FINAL REPORT

TO

MONSANTO CHEMICAL COMPANY

ON

DETERMINATION OF VAPOR PRESSURES OF AROCLORS

Project 526, Report 1

SOUTHERN RESEARCH INSTITUTE

BIRMINGHAM, ALABAMA

FEBRUARY 4, 1954

1876-526-V

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ABSTRACT

The vapor pressures of Aroclors 1242, 1248, and 1254 were measured by the gas-saturation method between 37.5 and 98° C. During each measurement of the vapor pressure the temperature was maintained within ±0.1° C.

The variation of vapor pressure with the temperature was correlated through the Clausius-Clapeyron equation

$$\log P = -\frac{\Delta H_v}{2.303R}\left(\frac{1}{T}\right) + \text{Constant}$$

or $$\log P = -A/T + B$$

Plots of log P against $1/T$ for the Aroclors have been constructed from the experimental data. The equation for the straight lines drawn on Figure 2 are

$$\log P = -\frac{4,240}{T} + 10.7, \text{ valid for Aroclor 1242}$$

$$\log P = -\frac{4,240}{T} + 10.2, \text{ for Aroclor 1248, and}$$

$$\log P = -\frac{3,780}{T} + 8.62, \text{ for Aroclor 1254.}$$

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DETERMINATION OF VAPOR PRESSURES OF AROCLORS

I. INTRODUCTION

The project was initiated to determine the vapor pressures of the Aroclors 1242, 1248, and 1254 over the temperature range of 25 to 100° C by the gas-saturation method.

The Aroclors are not definite compounds but are composed of mixtures of chlorinated biphenyls. The specific Aroclors in question, 1242, 1248, and 1254, are oily, viscous liquids, and have an average of three, four, and five chlorine substitutions per biphenyl molecule, respectively.

The vapor pressures of these Aroclors have been determined over the temperature interval of 150 to 300° C prior to this investigation. However, extrapolation of these data down to the temperature range of 25 to 100° C results in uncertainties in the vapor pressures at these temperatures of several hundred per cent.

II. GENERAL CONSIDERATIONS

For this particular project the gas-saturation method was judged superior to all other methods of measuring vapor pressures. It was by all odds the easiest procedure to get quickly into operation. Furthermore, if the mean extrapolations from the measurements at 150 to 300° C were not too much in error, the method should be reasonably convenient and accurate even down to room temperature.

In the gas-saturation method a current of inert gas is bubbled through or over the liquid whose vapor pressure is to be measured at a slow enough rate to insure saturation. The saturated mixture is next assayed for its vapor content. The vapor pressure of the liquid in question can then be calculated from the experimental data if Dalton's law is assumed to be valid, i.e., that the ratio of the vapor pressure to the total pressure is the same as the ratio of the volume of the vapor to the total volume of the vapor plus the inert gas.

In this investigation the evaporated Aroclor was absorbed in absolute alcohol and the inert gas was saturated with water by passing it through a bubbler before it was finally metered with a wet-test meter. If the ideal gas laws are assumed valid as well as Dalton's law then:

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$$P = \frac{WRT_s}{MP_s} \cdot \frac{T_m P_s}{T_s V_m} \cdot \frac{P_s - P}{P_m - pw}$$

where P, vapor pressure of Aroclor in mm Hg at T_s

R, gas constant, 62.361 mm-liters/°K

T_s, temperature of saturator, °K

M, average molecular weight of Aroclors, Aroclor 1242-258, 1248-292, 1254-326

P_s, pressure at saturator, mm Hg

T_m, temperature at wet-test meter, °K

V_m, measured volume from wet-test meter, liters

P_m, pressure at wet-test meter (atmospheric pressure), mm

pw, vapor pressure of water, mm at T_m

W, weight of Aroclor vaproized, grams

Since P is very small in comparison with P_s it can be neglected in the term $(P_s - P)$. Then

$$P = \frac{WRT_m}{MV_m} \cdot \frac{P_s}{(P_m - pw)}$$

The amount of Aroclor absorbed in the absolute alcohol during a run was determined spectrophotometrically.

III. EXPERIMENTAL DETAILS

A. Apparatus

Because the Aroclors are stable in air over the temperature range of 25 to 100° C, dry air can be used as the inert gas. Air was displaced from a narrow-mouth, five-gallon, glass jar by water; the air stream was dried with activated alumina before introducing it to the saturator.

