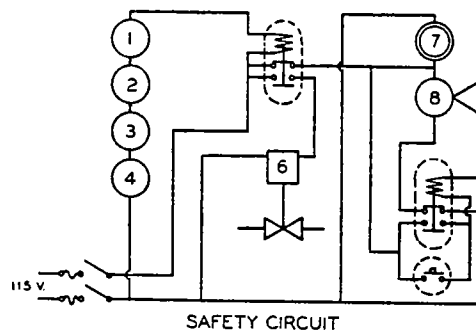


Figure 3. Control and Safety Circuit

HEATER DESIGN. The general requirements of the heater are compactness, ease of construction and service, and avoidance of direct flame impingement on the tubes.

Direct flame impingement is prevented by directing the gas flame through an enclosed channel with half-thickness fire brick protecting the tubes above until the high temperature of the flame is reduced by heat conducted through these bricks and radiated to the two bottom coils. The size of the heater is reduced to a minimum by using only 4.5 inches of insulating fire brick in the hottest areas and 2 inches of Eagle No. 66 insulation on the cooler spots.

Two sizes of units are used: One has a maximum capacity of 200,000 B.t.u. per hour, as shown in Figure 1. The larger has a range of 200,000 to 400,000 B.t.u.

The small size consists of 90 feet of 1-inch standard weight steel pipe made into three coils of six pipes each and connected in series. The larger size consists of 144 feet of 1.5-inch standard weight steel pipe arranged in the same fashion. Results of tests on the small-size heater covering temperatures from 150° to 300° C. show temperature rises to 10° to 20° C. in the Aroclor while circulating at a rate of 15 to 20 gallons per minute. The outlet gas temperature is consistently within 75° C. of the outlet Aroclor temperature. It is observed that the bottom two coils absorb the major part of the heat. The small unit indicates 50 to 60% efficiencies for capacities up to 200,000 B.t.u. per hour when a natural gas of 1000 B.t.u. per cubic foot is burned. A Surface Combustion Company high pressure inspirator and tunnel burner set is used in this installation.

Over-all heat-exchange coefficients (*U*) for the furnace are in the range of 7 to 10 B.t.u. per hour per square foot per degree Fahrenheit. Over-all heat-exchange coefficients for Aroclor 1248 to water in a double pipe heat-exchanger made from 1.25-inch pipe with a 2-inch pipe jacket are in the 120 to 180 range. These figures are calculated from test results on this installation.

COOLER. A very useful adjunct to the system is a double pipe cooler on the outlet of the heater shown in Figure 2. By turning water into the jacket, the Aroclor can be cooled and the temperature of the system lowered. This is helpful when it is necessary to cool a batch before removing it or when an exothermic reaction starts to get out of control.

PUMP. The pump for circulating the Aroclor 1248 may be any one of a number of standard centrifugal units designed for hot liquid service.

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TABLE VI. PIPING DETAIL

(Dimensions in inches)		
Pipe	1/4 through 1/2	Schedule 80, A.S.T.M. A53 or A106
Construction	1 through 6 1/4 through 1/2 1 through 6	Schedule 40, A.S.T.M. A53 or A106 Screwed Flanged Bend in shop and field where possible. Must be cleaned to remove scale
Ells, tees, and reducers	1/4 through 1/2	Forged steel screwed. Crane 300d series
Flanges	1 through 6	Welded fittings. Crane 300c Series 30 (to match valves)
Bolts	1 through 6	Machine bolts A.S.A. B-18.2 with hexagonal nuts for service below 500° F. Above use alloy steel. Crane triplex A.S.T.M. A96
Unions	1/4 through 1/2	Crane 252h forged steel
Dope		Crane 425 high temperature thread compound
Gaskets		Soft iron ring flat or corrugated
Shut-off valves	1/4 through 1/2 1 through 2 2 1/2 through 6	Crane 3606W, screwed, gate Crane 3615W, flange, gate Crane 33XR, flange, gate
Control valves	1/4 through 1/2 1 through 2 2 1/2 through 6	Crane 3640 XR, screwed, globe Crane 3656 XR, flange, globe Crane 151 XR, flange, globe
Check valves	1/4 through 1/2 1 through 2 2 through 6	Crane 3674 X, screwed Crane 3686 X, flanged Crane 159 X, flanged
Safety valves	3/4	Consolidated 1670 B.W. screwed
Relief valves	1 1/2 through 3	Consolidated 1612 W, flanged
Valve stem packing		Goetze 340D or Durametallic D-110
Gage and glass	1/4 gage	Type 100 PCPR Marsh O-100 lb./sq. inch gage siphon with Crane 222H bar stock valve. Jerguson Series R20 Reflex type liquid level gage
Strainers	1/2-3/4 1 through 3	821 Yarway threaded 822 Yarway flanged

