1-35

Chemical Research Report No. 833

CONFIDENTIAL

INTERIM REPORT

DEGRADATION OF AROCLORS

MONSANTO CHEMICAL COMPANY
RESEARCH AND ENGINEERING DIVISION
Chemical Research Department
Dayton, Ohio

Job No.: 4-4042

Written: July 29, 1954

Typed: November 5, 1954

Chemists:
A. S. Kenyon
W. A. White

Prepared by:
A. S. Kenyon
W. A. White

0690365

Chemical Research Report No. 833 Copy No. 3

DISTRIBUTION SHEET

	Copy No.
J. J. Healy - St. Louis	1
H. G. Johnson - "	2
Central Report Files- "	3
H. K. Nason - "	4
H. L. Hubbard - "	5
A. M. Ellenburg - "	6
E. W. Gluesenkamp	7
R. L. Jenkins	8
R. A. Ruehrwein	9
A. S. Kenyon	10
Extra	11
Extra	12
Extra	13

0690366

TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

TABLES

FIGURES

I. INTRODUCTION

Monsanto manufactures large quantities of chlorinated biphenyls (Aroclor series 12) which are sold as dielectric fluids. Research to improve the Aroclors is part of a continuing program within Monsanto for better products. Degradation of Aroclors, which leads to loss in electrical resistivity, is one of the shortcomings of these dielectrics, especially since only very minor degradation could cause serious breakdown in electrical equipment. The purpose of this study was to determine what factors are involved in degradation and what can be done to prevent the degradation. This study resulted from customer requests for higher stability in Aroclors in order that better electric equipment might be produced.

II. SUMMARY

Since the stability of Aroclors depends upon the degree of chlorination, the variation of Aroclor structure as it affects stability was determined by ultraviolet absorption spectra.

The variation between fractions of fractionated Aroclor 1242 and of unfractioned Aroclor 1254 was studied by ultraviolet absorption spectra. The thermal degradation of fractionated 1242 was measured at 250°C. and the amount of hydrogen chloride liberated was determined.

Aroclor 1242 was degraded by ultraviolet light in vacuo and the decrease in electrical resistivity with irradiation time was measured. It was possible to remove the conducting material and restore the resistivity to its original value by passing the degraded material over activated alumina. However further exposure of the purified Aroclor to radiation again lowered the resistivity. The plot of resistivity versus time of irradiation resembled a conductivity versus concentration curve for a weak electrolyte. The resistivity of the photodegraded Aroclor reached a constant value after approximately 24 hours irradiation but degradation evidently continued since the yellow color increased with time of irradiation.

Some information on the conducting material produced in Aroclor degradation was obtained by adding various types of compounds which could act as precursors for the conducting material and observing the effects of these additives when the mixture is irradiated. Possible precursors were used

because the conducting material could not be isolated from the degraded mixture.

Additional information on the degradation mechanism was obtained by prototype studies using chlorobenzene. As a result a reasonable mechanism has been postulated for the photodegradation of Aroclor and other halogenated aromatic compounds.

The effectiveness of several organometallic compounds as photostabilizers for Aroclor was measured; of those tested, tetraethyl lead was the most effective.

III. CONCLUSIONS

The loss of electrical resistivity is caused by the photodegradation of the Aroclor molecule itself but may also be affected to a minor extent by trace impurities. The amount of degradation is small but nevertheless sufficient to cause the resistivity to decrease below an acceptable minimum.

The thermal degradation of Aroclors is minor compared to the photochemical degradation. Thermal treatment causes release of a small amount of hydrogen chloride initially, but this evolution ceases after a short time. Such behavior is attributed to thermal degradation of impurities. If Aroclor is irradiated then exposed to a thermal treatment, appreciably more hydrogen chloride is liberated. This indicates that the hydrogen chloride is developed by a photoreaction and that the photodegraded material is more unstable than Aroclor itself.

The primary reaction occurring in the photodegradation of Aroclor or other halogenated aromatic compound at wave lengths greater than 2800 Å is the homolytic cleavage of the carbon-chlorine bond to give an aromatic or aromatic-substituted free radical and a free chlorine atom. This free chlorine atom can enter into further reactions in a number of ways. The chlorine atom can abstract a hydrogen atom and form hydrogen chloride or it may form an addition compound with Aroclor or a halogenated aromatic compound.

The loss of resistivity can be attributed to the formation of hydrogen chloride and a conducting chlorine addition compound which contains a number of phenyl groups attached to an aliphatic or alicyclic carbon bearing a chlorine. As such a complex possesses sufficient planarity for resonance

stabilization, a stable carbonium ion can be formed in the Aroclor medium.

Aroclors cannot be completely stabilized by additives which scavenge hydrogen chloride since the conductivity is only partially due to liberated hydrogen chloride. The proposed degradation mechanism indicates that the free chlorine atom and its reactions are responsible for the loss of resistivity. Elimination of chlorine atoms before they react will stabilize Aroclor against photodegradation. Stabilization by the use of metallic organic compounds, such as tetraethyl lead or diphenyl dibutyl tin, offers some possibility.

The ultraviolet absorption spectra for Aroclors show the characteristic absorption due to resonance of the coplanar benzene rings except for those Aroclors that possess resonance-restricting ortho substitution.

Aroclors will degrade photochemically regardless of the purity of the sample since the Aroclor molecule itself is unstable. No amount of purification will stabilize the Aroclor. Stabilization can only be accomplished by the use of additives.

The rate of degradation of Aroclors is accelerated by the addition of impurities such as phenyl alkanes or chlorine-substituted phenyl alkanes.

The degradation of chlorobenzene, a prototype for Aroclor, shows the formation of hydrogen chloride and the loss of electrical resistivity due to the formation of chlorine addition compounds which eventually lead to highly substituted phenyl alkanes. The mechanism of the chlorobenzene photodegradation is considered representative of Aroclor degradation.

IV. USES AND APPLICATIONS

Aroclors may be stabilized by certain metallic organic compounds. Tetraethyl lead exhibits the greatest stabilizing effect of many compounds tested but leads to a slight precipitate. This additive, as well as similar ones, should be further evaluated and its possible use as a photostabilizer should be brought to the attention of our customers.

V. REFERENCES

A. Literature References

1. Berberich, L. J., and Friedman, R., Ind. Eng. Chem. 40, 117 (1948).

2. Hantzch, A., and Jochem, E., Ber. 34, 3337 (1901).

3. Noyes, W. A., Organic Synthesis, Vol. 2, page 108.

4. Brown, H. C., and Fletcher, E. A., J. Am. Chem. Soc. 73, 2808 (1951).

5. Ziegler, K., and Mathes, W., Ann. 479, 111 (1930).

6. Pray, H.A.A., J. Phys. Chem. 30, 1477 (1926).

7. Lindsey, R. V., Jr., and Ingraham, J. N., J. Am. Chem. Soc. 75, 5613 (1953).

B. Patent References

1. Jenkins, R. L. (to Monsanto), U.S. 2,578,359. December 11, 1951. "Stabilization of halogenated organic compounds with dibutyl diphenyl tin."

2. Clark, F. M. (to General Electric), U.S. 2,468,544. April 26, 1949. "Stabilized halogenated compositions and electrical devices."

3. Jenkins, R. L. (to Monsanto), U.S. 2,646,403. July 21, 1953. "Halogenated aromatic hydrocarbon dielectrics.

4. Hardy, E. E. (to Monsanto), U.S. 2,566,196. August 28, 1951. "Chlorinated aromatic dielectrics."

5. Carothers, W. H. (to Du Pont), U.S. 2,008,003. July 16, 1935. "Lead phenolate."

6. Mack, G. P. (to Advance Solvents), U.S. 2,628,211. February 10, 1953. "PVC resins stabilized with polystannoxanediol esters."

C. Reference to Previous Work at Monsanto

1. White, W. A., and Ruehrwein, R. A., Central Research Report No. 543, January 11, 1949. "Light stability of electrical resistivity of Aroclor 1254.

VI. EXPERIMENTAL WORK

A. Raw Materials

All Aroclor samples used in these experiments were supplied by the Inorganic Division at Anniston, Alabama. The following Aroclors were used:

Aroclor 1221	Lot 47-741
Aroclor 1232	
Aroclor 1242	Lots 152 and 170
Aroclor 1248	Lot 1705
Aroclor 1254	Lot 1851
Aroclor 1260	Lot 1379
Aroclor 1262	Lot 16
Aroclor 1268	Lot 18.

The sources of the stabilizers, precursors, etc. are given in Tables IV and VI. All materials synthesized in this laboratory for these experiments are noted in these Tables and the syntheses are described elsewhere in this report.

B. Apparatus

1. Aroclor degradation

a. Thermal degradation

This apparatus, shown in Fig. 1, consists of a pot furnace containing Dow Corning Fluid 200 as an oil bath, a bubbler tube containing the Aroclor sample, and an HCl trap containing standardized NaOH. Nitrogen was bubbled through the oil bath to prevent polymerization and through the sample bubbler tube to sweep the HCl over into the HCl trap. Knobs were blown on the HCl trap to give the gas bubbles longer contact time with the NaOH solution.

b. Photochemical degradation

In the preliminary irradiations the samples, contained in a beaker and stirred with a magnetic stirrer, were irradiated by an S4 lamp, placed about 8 in. from the beaker. A reflecting baffle was placed around the entire set-up.

A calculation from the specific extinction coefficient of Aroclor 1242 showed that 50% of the light of 3000 Å was absorbed in a distance of 1 μ. Therefore, an

apparatus was set up, as shown in Fig. 2, in which an ever changing film of Aroclor could be irradiated. This apparatus consisted of an irradiation box with an elliptical reflecting surface inside. The sample tube was placed at one focal point of the ellipse and rotated by a motor to form a thin film on the wall of the sample tube. A S-4 sun lamp was placed at the other focal point of the elliptical reflecting surface. Two fans on the back of the apparatus pulled air through the box, thereby cooling the sample tube.

2. Continuous primary degradation of chlorobenzene

An attempt was made to degrade and to collect continuously the primary degradation products of chlorobenzene, without further degrading them. The apparatus used, shown in Fig. 3, consisted of a 200-ml. round-bottom distillation flask, a distillation column, a condenser, a quartz irradiation zone, a return line and trap and an AH-4 sun lamp. The flask was sealed to the distillation column and the return trap and was fitted with a thermometer well and filling tube. The chlorobenzene was charged to the flask, which was then sealed off under vacuum. The distillation column was wrapped with asbestos tape, while the flask, condenser and trap were protected from irradiation by tin foil; thus, only the quartz irradiation zone was exposed to light. An elliptical reflecting shield was placed around the irradiation zone and the AH-4 lamp and the apparatus was covered from above with tin foil. This increased the efficiency of the AH-4 lamp. The inner tube in the irradiation zone caused the distillate to spread in a thin film.

3. Resistivity measurements

The resistivities were measured with a General Radio Megohm bridge, Type 544B. The three conductivity cells, made by J. C. Balsbaugh Co., had an approximate capacity with air as the dielectric of 50 $\mu\mu$ f. and cell constants of 550, 555 and 574 cms. respectively. All resistivities were measured at 25° ± .03 C.

C. Experiments

1. Thermal degradation

Thermal degradation experiments were carried out at 250°C. on various Aroclors as shown in Table I and at 243°C. on various fractions of Aroclor 1242 as shown in Table II. The sample to be evaluated was placed in the apparatus, Fig. 1, and brought to the desired temperature.