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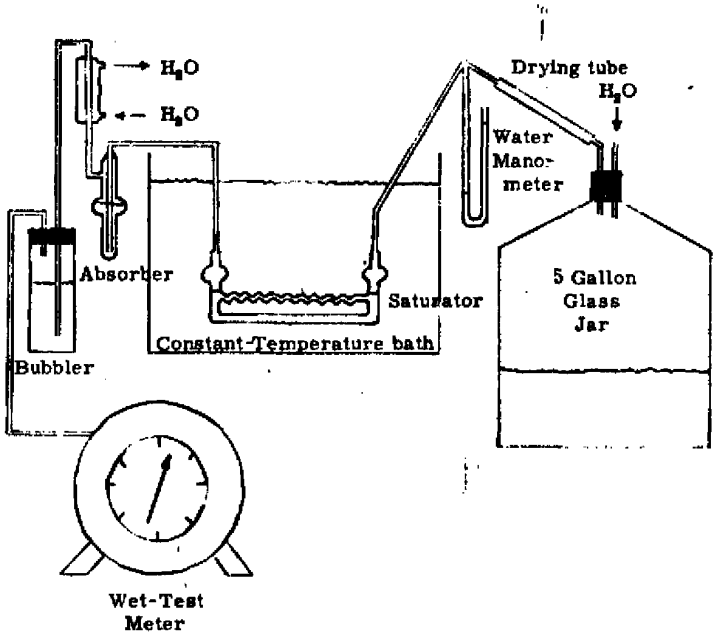

Figure 1

Apparatus used in Gas-Saturation
Method of Vapor - Pressure Measurement

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The system was constructed of Pyrex glass with spherical ground joints for pressure-tight, but yet flexible, connections. Duplicate systems were used to decrease the time required to gather the necessary data. The increase in pressure over atmospheric pressure at the saturator was measured with a water manometer. A gas-washing apparatus purchased from Ace Glass Company, Ace drawing No. 1740, part A, was used as the saturator. This saturator had several advantages: a large surface area was exposed, the pressure drop across the saturator was low, and if the flow rate were fast enough a circulation of the liquid within the saturator was obtained. The absorber was a 25-cc capacity bubbler with capillary inlet tube. A water-cooled condenser was attached to the exit tube of the absorber to condense the absolute alcohol that was vaporized into the gas stream.

The air stream passed from the water-cooled condenser to a gas-washing bottle filled with distilled water before it was metered by a wet-test meter. This procedure eliminates possible difficulties caused by incomplete saturation of the air stream with water in the wet-test meter. The wet-test meter previously had been calibrated by displacing a measured amount of air through the meter.

The temperature was regulated by a constant-temperature bath having a sensitivity of $\pm 0.1°$ C. At the higher temperatures the outside of the glass jar was wrapped in asbestos and the top covered to minimize any temperature differential existing in the bath caused by atmospheric cooling. The temperature variation throughout the bath was measured at 54 and 98° C. At both temperatures the differential was found to be not greater than $\pm 0.1°$ C.

B. Technique

Fill the clean, dry saturator with the Aroclor whose vapor pressure is to be measured to just above the level of the indentations. Add 15 to 20 milliliters of absolute alcohol to the clean, dry absorber. Connect the absorber and saturator using Dow-Corning high vacuum grease as the lubricant for the spherical joints. Lower saturator into the constant-temperature bath. Connect other apparatus, including condenser, wet-test meter, water manometer, glass jar. Allow apparatus to rest until the Aroclor in the saturator is at the temperature of the bath; if temperature equilibrium has not been reached, Schlieren effects will be observed when the flow is started.

Record time; reading of water manometer; temperatures of bath, meter, and room; meter reading; and barometric pressure. Then start water flowing into glass jar slowly but regularly. Record all readings every half hour during run whenever possible. Calculate from the approximate vapor pressure the necessary volume of air that must be passed through the system.

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The approximate vapor-pressure values can be obtained by extrapolation of the vapor pressures measured between 150 and 300° C. The volume of air will also depend on the limit of detection of the spectrophotometric method of analysis.

Stop water flow when sufficient air has been passed through the saturator and absorber. Disconnect glass jar and water manometer. Disconnect connection at top of water-cooled condenser. Wash down walls of condenser to drain. Lift saturator from the bath. Break connection next to saturator and wipe joint clean. Wash outside of piece carefully in acetone if bath liquid is mineral oil. Pour alcohol in 50- or 100-ml volumetric flask and wash absorber repeatedly with warm alcohol to make solution up to volume. Determine concentration of Aroclor in alcohol with a Beckman DU spectrophotometer using absolute alcohol as a blank.

Calculate the vapor pressure of Aroclor and compare with other determinations by plotting value on a graph of log P against $\frac{1}{T}$. Repeat determination as an additional check.

