ORGANIC CHEMICALS DIVISION RESEARCH Report

Report No. P-688 Job No. 2-02-750.01-3040

TENTATIVE PROCESS
FOR
CONTINUOUS CHLORINATION OF BIPHENYL

March 23, 1956 R. A. Simone

MONSANTO
ST. LOUIS, MO.

St. Louis Research Report No. P-688

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P. Anniston Plant
Tech. Dept.

SAFETY REVIEW COMMITTEE
APPROVED BY
APPROVED

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Monsanto Chemical Company
Organic Chemicals Division
St. Louis Research Department

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INTRODUCTION

The Anniston production group requested that the Research Department investigate the possibility of producing Aroclors (chlorinated biphenyl) by a continuous process in order to increase the production efficiency over the present batch operation. The advantages that should be realized by continuous manufacture are increased production, decreased labor costs, and product uniformity.

The object of the research laboratory work was to develop a continuous operation that would produce Aroclors favorable in quality to batch processed material. Satisfactory continuously produced Aroclor 1242 and 1254 have been demonstrated in the laboratory.

The process reported herein is for the continuous production of Aroclors 1142, 1148, 1154, and 1160 and is based on laboratory work.

SYNOPSIS OF PROCESS

Aroclors are manufactured continuously by a four stage chlorination of biphenyl in the presence of iron catalyst and at elevated temperatures. Biphenyl and chlorine gas are introduced into the first chlorinator at controlled rates. The overflow from the first stage chlorinator flows into the second stage reactor and is further chlorinated under controlled conditions and discharged into the third stage, etc. The process is controlled in such a manner that the overflow product from the fourth stage is of the required chlorination level for the crude Aroclor desired, as indicated by specific gravity measurement. The different Aroclors are made by varying the ratio of the chlorine to biphenyl and chlorinated biphenyl in the four stages.

The crude Aroclors are further processed to refined material in the same manner as in the present Aroclor manufacture. By-product HCl is absorbed in water for the production of muriatic acid.

BILL OF MATERIALS

The materials theoretically required for 100 pounds of various crude Aroclors are as follows:

Aroclor	Chlorine - Lbs.	Biphenyl - Lbs.
1142	84.9	58.7
1148	96.6	53.0
1154	109.7	46.7
1160	120.0	40.4

The raw materials used in the continuous chlorination are the same as in the present Aroclor batch process consisting of biphenyl,

chlorine, and iron turnings catalyst. The theoretical feeds for the continuous production of Aroclors 1142, 1148, 1154, and 1160 are given in Table I of the appendix of this report.

EQUIPMENT LIST

The continuous chlorination process makes use of the present chlorinators which are 3' I.D. x 16' vertical tanks equipped with cooling coils, chlorine distributors, circulating pumps, biphenyl inlets and off-gas lines. The following additions and modifications will be necessary for conversion to satisfactory continuous operation:

Biphenyl Feed Pump - This pump should be capable of accurately delivering molten biphenyl at rates from 1300 to 3400 pounds per hour against the hydrostatic head in the first stage chlorinator. Auxilliary equipment, such as a flow recorder and line thermocouple should be installed to assure accurate biphenyl feed. Lines to and from the pump must be steam traced or jacketed to avoid freezing.

Chlorinators - The first three chlorinators should be elevated to the proper levels to assure discharge by gravity of the overflow from one stage to the next. That is, the differential in adjacent reactor levels should be sufficient to overcome the hydrostatic pressure in the receiving reactor, which will contain material of a higher gravity. The gravity differential will be greatest in the manufacture of Aroclor 1160. If the proper elevation of the chlorinator is not feasible, transfer pumps will be necessary in the overflow lines. The overflow outlets should be set at the 700 gallon level of each chlorinator.

Cooling capacity must be sufficient to maintain desired temperature control.

Biphenyl should be introduced into the first chlorinator well below the surface in order to avoid short circuiting. The overflow line to the succeeding stages should likewise be extended to the lower region of reactors. The lower ends of these dip pipes should be perforated to aid in mixing with chlorinator material. Each overflow line should be equipped with a sampling cock.

Agitation is accomplished with the circulating pump presently installed. Each chlorinator should be equipped to allow conversion to batch operation with a minimum of effort.