Nitrogen was passed through the sample to sweep the HCl liberated by the thermal degradation into the HCl trap. After various heating cycles, as shown in Tables I and II, the sample of 0.02N NaOH in the HCl trap was removed and acidified with 2 ml. of 0.9N HNO_3. Then, 2 ml. of 0.018N $AgNO_3$ was added and the chloride ion was determined turbidimetrically. It was found that hydrogen chloride was only evolved during the first 3-1/2 hrs. and that additional heating produced no more hydrogen chloride. The additional 1-1/2 hr. or a total of 5 hrs. heating was adopted to insure complete removal of all hydrogen chloride.

Aroclor 1242, Lot 170, was photodegraded in air for 240 hrs. and then thermally degraded at 243°C. for 5 hrs. The photodegraded Aroclor liberated 22.6×10^{-6} g. of HCl per gram of Aroclor during the above thermal degradation, compared to 2.13×10^{-6} g. of HCl when this Aroclor was subjected to heat alone.

2. Ultraviolet absorption spectra

The ultraviolet absorption spectra of Aroclors 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 and various fractions of Aroclors 1242 and 1254 were measured with a Cary Recording Ultraviolet Spectrophotometer. These spectra were measured on approximately 0.0006% solutions of the Aroclors in absolute alcohol using a 1-cm. cell. The results are shown in Figs. 4-10 expressed as specific extinction coefficient versus wave length in mμ's. The specific extinction coefficient is defined as

$$K = \log {}^{I_0}/_{I} \Big/ {}_{bc} \quad \text{or} \quad \frac{\text{optical density}}{\text{cell thickness in cms} \times \text{conc. in g./liter}}$$

The ultraviolet absorption spectra were also measured on several lots of Aroclor 1242 submitted by Anniston. The results are shown in Table III for Aroclor 1242, Lots 166, 170, 174, 179, 181. These results are tabulated since plots of extinction coefficients vs. wave length were so similar that little or no difference was detectable. The slight differences between lots are more clearly shown in the Table giving optical density and specific extinction coefficient for each wave length.

3. Photodegradation

Aroclor 1242 was photodegraded in air for 100 hrs.,

in the first photodegradation apparatus described above. During this treatment the volume resistivity of the Aroclor changed from 9.7×10^{11} ohm cms. to 1.4×10^{11} ohm. cms. A 50% solution of the degraded Aroclor in heptane was then separated chromatographically by passage through a column of activated alumina. A very dark yellow band appeared at the top of the column while the Aroclor-heptane solution was clear, resembling unirradiated Aroclor. After the heptane was distilled off, the recovered Aroclor 1242 had a resistivity of 1.2×10^{12} ohm cms. The recovered Aroclor was again exposed to the S-4 lamp for 240 hrs. and the irradiated sample was recovered as described; its resistivity was 1.3×10^{11} ohm. cms.

The isolation of the degraded material from Aroclor which was adsorbed on alumina was attempted by treatment of the column with heptane. After 50 washes with heptane, the eluate still contained 0.0118 g. Aroclor 1242/liter, while the brown layer had not moved during elution. Other solvents ranging in polarity from hydrocarbons to water were tried as eluants but none was effective. Since these washings did not separate the adsorbed material, isolation of the degraded materials by this method was abandoned.

Aroclor 1242 was irradiated in vacuo for a total of 210 hrs. by the S-4 lamp in the elliptical irradiation apparatus (Fig. 2). At intervals samples were removed and the resistivity was measured. A plot of resistivities vs. time of irradiation is shown in Fig. 11. The initial resistivity of 1×10^{12} ohm cms. dropped rapidly during the first 24 hrs. of irradiation but the drop thereafter was only slight. The final resistivity after 210 hrs. exposure was 1×10^{11} ohm cms.

The resistivity stability of Aroclor 1262 was compared with that of Aroclor 1242 upon irradiation for one-half and for five hrs. Benzene (25% by weight) was added to the Aroclor 1262 to facilitate handling. The measured resistivities (ohm cms.) are as follows:

	Initial	1/2 hr.	5 hrs.
Aroclor 1242	7.7×10^{11}	6.9×10^{10}	9.9×10^{9}
75% Aroclor 1262, 25% benzene	1.2×10^{12}	2.1×10^{11}	7.3×10^{10}

It was considered that Aroclor could contain some impurities which would lead to the formation of conducting materials on irradiation and that such impurities might be oxygen-, nitrogen-, or sulfur-containing compounds which should be removable by washing with conc. H_2SO_4. Aroclor 1242, Lot 152, was extracted three times with conc. H_2SO_4 and then washed with water, alcoholic KOH and finally with distilled water until the washings were neutral. The Aroclor was dried by a vacuum technique. Its resistivity was 1.93×10^{10} ohm-cms. compared to 7.7×10^{11} ohm cms. The Aroclor was then passed over alumina, and the resistivity rose to 8.2×10^{12} ohm cms. The H_2SO_4-washed Aroclor was irradiated 20 hrs. by the S-4 lamp and the resistivity dropped to 1.9×10^{10} ohm cms. compared to a resistivity of 2.5×10^{10} ohm cms. for untreated Aroclor after 20 hrs. irradiation. From these results it was concluded that acid washing did not affect the degradation.

The photodegradation of Aroclor 1242 in the presence of diphenyl picryl hydrazyl (DPPH) was also followed by its change in resistivity. Very little change was observed since the conductivity of the DPPH was high, causing low initial resistivity.

4. Effect of added impurities

Phenyl-substituted methyl chlorides have been shown to be electrolytes in non-aqueous media (A.5) and it was considered likely that this type of compound could be material formed upon irradiation of Aroclor. It was further thought that this type of conducting material could be formed from small amounts of impurities, such as phenyl alkanes or their chlorinated derivatives, which could be present in Aroclor. For example, it is known that stilbene is an impurity in raw biphenyl.

Accordingly a number of compounds were added to Aroclor at a concentration of 0.5% to determine if the loss of resistivity would be accelerated upon irradiation in the presence of these additives. It was believed that such experiments might reveal the kind of impurity that could be acting as a precursor for the conducting substance. The Aroclor solutions were irradiated for 5 hrs. by the S-4 lamp, samples being removed after 1/2 hr. for resistivity measurements. The results of these additives are shown in Table IV.

Compounds of the triphenylmethyl chloride type were shown to be conductors in an Aroclor media by measuring

the resistivities of Aroclor 1242, Lot 170, containing various concentrations of triphenylmethyl chloride (up to 0.37%) at 25°C. The plot of concentration of triphenylmethyl chloride vs. resistivities is shown in Fig. 12. The resemblance of this curve to the conductivity curve of a weak electrolyte indicates that triphenylmethyl chloride acts as a weak electrolyte in Aroclor. It was considered that the presence of a substance containing an excess of electrons might be essential for the stabilization of the carbonium ions; however, when this was tried, using benzophenone as the source of excess electrons, a negligible effect on the resistivity resulted, which indicated that the carbonium ion needed no further stabilization.

Aroclor 1242 could contain as an impurity a small amount of a substance bearing an excess of electrons which could stabilize the carbonium ion formed upon addition of triphenylmethyl chloride. Such an impurity, if present, should be removable by conc. H_2SO_4. If it is necessary to have a compound bearing an excess of electrons in order to stabilize triphenylmethyl chloride, then H_2SO_4-washed Aroclor should not conduct when triphenylmethyl chloride is added. Acid washed and dried Aroclor 1242 containing added triphenylmethyl chloride had the following resistivities:

Wt. % ϕ_3CCl	Resistivity at 25°C.
0.000	2.1×10^{12} ohm cms.
0.0652	2.4×10^{9} ohm cms.
0.314	3.7×10^{8} ohm cms.

5. Reduction of resistivity by hydrogen chloride

Hydrogen chloride has been reported to be a conducting material in Aroclor (A.1). Further measurements on the conductivity of hydrogen chloride in Aroclor were made by modifying a Balsbaugh conductivity cell so that dry hydrogen chloride gas was bubbled directly into the cell containing Aroclor 1242 and the resistivities of the solution were followed as a function of time. The results and conditions of the experiments are shown in Table V. In 10 minutes the resistivity had dropped from 5×10^{12} ohm cms. to 2.4×10^{10} ohm cms., at which point the minimum resistivity level had been reached and additional hydrogen chloride bubbling did

not further decrease the resistivity. The cell was heated to 100°C. and dry nitrogen was bubbled through the Aroclor to sweep out the entrained hydrogen chloride. The resistivity returned to 2.0×10^{12} ohm cms., or essentially the original value.

Aroclor 1242 was photodegraded until its resistivity was 7.8×10^{9} ohm cms. Nitrogen was bubbled through this degraded Aroclor in the conductivity cell at 100°C. The resistivity level after the bubbling was 4.4×10^{10} ohm cms.

Hydrogen chloride was added to chlorobenzene and the resistivity was measured. The addition of HCl reduced the resistivity from 3.2×10^{12} ohm cms. to 6.3×10^{8} ohm cms., but bubbling nitrogen through the solution (that is, sweeping out the HCl) raised the resistivity to 1.5×10^{11} ohm cms. Failure of the chlorobenzene to return to its original resistivity may be partially due to dissolved hydrogen chloride, since no heat was applied during the nitrogen sweeping.

6. Chlorobenzene reactions

a. Reaction of chlorobenzene with benzenediazonium chloride

Since benzenediazonium chloride splits thermally to give a phenyl radical and a chlorine atom, its reaction products in the presence of chlorobenzene should be similar to products obtained during chlorobenzene photodegradation. This is based on the assumption that the primary photochemical reaction of chlorobenzene is the homolytic cleavage of the carbon-chlorine bond.

To 150 ml. of distilled chlorobenzene in a 300 ml. flask 28.5 g. benzenediazonium chloride was added. The reaction mixture was allowed to stand for four weeks at room temperature, protected from atmospheric moisture by a calcium chloride drying tube. The rate of reaction was so slow that very small bubbles of nitrogen could be seen coming off only occasionally. After four weeks at room temperature, reaction was allowed to continue for 16 hours at 45°C. and 24 hours at 50°C. The reaction at the elevated temperatures was carried out in a bomb room, by remote control.

After the above treatment, the excess benzenediazonium chloride was filtered off. Hydrogen chloride was identified as one of the reaction products. The filtrate

was distilled by a high-vacuum and low-temperature distillation and separated into three fractions. The refractive indices of the fractions were as follows:

	N_{25}^{D}
Number 1	1.5095
Number 2	1.5212
Number 3	1.5215
Distilled chlorobenzene	1.5214

The fractions and the residue were analyzed by infrared and the results showed little or no difference between samples.

b. Photodegradation of chlorobenzene

The continuous irradiation apparatus shown in Fig. 3 was charged with 150 ml. of distilled chlorobenzene. The liquid was frozen with liquid nitrogen and the apparatus was evacuated. The freezing, pumping and thawing cycle was continued until all dissolved gases were removed. The liquid and apparatus was finally pumped to a pressure of 1 x 10^{-5} mm. of Hg and sealed off. The liquid was distilled from the reservoir, condensed in the irradiation zone and then returned to the reservoir. This continuous distillation and irradiation was continued for 482 hours. Initial boiling point of the chlorobenzene was 50°C., and the final boiling point was 60°C.

The reaction mixture was analyzed by infrared and ultraviolet. The ultraviolet spectra of irradiated chlorobenzene and the reaction products of chlorobenzene and benzenediazonium chloride showed strong absorption at 287 mμ, attributed to an addition compound of chlorobenzene and chlorine. Infrared analyses were not significant.

c. Chlorine addition to chlorobenzene

An addition compound of chlorine to chlorobenzene was made by filling a 500-ml. flask with chlorine and adding 10 ml. of distilled chlorobenzene. The flask was stoppered and irradiated by an AH-4 lamp for a short time. The liquid was freed of the excess chlorine by a low-temperature distillation. An ultraviolet spectrum of this addition mixture, compared with that of chlorobenzene, showed a very strong absorption at 287mμ.

