ORGANIC CHEMICALS DIVISION RESEARCH *Report*

REPORT NO.- P-1592 JOB NO.- 2-02-760.01-1348305

TENTATIVE PROCESS
ON
MCS 1016A

DATE - March 22, 1971 WRITTEN BY - D. R. Cova

Monsanto

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ORGANIC CHEMICALS DIVISION RESEARCH *Report*

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MONSANTO COMPANY
ORGANIC CHEMICALS DIVISION
TECHNOLOGY DEPARTMENT

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Report No. P-1592 Job No. 2-02-760.01-1348305

TENTATIVE PROCESS ON MCS 1016A

Date: March 22, 1971

Written by: D. R. Cova

Work done by:

D. R. Cova
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INTRODUCTION

MCS 1016 or MCS 1016A will replace Aroclor 1242 in the functional fluids product line for the following reasons. Recent scientific data suggest that non-biodegradable polychlorinated biphenyls cause considerable ecological damage when dumped into the environment. Although conclusive scientific evidence on all polychlorinated biphenyls has not been developed, public opinion has been aroused. Aroclor 1242 does contain appreciable amounts of slowly biodegradable polychlorinated biphenyls and the use of Aroclor 1242 causes some of this material to be dumped into the environment. From the viewpoints of both ecology and public relations there is an urgent need to produce a more biodegradable substitute for Aroclor 1242. MCS 1016 or MCS 1016A will be the substitute.

MCS 1016 is Aroclor 1242 from which some of the slowly biodegradable components have been removed. Since this product may be less fire resistant than Aroclor 1242, it may be necessary to produce MCS 1016A, MCS 1016 from which part of the material containing less than 3 chlorines/mol has been removed in order to bring the average chlorine content to a value nearly equal to that of Aroclor 1242. Laboratory evidence indicates that the least biodegradable components in Aroclor 1242 are the higher boiling components. Aroclor 1242 is produced by a straight takeover distillation of Aroclor 1142. By fractionating Aroclor 1142 most of the higher boiling components can be removed. Laboratory evidence confirms that fractionated Aroclor 1142 is more biodegradable than Aroclor 1242. The low-biodegradable residue from this fractionation is used to make Aroclor 1254 and Aroclor 1260 which are unlikely to find their way into the environment.

Fractionation data on Aroclor 1142 was generated by the Process Technology section. This report describes how the present Aroclor 1242 process can be changed to produce MCS 1016A. This report supplements Report No. P-1579 which describes a process for MCS 1016. MCS 1016A differs from MCS 1016 in that a forefraction is also removed from Aroclor 1142 to make MCS 1016A. This is done to raise the average chlorination level of the final product.

NOMENCLATURE

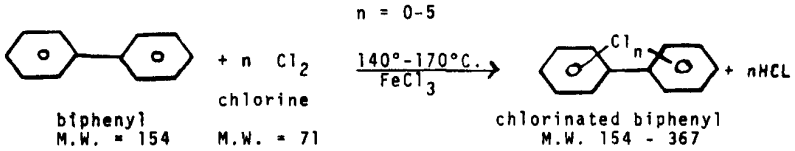
The Aroclor nomenclature is the standard nomenclature used for Aroclors.

The abbreviation C. B. will be used to refer to chlorinated biphenyls. This abbreviation followed by an interger refers to a chlorinated biphenyl containing that number of chlorine atoms per molecule.

SYNOPSIS OF THE PROCESS

The present Aroclor 1242 process is converted to an MCS 1016A process by changing the distillation process steps. Since the other process steps are unchanged, well documented, and current plant practices, they will not be discussed at length.

The process steps required to produce Aroclor 1142 are essentially unchanged. Biphenyl is reacted with chlorine gas in the presence of a Ferric Chloride ($FeCl_3$) catalyst at 140-170°C. This is an aromatic substitution reaction and the product is a distribution of biphenyl and C.B. isomers which contain from one to five chlorine atoms per molecule. The following is a schematic representation of the reaction.



The reaction product is blown with dry air to remove free HCL gas. The blown reaction product is Aroclor 1142.

The Aroclor 1142 is vacuum distilled through a 30 plate, sieve tray column. The fractionation is carried out in the batch mode. A forefraction comprising 10 to 20% of the charge is distilled off. This fraction is recycled to one of the chlorination stages. The main fraction is taken off until a total of 82% of the charge has been distilled. This main fraction is sent to porocel treatment to make MCS 1016A. The residue (comprising 18% of the charge) is subjected to vacuum, straight takeover distillation. 97-98% of the residue is recovered in this way for further chlorination to make the solid Aroclors. The residue remaining in the straight take-over still is incinerated.

The final process step is unchanged from the Aroclor 1242 process. MCS 1016A is circulated through a porocel column to remove moisture and ionic material. The finished product is stored or drummed for sale.

MATERIAL BALANCE AND FLOW SHEET

The material balance and flow sheet cover only the distillation area. The remainder of the process is unchanged except for the recycle of forefraction from the distillation to an appropriate chlorination stage.

The material balance is based on a forecut comprising 10% of the still charge. This forefraction can be as high as 20% of the charge depending on the results of MCS 1016A product tests now in progress.

PROCESS IN DETAIL

Except for the distillation steps, the process to produce MCS 1016A is essentially the same as the process currently used to produce Aroclor 1242 at W. G. Krummrich and Anniston, Alabama plants. The process steps which remain unchanged are:

1. Chlorination

Biphenyl is reacted with chlorine gas in the presence of a ferric chloride catalyst in four continuous reactors in series. The unreacted biphenyl and C.B.'s produced are transferred to the blow tanks for aeration.

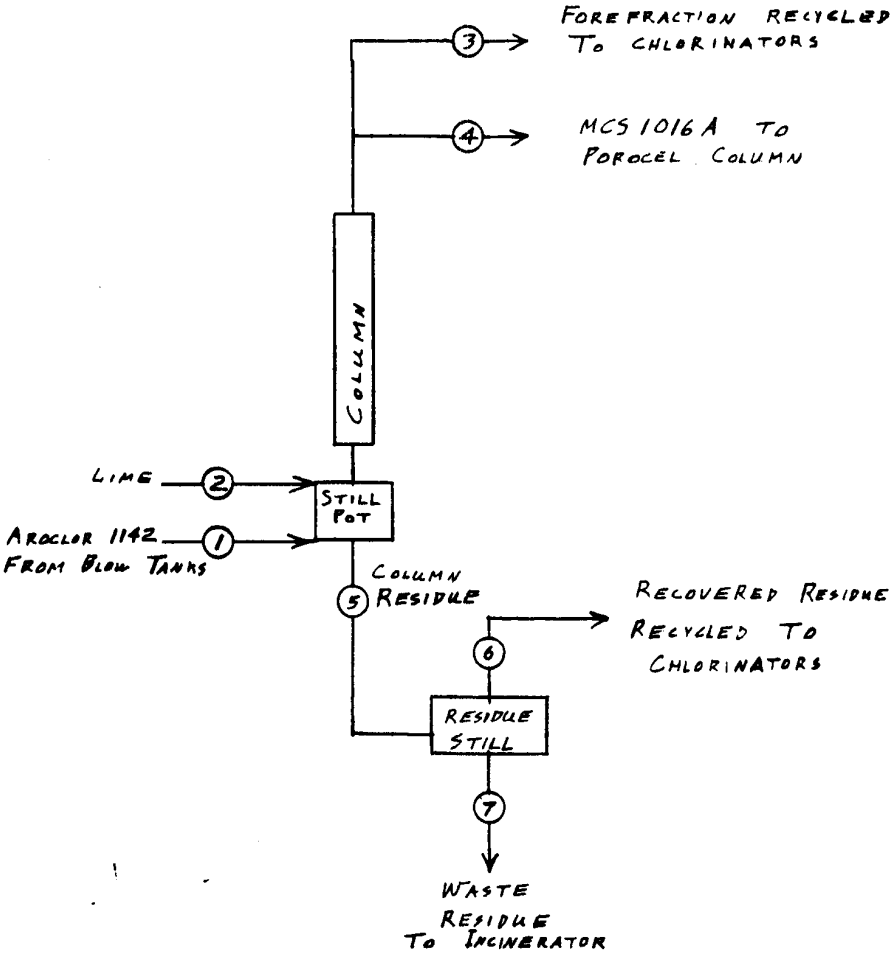
The one change in this area is the recycle of the forefraction from distillation. This forefraction should be fed into one of the chlorination stages. The appropriate stage should be selected by matching the composition of the feed to that stage with the composition of the forefraction. Since the amount of recycle is not yet known, neither is its composition. Complete definition of this portion of the process must await a decision on forecut size.