Chlorine Feed Regulators - The chlorine feed to each stage should be accurately controlled as indicated by the specific gravities of the overflow streams. This will require the monitoring of each overflow stream with an automatic gravity recording and regulating device which is capable of proportional control of the chlorine valves. The controller should be so located as to keep lag at a minimum. In addition, the chlorine feed line of each stage should

Figure I - Flow Diagram
Four Stage Continuous Chlorination of Biphenyl

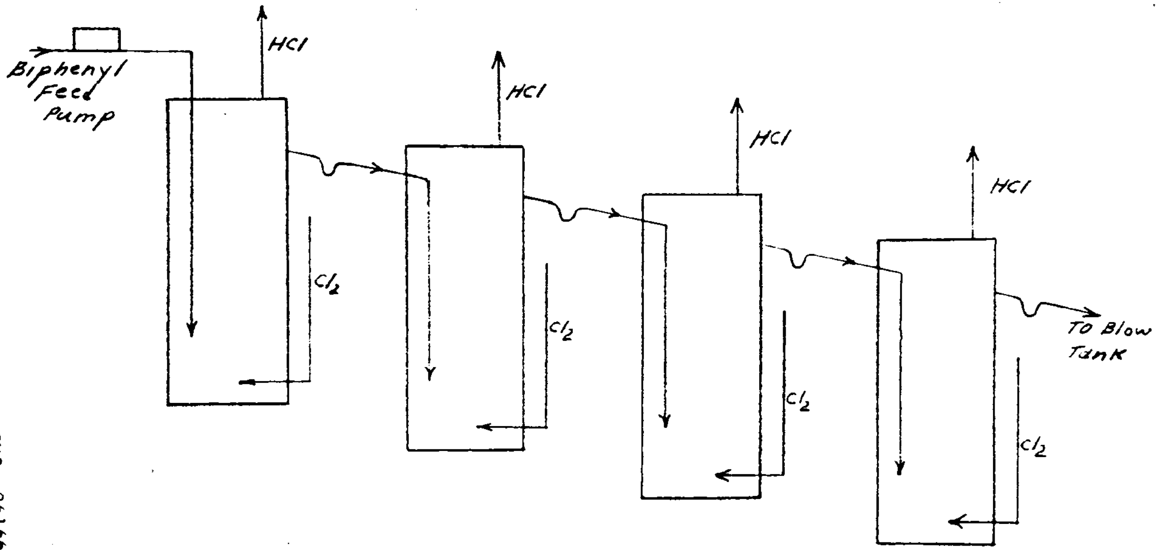
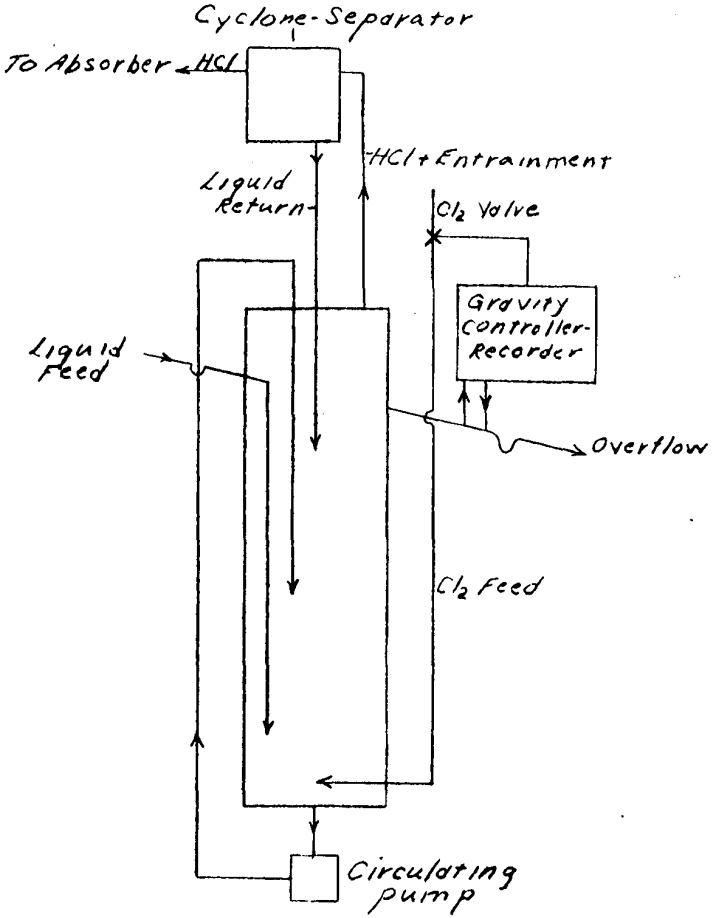


Figure II

Diagram of Continuous Chlorination Stage



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be equipped with a flowrator capable of measuring flows of 500 to 800 pounds per hour. The main chlorine line feeding all stages should be equipped with a pressure regulator.