Infrared spectra of (1) photodegraded chlorobenzene, (2) benzenediazonium chloride-chlorobenzene reaction product and (3) chlorobenzene with known addition compounds showed (Fig. 14) a slight shoulder on the C-H aromatic band, which indicated that an aliphatic or alicyclic structure is present in all mixtures.

7. Stabilizers

The stabilizing effects of various additives were determined by measuring the volume resistivities of the Aroclor containing the additive before and after 5 hours irradiation. All irradiations were carried out in the irradiation apparatus shown in Fig. 2. The concentration of the additive was 0.1% by weight unless noted otherwise. The compounds tested and the resistivities of Aroclor containing them are shown in Table VI.

8. Syntheses of compounds

a. Triethanolamine borate

Triethanolamine borate was synthesized from triethanolamine and boric acid in 68% yield, using the method described by H. C. Brown and E. A. Fletcher (A.4).

b. Trisdibutylstannanediol

Trisdibutylstannanediol was prepared by hydrolyzing dibutyl tin diacetate by steam. This procedure is described in U.S. Patent 2,628,211 (B.6) issued to Mack of Advance Solvents & Chemical Corp.

c. Triethyl lead phenolate

Triethyl lead phenolate was prepared by the action of tetraethyl lead upon phenol as described by Carothers in U.S. Patent 2,008,003 (B.5).

d. Chlorinated diphenylmethane

Diphenylmethane was vacuum distilled through a Vigreux column pressure and the fraction boiling at 132°C./14 mm. was collected; $N_D^{25} = 1.5734$ ($N_D^{17} = 1.57884$ reported). The purified diphenylmethane was chlorinated by bubbling chlorine gas through 34.5 g. of the hydrocarbon at a rate of 1/3 mole per hour, with the temperature maintained at 120°C. Iron clippings were used as a catalyst. In order to prevent

chlorination by a free radical mechanism, light was eliminated from the glass tube reactor by immersing it in a sand bath surrounded by a steel casing. After 4-1/2 hours, the chlorination was stopped, the product was distilled and the distillate was collected at 130-152°C./1-5 mm., b.p.=130°C./1 mm.

Anal. Calc. for $C_{13}H_{11}Cl$: C, 77.41; H, 5.46; Cl, 17.13. Found: C, 80.64; H, 5.91; Cl, 13.45 (by diff.).

The tarry residue was dissolved in benzene and extracted with water. The benzene solution was distilled to remove the water and solvent. The dry product was a fine brown powder melting near 95°C. (not sharp) was obtained. Analysis showed 9.25% chlorine.

e. Chlorinated triphenylmethane

Triphenylmethane (10.8 g.) was chlorinated in the same manner as the preceeding synthesis. The temperature was allowed to reach 142°C. After 1-1/2 hours, the chlorine flow was stopped and the material crystallized into a dark reddish brown mass upon cooling.

Anal. Calc. for $C_{13}H_{15}Cl$: C, 82.16; H, 5.41; Cl, 12.43. Found: C, 86.74; H, 6.56; Cl, 6.7 (by diff.).

In both of the above reactions the desired degree of chlorination was not reached; however, it was thought that some of the desired product was present.

f. Benzenediazonium chloride

Benzenediazonium chloride was prepared according to Hantzch and Jochem (A.2) by reaction of amyl nitrite with aniline hydrochloride. The amyl nitrite was prepared as described by Noyes (A.3). In this synthesis 38 g. (0.55 moles) C.P. sodium nitrite was dissolved in 150 cc. of water and cooled to 0°C. To this cooled mixture a solution containing 10 cc. water, 13.6 cc. conc. H_2SO_4 and 44 g. n-amyl alcohol was added dropwise in 1-1/2 hours. The water layer was separated and the amyl nitrite was washed with sodium bicarbonate and sodium chloride solutions and finally was dried over anhydrous sodium sulfate.

A mechanically stirred mixture of 22 g. of aniline hydrochloride dissolved in 60 ml. of glacial acetic acid was cooled to 0°C. To this was added during 2 hours

25 g. of amyl nitrite. The benzenediazonium chloride was precipitated by slowly dropping in anhydrous ether (two volumes of ether to one of solution). This addition required 3-1/4 hours. The precipitated diazonium compound was filtered off and washed with anhydrous ether until free of acetic acid. The benzenediazonium chloride could be stored under ether but at no time was it allowed to be dry. Benzenediazonium chloride is explosive and must be handled with extreme care.

VII. DISCUSSION

A. Thermal Degradation of Aroclors

Aroclors 1221, 1232, 1242, 1248 and 1254 were thermally degraded at 250°C. and all liberated hydrogen chloride. It is seen from Table I that 1221, 1232 and 1242 liberate approximately the same amount of hydrogen chloride, while less is liberated from Aroclors 1248 and 1254. Apparently the higher Aroclors are more stable to thermal degradation. Since any of the Aroclors contains a mixture of compounds of various degrees of chlorination, it is reasonable to expect that all would produce some degradation products. It seems that 1242 contains such a possible combination as to give maximum degradation.

The Research Laboratory at Anniston, Alabama, fractionated Aroclor 1242 into ten fractions and these fractions were thermally degraded at 250°C. for 5 hours (Table II). Only the first three fractions liberated hydrogen chloride, the greatest amount being liberated from the first fraction. Fraction No. 4 showed only a slight trace of hydrogen chloride while higher fractions liberated none at all.

It was also significant that hydrogen chloride was no longer liberated from any of the samples after approximately the first 3-1/2 hours. These data would indicate that the degradation by some trace impurity was occuring and after depletion of this material no further thermal degradation took place during this heating cycle. When these fractions were photodegraded and then heated, additional hydrogen chloride was liberated. These data would indicate that unstable impurities could be formed within the Aroclor as a result of photodegradation or aging and that the loss of resistivity could be attributed to products arising from the Aroclor molecule itself.

Thermal degradation studies on fractionated Aroclor 1254 were not performed but it is expected that results similar to those with Aroclor 1242 would have been obtained; that is, hydrogen chloride would have been released in the early fractions, but not from the higher boiling fractions.

B. Ultraviolet Spectra of Aroclors

The plots of specific extinction coefficient against wave length in millimicrons (Figs. 4 and 5) for Aroclors 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268 show a gradual decrease in the absorption band at 246 mμ which disappears in Aroclor 1248 and those higher. This absorption band is due to coplanarity resonance between the benzene rings. It is absent in Aroclors higher than 1248, in which coplanarity resonance is hindered by ortho chlorination: even one chlorine atom in the ortho position is sufficient to eliminate this resonance.

The ultraviolet absorption spectra of fractionated Aroclor 1242 show little difference between fractions, with the exception of Fraction No. 1: the absorption curve for Fraction No. 1 shows little absorption due to coplanarity resonance, whereas curves for other fractions show a strong band at mμ. This fraction also liberated the greatest quantity of hydrogen chloride during thermal degradation.

The ultraviolet absorption spectra of various lots of Aroclor 1242 show little or no difference between lots.

C. Photodegradation of Aroclors

It is shown in Fig 11 that the resistivity of Aroclor 1242 rapidly decreases during irradiation, but reaches an essentially constant lev after approximately 24 hours. The shape of this plot resembles the plot of conductivity versus concentration for a weak electrolyte. Even though the resistivity reaches a constant value, degradation continues since the color continues to darken.

The colored material can be adsorbed from the Aroclor by activated alumina and the resistivity of the recovered Aroclor is thereby restored to its original high value. Further exposure of the purified Aroclor to irradiation causes a further decrease in resistivity. If this colored extract from the Aroclor is added to untreated Aroclor, a drop in the resistivity occurs, showing that the conducting material is contained in the colored extract.

It was shown that hydrogen chloride in Aroclor lowers its resistivity but that hydrogen chloride can be freed from the Aroclor by bubbling nitrogen through the Aroclor, thereby restoring the original high resistivity. Photodegraded Aroclor could not be returned to its original resistivity by bubbling nitrogen through the degraded Aroclor at 100°C. for a period of 24 hours. Since the resistivity was restored partially by this treatment, it is believed the hydrogen chloride was removed but some other conducting material remained. These results indicate that the conducting materials in degraded Aroclor could be hydrogen chloride and some high-boiling material.

Photodegradation of Aroclor takes place in the presence or absence of oxygen with loss of resistivity; however, the reduction of resistivity is more pronounced in the absence of oxygen. All experiments in this study were carried out in the absence of oxygen.

Trace impurities are always a possible source of degradation reactions in any system. Impurities were considered to be present in the Aroclor and these were considered to be nitrogen-, sulfur- or oxygen-containing compounds which should be removable by concentrated H_2SO_4 washes. After several treatments with concentrated H_2SO_4, the purified Aroclor underwent photodegradation with loss of electrical resistivity at essentially the same rate as unpurified Aroclor. These data indicate that the degradation products were being developed from the Aroclor itself.

The thermal degradations indicated that hydrogen chloride was produced from some impurity and after depletion of this impurity, no further hydrogen chloride was liberated. To determine the source of the degradation, Aroclor 1242, Lot 170, was irradiated and then heated. The amount of hydrogen chloride liberated from this Aroclor was ten times greater than from Aroclor subjected to thermal degradation alone. It is concluded that a thermally unstable compound which liberates hydrogen chloride is produced in the photodegradation, and it is also reasonable to believe that the Aroclor contains traces of such a compound, developed during handling and storage.

Determination of the chemical constitution of the conducting material was attempted by first isolating the material on activated alumina. The color was removed from the degraded Aroclor and the resistivity was restored by the alumina adsorption purification. However, the material was

so tightly bound to the alumina that it could not be completely eluted. After 50 washes with heptane, the heptane still showed 0.0118 g. of Aroclor per liter, indicating some original Aroclor on the alumina. The alumina was then eluted with ethanol and finally with 0.1N KOH. Even after all these treatments, the colored band remained on the alumina. Other materials for adsorbing the conducting material were tried (silica gel, sugar, charcoal, etc.) but without success. Since it could not be ascertained whether some reaction occurred with the alumina and since the colored material could not be completely eluted from the alumina, this method of isolating the conducting material was abandoned.

Extraction of the photodegraded Aroclor was tried with conc. H_2SO_4. The acid washings were diluted 5:1 with water and the temperature was kept below 50°C. The benzene extract of the acid washings yielded a brown, waxy material, the infrared and ultraviolet spectra of which were anomalous.

Since attempts to isolate and identify the conducting material had failed, it was considered possible that insight as to the nature of the precursor for the conducting material might be obtained by addition of various types of compounds to the Aroclor. The additives tried are described in Sect. VI-C-4.

D. Effect of Addition of Impurities

Phenyl-substituted methyl chlorides have been shown to be electrolytes in non-aqueous solvents (A.5), and it is possible that compounds of this type would be the conducting material in Aroclor. This possibility was explored by adding triphenylmethyl chloride to Aroclor and following the resistivity as a function of concentration. The resulting curve was similar to the equivalent conductance curve for a weak electrolyte.

For such compounds to be conductors they must have resonance stabilization of the carbonium ion or there must be present some trace materials possessing an excess of electrons for stabilization. Benzophenone is known to act as a stabilizer for carbonium ions. However, the addition of benzophenone to Aroclor containing a small amount of triphenylmethyl chloride does not further lower the resistivity of the mixture. If stabilization of the carbonium ion had required the presence of an excess of electrons, then the addition of benzophenone should have lowered the resistivity considerably. It was concluded that substances such as

triphenylmethyl chloride posses sufficient resonance stabilization to render the carbonium ion stable.