IV. RESULTS

All of the experimental data on Aroclors 1242, 1248, and 1254 are summarized in Table I. Plotted in Figure 2 are the calculated vapor pressures against the temperature.

V. DISCUSSION

A. Evidence of Validity of Method

The technique and the apparatus involved in the gas-saturation method were first checked by measuring the vapor pressure of diethylphthalate. This compound was selected as the reference liquid because its vapor pressure had been measured accurately by the gas-saturation method by P. W. Small, K. W. Small, P. Cawley, "The Vapor Pressures of Some High Boiling Esters," Trans. Faraday Soc., 44, 810 (1948), between 25 and 56° C. This measured vapor pressure fell within the range of vapor pressures of the Aroclors. In addition diethylphthalate was similar to the Aroclors in viscosity and could be obtained readily in the requisite purity.

A comparison of the known value of the vapor pressure of diethylphthalate at 54° C, 1.23×10^{-2} mm Hg, with those determined experimentally, 1.23×10^{-2} a flow rate of 30 cc per minute and 1.16×10^{-2} at a flow rate of 5 cc per minute indicates that reasonable agreement is obtained. It can be assumed that the method will give just as reliable values for the unknown vapor pressures under similar conditions.

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Table I

Summary Of All Vapor Pressure Determinations

Temp. in ° C	Aroclor 1242, Lot 166 Calculated Vapor Pressure in mm Hg	Aroclor 1242, Lot 166 Average Flow Rate cc/min	Aroclor 1248, Lot E-5 Calculated Vapor Pressure in mm Hg	Aroclor 1248, Lot E-5 Average Flow Rate cc/min	Aroclor 1254, Lot 1923 Calculated Vapor Pressure in mm Hg	Aroclor 1254, Lot 1923 Average Flow Rate cc/min
37.5	9.3×10^{-4}	5	5.3×10^{-4}	6	2.87×10^{-4}	9
	1.14×10^{-3}	10			2.76	10
54.0	6.0×10^{-3}	7	1.98×10^{-3}	4	1.18×10^{-3}	6
	6.5	6	1.84	42		
71.0	2.30×10^{-2}	11	9.2×10^{-3}	6	3.2×10^{-3}	7
	2.61	7	9.2	5	4.2	14
	2.52	6	8.6	9	4.2	8
					3.3	5
98.0	1.82×10^{-1}	25	7.6×10^{-2}	12	2.52×10^{-2}	12
	1.77	22	7.8	68	2.75	10
	1.53	39	7.5	39	2.76	43
	1.53	25	7.6	12	1.43	38
	1.71	10			2.34	16
	1.73	13			2.88	10
	1.76	8				

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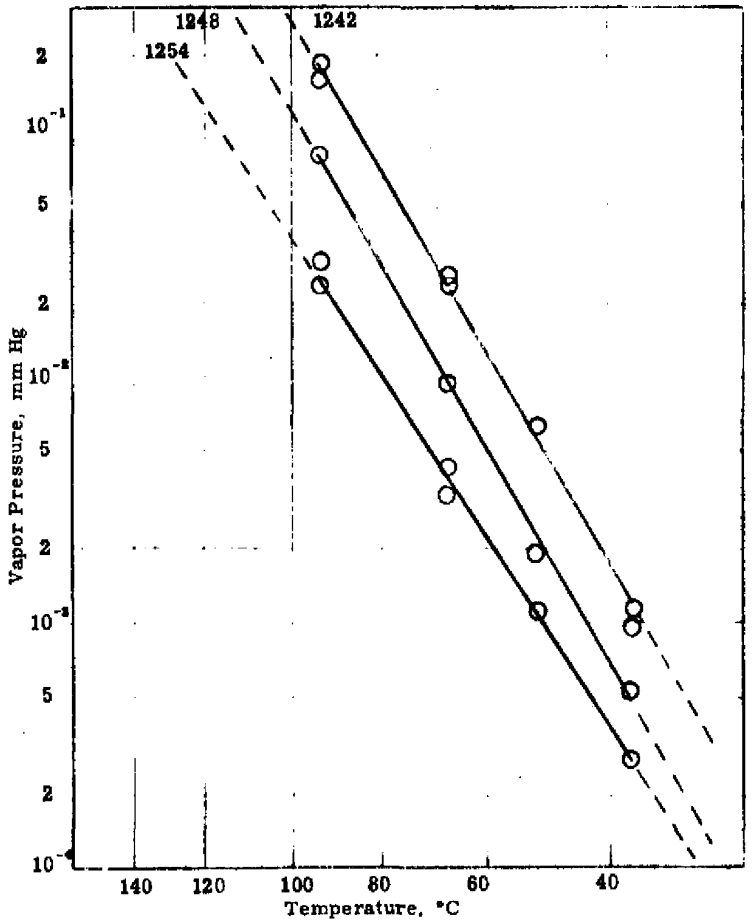