Cyclone Separators - Each chlorinator should be equipped with a cyclone separator to remove sublimed or entrained material from the off-gas. The separated material is dropped back to the chlorinator, with the return line extending below the surface of the chlorinator liquid. The return line outside the chlorinator should be steam traced. A sampling outlet on the exit line to the absorber will be necessary to determine chlorine efficiency.

PROCESS IN DETAIL

Instrumentated Operation

The four chlorinators are charged with biphenyl, the amount depending on the Aroclor to be produced. Allowance should be made for the molar expansion of biphenyl upon batch chlorination in each reactor. The biphenyl in each stage is chlorinated batchwise to the desired level for the Aroclor to be produced as listed in Table I. When the proper gravity is obtained in each stage, the liquid surface should be at the overflow level. The gravity controls are then adjusted to the proper setting. The biphenyl delivery is set at the required feed for the corresponding Aroclor to be produced as listed in Table I. The continuous operation is then started by simultaneous feed of biphenyl and chlorine. The gravity of each overflow line should be determined periodically by hydrometer to check the operation of the gravity recorder-controllers. The temperature of each stage should be held uniformly.

Manual Operation

During the plant demonstration run, it is contemplated at present that the chlorination will not be fully instrumentated and chlorine flow will have to be manually controlled, based on flowrator readings. If the flowrators are calibrated against the hydrostatic pressure expected in each chlorinator, the process is started in the same manner as described under "Instrumentated Operation", with the gravity of the overflow streams being determined manually every half hour. The chlorine feeds are adjusted accordingly by operation of the chlorine valves. The maintainance of uniform reactor temperatures is important in order to avoid flowrator fluctuations due to the temperature-gravity relationship.

In case the flowrators cannot be accurately calibrated against the hydrostatic pressures expected in the chlorinators, the correct feed will have to be determined by trial and error. In order to avoid production of off-grade material due to poor control, the operation should be started stagewise. Biphenyl is charged to the first stage and chlorinated batchwise to the desired level. Continuous

operation is then started and the correct chlorine feed is determined as indicated by the proper uniform overflow gravity. The overflow is discharged into the second stage reactor until nearly overflowing. The flowrator reading is noted and the operation stopped. The second stage is then chlorinated batchwise to the desired gravity. Continuous operation is then resumed and the correct chlorine feed is determined for the second stage in the same manner. The procedure is repeated until all four stages are operating continuously at the desired chlorination levels. When the chlorine feeds are determined in this manner, the gravity of the overflow gravities should remain relatively constant, providing that reactor temperatures and chlorine pressure are uniform.

DISCUSSION OF IMPORTANT VARIABLES

The stagewise startup for manual operation is recommended in cases where chlorine feed cannot be accurately predetermined. If startup of all four stages were attempted without accurate knowledge of chlorine feed, control of the over-all operation would be extremely difficult and before the system could be brought into balance, considerable material of incorrect gravity overflowing from the fourth stage could be produced.

The suggested feeds listed in Table I are theoretical and assume 100% utilization of chlorine, biphenyl, and chlorinated biphenyl. Allowance for any entrainment losses and chlorine inefficiency will have to be made in practice.

The suggested feeds in Table I give four production rates for each Aroclor. Each rate results in a different sojourn which will influence the character of the final product. These differences may be minor but should be determined by infrared analysis when shifting from one rate to another. Two alternatives are given in Table I for production of Aroclor at the 2400 and 2800 pounds of chlorine per hour over-all rates. In one case the chlorine feed is distributed equally to each stage and in the other the feed is staggered, with the first two stages operating at below over-all average chlorine feeds. The latter alternative is suggested if sublimation and entrainment becomes a severe problem at high chlorination rates in the first and second stages.