If phenyl-substituted aliphati. .hloride compounds are the conductors formed in irradiated Aroclor, the question arises whether these compounds are formed from impurities or from Aroclor itself. It was thought that the effects of various phenyl-substituted methanes and their chlorine derivatives (Table IV) on Aroclor resistivity would give some idea of the nature of the precursor for the conducting material in Aroclor. A comparison of the drop in resistivity of Aroclor upon irradiation in the presence of the various additives with that of the Aroclor alone reveals that all of the additives accelerate the loss of resistivity. It is therefore concluded that, in general, a phenyl alkane can be a precursor for conducting material. It is not necessary for the phenyl alkane to be chlorinated initially, as the dissociating chlorine atom, which leads to conduction by the assumed conducting material, is added to the precursor during the photochemical reactions. Addition of phenyl alkane chlorides, for example, causes decrease in the resistivity, even without irradiation. It is known that the greater the phenyl substitution on the aliphatic chlorine-bearing carbon, the greater is the conductivity.

Carbonium ion must be planar in order to be stable. Compounds produced in the degradation of Aroclor could possess a number of phenyl groups and could possess sufficient planarity for resonance stabilization of the carbonium ion. However, if the ortho positions are filled in Aroclor, then the compounds produced could not arrange themselves into a planar configuration and therefore no conducting material could be produced through the formation of carbonium ions. The fact that Aroclor 1262 (62% chlorinated) is more stable than Aroclor 1242 (42% chlorinated) indicates that less conducting material is formed when the ortho position is blocked. Since Aroclor 1262 contains some molecules that are not chlorinated in the ortho position, it is expected that some degradation should occur. The higher degree of chlorination aids in the photostability of the Aroclors due to restriction of the resonance and thus reduces the concentration of the carbonium ion formed.

The photodegradation of Aroclor undoubtedly proceeds via a free radical mechanism. An attempt was made to follow the rate of generation of the free radicals by reaction with diphenyl picryl hydrazyl (DPPH) dissolved in Aroclor and observing the change in resistivity with time. The diphenyl

picryl hydrazyl solution was placed in a special cell arranged so that the irradiation took place in a portion of the cell where light could not strike the metal surfaces of the electrodes. Significant results were not obtained since the DPPH had some initial conductivity and degradation produced only a very small change in the resistivity. No further work was done to purify the DPPH.

The study with possible precursors had given some insight into how conducting substances could be formed but determination of the actual compound was difficult due to the complexity of the Aroclors. These complications led to the use of a prototype, chlorobenzene, for further identification of the conducting material.

E. Prototype Studies

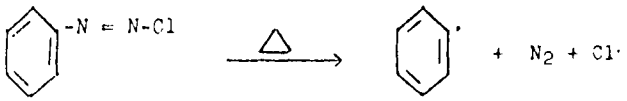
Chlorobenzene has an absorption band at approximately 2200 Å due to the cleavage of the carbon-chlorine bond. This is measured on very dilute solutions. In pure chlorobenzene this absorption is shifted to higher wave lengths and the absorption is apparently sufficient at wave lengths above 3000 Å to cause some degradation, since it was shown that the resistivity of pure chlorobenzene was lowered by irradiation.

As with Aroclor 1242, it was not possible to restore photodegraded chlorobenzene to its original high resistivity by bubbling dry nitrogen through the degraded material. An attempt to remove the conducting material by freezing, evacuation, thawing, refreezing and re-evaluation was not effective.

Fractionation of photodegraded chlorobenzene yielded a dark residue as the final fraction. The infrared spectrum of this residue, compared to that of chlorobenzene, indicated a shift in the CH absorption band, attributable to a trace of aliphatic or alicyclic carbon. There were also indications of para and meta substitution. Ultraviolet spectra show a strong absorption at 287 mμ.

The logical photodissociation of chlorobenzene would be the homolytic cleavage of the C-Cl bond to give a phenyl radical and a chlorine atom as the primary reaction. To test these reactions, the thermal degradation of benzenediazonium chloride in presence of chlorobenzene was studied since several workers (A.6,7) have shown that benzenediazonium chloride

is thermally unstable and the reaction is as follows:



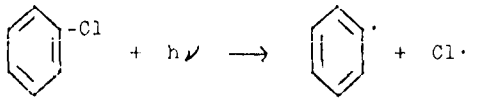
Considerable proof exists for this reaction and the resulting products formed through the free radical mechanism. If such radicals are produced thermally, then the reaction of these radicals with chlorobenzene should produce the same products as the photodegradation of chlorobenzene if the primary reaction is the homolytic cleavage of the carbon-chlorine bond. The ultraviolet and infrared spectra of the products of the reaction of the diazonium chloride with chlorobenzene were similar to spectra of photodegraded chlorobenzene.

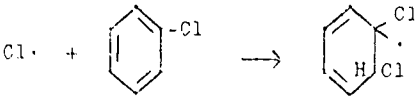
Lindsey and Ingraham (A.8) have studied the photodegradation of 1-chlorocyclohexene and have concluded that the primary reaction is the homolytic cleavage of the carbon-chlorine bond. They found cyclohexene, cis-1,2-dichlorocyclohexane, 3,3'-dichloro-1,1'-bi-2-cyclohexenyl and 3-(1'-cyclohexenyl)-1-chlorocyclohexene as reaction products. These products show that all possibilities are formed from the radicals and that the chlorine atom can add to the double bond in the cyclohexene ring. From these results it is reasonable to expect that aromatic compounds such as chlorobenzene could undergo essentially the same types of reactions, especially the homolytic cleavage of the carbon-chlorine bond plus the addition of the chlorine to the aromatic ring. Such reactions would be expected to take place to a lesser extent with the aromatic compounds, however.

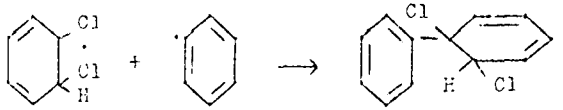
It is seen in Fig. 13 that the ultraviolet spectra of (1) a chlorine addition compound of chlorobenzene (Curve B), (2) the reaction products of benzenediazonium chloride (with chlorobenzene (Curve A) and (3) irradiated chlorobenzene show a characteristic absorption band near 285 mμ, when compared with the spectrum of distilled chlorobenzene. The infrared spectra of these three preparations plus the spectrum of chlorobenzene are shown in Fig. 14. Curve I in Fig. 14 shows only the characteristic C-H absorption of an aromatic group in the 3.3μ region. Curves II, III and IV show similar absorption plus an additional absorption at slightly longer wave lengths, attributable to the presence of addition compounds. It is to be noted in Curve III, Fig. 14, that the

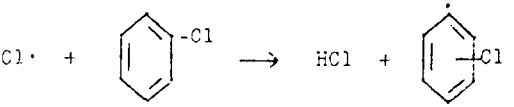
residue from photodegraded chlorobenzene (Curve B, Fig. 13) shows considerable shift, indicating that the addition products are concentrated in the higher boiling residue. Also the resistivity of all the treated chlorobenzene mixtures are low. From these data, it can be concluded that the conducting material arises from the chlorine addition compounds which contain some aliphatic carbons bearing a chlorine atom.

From the data and those of Lindsey and Ingraham (A.7) it is possible to write a mechanism for the photodegradation of chlorobenzene as follows, to account for the behavior of chlorobenzene under photodegradative conditions:

(1) 

(2) 

(3) 

(4) 

Reaction (1) is the homolytic cleavage of C-Cl bond and represents the primary reaction. Reaction (2) shows the addition of the chlorine atom to the benzene ring. Reaction (3) shows the reaction of the addition complex with phenyl radicals to produce a compound which could possess sufficient resonance energy so that the carbonium ion would be stable. The exact nature of the conducting material was not identified. With such radicals produced in the primary reaction, hydrogen chloride could be produced by the action of a chlorine atom with a hydrogen on the ring. In any case the

conducting material in the chlorobenzene degradation must arise from secondary reactions of the chlorine atom.

The phenyl radicals are free to enter into other reactions, which could produce color or polyphenyls but it is not considered possible that they could produce conducting materials. The reaction of Aroclors and other chlorinated organic compounds could be expected to follow a similar pattern.

F. Aroclor Stabilization

From the postulated mechanism for the degradation of chlorobenzene, it is seen that elimination of the free chlorine atom is essential if the Aroclor is to be successfully stabilized. Stabilizers must have the following characteristics:

(1) The stabilizer must be a non-conductor.
(2) The stabilizer must react rapidly with chlorine atoms.
(3) The resulting product must be non-conducting.

Stabilizers for Aroclor which operate by scavenging the hydrogen chloride liberated cannot be expected to do an efficient stabilization job since they are ineffective in preventing the formation of the chlorine addition complex.

Although not investigated here to any extent, another effective stabilization method could be the elimination of the primary reaction by screening out that radiation which causes the cleavage of the C-Cl bond.

From the results listed in Table VI it is seen that tetraethyl lead was the most effective stabilizer tested. A slight precipitate occurred with this stabilizer which might affect its use. Diphenyl dibutyl tin was not quite so effective.

Compounds such as Uvinul 490, 2-dodecyl-9,10-anthraquinone and Ponsul Yellow could only act as ultraviolet screening agents and would not be effective in removing the hydrogen chloride or the chlorine atoms. None of these additives was an effective stabilizer.

A number of the additives tried as stabilizers caused an initial decrease in resistivities of the Aroclor, but it is suspected that in many cases this is due to trace impurities which are conductors.

It has recently been found at Anniston that phenoxypropene oxide is a good thermal stabilizer and is not covered by adverse patents. This compound was evaluated as a light stabilizer but was found to be ineffective.

Many of the additives that were found to be photostabilizers for Aroclors are covered by patents, which claim such compounds as hydrogen chloride scavengers but which do not cover photostabilization.

VIII. RECOMMENDATIONS

Aroclors can be stabilized by certain metallo-organic compounds such as tetraethyl lead. It is not certain what effects this compound will have on electrical equipment since a slight precipitate was formed during photodegradation of Aroclor containing it. It is to be pointed out that the degradations in this study represent accelerated and more severe degradation conditions than those obtained under use conditions. General Electric holds the basic patent on the addition of compounds of R_xM type to chlorinated biphenyls. It is also felt that G.E. has never studied the effect of this additive in Aroclor under photodegradative conditions since their original intent was a hydrogen chloride scavenger. The effect of tetraethyl lead as a photostabilizer for Aroclors should be brought to the attention of General Electric.

Monsanto holds the patent on diphenyl dibutyl tin as an additive for Aroclor. Although this compound is not as effective as tetraethyl lead, it does exhibit a marked photostabilizing action and further evaluation is in order.

The search for a more efficient stabilizer should be continued with attention to those compounds which will react readily with free chlorinators.

Additional Aroclor degradation studies should place more emphasis on prototype studies since with a prototype the number of product possibilities is reduced. From the data of this study, it is seen that the mechanism of degradation for the Aroclor prototype, chlorobenzene, is given from reasonably good evidence but has not been absolutely proved. Further study on the proof of this mechanism is indicated. Studies should include a positive identification of the products, quantum yields, and the wave length ranges effective in degradation.

Emphasis should not be placed solely upon purification of Aroclors as a means of stabilization since degradation has been shown to arise from Aroclor itself.

IX. DESCRIPTION OF RECOMMENDED PROCESS

Not applicable.

X. PATENT STATUS

A disclosure on the use of tetraethyl lead as a photostabilizer was submitted, but it is expected that this will be in direct comflict with a previous patent issued to Clark of General Electric (B.2).

Diphenyl dibutyl tin is protected by a Monsanto patent (B.1).

XI. COST ESTIMATES

Not applicable.