2. Aeration

Dry air is blown through the biphenyl and C.B.'s to remove free HCL gas. The aerated material, Aroclor 1142, is transferred to the distillation step.

3. Porocel treatment

The distillate from the distillation step is circulated through a column packed with Porocel to give the finished product.



FLOW SHEET FOR MCS1016 A DISTILLATION

MONS 040809

MATERIAL BALANCE FOR MCS1016A
DISTILLATION AREA

PROCESS STREAM / COMPONENT	① AROCLOR CHARGE TO STILL	② LIME	③ FORECUT	④ MCS1016A	⑤ COLUMN RESIDUE	⑥ RECOVERED RESIDUE	WASTE RESIDUE
LOW BOILERS	13.89		13.89				
MCS1016A	100.00			100.00			
HIGH BOILERS	24.25				24.25	24.25	
TARS & CATALYST	.75				.75		.75
$Ca(OH)_2$		.14			.14		.14
TOTAL	138.89	.14	13.89	100.00	25.14	24.25	.89
TEMP., °C	160	20	200-210	210-240	290	300	250-300
PRESSURE TORR			40	40			
PSIG	0	0			25	0	25

BASIS: 100 lb. OF MCS1016A

MONS 040810 FORECUT IS 10 % OF CHARGE.

Since these steps are unchanged they will not be described in detail. A detailed description of these steps may be found in the Standard Manufacturing Process for Aroclors in Dept. 27 at Anniston and Dept. 246 at W. G. Krummrich.

The process steps described here take Aroclor 1142 from the blow tank and produces MCS 1016A which goes to the Porocel column. The following is based on producing 100 lbs. of MCS 1016A for Porocel treatment.

1). Aroclor 1142 Fractionation

138.89 lbs. of Aroclor 1142 from the blow tank and 0.14 lbs. of hydrated lime are charged to the still pot of a 30-plate, sieve tray column. The pressure at the head of the column is reduced to 40 torr, and heat is applied to the reboiler. The column is brought to reflux and is run at total reflux until the head and reboiler temperatures have lined out. Projection from laboratory data indicates that these two temperatures will line out in the ranges of 205-215°C. and 255-265°C. for the plant column. Distillate is then taken forward at a reflux ratio of 3/1. This distillate is collected in the forecut receiver until 13.89 lbs. of distillate has been collected. This material is recycled to the chlorinators for conversion to Aroclor 1142. The distillate flow is now diverted to the main fraction receiver. When 43.05 lbs. of main fraction have been collected (at this point, 56.94 lbs. of the charge has been distilled off), the reflux ratio is changed to 5/1. Distillate continues to flow to the main fraction receiver until a total of 100.00 lbs. of main fraction has been collected. At this time, distillation is stopped. The main fraction is sent forward for Porocel treatment. The column residue (25.14 lbs. of material) is transferred to the residue still.

2). Residue Still

25.14 pounds of residue from the fractionation column are charged to a straight takeover still. The pressure in the still is reduced to 40 Torr. The still is heated and distillate begins to boil over at 250°C. The distillation is stopped when the still temperature reaches 300°C. Approximately 24.25 pounds of material are boiled over. The distillate from this still contains approximately 50% by weight chlorine. This material is recycled for further chlorination to make Aroclor 1254 or Aroclor 1260. The residue (0.89 lbs.) which consists of tars, $FeCl_3$ catalyst and lime is transferred hot to an incinerator.

DISCUSSION OF IMPORTANT VARIABLES

A. Aroclor 1142 Fractionation

1. Control

There are three important control points in the fractionation cycle: (1) the end of the forecut. (2) the change in reflux ratio from 3/1 to 5/1, and (3) the end of the main fraction.

The end of the forecut is signaled when 10 to 20% of the charge has been collected as distillate (the exact percentage required has not been determined yet). The purpose in removing the forecut is to increase the chlorination level of the main fraction. Since this changes slowly with forecut size, a larger error in forecut size can be tolerated. A maximum error in forecut size of ± 1% of the charge will be adequate for the plant system.

The change in reflux ratio is to take place when 41% of the charge has been distilled. Here also, a maximum error of ± 1% of the charge can be tolerated in changing reflux ratio.

The end of the main fraction is the most important cut point. It determines the concentration of highly chlorinated biphenyls in the product. The entire purpose of this fractionation is to reduce this concentration to an acceptable level. The end of the main fraction comes when 82% of the charge has been distilled. The concentration of highly chlorinated biphenyls in the product is very sensitive to this cut point. It was found experimentally that an error in this cut point of + 1% of the charge causes a 30% change in the concentration of C.B. 5's in the product (i.e., 81, 82 and 83% of the charge distilled would give products containing .28, .40 and .52% C.B. 5's). The error in this cut point should be minimized.

The control points can be determined by material balance if some means is provided for measuring total distillate. Reboiler and head temperatures change rather slowly with percent distilled. Because of the large number of components, there are no "breakpoints" or plateaus in the temperature profile (see Figure 2 in Appendix C). Near the end of the fractionation, the temperature change is less than 1°C. for each percent of the charge distilled. Since pressure can also affect temperature, it would not appear that temperature would be a suitably accurate means of controlling the end of fractionation.

2. Cycle Time

High temperatures and long distillation cycle times can cause trace decompositions in the reboiler which can adversely affect the electrical properties of the distillate. A laboratory fractionation has shown that a distillation time of 60 hours with a reboiler temperature range of 260°C. to 290°C. had no adverse effects on the distillate. Plant distillation times and reboiler temperatures should not exceed these demonstrated values. CED's proposed design is not expected to exceed these conditions.

3. Pressure

The reboiler temperature is directly related to the reboiler pressure. In the discussion of "cycle time", the plant reboiler temperature range was restricted to be equal to or less than 260°C. to 290°C. This temperature range occurs at 147 torr. Therefore, the reboiler pressure should not exceed 147 torr. CED's proposed design specifies a column head pressure of 40 torr and estimates a reboiler pressure of 140 torr.

4. Portion distilled

The portion distilled is 82% of the Aroclor 1142 charge. This number is based on projected production of MCS 1016A, Aroclor 1254 and Aroclor 1260. If the quantity of residue produced in the MCS 1016A fractionation exceeds the need for Aroclor 1254 and Aroclor 1260, it must be incinerated. The cost of incineration makes this undesirable. The portion distilled is set at 82% to secure adequate reduction of higher chlorinated biphenyls and to balance residue production with expected Aroclor 1254 and Aroclor 1260 requirements.

5. Number of plates and reflux ratios

The selection of reflux ratios and number of plates is not based entirely on distillate composition. This circumstance is the result of the following:

a. MCS 1016A is not intended to be completely biodegradable but is defined to be more biodegradable than Aroclor 1242.

b. There are no standard methods for measuring biodegradability.

c. There is not enough scientific evidence to single out all of the non-biodegradable components in Aroclor 1242.

The available laboratory evidence indicates that the highest boiling C.B.'s, C.B.4's and C.B.5's, contained in Aroclor 1242 are the least biodegradable. Laboratory experiments confirm that fractionated Aroclor 1142 is more biodegradable than Aroclor 1242. This fractionated Aroclor 1142 was produced by batch distilling 82% of an Aroclor 1142 charge through a 25 plate, sieve tray column at reflux ratios of 3/1 and 5/1. This fractionated Aroclor 1142 contained 0.39% C.B.5's. This concentration was selected as an approximate upper limit for MCS 1016A.

A 30 plate column was selected rather than a 25 plate column. The extra five plates were added because a need may develop to produce fractionated Aroclor 1130 to replace MCS 1016A. Fractionated Aroclor 1130 is more biodegradable than MCS 1016A and an Aroclor 1130 fractionation would produce less residue. Laboratory fractionations indicate that 30 plates are required to obtain a feasible recovery for this fractionation. A 30 plate column was selected to make the MCS 1016A process adaptable to Aroclor 1130.