When production demands require the manufacture of a different Aroclor than previously produced, two possible situations may arise. The required Aroclor may be of a higher or lower chlorination stage than the one previously manufactured. In case the required Aroclor is higher, the individual stages are chlorinated batchwise to the proper levels before continuous operation is started. An intermediate Aroclor will be discharged from the system during the batch chlorinations due to molar expansion. When a lower Aroclor is required, the fourth stage is pumped out and processed to finished goods. The first three stages are then pumped forward and adjusted batchwise to the correct gravity before continuous operation is resumed. If a shift

from Aroclor 1160 to 1142 or 1148 were required, the third stage would also have to be drained. An alternative when such a shift is necessary would be to chlorinate the third stage batchwise to Aroclor 1160 and drain the reactor. The overflow should be closed during the batch chlorination to avoid overflow due to molar expansion.

The product from the fourth stage should not be considered truly representative of a continuous operation until at least 3500 gallons have been discharged. The intermediate material will be partially composed of varying degrees of batch material.

MATERIAL SPECIFICATIONS, ANALYTICAL METHODS

The raw, crude and finished material specifications are the same as those given by present product specifications.

The analytical methods for finished Aroclors are the same presently used on present production. In addition, infrared spectra of 10% carbon disulfide solutions of finished Aroclors are to be run by the St. Louis Research Department during the initial continuous production of each product or whenever sojourn time for any Aroclor is initially changed.

TOXICITY AND HAZARDS

Chlorine - Chlorine is an extremely toxic gas. The allowable concentration for an eight hour day is reported to be from 0.35 to 2 parts per million. High concentrations causes pneumonitis and edema of the lungs. An exposure of 1000 ppm is rapidly fatal. However, sufficient warning of its presence is given since the gas is detectable by odor at a concentration of 3.5 ppm, and 15.1 ppm gives throat irritation. Respiratory equipment should be available to those working on chlorination equipment.

Reference: Sax, N. I., "Handbook of Dangerous Chemicals", Rheinhold Publishing Company, New York, 1951, p. 93.

Biphenyl - Large concentration of biphenyl vapors causes intoxication. Respiratory equipment should be worn when working in contact with its vapors. The material is flammable and should be kept away from areas of acute fire hazard.

Reference: Opus Cit., p. 151.

Chlorinated Biphenyl (Aroclors) - Aroclors can give rise to dermatitis when contacted with the skin. Inhalation of vapors is usually followed by systemic poisoning. The liver is affected by serious exposure to vapors. Toxicity increases with increasing degree of chlorination. The proper protective clothing should be worn when handling Aroclors. Respiratory equipment should be used when vapor contact is anticipated.

Reference: Opus Cit., p. 92

These materials have been handled for many years in Monsanto so no difficulty is expected in the operation of this process.

R. A. Simone

Approved: A. M. Ellenburg

dm
3-28-56

APPENDIX

(1) Physical Constants Sheet for Biphenyl.

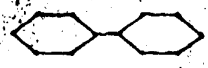
(2) Graph I - Percent Chlorine vs. Specific Gravity for Chlorinated Biphenyl.

(3) Table I - Suggested Feeds for the Continuous Chlorination of Biphenyl.