XII. ANALYTICAL PROCEDURE

The Balsbaugh conductivity cells must be subjected to a very rigorous cleaning procedure. This procedure was recommended by the research group from Anniston and is also that used by General Electric. Unless the cells are thoroughly cleaned as described below reproducible results cannot be obtained. The cleaning procedure recommended is as follows:

(1) Drain cell and fill with trichlorobenzene and heat at 100°C. for 15 minutes.

(2) Drain hot trichlorobenzene and rinse with cold trichlorobenzene.

(3) Rinse at least twice with methanol.

(4) Rinse with water.

(5) Fill with a saturated solution of trisodium phosphate and heat at 100°C. for 15 minutes.

(6) Rinse with distilled water several times and dry in an oven at 120°C. for at least 1 hour.

The resistance of the Balsbaugh cell shows a drift with time after the voltage from the Megohm bridge is applied across the cell. This is due probably to polarization of the electrodes. The A.S.T.M. recommends that the voltage be applied for one minute and then the resistance be measured. Drift after one minute has been found to cause less than 10% change in the resistance. All resistivities were measured after the voltage had been applied for one minute. Care must be exercised in handling the cell in order to keep electrical leakage as low as possible when measuring these very high resistances.

The amount of hydrogen chloride liberated from the Aroclor was determined turbidimetrically by precipitating the chlorine as silver chloride and observing the quantity of light scattered at 90° by a Debye light scattering instrument. The amount scattered was compared with a calibration chart for determination of chloride ion present.

XIII. TOXICITY AND HAZARDS

The stabilizers used for Aroclors consist chiefly of metallo organic compounds such as tetraethyl lead or diphenyl dibutyl tin. These compounds are toxic and care should be exercised in handling them.

XIV. ACKNOWLEDGMENT

The assistance of Miss Ulm, Messrs. Beasecker and Loucks of the Spectrographic Group is acknowledged. Many helpful discussions were held with Drs. Johns and Ruehrwein and their suggestions were particularly valuable. Prof. Fuoss also contributed much to the discussions.

XV. APPENDIX

This report covers work recorded in the following note book pages:

257780
257784-87
261937
270638
270643-50
275151-59
275161
275171
275173-75
275181-82
275184-95
275197-200
279851-80
279885-87

Notebook pages continued.

279890-94
279896-900
280906-50
284652-54
284655-62
284664-68
284675
284693
287901-04
289905
289909
289912-13
289916
289922
289924
289928
289938-50
294004-05
294007
294009-20
294041
294046-47
297678

Je

TABLE I

THERMAL DEGRADATION OF AROCLORS AT 250°C.

Aroclor	g. of HCl/g. x 10^6	Heating Time
1221	3.34	1 hr.
	6.73	2 hr.
	11.07	5 hr.
1232	3.91	1 hr.
	6.42	2 hr.
	9.81	5 hr.
1242 Lot 152	5.96	1 hr.
	9.58	2 hr.
	13.00	5 hr.
1248	3.61	1 hr.
	5.44	2 hr.
	8.48	5 hr.
1254	3.43	1 hr.
	3.96	2 hr.
	6.43	5 hr.

0690398

TABLE II

THERMAL DEGRADATION OF FRACTIONATED AROCLOR 1242 AT 243°C.[1,2]

Fraction	Wt. % of Charge	B.P. Range °C./mm.[3]	g. HCl/g. Aroclor
1	4.6	146-169/ 10-11 mm.	6.6×10^{-6}
2	9.5	168-186/ 11-26 mm.	0.36×10^{-6}
3	10.0	169-196/ 26-40 mm.	0.35×10^{-6}
4	10.0	138-157	Very slight trace
5	10.1	157-159	0
6	10.1	159	0
7	10.4	159-162	0
8	10.3	162-167	0
9	10.3	154-177	0
10	11.4	177-197	0
Still bottom	2.4		

[1] The Aroclor was fractionated by the Inorganic Division at Anniston.

[2] All samples were heated 5 hrs. at 243°C. with N_2 bubbling through them.

[3] Pressure is 3 mm. except as noted.

0690399

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF AROCLOR 1242

Aroclor 1242, Lot 166
C=15.80 x 10^{-3} g./l.

λ	O. D.	Specific Extinction Coefficient
220	1.25	79.11
230	.68	43.04
240	.485	30.70
250	.44	27.85
260	.32	20.25
270	.163	10.32
280	.070	4.43
290	.03	1.90

Aroclor 1242, Lot 170
C=10.2 x 10^{-3} g./l.

λ	O. D.	Specific Extinction Coefficient
220	.892	87.45
230	.470	46.08
240	.33	32.35
250	.312	30.59
260	.21	20.59
270	.108	10.59
280	.050	4.90
290	.015	1.47

0690400

TABLE III (Contd.)

ULTRAVIOLET ABSORPTION SPECTRA OF AROCLOR 1242

Aroclor 1242, Lot 174
C=14.9 x 10^{-3} g./l.

λ	O. D.	Specific Extinction Coefficient
220	1.335	89.60
230	.71	47.65
240	.49	32.88
250	.44	29.53
260	.32	21.47
270	.163	10.94
280	.067	4.50
290	.031	2.08

Aroclor 1242, Lot 179
C=14.8 x 10^{-3} g./l.

λ	O. D.	Specific Extinction Coefficient
220	1.36	91.89
230	.725	48.99
240	.50	33.78
250	.455	30.74
260	.33	22.30
270	.16	10.81
280	.07	4.73
290	.033	2.23

Aroclor 1242, Lot 181
C=18.1 x 10^{-3} g./l.

λ	O. D.	Specific Extinction Coefficient
220	1.68	92.82
230	.895	49.45
240	.60	33.15
250	.55	30.39
260	.40	22.10
270	.19	10.50
280	.090	4.97
290	.035	1.93

TABLE IV

EFFECT OF VARIOUS ADDITIVES AS IMPURITIES IN AROCLOR 1242

Precursor, 0.5 Wt. %	Source of Additive	Resistivity in Ohm-cm. At Start	After 1/2 hr. Irradiation	After 5 hr. Irradiation
p-Chlorotoluene	E. K.	2.0×10^{12}	3.4×10^{10}	3.3×10^{10}
o-Chlorotoluene	E. K.	4.2×10^{12}	4.8×10^{10}	1.5×10^{10}
Toluene	C. R.	3.0×10^{12}	4.7×10^{10}	1.3×10^{10}
Aroclor 1242	Monsanto	7.7×10^{11}	6.9×10^{10}	9.9×10^{9}
Trans Stilbene	E. K.	1.5×10^{12}	1.0×10^{11}	9.8×10^{9}
Benzyl Chloride	Gen. Chem.	3.5×10^{10}	1.9×10^{10}	7.9×10^{9}
*Chlorinated triphenylmethane		8.0×10^{9}	4.6×10^{9}	3.2×10^{9}
Diphenylmethane	E. K.	1.7×10^{12}	6.1×10^{10}	2.0×10^{9}
*Chlorinated diphenylmethane	(Liq.)	5.3×10^{11}	5.3×10^{10}	1.0×10^{9}
*Chlorinated diphenylmethane	(Solid)	1.9×10^{12}	1.0×10^{10}	--
Triphenylmethane	E. K.	5.5×10^{11}	8.3×10^{9}	1.0×10^{9}
Triphenylmethyl Chloride	E. K.	5.0×10^{8}**	--	--

* Synthesized during this investigation.

** 0.369 Wt. %.

0690402

TABLE V

EFFECT OF DISSOLVED HCl ON THE RESISTIVITY OF AROCLOR 1242

Treatment	Resistivity of Non-Irradiated Aroclor	Resistivity of Irradiated Aroclor
START	5×10^{12} ohm-cm.	7.8×10^{9} ohm-cm.
HCl bubbled through at 25°C. until resistivity became constant	2.4×10^{10} ohm-cm.	Not treated
N_2 bubbled through at 100°C. for 2.5 hrs.	3.6×10^{11} ohm-cm.	2.2×10^{9} ohm-cm.
N_2 bubbled through at 25°C. for 16 hrs.	2.0×10^{12} ohm-cm.	3.8×10^{10} ohm-cm.
N_2 bubbled through at 100°C. for 4 hrs.	1.0×10^{12} ohm-cm.	--
N_2 bubbled through at 100°C. for 5 hrs.	--	4.4×10^{10} ohm-cm.

0690403

TABLE VI

STABILIZATION OF RESISTIVITY OF AROCLOR 1242

CONTAINING EXPERIMENTAL STABILIZERS**

Stabilizer	Source	Volume Resistivities at 25°C. in ohm-cms. Before	After 5 hrs. Irradiation
None		1.0×10^{12}	1.0×10^{10}
Tetraethyl lead	Ethyl Corp.	1.7×10^{12}	9.3×10^{11}
Diphenyldibutyl tin	Metal and Thermite	5.0×10^{11}	7.0×10^{10}
Di-2-ethylhexyl phenyl phosphate	C. R.	1.65×10^{11}	--
Dibutyl tin dilaurate	C. R.	5.86×10^{11}	7.6×10^{10}
Triethanolamine borate*		1.46×10^{11}	3.2×10^{10}
Bis(2-ethylhexyl)benzene phosphonate	C. R.	9.9×10^{10}	--
Diphenyl tin oxide	Metal and Thermite	Insoluble	
Triphenylstibine	E. K.	1.73×10^{11}	8.6×10^{8}
Dibutyl tin salicylate	C. R.	3.3×10^{11}	2.25×10^{10}
Benzalamine	Mathieson	7.9×10^{11}	8.65×10^{9}
Dibasic lead phosphite	Natl.Lead	Insoluble	
Barium-Cadmium laurate	Ferro	Insoluble	
Diacetate of dianhydro-trisdibutyl stannanediol*		5.75×10^{10}	--
Tetraethyl silicane	C. R.	1.39×10^{12}	1.06×10^{10}
Tetrabenzyl silicane	C. R.	1.27×10^{12}	3.3×10^{9}

0690404

TABLE VI (Contd.)

STABILIZATION OF RESISTIVITY OF AROCLOR 1242
CONTAINING EXPERIMENTAL STABILIZERS**

Stabilizer	Source	Volume Resistivities at 25°C. in ohm-cms. Before	After 5 hrs. Irradiation
Dibutyl tin maleate	Metal and Thermite	3.6×10^{10}	--
Triphenyl phosphite	C. R.	2.48×10^{11}	2.3×10^{9}
Diphenyl picryl hydrazyl	Harvard	4.2×10^{9}	--
General Dyestuff Corp. Uvinul 490		1.3×10^{10}	6.8×10^{9}
0.5 wt. % 2-dodecyl 9-10-anthraquinone	C. R.	1.2×10^{11}	3.8×10^{8}
0.15 wt. % aluminum isopropylate	Mathieson	2.5×10^{12}	1.8×10^{9}
Ponsul Yellow	C. R.	--	--
Phenyl salicylate	C. R.	--	--
1.0 wt. % d-limonene	E. K.	2.4×10^{11}	1.5×10^{10}*
Tetraphenyl germanium	C. R.	--	--
Hexaphenyl digermane	C. R.	--	--
Epoxidized Soybeanoil	Du Pont	--	--
Triethyl lead phenolate		1.43×10^{11}	--
0.5 wt. % Pinene	C. R.	--	1.5×10^{10}
0.5 wt. % Metal & Thermite's RS 31		--	4.7×10^{10}
Phenoxy propene oxide		8.9×10^{11}	8.6×10^{9}

C.R. - Chemical Research stock - source unknown or made in Laboratory previously.

* 20 hrs. Irradiation.
** Stabilizer concentration was 0.1% unless otherwise noted.