The reflux ratios of 3/1 and 5/1 were selected to meet tray hydraulics and product volume requirements as estimated by CED for the column. A laboratory simulation of the proposed fractionation produced MCS 1016A which contained .41% C.B.5's. This was with a 10% forecut. A larger forecut of 20% would increase the concentration of C.B.5's in the MCS 1016A to about .48%,

6. Column Holdup

The effect of column holdup is to decrease the separating efficiency of the column. The plant column should have an operating holdup of about 3% of the charge. In a laboratory simulation with a 3% holdup, the product was found to contain .41% C.B.5's. In an approximately similar experiment where the holdup was reduced to .34% of the charge the concentration of C.B. 5's in the product was .07%.

7. Effect of variations in feed composition

The cut points in the distillation will most likely be controlled by material balance. This means that variations in the composition of the still charge can have a large effect on product composition. Thus, a charge of material having a higher degree of chlorination would give MCS 1016A with a higher concentration of C.B.5's. We do not have quantitative data in this area, and so it is recommended that this be followed closely in the plant, especially during startup.

Each still charge should be analyzed for the degree of chlorination (by measuring density or refractive index as an indication of the degree of chlorination or by analysis for chlorine). In this way it should be possible to correlate one of these measurements with the concentration of C.B. 5's in the product. From this a plan of action can be developed to counteract the effect of charge composition on product composition (as,for example, changing the percent distilled according to the density or refractive index of the charge).

8. Tail Fraction

The process as described makes no provision for taking a tail fraction after the main fraction. It may be advantageous to do so. The tail fraction could be recycled to the still with the next distillation charge. It should be possible in this way to reduce the concentration of C.B.5's in the product (by stopping the main fraction at 78 to 80% of the charge distilled). Also, by continuing to collect tail fraction past 82% distilled it should be possible to reduce the percentage of material going to the residue still. This may be desirable if Aroclor 1254 and Aroclor 1260 requirements are lower than expected.

9. Corrosion

The corrosion status is not expected to be different from the Aroclor 1242 process. No work was done on corrosion.

10. Blending

The composition of the distillate varies during the Aroclor 1142 fractionation. Customers who analyze MCS 1016A by infrared spectroscopy would be able to detect large difference between the lower and higher boiling portions of the distillate. Therefore, each distillate batch should be thoroughly mixed to insure that any portion of the batch is representative of the entire distillation range.

B. Residue Still

1. Semi-continuous operation

The residue still can be operated semi-continuously. Residue from the MCS 1016A fractionation can be fed continuously to the still during the distillation. When the still temperature approaches 300°C. the feed is stopped. The other operating condition of the distillation remain unchanged.

2. Pressure and Temperature

The residue fed to the laboratory still was at 25°C. In the plant, residue can be fed directly from the fractionation column at 290°C. The residue will begin to boil at 165 torr. at this temperature. Therefore, reducing the still pressure to 40 torr. will cause a portion of the residue to boil over without additional heat input.

The still is heated to an end point of 300°C. at 40 torr. The pressure of 40 torr. was chosen to achieve a 97% plus recovery of residue with a maximum still temperature of 300°C. The maximum temperature is set at 300°C. for the same reasons mentioned in discussion of "cycle time" for the fractionation column.

MATERIAL SPECIFICATIONS AND PHYSICAL CONSTANTS DATA

Except for MCS 1016A, all material specifications and physical constants data are the same as in the Aroclor 1242 process. Proposed MCS 1016A and the available material specifications and physical constants sheets are presented in Appendix A.

TOXICITY AND HAZARDS

No change is expected from the Aroclor 1242 process. Toxicity and safety data are presented in Appendix B.

POLLUTION CONTROL

In addition to the pollution controls in existence for the Aroclor 1242 process, a sump tank is to be installed in the water disposal line for the jet ejector system for the fractionation column. Any C.B.'s in the water will be collected in this tank. These C.B.'s and the tars from the residue still will be burned in the Aroclor incinerator.

ENGINEERING DATA

The available engineering data is presented in Appendix C.

ANALYTICAL METHODS

Except for GLC analysis of MCS 1016A, the analytical methods are the same as used in the Aroclor 1242 process. The standard analytical procedure identifications and a tentative GLC procedure are presented in Appendix D.

D. R. Cova

ds
3/29/71

Approved by:

W. R. Richard Date

O. DeGarmo Date

J. R. Savage Date

Appendix A

Material Specifications and Physical Constants Data

1. Raw material specification
   a. Diphenyl(Biphenyl)
   b. Chlorine gas
   c. Ferric Chloride
   d. Lime
   e. Porocel

2. MCS 1016A - Typical Properties

3. Physical Constants Data

   Aroclor 1142
   Biphenyl

Monsanto
ORGANIC CHEMICALS DIVISION

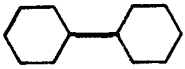
RAW MATERIAL SPECIFICATION

MATERIAL CODE	MATERIAL
82601	DIPHENYL (BIPHENYL)
PLANT	**USING DEPTS.**
WGK	246
DATE EFFECTIVE	**SUPPLIER**
10/23/70	Anniston Plant

APPROVALS

PRODUCTION	RESEARCH
B. W. Corlew	M. A. Terpstra G. W. Miller
PROCUREMENT	**QUALITY CONTROL (Chief Chemist)**
J. Leyerle	R. Blowers

GENERAL DESCRIPTION



mol wt. 154.20

CHEMICAL FORMULA

SUPERSEDES SPEC'S OF	SAMPLE FOR ANALYSIS	ISSUED BY
2/6/69	2 x 16 oz. W.M. Bottles	S. Shaulter/G. Stites

CHARACTERISTIC		LIMITS	METHOD
UNRESTRICTED INFORMATION			
(R)	Appearance and Color	Light Yellow Cryst. Solid	10,252
(R)	Crystallizing Point	68.7°C., min.	10,298
(R)	H_2O	250 ppm max.	13,155
GENERAL INFORMATION			
	Distillation Range:		
	First Drop to	2.5°C., max.	10,299
	Dry Point	Must include 255°C. within range	

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MONS 040819

(R) Routine Analysis. All others Analyzed by request only.

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ORGANIC CHEMICALS DIVISION

FINISHED PRODUCT SPECIFICATION

PRODUCT		DEPT.
Chlorine (Snift Gas)		232
PLANT: WGK	PRODUCT CODE: 81069 81064	USE: Internal
DATE EFFECTIVE: 11/69	SALES CODE:	

APPROVALS

PRODUCTION: J. Molloy, E. Malone, T. W. Dalton	RESEARCH: M. A. Terpstra
SALES:	QUALITY CONTROL (Olin Chemicals): R. M. Blowers

GENERAL DESCRIPTION: Mixture

CHEMICAL FORMULA:

MOL WT.

SUPERSEDES SPECS. OF	SAMPLE FOR ANALYSIS	ISSUED BY
10/66	100 c.c. Gas Burette	Higgerson/Stites

CHARACTERISTIC	LIMITS	METHOD

UNRESTRICTED INFORMATION

	Typical Analyses
Chlorine (Cl_2)	86%, By Volume
Oxygen (O_2)	3% " "
Carbon Dioxide (CO_2)	1.5% " "
Carbon Monoxide (CO)	0.1% " "
Hydrogen (H_2)	1.0% " "
Inert Gasses (By difference)	8.4% " "
Moisture (H_2O) @ Std. Conditions	2.4×10^{-5} lbs./ft.^{3} (Average)

Direct pipeline transfers to using Depts.

233, 236, 237, 246

This specification is for internal use at WGK Plant only.