Figure 2
Application of Clausius - Clapeyron
Equation to Experimental Data

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The effect of the flow rate of the inert gas through the system was investigated. Only the total volume of gas saturated by the Aroclor is needed in the calculations and so constancy of gas flow is not essential if the rate is always kept below the maximum flow rate for saturation. A study of the data in Table I will reveal that the differences in vapor pressure obtained with widely differing flow rates up to 70 cc per minute were no greater than duplicate determinations using identical flow rates. Saturation of the air stream by the Aroclor at the flow rates used experimentally seems assured. However, additional tests were made in which two saturators filled with the same Aroclor were connected in series. Table II shows that data from these runs were no different from those recorded from the usual setup, and confirms the fact that saturation is obtained at the flow rates used experimentally.

Table II

Comparison of Data Obtained at 98° C By Using Two Saturators In Series With Representative Data Gathered Normally

	Usual Setup		Two Saturators	
Aroclor	Calculated Vapor Pressure in mm Hg	Flow Rate in cc/min	Calculated Vapor Pressure in mm Hg	Flow Rate in cc/min
1242	1.73×10^{-1}	13	1.76×10^{-1}	7
1248	7.5×10^{-2}	39	7.6×10^{-2}	12
1254	2.76×10^{-2}	43	2.88×10^{-2}	10

Spot checks were make to determine the efficiency of the bubblers. In these checks two such traps were connected in series and the amount of Aroclor passing through the first trap was determined. Only gamma quantities of Aroclor escaped the first trap. Table III indicates that the bubblers are very efficient and for all practical purposes absorb 100% of the Aroclor vapor.

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Table III

Spot Checks On The Efficiency Of Absorbers

Aroclor	Volume of Air Passing Through System	Flow Rate of Air Stream in cc/min	Aroclor Passing First Absorber / Amount of Aroclor Vaporized x 100
1242	9.82	7	0.01%
1248	16.7	12	0.00%
1254	13.4	10	0.09%

The final check on the method was on the accuracy of the spectrophotometric method of analysis. The quantitative curves at the selected wavelengths of absorbance versus concentration indicated that the solutions obeyed Beer's law satisfactorily, but there was some doubt as to the accuracy and reproducibility of the analysis since it was not possible to select a wavelength where the specific extinction coefficient was not changing rapidly. Figure 3, a plot of the specific extinction coefficient versus wavelength, shows a shoulder on the curve at a wavelength of 244-245 mμ for Aroclor 1242 and 1248 and this was the wavelength used for the analysis of these Aroclors. However, there is no shoulder at all in the curve of 1254 so the absorbance was read at three wavelengths, 245, 260, and 275 and the results were averaged. The averaged error in the analysis for Aroclor 1242 and 1248 was 0.62 and 2.30%, respectively. The average error inherent at the three wavelengths at which the analysis of 1254 was determined was 1.95% for 245 mμ, 1.65% for 260 mμ and 1.68% for 275 mμ.

Runs were made in which the Aroclor was condensed in a cold trap and the condensate of Aroclor was weighed. This Aroclor was then washed from the trap with warm alcohol into a volumetric flask and the concentration of Aroclor determined spectrophotometrically. Satisfactory checks were obtained with Aroclor 1242, 32.6 mg weighed against 31.5 mg determined spectrophotometrically, and with Aroclor 1254, 12.1 mg both weighed and analyzed.

It was not possible to obtain evidence of fractionation of any of the Aroclors during the vapor pressure measurements. The curves of specific extinction coefficient divided by the concentration versus the wavelength in millimicrons of the Aroclors evaporated and absorbed in the alcohol were always identical to the original. If appreciable fractionation had occurred the absorbed