PHYSICAL CONSTANTS OF Biphenyl

COMPILED BY W. F. Metzner

DATE 2-12-43
Corrected 6-22-43
Corrected 1-11-44



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NAME		SOURCE	
Formula	$C_6H_5.C_6H_5$		
Appearance	Monoclinic	Chem. Rubber Handbook	19[illegible]
Molecular weight	154.20	" " "	
Boiling point at 760mm	255°C.	Int. Crit. Tables	1926
Boiling point at 104 mm	118	*Swann file #137	1932
Crystallizing point	69.0°C.	*Swann curves	1934
Melting point	69°C.	Int. Crit. Tables	1926
Solution point			
Specific gravity @ 77/4°C.	0.9896	Int. Crit. Tables	1926
Specific gravity @ 20/4°C.	1.041	" " "	"
Refractive index @ 77.1°C.	D = 1.58822	" " "	"
Viscosity @ 100°C.	28.8 Say. Sec.	*Swann File #137A	1930
Viscosity @ 70°C.	31.2 " "	" " "	"
Surface tension @ 129.2°C.	29.5 dyne/cm	Int. Crit. Tables	1926
Solubility in water @ 80°C.	Insoluble	Dow	19[illegible]
Solubility in [illegible] alc. @ 19.5°C.	9.98 g./100 g. solvent	Seidell	19[illegible]
Solubility in 100% Methanol @ 19.5°C.	6.57 g./100 g. solvent	Seidell	1941
Benzene @ 27.9°C.	137 g./100 g. solvent	Seidell	1941
Heptane @ 26.5°C.	25.1 g./100 g. solvent	Seidell	1941
Flash point °F (method)	235°F. - closed cup 255°F. - open cup	Ind. & Eng. Chem. 32,882	1940
Fire point °F	124°C.	Dow	1943
Heat of combustion Kg-cal(15)	per gm. mol = 1504.4	Int. Crit. Tables	1926
Latent heat of vap @ 69.2°C.	190.9 BTU per lb.	*Swann File #137A	1930
Specific heat @ 40°C.	1.61 joule/gm.	Int. Crit. Tables	1926
Critical temperature			
Critical pressure			
Pounds per gal. @ 77 °C	8.23 lbs. per gal.	Swann File #137A	1930
Latent heat of fusion	28.8 gm-cal per gm. (53.1 BTU/lb.)	Lange Handbook	1937
Toxicity (give reference) (1)	Dr. McLester, Anniston	Plant Report-	
	Copy in St. Louis physician's file		1937
(2)	Percy May-"Chemistry of Synthetic Drugs"		
	3rd Edition, p. 19.		

*NOTE: Files of W. F. Metzner

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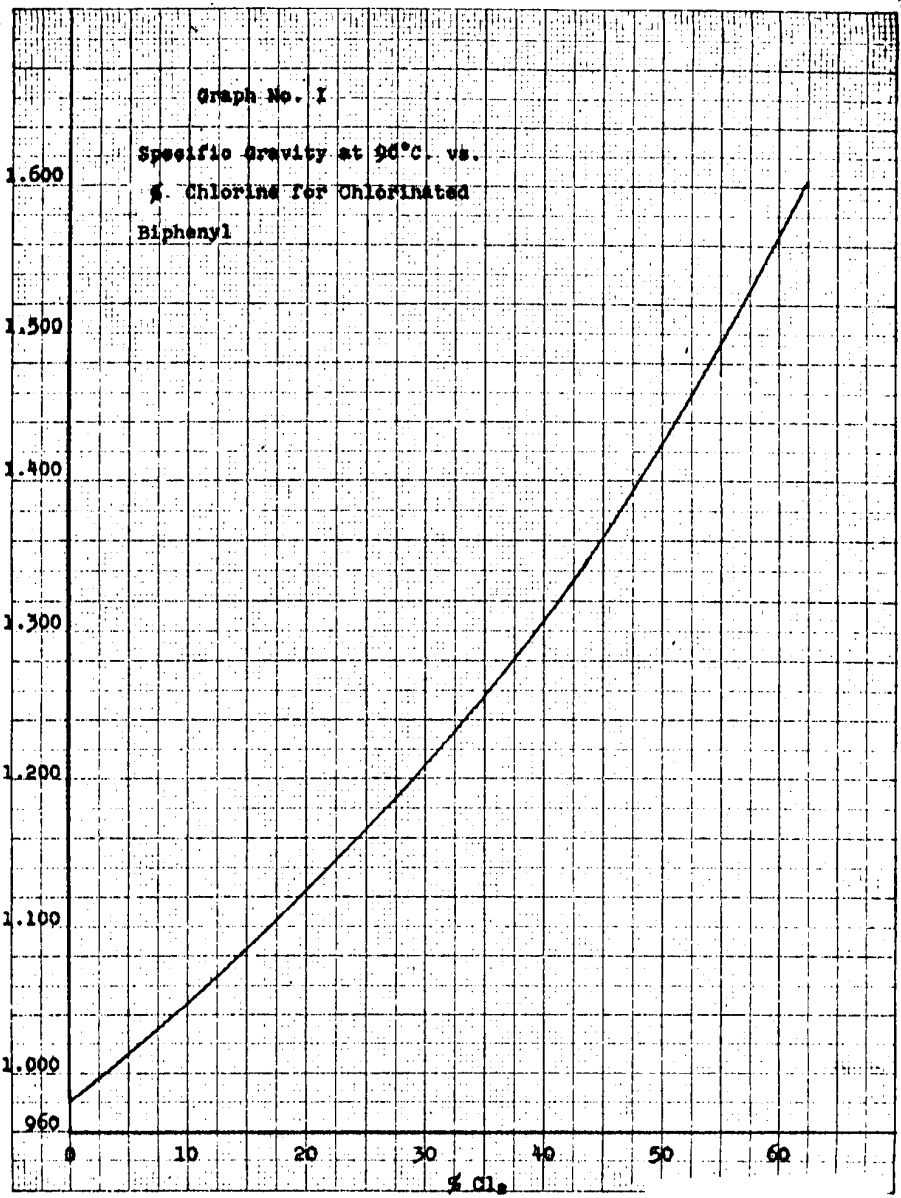
Graph No. I
Specific Gravity at 96°C. vs.
% Chlorine for Chlorinated
Biphenyl
1.600
1.500
1.400
1.300
1.200
1.100
1.000
960
0
10
20
30
40
50
60
% Cl₂