RAW MATERIAL
Date Approved_____
For Dept. 233, 236, 237, 246

MONS 040820

(R) Routine Analysis. All others Analyzed by request Only

Monsanto
ORGANIC CHEMICALS DIVISION
W. G. Krummrich Plant
RAW MATERIAL
SPECIFICATION

MATERIAL CODE	MATERIAL
33500	Ferric Chloride Anhydride
PLANT: WGK	USING DEPTS.: 233
DATE EFFECTIVE: Jan. 31, 1969	SUPPLIER: McKesson & Robbins

APPROVALS

PRODUCTION: T. W. Dalton	RESEARCH: M. A. Terpstra
PROCUREMENT: J. Leyerle	QUALITY CONTROL (Chief Chemist): R. Blowers

GENERAL DESCRIPTION — CHEMICAL FORMULA

$FeCl_3$

mol wt. 162.21

SUPERSEDES SPECS OF	SAMPLE FOR ANALYSIS	ISSUED BY
1/7/66	1 x 8 oz. W.M. Bottle	Higgerson/Stites

UNRESTRICTED INFORMATION

CHARACTERISTIC	LIMITS	METHOD
		J.F.Q.
Appearance	Black powder or Granules	16-A
Assay	97.0%, min.	22-570
Sulfates	0.05%, max.	120-570
Ferrous Salts	Trace, max.	S-570-1
Solubility:		112-B
10:10 of Water	Complete to slightly turbid, max.	
10:10 of Formula 30 Alcohol	Complete to slightly turbid, max.	

MONS 040821

(R) Routine Analysis. All others Analyzed by request only.

Monsanto
ORGANIC CHEMICALS DIVISION
W. G. Krummrich Plant
RAW MATERIAL
SPECIFICATION

MATERIAL CODE: 38800	MATERIAL: Lime, Hydrated
PLANT: WGK	USING DEPTS.: 287, 750, 246
DATE EFFECTIVE: 4/7/70	SUPPLIER: Mississippi Lime Co.

APPROVALS

PRODUCTION: T. W. Dalton ~~B. Corlew~~	RESEARCH: M. E. Gibbs
PROCUREMENT: J. Leverle	QUALITY CONTROL (Chief Chemist): R. Blowers

GENERAL DESCRIPTION

CHEMICAL FORMULA

$Ca(OH)_2$

SUPERSEDES SPEC OF	SAMPLE FOR ANALYSIS	ISSUED BY
8/13/69	1 x 16 oz. W.M. Bottle	Higgerson/Stites

CHARACTERISTIC	LIMITS	METHOD
Appearance	Fine white or slightly gray powder, free from lumps or gritty material	10,188
Assay ($Ca(OH)_2$)	92.00%, min.	10,191
Carbonates as ($CaCO_3$)	3.00%, max.	10,193
Magnesium	0.50%, max.	10,192
Sulfates (as SO_3)	0.30%, max.	10,189

Supplier's certificate of analysis to be sent on day of shipment to:

Chief Chemist, Monsanto Co., Sauget, Illinois

MONS 040822

(R) Routine Analysis. All others Analyzed by request only.

WGK-814

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RAW MATERIAL
SPECIFICATION

MATERIAL CODE	MATERIAL
48289	REGULAR POROCEL
PLANT: WGK	USING DEPTS.: 246
DATE EFFECTIVE: 8/3/70	SUPPLIER: Porocel Corp. (A Subsid. of Mineral & Chemicals Phillip Corp.)

APPROVALS

PRODUCTION	RESEARCH
R. W. Corlew	M. E. Gibbs
PROCUREMENT	QUALITY CONTROL (Chief Chemist)
J. Leverle	R. M. Blowers

GENERAL DESCRIPTION: ACTIVATED BAUXITE

CHEMICAL FORMULA:

SUPERSEDES SPECS OF	SAMPLE FOR ANALYSIS	ISSUED BY
9/69	2 x 16 oz. W. M. Bottles	Higgerson/Stites

CHARACTERISTIC	LIMITS	METHOD

UNRESTRICTED INFORMATION

(R)	Appearance	Free from lumps and foreign material	
(R)	Mesh Test:		10,692
	Less than 60 mesh:	3%, max.	
	20 to 60 mesh inclusive:	67%, min.	
	Greater than 20 mesh:	30%, max.	
(R)	Water	1%, max.	10,100
	Volatile Matter (at 1000°C. to constant weight)	2%, max.	

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(R) Routine Analysis. All others Analyzed by request only.

MCS-1016A

TYPICAL PROPERTIES

COLOR (APHA)	10
CONDITION	CLEAR
SP. GR. @ 25/15.5°C	1.363
ACIDITY (Mg. KOH/g.)	0.001
MOISTURE (PPM)	40
REFRACTIVE INDEX @ 25°C	1.6210
INORGANIC (FREE) CHLORIDES (PPM)	0.02
POUR POINT (°C)	-18
DIELECTRIC CONSTANT (1000 CYCLES @ 100°C)	4.96
RESISTIVITY (500 VDC @ 100°C, D.1" GAP) AS OHM-CM X 10^9	353×10^3
HYDROLYSIS STABILITY (PPM AS CHLORIDES)	0.10
MONSANTO STABILITY (PPM AS CHLORIDES)	0.06
DISTILLATION RANGE (ASTM D-20, CORRECTED)	
10% DISTILLED (BY WT.) °C	324
90% DISTILLED (BY WT.) °C	342
DIELECTRIC STRENGTH @ 25°C (KV)	50
FLASH POINT (°F)	354
FIRE POINT (UP TO B.P.)	NONE
VISCOSITY @ 100°F (SUS)	70.6
FIXED CHLORIDE (%)	41.3
(G-E) THERMAL CHEM. CHLORIDES (PPM)	0.16
(WESTINGHOUSE) HYDROLIZABLE CHLORINE (PPM)	0.26

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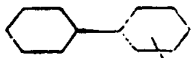
PHYSICAL CONSTANTS DATA

AROCLOR 1142 (Technical)

STRUCTURAL FORMULA



DATE 1947

Prepared by A. M. Ellenburg 7/5/57

NAME		SOURCE & DATE
Formula	$C_{12}H_7Cl_3$	Total Cl_2 41.5 - 42.5% Specs 12-21-54
Molecular Weight		
Appearance		Brown to black oily liquid Specs 12-21-54
Boiling Point at 760 mm		
Boiling Point at mm		
Boiling Point at mm		
Crystallizing Point		
Melting Point		
Softening Point		
Specific Gravity 65/15.5°C		1.348-1.360 Specs 12-21-54
Specific Gravity 25/15.5°C		1.384-1.397
Pounds per Gal. @ 25 °C		10.5
Coefficient of Expansion		
Refractive Index $n_D^{\ }$		
Infrared Spectrum *(Reference)*		
Ultra Violet Spectrum *(Reference)*		
Viscosity		
Volatility		
Surface Tension		
Solubility in Water		
Solubility in		
Solubility in		
Sp. Gr. Temp Coeff. (50-105°C)		0.0009/°C Specs 12-21-54
Flash Point °F *(Method)* C. O. C.		350 Aroclor Bull. C
Fire Point °C		None
Heat of Combustion		
Heat of Formation		
Thermal Stability (cal./kg/min.)		
Latent Heat of Fusion		
Latent Heat of Vap.		
Specific Heat		
Critical Temperature		
Critical Pressure		
Dissociation Constant		
Other Constants		
		MONS 040825
Toxicity *(Give Reference)*		Schwartz, U. S. Pub. Health Service Bull. #22
		"Industrial Poisons, Hazards and Solvents"
		Jacobs Vol. 1, p. 463-464 1941

NOTE: *These data should not be released outside of Monsanto Chemical Company. Use additional sheets if necessary.*

PHYSICAL CONSTANTS (Cont'd.)

PHYSICAL AND CHEMICAL DATA

Diphenyl

Specific Gravity: 0.992 at 75°C/4°C.

The Swann Chemical Company bulletin of 1950 gave thermal data on diphenyl.

Viscosity of Diphenyl (from Anniston Files)

°F.	Centipoises
160	1.439
170	1.309
180	1.208
190	1.114
200	1.034
220	0.901
250	0.752
300	0.574
350	0.459
400	0.374
450	0.313
482	0.283

Specific Heat (from Anniston Files)

°F.	B.T.U./lb.
200	0.416
300	0.470
400	0.547
500	0.616
600	0.658
700	0.679
800	0.686
900	0.690
1000	0.696

PHYSICAL AND CHEMICAL DATA (Cont'd.)

Diphenyl (Cont'd.)

Another record gives the following values for liquid diphenyl:

°C.	Sp. Heat cals./gram
100	0.360
150	0.380
200	0.412
250	0.460
300	0.518
350	0.575
400	0.610
450	0.625

Vapour CP = $\frac{0.460}{250°C.}$

$\frac{0.625}{450°C.}$ (D. A. Roper, Design Data for Units 4 & 5)

Density of Liquid Diphenyl (from Anniston files)

°C.	Grams./cc
75	0.9885
100	0.9695
150	0.9294
200	0.8885
250	0.8470
300	0.8010
350	0.7510
400	0.6918
450	0.6180

Heat of Vaporization:

65.4 g. cal./g. at 258.5°C.