The Dayton Dowd Type C pump is an example of the type required. It should be made of cast steel and have a water-cooled stuffing box and water-cooled bearings. The stuffing box should have room for at least six rings of packing and a lantern ring. Durametallic No. D-110 or Garlock No. 234 may be used for packing the pump. An open impeller is desirable, as it will handle the cool, more viscous liquid on starting the system better than will a closed impeller. Enough horsepower for the most viscous conditions is required.

PIPING SYSTEM AND EXPANSION TANK. The detail of the piping system for Aroclor 1248 used up to temperatures of 300° C. (572° F.) and 100 pounds per square inch pressure is given in Table VI. The valves and specialties given indicate the type required. All piping larger than 0.75 inch is flanged or welded; experience has shown that hot Aroclor penetrates screwed joints of the larger sizes. Steel and cast steel are used throughout.

The system requires an expansion tank located at the highest level of the installation. The size of this tank is normally about 25% of the capacity of the Aroclor system. Connections with valves, made on either side of the pump, enable the operator to connect a flexible hose and to pump in or out as required.

For operation in locations where the Aroclor temperature may drop to where the attendant viscosities may make pumping impractical in the system as designed, it may be desirable to steam-jacket the Aroclor circulating lines to facilitate rapid start-up. Suitable safety provisions, such as safety pop-off valves, must be installed in the steam jacket system to prevent pressure ruptures which would develop if any condensate remained in a closed system during high temperature operation.

In order to establish operating conditions and to check the operation of the heater itself, it is often desirable to measure the temperatures of the Aroclor in and out of the heater and cooler. Items 9, 10, and 11 (Figure 2) provide for this. They may be dial thermometers or mercury bulb thermometers of any commercially available type recommended for the service.

TABLE VII. SAFETY AND CONTROL EQUIPMENT

1. High pressure alarm (detects stoppage of pipe)	Mercoird DA-31, open circuit on high pressure. Actual settings depend on individual layout
2. Low pressure alarm (detects stoppage of pump)	Mercoird DA-31-3, open circuit on low pressure. Actual settings depend on individual layout
3. Thermostat (detects excessive heating hence obstruction of flow)	Fenwal 18002. Contacts open on temperature increase
4. Float switch (detects leakage from system)	Mercoird Figure 40. S.P. switch. Open at low level
5. Flame failure system (cuts off gas if pilot flame goes out)	Combustion Control Corp. Fireye FF6. Flame failure control for manual ignition gas burner systems
6. Gas valve (cuts off in case preceding devices act)	General Control Corp. K-10-2. Closes with current off
7. Red light (alarm)	Killark VA-1 60 W, or Benjamin 7013-V
8. Horn (sounds alarm)	Edwards 312
Alarm relay	Type C-1104 1-NO, 1-NC watertight (1)
Stop horn relay	Type C-1104 1-NO, 1-NC, watertight (1)
Stop horn button	1-HA-4 (2)
9. Thermometer well (visual check of heater performance)	0-350° C. mercury bulb thermometer
10. Thermometer well (visual check of heater performance)	0-360° C. mercury bulb thermometer
11. Thermometer well (visual check of cooler performance)	0-360° C. mercury bulb thermometer
12. Solenoid valve	General Control K-10-2. Controls Aroclor temperature to meet demands of system

For automatic temperature control a solenoid valve, item 12, is indicated in a by-pass arrangement with a manually operated needle valve. The needle valve is adjusted to give almost enough heat to meet the requirements and the actual control is carried on by the solenoid valve, which opens and closes as directed by a temperature-control instrument connected to the equipment being heated.

One unit was set up with temperature control using a Leeds & Northrop Model S all-electric control with droop corrector. Very close control over a wide range of heat demand resulted, when a throttling range adjustment of 4 was used on this control device.

SAFETY CIRCUIT. Figure 3 shows a safety circuit which automatically protects the system by closing off the gas supply in the event of faulty operating conditions. Provision is made for shutting off the warning horn while the system is being put back into operation after a safety shutdown.

A detailed list of the safety and control equipment is given in Table VII. The equipment named indicates the type required.

ACKNOWLEDGMENTS

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