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TABLE I

Suggested Approximate Operating Conditions of 4 Stage Continuous - ~~100% Conversion~~ Chlorination of Aroclors - 700 Gal. Chlorinator Volume

Aroclor	Stage	Cl_2 Feed Lbs./Hr.	Liq. Feed Lbs./Hr.	Outage Lbs./Hr.	Sp. Gr. at 90°C.	Chlor. Temp. °C.	Sojourn Hrs.	Total Sojourn	% Cl_2
1142	1	500	1353	1593	1.092	110	3.9		15.65
	2	500	1593	1836	1.184	120	3.7		27.17
	3	500	1836	2079	1.268	130	3.4		36.00
	4	500	2079	2323	1.332	140	3.2	14.2	43.00
1142	1	600	1625	1917	1.092	110	3.3		15.65
	2	600	1917	2208	1.184	120	3.1		27.17
	3	600	2208	2500	1.268	130	2.8		36.00
	4	600	2500	2791	1.332	140	2.7	11.9	43.00
1142	1	400	1625	1819	1.054	110	3.3		10.99
	2	500	1819	2062	1.140	120	3.2		21.82
	3	700	2062	2402	1.236	130	2.9		33.30
	4	800	2402	2791	1.332	140	2.7	12.1	43.00
1142	1	700	1896	2236	1.092	110	2.8		15.65
	2	700	2236	2576	1.184	120	2.6		27.17
	3	700	2576	2916	1.268	130	2.4		36.00
	4	700	2916	3256	1.332	140	2.3	10.1	43.00
1142	1	500	1896	2139	1.056	110	2.8		11.69
	2	700	2139	2479	1.156	120	2.7		24.20
	3	800	2479	2868	1.256	130	2.5		34.87
	4	800	2868	3256	1.332	140	2.3	10.3	43.00
1142	1	800	2166	2555	1.092	110	2.5		15.65
	2	800	2555	2943	1.184	120	2.3		27.17
	3	800	2943	3332	1.268	130	2.1		36.00
	4	800	3332	3721	1.332	140	2.0	9.0	43.00

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TABLE I (Cont.)
Page 2

Aroclor	Stage	Cl_2 Feed Lbs./Hr.	Liq. Feed Lbs./Hr.	Outage Lbs./Hr.	Sp. Gr. at 90°C.	Chlor. Temp. °C.	Sojourn Hr.	Total Sojourn	% Cl_2
1148	1	500	1111	1354	1.110	110	4.7		18.46
	2	500	1354	1597	1.226	120	4.0		31.91
	3	500	1597	1840	1.314	130	4.0		40.76
	4	500	1840	2083	1.396	140	3.8	16.5	48.00
1148	1	600	1334	1626	1.110	110	3.9		18.46
	2	600	1626	1917	1.226	120	3.4		31.91
	3	600	1917	2209	1.314	130	3.4		40.76
	4	600	2209	2500	1.396	140	3.2	13.9	48.00
1148	1	400	1334	1528	1.068	110	4.0		13.10
	2	500	1528	1771	1.168	120	3.8		25.41
	3	700	1771	2111	1.284	130	3.5		37.90
	4	800	2111	2500	1.396	140	3.2	14.5	48.00
1148	1	700	1557	1897	1.110	110	3.4		18.46
	2	700	1897	2237	1.226	120	2.9		31.91
	3	700	2237	2557	1.314	130	2.9		40.76
	4	700	2577	2917	1.396	140	2.7	11.9	48.00
1148	1	500	1557	1800	1.076	110	3.2		13.89
	2	700	1800	2140	1.190	120	3.2		28.04
	3	800	2140	2529	1.300	130	2.9		39.54
	4	800	2529	2917	1.396	140	2.7	12.0	48.00
1148	1	800	1778	2167	1.110	110	2.9		18.46
	2	800	2167	2556	1.226	120	2.5		31.91
	3	800	2556	2945	1.314	130	2.5		40.76
	4	800	2945	3334	1.396	140	2.4	10.3	48.00