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APPENDIX B

"Safety and Toxicity Data"

taken from The Standard Manufacturing Process for the Manufacture of Aroclors, in Dept. 246, W. G. Krummrich Plant.

CHLORINE (Cl_2) (Cont'd.)

Fire Hazard: There is no fire hazard under normal conditions, but there is an explosion hazard if chlorine is mixed with a strong reducing agent such as hydrogen or hydrocarbons at high temperature.

Other Hazards: This material causes eye, skin, and mucous membrane irritation

Treatment and Antidotes: The patient should be given oxygen immediately and treated for shock. Call a physician.

Storage and Handling: This material should be stored in a ventilated and cool place away from fire hazards. When handling, wear a gas mask or approved respirator, clothing and rubber or chemical safe goggles. In strong chlorine concentrations, wear canister gas masks, Scott air pack, or oxygen breathing apparatus.

Shipping: The shipping containers must have a green gas label and a non-flammable label on. Ship in steel cars or cylinders.

ATTAPULGUS EARTH:

Toxicity: This earth is not toxic in general.

Fire Hazard; There is no fire hazard.

Other Hazards: Attapulgus earth can create a dust hazard similar to other dusts that contain silica.

Treatment and Antidotes: Consult a physician.

Storage and Handling: Attapulsug earth presents no special storage problem and should be handled by persons wearing an approved respirator.

Shipping: There are no special restrictions on shipping.

HYDROGEN CHLORIDE (HCl)

Toxicity: This material is a gas under normal conditions and is very toxic. The M.A.C. is 5-10 ppm and a concentration of 1500-2000 ppm would be fatal to humans in a few minutes.

Fire Hazard: There is no fire hazard under normal conditions, but wet gas reacts with some metals to form hazardous hydrogen.

Other Hazards: This material is hazardous to teeth, skin, eyes, and mucous membranes.

Treatment and Antidotes: Wash profusely with water, if ingested, eat chalk, magnesium hydroxide, egg whites, and milk, and also administer oxygen. Call a physician.

Storage and Handling: This material should be stored in a cool, well ventilated area away from oxidizing agents. This material can be stored in rubber lined, glass, or tantalum vessels. People handling this material should wear suitable clothing like rubber aprons, shoes, and gloves. Also rubber goggles or chemical safe grades and approved pack or canister gas masks.

Shipping: Shipping containers must have a white warning label and a non-flammable label. Ship in appropriate containers such as rail car or carboy.

CHLORINE (Cl_2)

Toxicity: This material is a gas under normal conditions and is very toxic. The M.A.C. is .35 to 2 ppm. A concentration of 1000 ppm would be rapidly fatal. Least concentration with detectable odor is 3.5 ppm

DIPHENYL ($C_6H_5C_6H_5$) (Cont'd.)

Treatment and Antidotes: Wash eyes with water and get the patient to fresh air. Try to get patient to vomit, and call a physician.

Storage and Handling: This material can be stored in steel containers away from fire hazards and oxidizing agents. Wear suitable clothes and approved goggles when handling diphenyl.

Shipping: Ship in cars or other suitable containers with a red warning label of flammability.

LIME $Ca(OH)_2$

Toxicity: Lime is not dangerously toxic, and it is regarded as more of a nuisance. This material is a solid or slurry.

Fire Hazard: This material is not flammable.

Other Hazards: Lime is very hazardous to the eyes. It will burn the skin also, and the dust will affect the mucous membranes.

Treatment and Antidotes: Flood eyes and skin with large quantities of water. If lime is ingested, get patient to vomit and call physician.

Storage and Handling: Lime can be stored in steel containers, and people should wear protective clothing, respirators, and rubber or chemical safe goggles when handling lime.

Shipping: There are no special restrictions for shipping, but the containers should have a white label, a caustic warning.

Other Hazards: This material can cause dermatitis, systemic poisoning from the fumes, and yellow atrophy of the liver. There are skin, mucous membranes and eye hazards encountered in handling this material.

Treatment and Antidotes: Call a physician and remove patient from fumes.

Storage and Handling: Protect the skin, lungs, and eyes by wearing approved protective clothing, respirator, and goggles. People who handle this material at elevated temperatures should have medical supervision, and the air should be sampled to insure compliance with M.A.C. There are no special storage restrictions under normal conditions except store in a ventilated area.

Shipping: There are no special shipping restrictions.

FERRIC CHLORIDE ($FeCl_3$)

Toxicity: This material is a solid under normal conditions and is non-toxic or has a rating as low.

Fire Hazard: There is no fire hazard under normal conditions, but it will emit toxic fumes at high temperatures.

Other Hazards: Some people are allergic to this material and may develop skin rash, and there is an eye hazard.

Treatment and Antidotes: Call a physician.

Storage and Handling: Protect the skin with approved protective clothing, avoid the breathing of $FeCl_3$ duet, wear approved respirator with adequate cartridge, and protect the eyes with approved goggles. There are no storage regulations.

Shipping: There are no shipping restrictions.

DIPHENYL ($C_6H_5C_6H_5$)

Toxicity: This material is a solid at normal conditions and is medium toxic. The M.A.C. of vapor is 2 mg/cubic meter of air. If ingested the lethal dose is 2.4 g/Kg of body weight. The fumes are not dangerously deadly, but they are poisonous over a prolonged time.

Fire Hazard: Diphenyl is very flammable and will burn when exposed to heat or flame or oxidizing materials.

Other Hazards: Diphenyl is not too corrosive to skin, but it will affect the eyes.

Safety Precautions (Cont'd.)

2. Sampling of Crude Aroclor
The samples of Aroclor taken during the chlorination reaction are hot (170°C.). Precaution must be taken to avoid skin contact of samples and inhalation of Hydrogen Chloride, Chlorine and Aroclor vapors.

3. Fires
Fires may result from the ignition of leaking gas, Xylene, Diphenyl, rags, paper, wood, etc. Automatic fire extinguishers and sprinklers have been installed to combat fires.

4. Explosions
Explosions may be caused from accumulated pockets of natural gas or a rapid burning of Diphenyl in a closed container such as a Chlorinator. Chlorinators are equipped with a 10" diameter pressure relief line with a rupture disc made to burst at 22 psi in case Diphenyl within the Chlorinator ignites.

5. Toxicity
Toxicity does not present a serious problem. However, a complete daily change of clean clothes is supplied to each person and time is allotted at the end of each shift to take a bath. Instructions are also issued to avoid actual skin contact with Biphenyl and Aroclor as much as possible and to wash hands and face before eating.

6. Miscellaneous
There are many accidents that can occur that may be classified as health and safety hazards. These accidents may result from such things as broken process lines, acid leaks, steam leaks, etc.

The worst inherent hazards are as follows:

1. Free Chlorine from ruptured line or major leak.
2. HCl Gas from ruptured line or major leak.
3. Dropping bottoms from stills.
4. Hot Aroclor & Diphenyl.

AROCLOR

Toxicity: This material is a liquid under normal conditions and has a medium toxicity range for liquid ingestion and high toxicity for vapor inhalation. The maximum allowable concentration (M.A.C.) is 1 mg/cubic meter.

Fire Hazard: There is no fire hazard under normal conditions. Aroclor mixes (Xylene, Toluene, Butyl Acetate, etc.) may burn and explose at high temperatures when exposed to flames.

Safety Equipment

The following is a list of safety equipment (personal and departmental) required in department 246.

1. Fire extinguishers:

   A. Dry Chemical (3) - Southwest corner Bldg. CR - Main Floor.

   - West wall at top of stairs of Second Floor.

   -

   B. Carbon Dioxide Snow - Southwest corner of Bldg. CR, ground level.

2. Chlorine Gas Masks (4) - Southwest corner, second floor

   - Control room, second floor

   - East side, outside control room

   - Wall, Southwest corner of sprinkler house, main floor.

3. Scott Air Masks - West of Lean-To

4. Safety Showers (2) - Southeast corner of Bldg. CR, ground level.

   - Southeast corner of Bldg. CR, 2nd Floor.