0690405

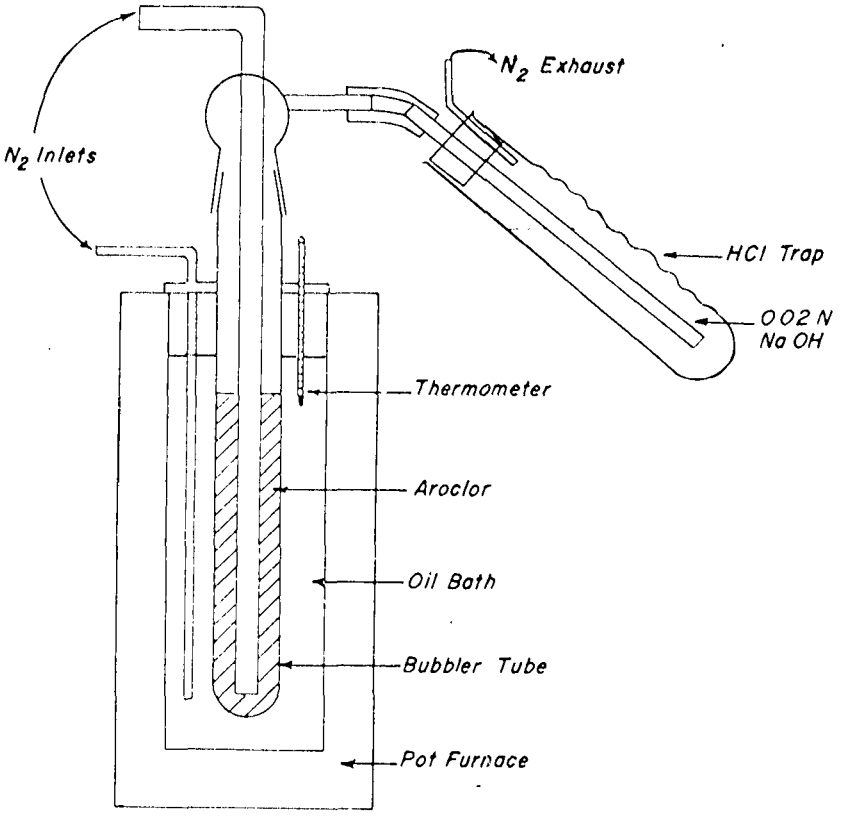
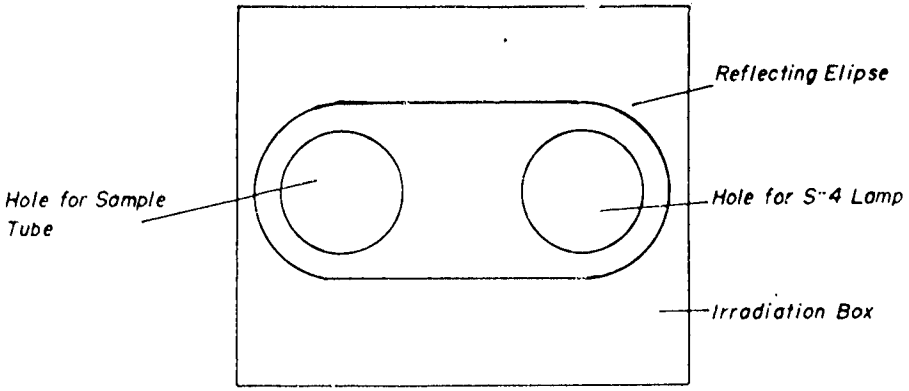


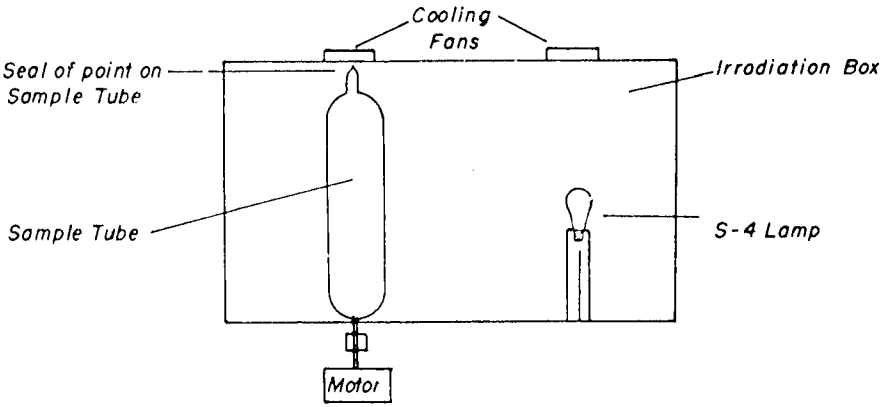
Fig. 1

THERMAL DEGRADATION APPARATUS

0690406



FRONT VIEW



TOP VIEW

Fig. 2

PHOTOCHEMICAL DEGRADATION APPARATUS

0690407

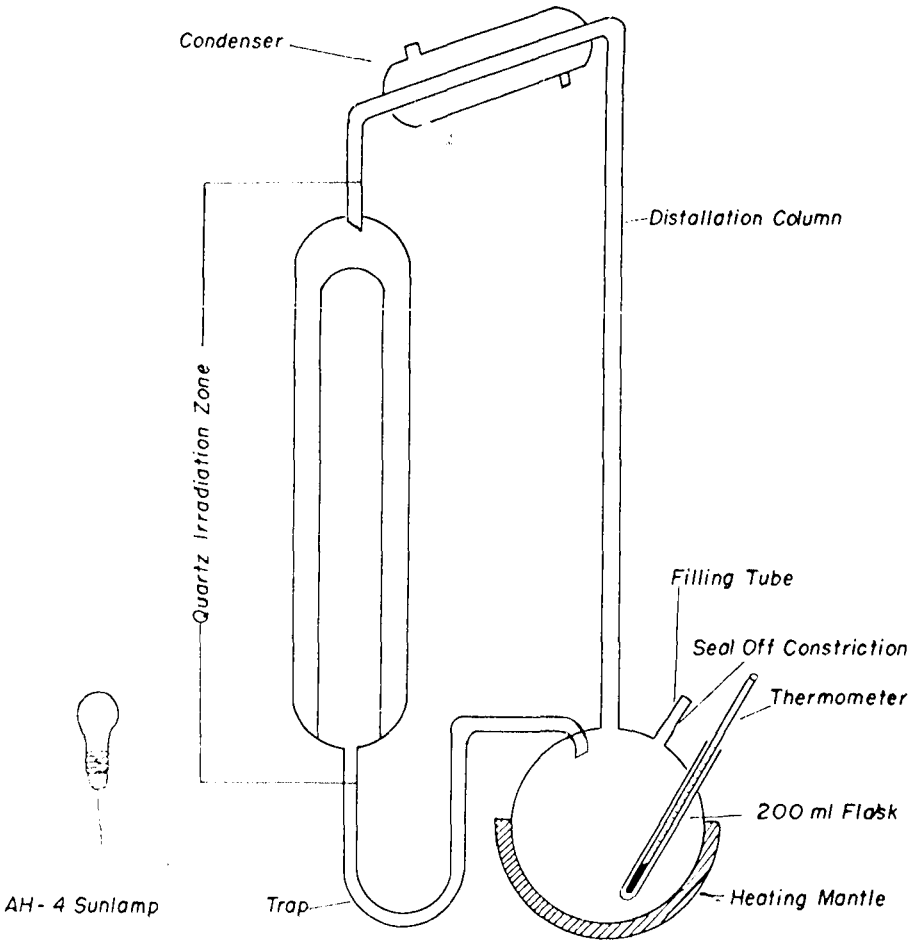
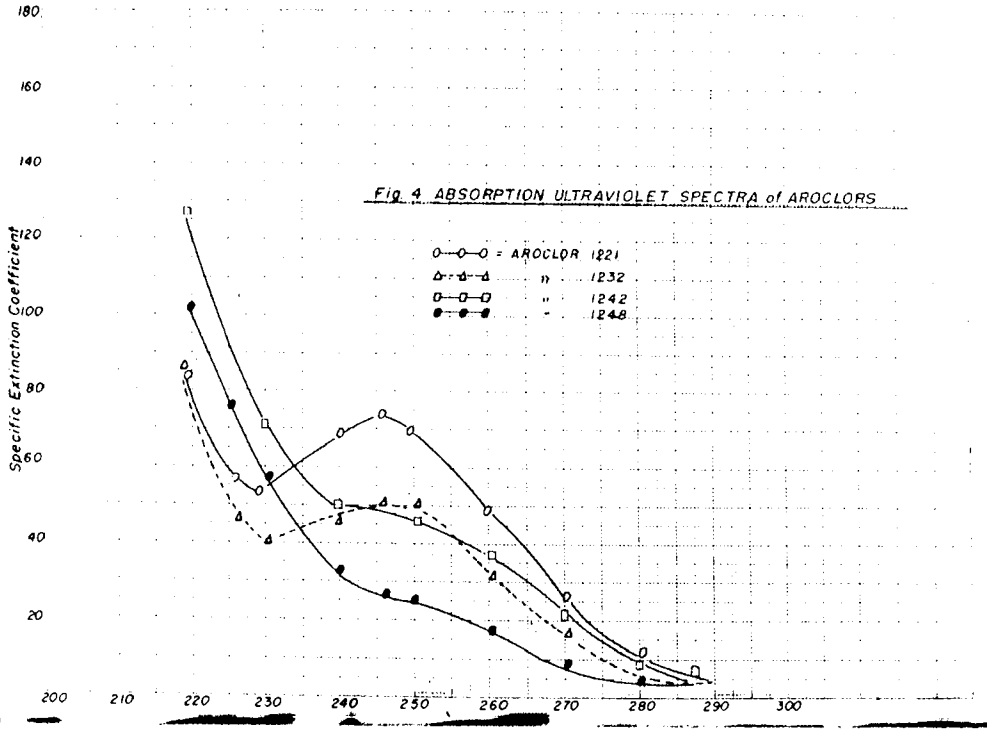