TABLE I (Cont.)
Page 3

Aroclor	Stage	Cl_2 Feed Lbs./Hr.	Liq. Feed Lbs./Hr.	Outage Lbs./Hr.	Sp. Gr. at 90°C.	Chlor. Temp. °C.	Sojourn Hr.	Total Sojourn	% Cl_2
1154	1	500	846	1089	1.156	110	6.1		23.96
	2	500	1089	1332	1.280	120	5.5		37.54
	3	500	1332	1575	1.390	140	5.0		47.62
	4	500	1575	1818	1.486	150	4.6	21.2	55.00
1154	1	600	1016	1308	1.156	110	5.1		23.96
	2	600	1308	1599	1.280	120	4.6		37.54
	3	600	1599	1891	1.390	140	4.2		47.62
	4	600	1891	2182	1.486	150	3.8	17.7	55.00
1154	1	400	1016	1210	1.096	110	5.2		16.67
	2	500	1210	1453	1.216	120	4.8		30.97
	3	700	1453	1793	1.354	140	4.3		44.62
	4	800	1793	2182	1.486	150	3.8	17.8	55.00
1154	1	700	1185	1525	1.156	110	4.4		23.96
	2	700	1525	1865	1.280	120	3.9		37.54
	3	700	1865	2205	1.390	140	3.6		47.62
	4	700	2205	2545	1.486	150	3.3	15.2	55.00
1154	1	500	1185	1428	1.102	110	4.5		17.51
	2	700	1428	1768	1.244	120	4.0		33.94
	3	800	1768	2157	1.376	140	3.6		46.36
	4	800	2157	2545	1.486	150	3.3	15.4	55.00
1154	1	800	1354	1743	1.156	110	3.8		23.96
	2	800	1743	2132	1.280	120	3.5		37.54
	3	800	2132	2521	1.390	140	3.1		47.62
	4	800	2521	2916	1.486	150	2.9	13.3	55.00

TABLE I (Cont.)
Page 4

Aroclor	Stage	Cl_2 Feed Lbs./Hr.	Liq. Feed Lbs./Hr.	Outage Lbs./Hr.	Sp. Gr. at 90°C.	Chlor. Temp. °C.	Sojourn Hr.	Total Sojourn	% Cl_2
1160	1	500	695	938	1.176	110	7.3		26.65
	2	500	938	1181	1.326	120	6.5		42.34
	3	500	1181	1424	1.456	140	5.8		52.67
	4	500	1424	1667	1.562	150	5.3	24.9	60.00
1160	1	600	834	1226	1.176	110	5.6		26.65
	2	600	1126	1417	1.326	120	5.4		42.34
	3	600	1417	1709	1.456	140	4.8		52.67
	4	600	1709	2000	1.562	150	4.4	20.2	60.00
1160	1	400	834	1028	1.118	110	6.5		19.45
	2	500	1028	1271	1.260	120	5.7		35.40
	3	700	1271	1611	1.416	140	5.0		49.66
	4	800	1611	2000	1.562	150	4.4	21.6	60.00
1160	1	700	973	1313	1.176	110	5.2		26.65
	2	700	1313	1653	1.326	120	4.6		42.34
	3	700	1653	1993	1.456	140	4.1		52.67
	4	700	1993	2333	1.562	150	3.8	17.7	60.00
1160	1	500	973	1216	1.126	110	5.3		20.56
	2	700	1216	1556	1.288	120	4.8		38.56
	3	800	1556	1945	1.440	140	4.2		51.41
	4	800	1945	2333	1.562	150	3.8	18.1	60.00
1160	1	800	1112	1501	1.176	110	4.5		26.65
	2	800	1501	1890	1.326	120	4.0		42.34
	3	800	1890	2279	1.456	140	3.6		52.67
	4	800	2279	2668	1.562	150	3.3	15.4	60.00