5. Davis Vapotester

6. Eye Baths

7. Sprinkler System

Safety Precautions

The folliwing are safety precautions followed in the operation of department 246.

1. Safety Equipment of Employee
   Each employee has the following safety equipment: (1) Hard hat (2) Safety glasses (3) Goggles (4) Rubber and canvas gloves (5) Rubber overshoes. Special equipment may be issued as necessary for performing a particular job in a safe manner.

Appendix C

Engineering Data

1. Vapor pressure equations for biphenyl
2. Boiling Temperature versus pressure curve for the residue from the MCS 1016 distillation.
3. Reboiler Temperature versus Percent Distilled
4. Component material balance for MCS 1016 fractionation column

Biphenyl vapor pressure equations:

For temperature 70°C. to 254.9°C.

$$\text{Log } P = 7.0220 - (1723/T) - (245{,}700/T^2)$$

p = pressure in mm. Hg.

T = temperature in degrees Kelvin

For temperature 250°C. to [illegible]°C.

$$\text{Log } P = 4.76 - \frac{2123.3}{t + 230}$$

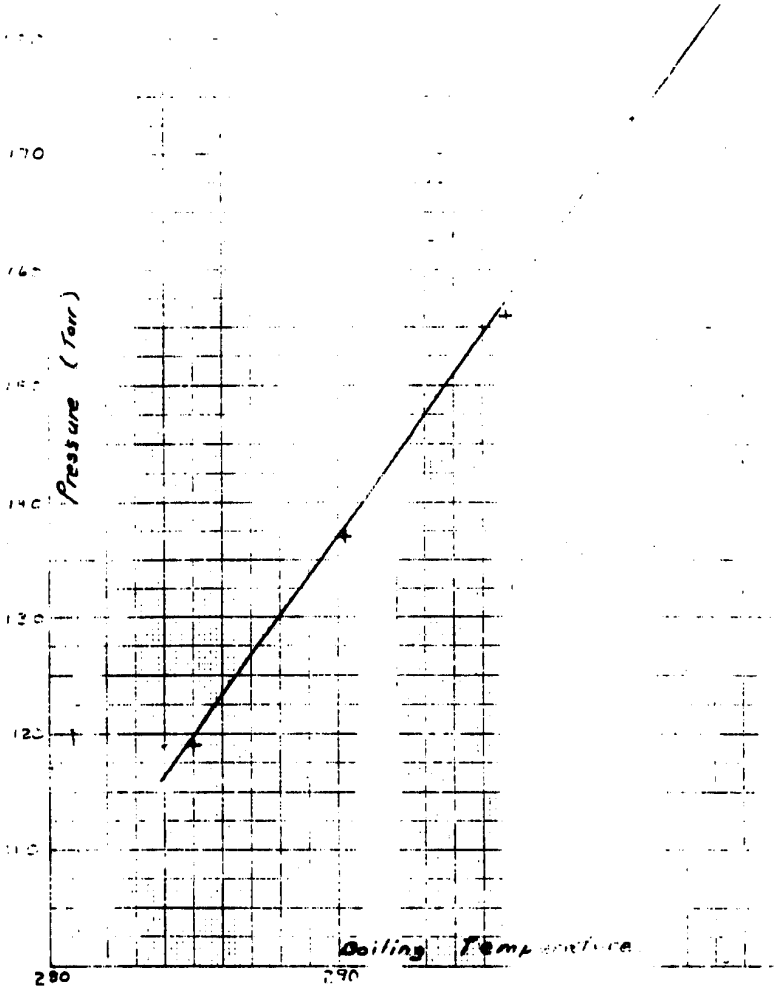
p = pressure in atmospheres

t = Temperature in degrees centigrade

The vapor pressure equations were obtained from Vapor Pressure of Organic Chemicals, J. Earl Jordan, Interscience Publishers, 1954, page 14.

MONS 040836

Boiling Point vs Pressure
for
Residue from MCS Distillation



MONS 040837

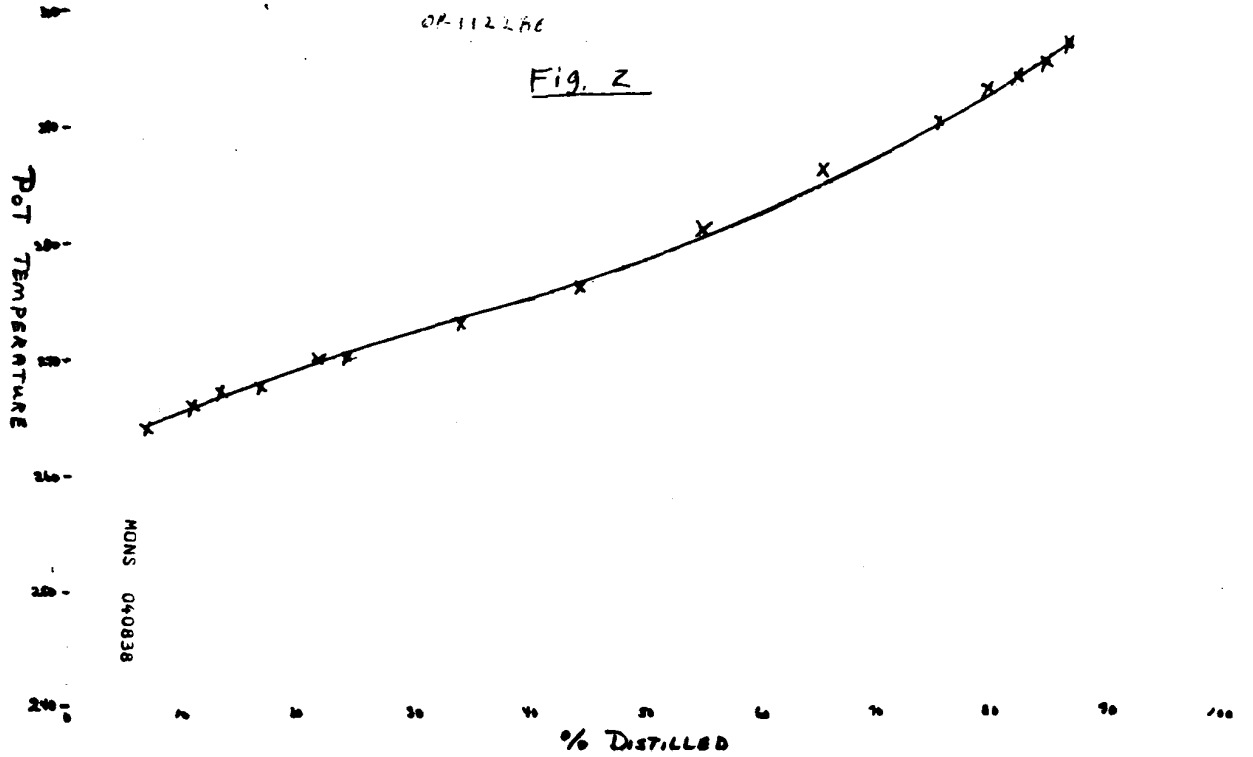
REBOILER TEMP. VERSUS PERCENT DISTILLED

A ROCLOR 1242 DISTILLATION

POT PRESSURE [illegible] mm Hg

OR-112286

Fig. 2



MONS 040838

Component Material Balance

The following table is a component balance for Aroclor 1142 in the MCS 1016 fractionation column. The weights are based on GLC analyses of a laboratory fractionation.