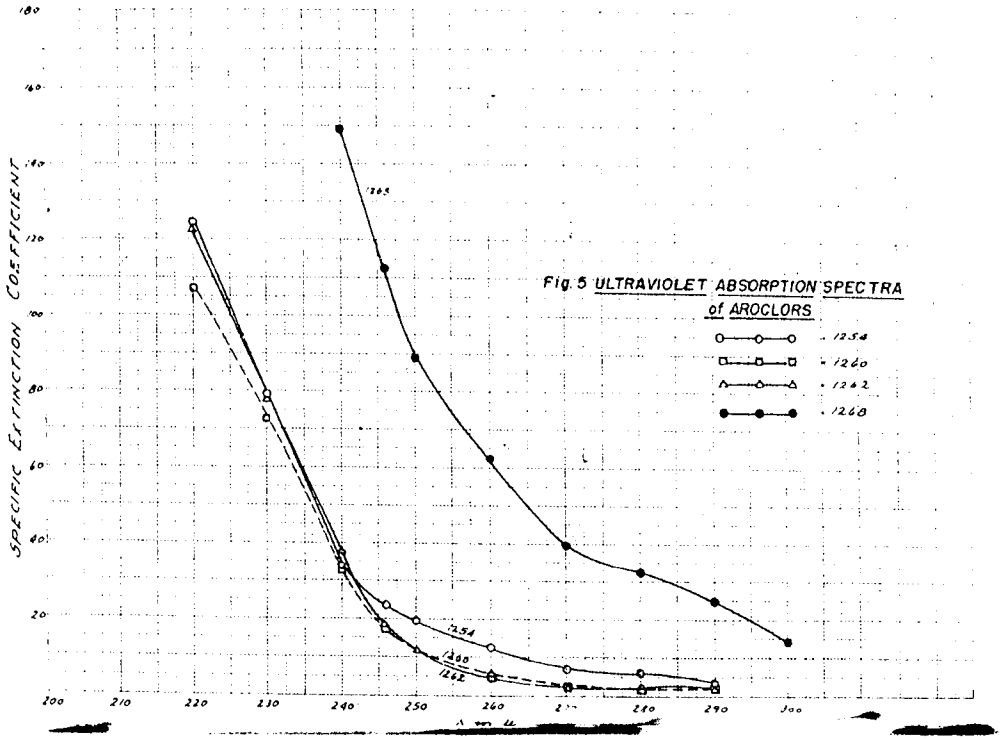
Fig. 3

CONTINUOUS PHOTOCHEMICAL DEGRADATION APPARATUS
for CHLOROBENZENE

0690408



0690409



0690410

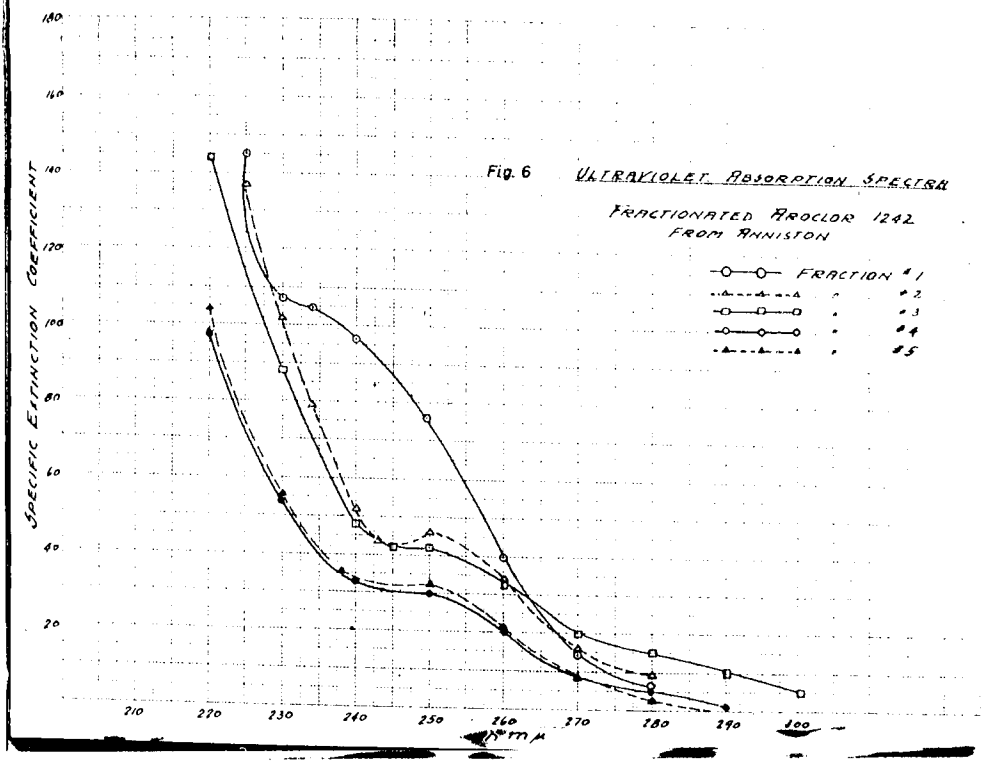


Fig. 6 ULTRAVIOLET ABSORPTION SPECTRA

FRACTIONATED AROCLOR 1242
FROM ANNISTON

0690411

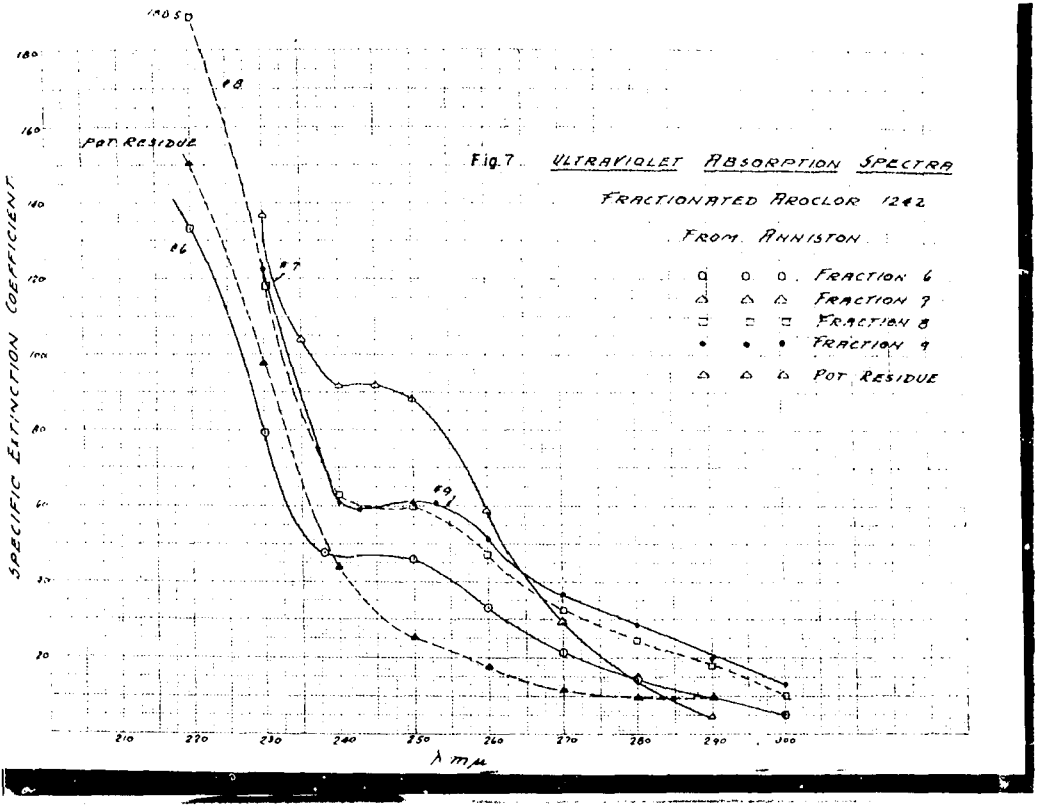


Fig. 7 ULTRAVIOLET ABSORPTION SPECTRA
FRACTIONATED AROCLOR 1242
FROM ANNISTON

0690412

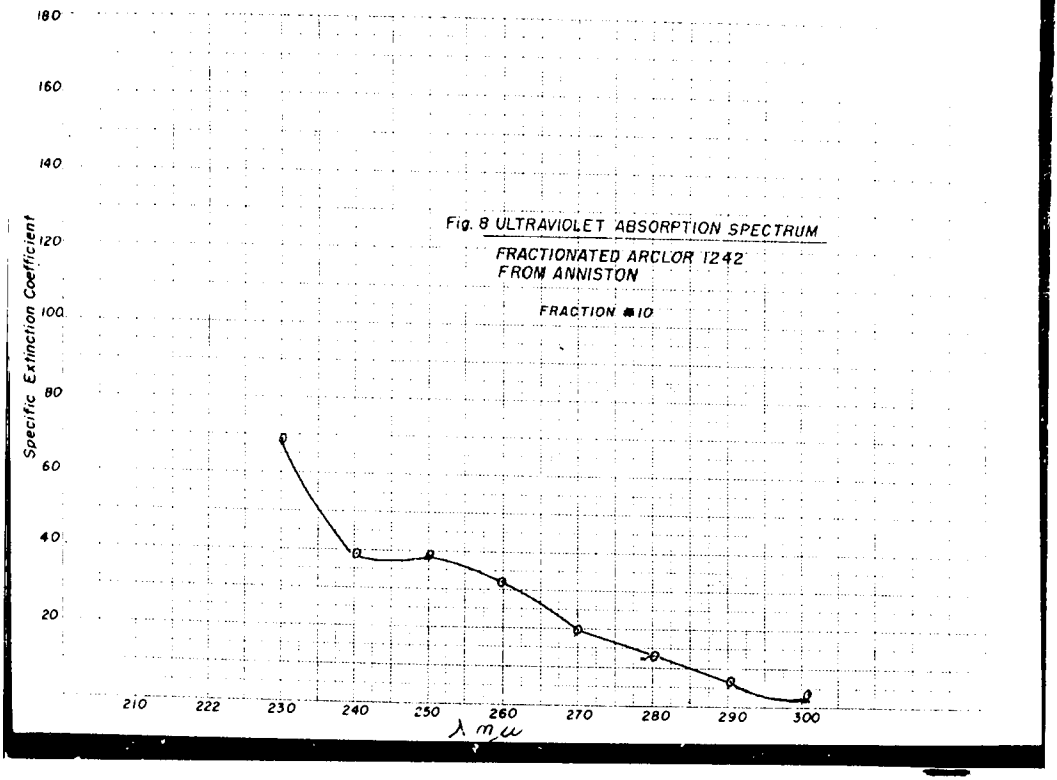
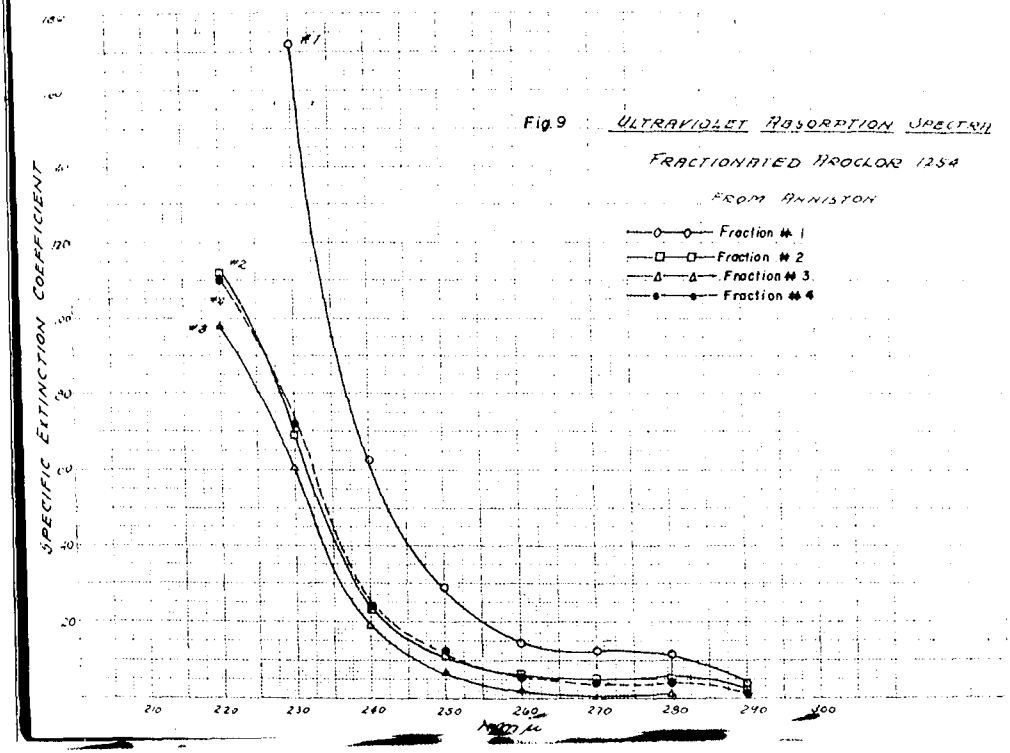
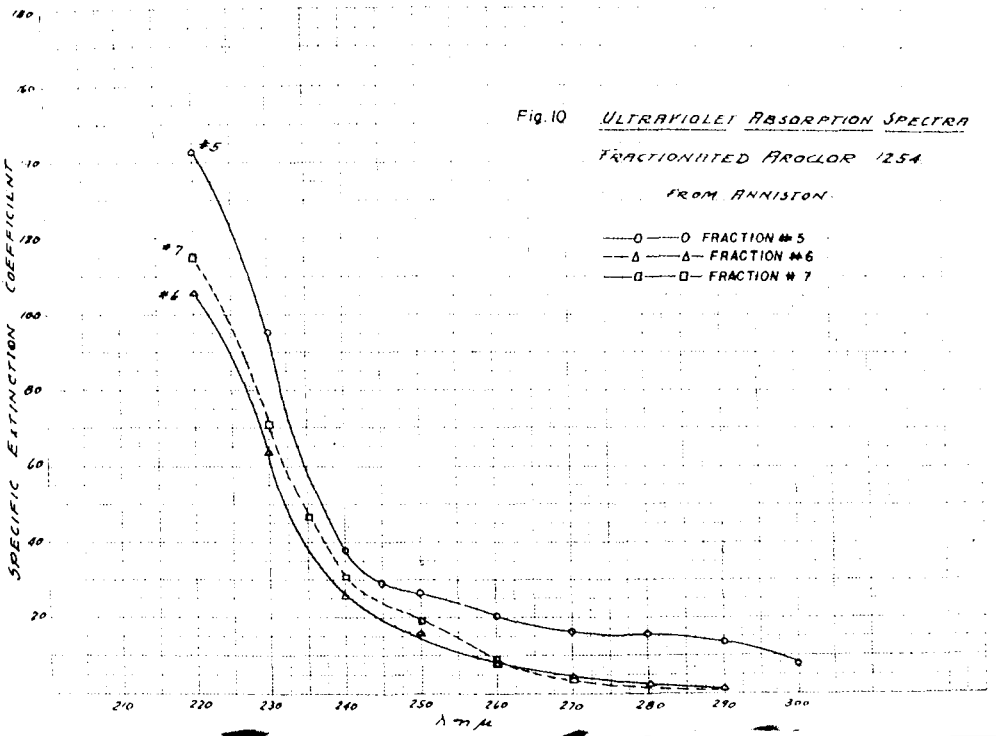