	Component	Pounds of Feed	Pounds of Residue	Pounds MCI 1016
1	BIPHENYL	0.02		0.01
2	ORTHO C.B1	0.70		0.73
3	META C.B1	0.04		0.02
4	PARA C.B1	0.21		0.16
5	2,6 C.B2	0.12		0.13
6	2,2' C.B.2	4.27		5.21
7	2,[illegible] C.B.2	0.94		
8	[illegible] C.B.2			0.77
9	3,3 C.B2	1.93		2.81
10	2,4' C.B2	9.77		10.93
11	C.B. 3	1.10		0.94
12	2,5,2' C.B.3	14.90		16.77
13	3.3' C.B.2	0.33		0.12
14	[illegible] C.B2	[illegible]		0.46
15	3,4' C.B2	0.35		0.25
16	C.B.2	1.99		2.01
17	4,4' C.B 2	2.24		2.58
18	2,3,2'C.B.3	6.42		7.15
19	C.B.3	16.16	0.08	17.21
20	C.B.3	1.12		0.61
21	C.B.3	6.55	0.02	6.13
22	C.B.3	0.91		0.58
23	C.B.3			
24	C.B.3			
25	C.B.3	10.02	0.09	9.91
26	C.B.3			
27	2,4,4' C.B.3	3.65	0.01	3.10
28	C.B.4	0.63		0.04
29	C.B.4	0.56		0.09
30	C.B.4	5.88	0.14	5.08
31	C.B.4			
32	C.B.4	1.56	0.08	.12
33	C.B.4	3.65	0.13	2.40
34	C.B.4		0.08	
35	C.B.1	2.38	1.67	0.32
36	C.B.1	0.08		tr
37	3,4,4'C.B 3	2.26	0.06	1.21
38	C.B.4	0.99	9.34	0.13
39+42	C.B.4	10.43		1.90
43	C.B.5	0.06	0.06	tr
44+45	C.B.5	4.73	5.43	0.06
47	C.B.5	0.55	0.65	
48	C.B.5	0.29	0.27	
49	C.B.5	0.90	1.11	
50	C.B.5	0.02	0.03	
51	C.B.5	0.06	0.05	
52	C.B.5	0.49	0.42	
53	C.B.5	0.23	0.25	
54	C.B.5	tr	0.01	
55	C.B.5	0.12	0.35	
56	C.B.5	0.01	tr	
57	C.B.5	0.01	tr	
58	C.B.5	tr	0.01	
59	C.B.5	0.05	0.01	
60	C.B.5	0.33	0.60	
	TOTAL	121.95	21.95	100.00

MONS 040840

APPENDIX D

Analytical Methods

1. Current analytical procedures

2. Tentative GLC procedure

The following is a list of analytical tests used at W. G. Krummrich Plant.

Number	Procedure for Determining
10084	Color (ASTM)
10084	Condition
10114	Specific gravity at 25/15.5°C.
10620	Moisture
10175	Refractive index at 25°C.
12741	Inorganic chloride content
10115	Pour point
11608	Dielectric constant at 1000 cps at 100°C.
11607	Resistivity
12672	Hydrolysis stability
11503	Monsanto stability
12169	Sulfates content
10117	Distillation range
11605	Dielectric strength at 25
10123	Flash point, fire point
10126	Corrosion
10086	Viscosity

Physical Chemistry
Method No. 71-11
Job No. 1348522

GAS CHROMATOGRAPHIC DETERMINATION OF PENTA- AND HEXA-CHLOROBIPHENYLS IN AROCLOR 1242 AND MCS 1016

PURPOSE OF ANALYSIS

This is a rapid, simplified method to be used to determine the level of high boilers (mainly pentachlorobiphenyls) in MCS 1016 obtained from the fractionation of Aroclor 1142. It is not intended for general analysis of chlorinated biphenyl mixtures. Physical Chemistry Method No. 70-20 should be used for that purpose.

CHROMATOGRAPHIC CONDITIONS

Instrument: Perkin-Elmer 800, Hewlett-Packard 7624A or Equivalent

Type Detector: Flame Ionization

Column: 50' X 0.02" I.D. FFAP S.C.O.T. (Support-Coated Open Tubular) Capillary (Perkin-Elmer Part No. 008-0804)

Column Temperature: 220°C

Detector Block Temperature: 300°C

Injection Port Temperature: 320°C

Sample Volume Injected: 0.005 ml
Split 25 to 1

Flow Rates

Column Helium: 8 ml/min (7 PSIG)
Inlet Splitter: 210 ml/min
Auxiliary Helium: 50 ml/min
Hydrogen: 50 ml/min
Air: 400 ml/min

RETENTION TIMES (UNCORRECTED) OF COMPONENTS SEPARATED (CHROMATOGRAMS ATTACHED)

Biphenyl, Mono-, Di-, Tri- and Most Tetra-Chlorobiphenyls (1.0 to 5.0 min); High Boilers (Mostly Penta- and Hexa-Chlorobiphenyls)(5.5 to 11.2 min).

CALCULATION TECHNIQUE

Peak area normalization. The lack of pure knowns prevents the accurate determination of response factors (area correction factors) for the individual components. Therefore, the specification for MCS 1016 is simply based on area percent of total high boilers.

PRECISION

Reference samples* of MCS 1016 (Drum 2) and Aroclor 1242 (Lot KK 491) were analyzed in duplicate on the two instruments listed using both the Disc chart integrator and an electronic integrator (Infotronics CRS-100 on the Perkin-Elmer 800 chromatograph and Hewlett-Packard 3370A on the Hewlett-Packard 7624A chromatograph). The same column was used in both instruments. Results reported as Area % High Boilers:

MCS 1016 (Drum 2):

	Method of Integration		
Chromatograph	Disc Chart	Infotronics CRS-100	Hewlett-Packard 3370A
Perkin-Elmer 800	0.30, 0.27	0.23, 0.21	-
Hewlett-Packard 7624A	0.30, 0.30	-	0.27, 0.28
Aroclor 1242 (Lot KK 491):			
Perkin Elmer 800	5.88, 5.78	6.22, 5.94	-
Hewlett-Packard 7624A	6.14, 6.32	-	6.63, 6.50

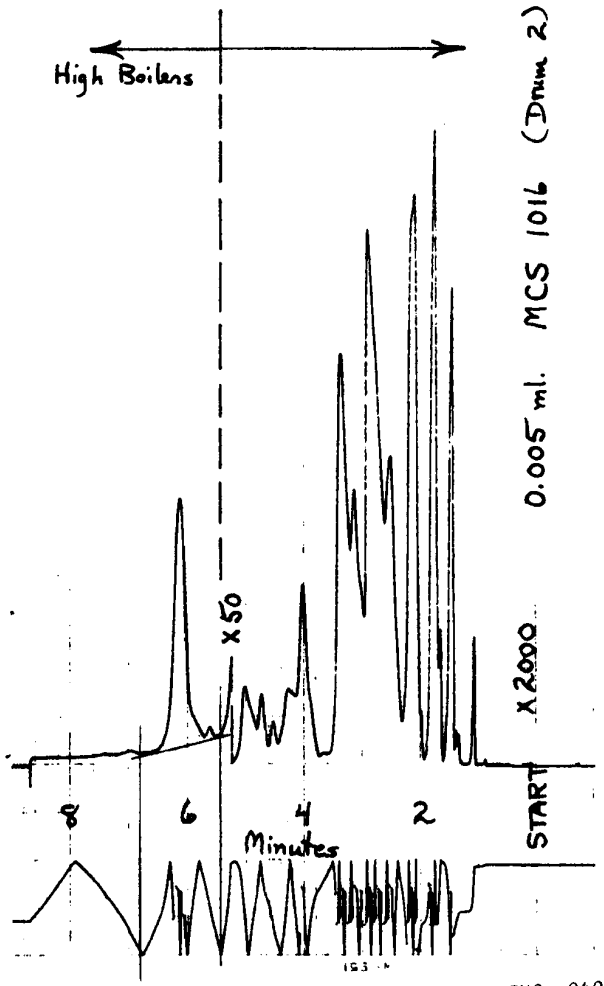
*Portions of these samples are available to those Monsanto laboratories that are setting up this method for control of MCS 1016 manufacture.

db

Monsanto Company
Organic Chemicals Division
Applied Sciences Section
St. Louis, Missouri

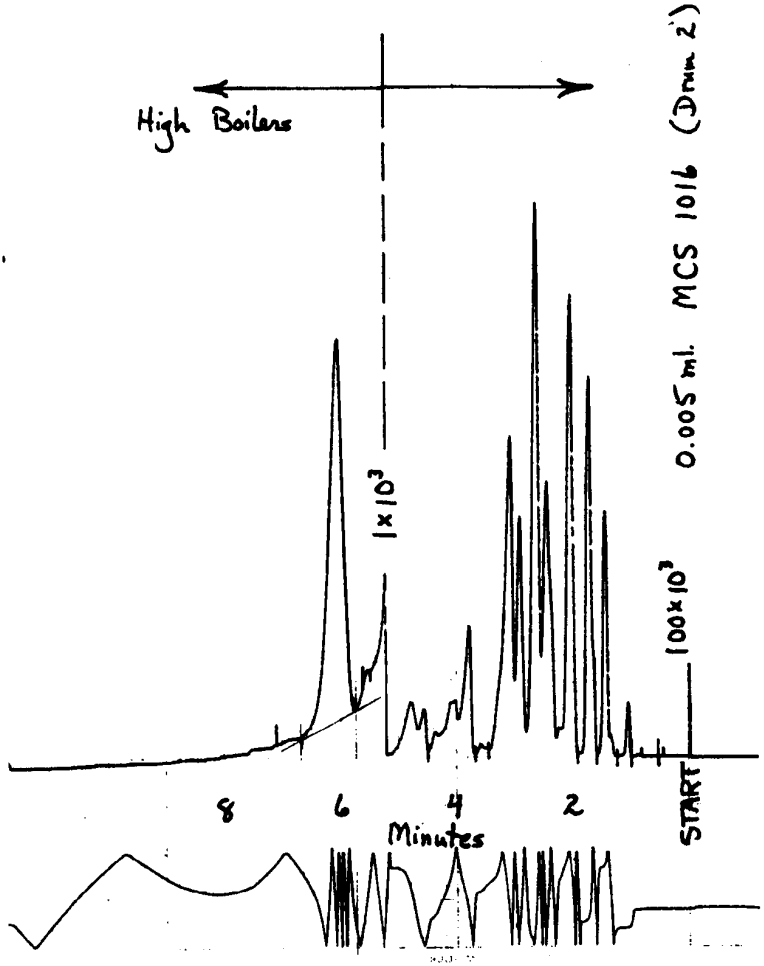
5/71 - G. M. Gasser, E. M. Emery

Perkin-Elmer 800

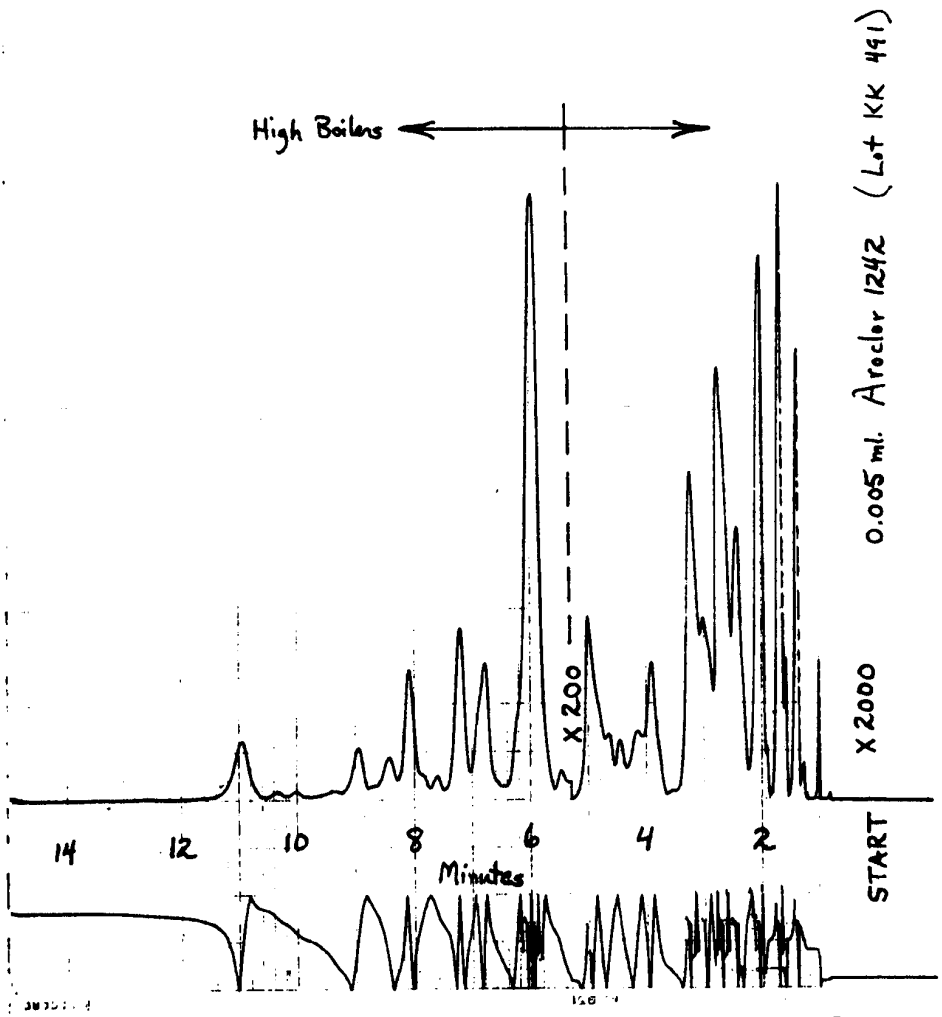


MONS 040845

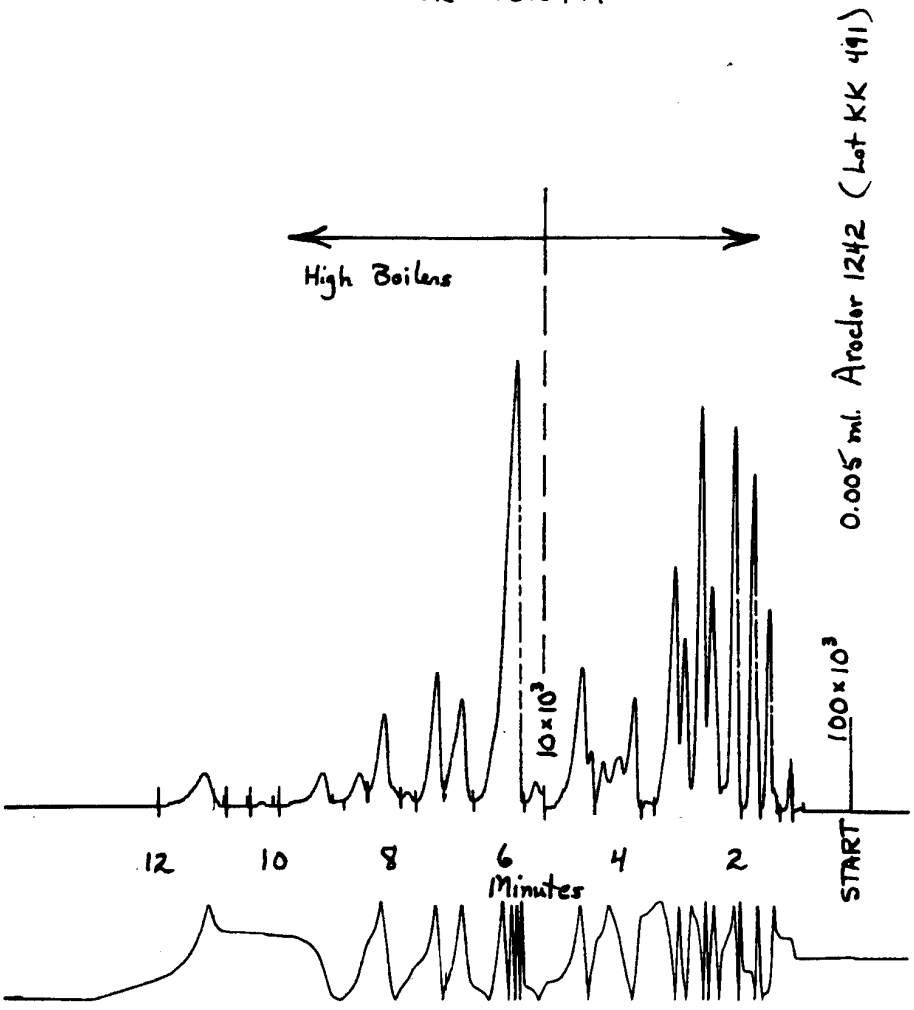
Hewlett-Packard 7624A



MONS 040846


Perkin - Elmer 800
High Boilers
0.005 ml. Aroclor 1242 (Lot KK 491)
X 200
X 2000
START
14
12
10
8
6
4
2
Minutes
MONS 040847

Hewlett-Packard 7624A



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