Fig. 8 ULTRAVIOLET ABSORPTION SPECTRUM
FRACTIONATED ARCLOR 1242
FROM ANNISTON
FRACTION #10

0690413



0690414



0690415

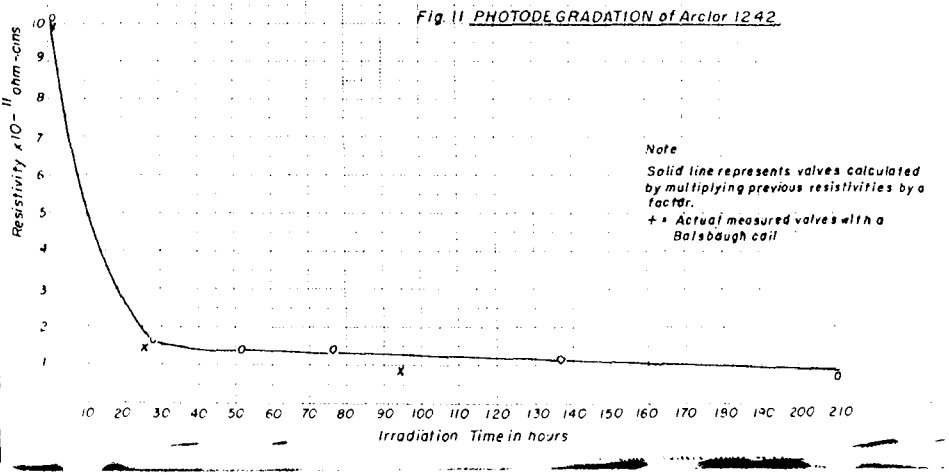


Fig. 11 PHOTODEGRADATION of Arclor 1242

0690416

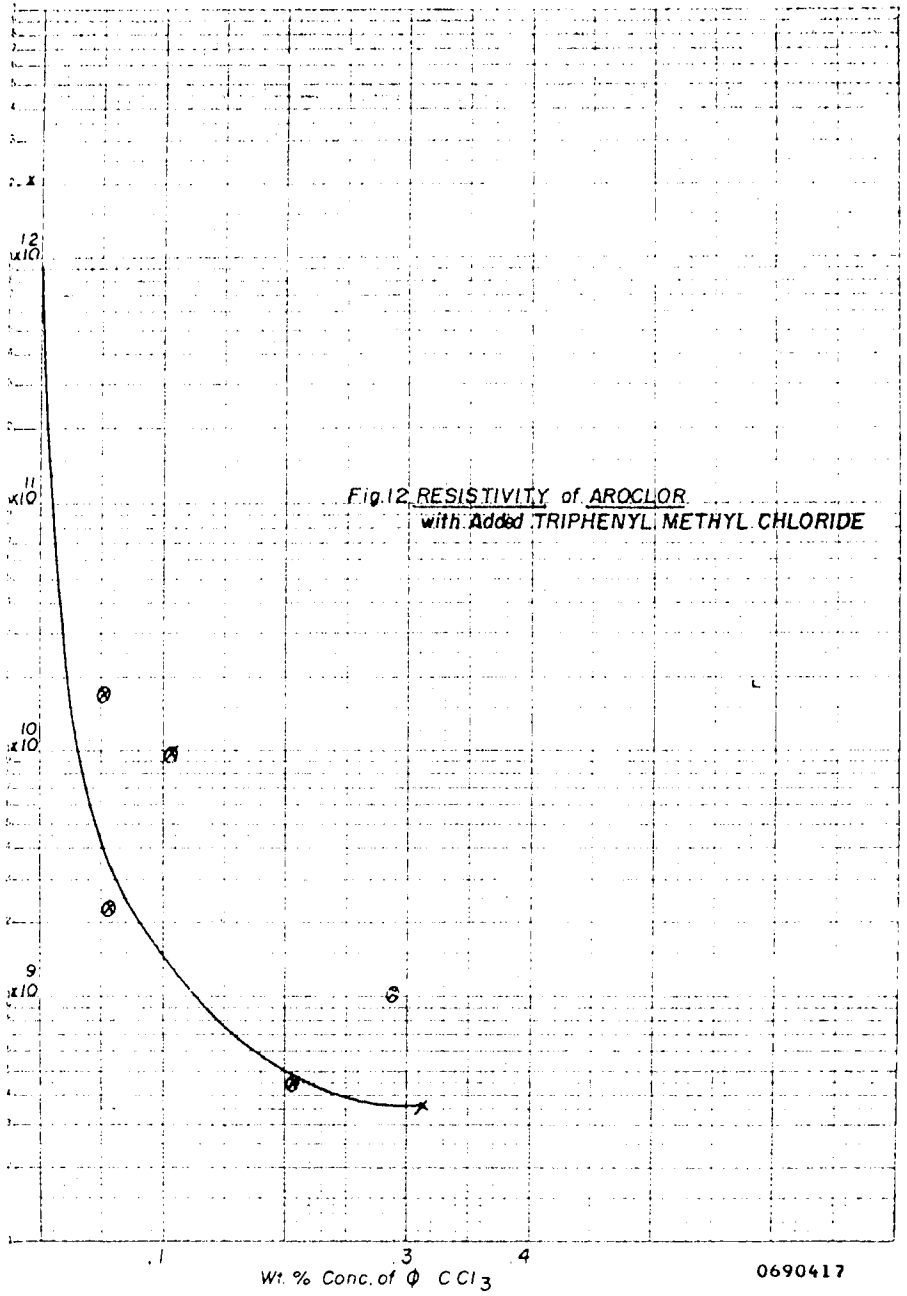
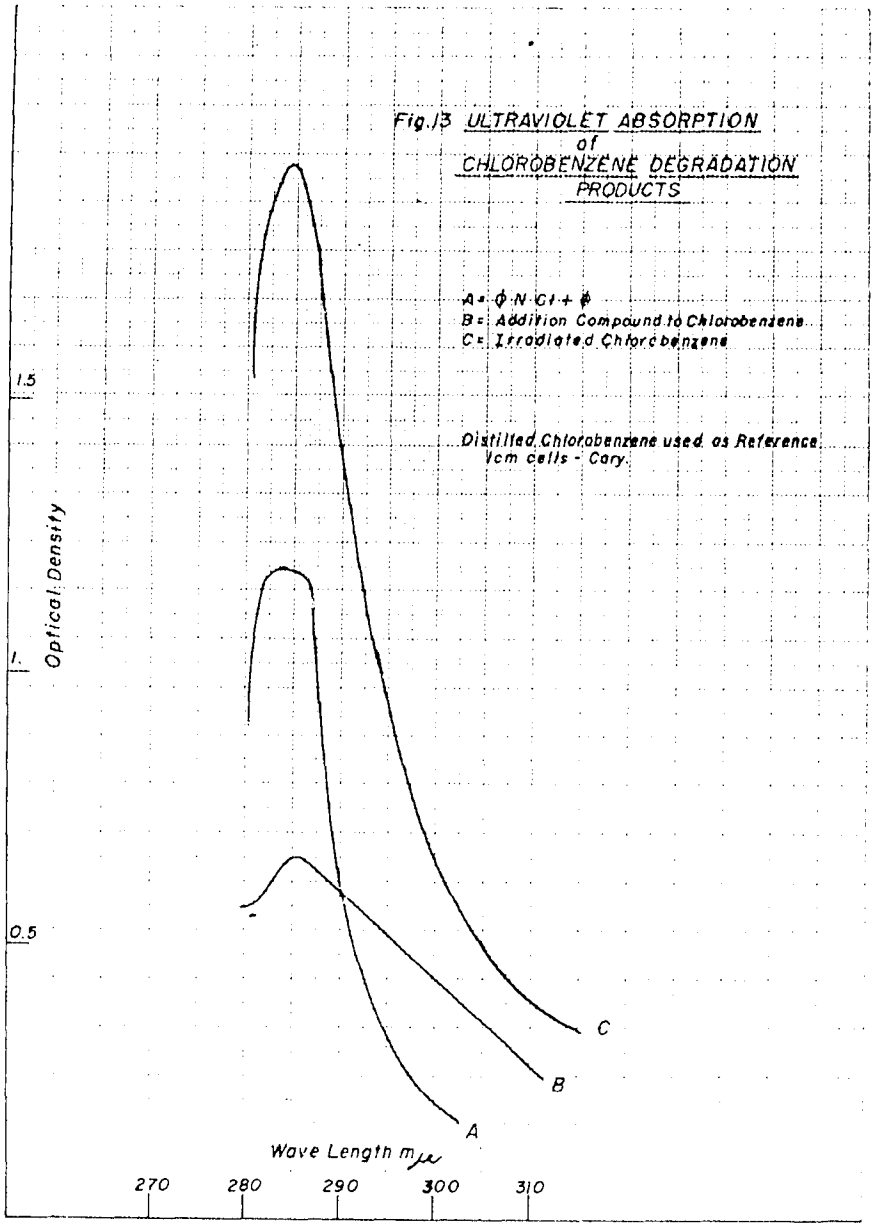


Fig.12 RESISTIVITY of AROCLOR with Added TRIPHENYL METHYL CHLORIDE

Fig. 13 ULTRAVIOLET ABSORPTION of CHLOROBENZENE DEGRADATION PRODUCTS



0690418

Fig. 14 INFRARED ABSORPTION SPECTRA of CHLOROBENZENE DEGRADATION PRODUCTS