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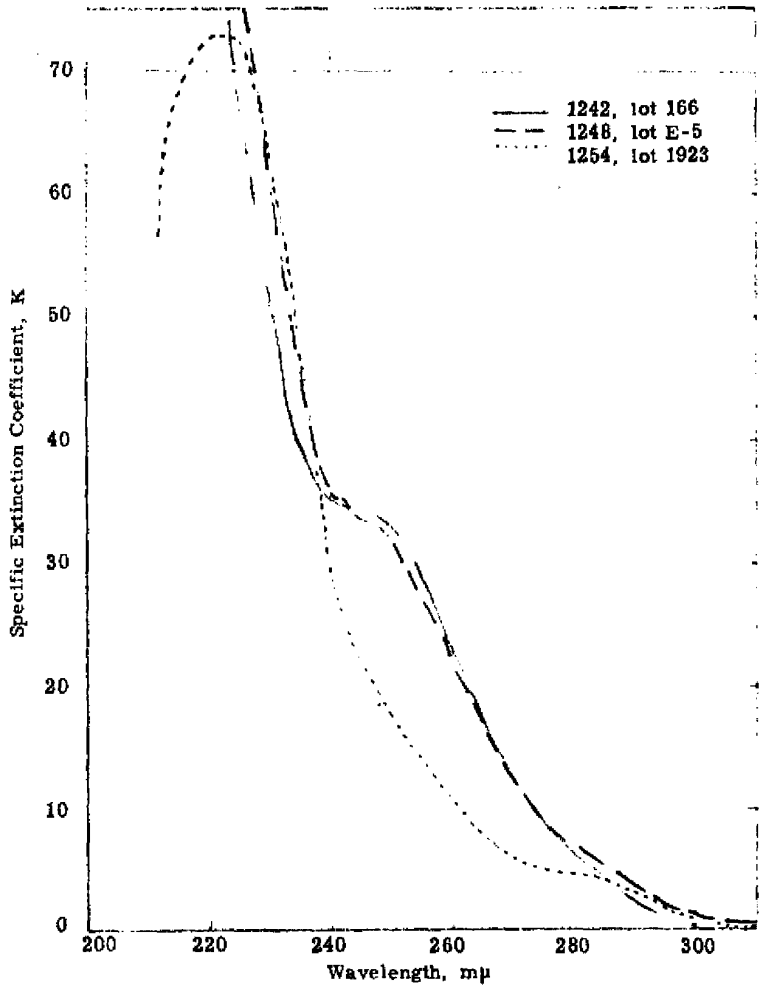

Figure 3
Spectra of Aroclor 1242, 1248 and 1254
in absolute Alcohol, K = A/(bc) in which
A = specific absorbancy, b = cell thickness
and c = concentration of Aroclor

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Aroclor would have had a different curve. The percentage evaporated during a run was much less than 0.1% by weight of the Aroclor in the saturator. In Figure 4 curves of specific absorbancy versus wavelength for fractions of Aroclor 1242 of approximately 0.1% which were distilled at 3 mm Hg at 135-140° C (Monsanto notebook reference 92919) showed very little deviation from the curve of the unfractionated sample. This would indicate that very little fractionation takes place initially even on boiling under reduced pressure.

A blank run, in which the apparatus was connected as usual but no air was passed through the system, was made to determine if the thermal diffusion of the Aroclor vapor to the absorber was appreciable. Less than 0.03 mg of Aroclor were detected in the absorber after over 144 hours of exposure at a temperature of 98° C. This quantity of Aroclor would be less than 1% of the amount evaporated during a vapor-pressure determination at 98° C.

B. Correlation of Results

The calculated vapor pressures were correlated by plotting log P against the reciprocal of the absolute temperature, $\frac{1}{T}$. The Clausius-Clapeyron equation

$$\log P = - \frac{\Delta H_{\sim}}{2.303R} \left(\frac{1}{T}\right) + C$$

predicts that the curve will be a straight line with a slope equal to $- \frac{\Delta H_{\sim}}{2.303R}$ and Figure 2 shows that fairly straight line relationships do result for each Aroclor. The slopes of the three lines representing Aroclors 1242, 1248, and 1254 are very similar and perhaps even identical. This would imply that, if the slopes are similar, the heats of vaporization of the Aroclors are approximately equal. This is reasonable and was an expected behavior.

Figure 5 gives the relationship of the vapor pressures previously measured between 150 and 300° C with those measured between 25 and 100° C by again plotting the vapor pressure against the temperature. It can be seen that rather good agreement between the two sets of data was obtained. The lowest point for Aroclor 1242, at 37.5° C, is low when a straight line is drawn through the remaining points. Likewise the values of the vapor pressure of Aroclor 1242 and 1248 at the higher temperatures tend to fall off a straight line drawn through the bulk of the data. For the Clausius-Clapeyron equation to be valid the constancy of $\Delta H_{\sim}$ is assumed. This will hold for rather narrow ranges of temperature but will not be necessarily valid for the wide spread of temperatures recorded in Figure 5.

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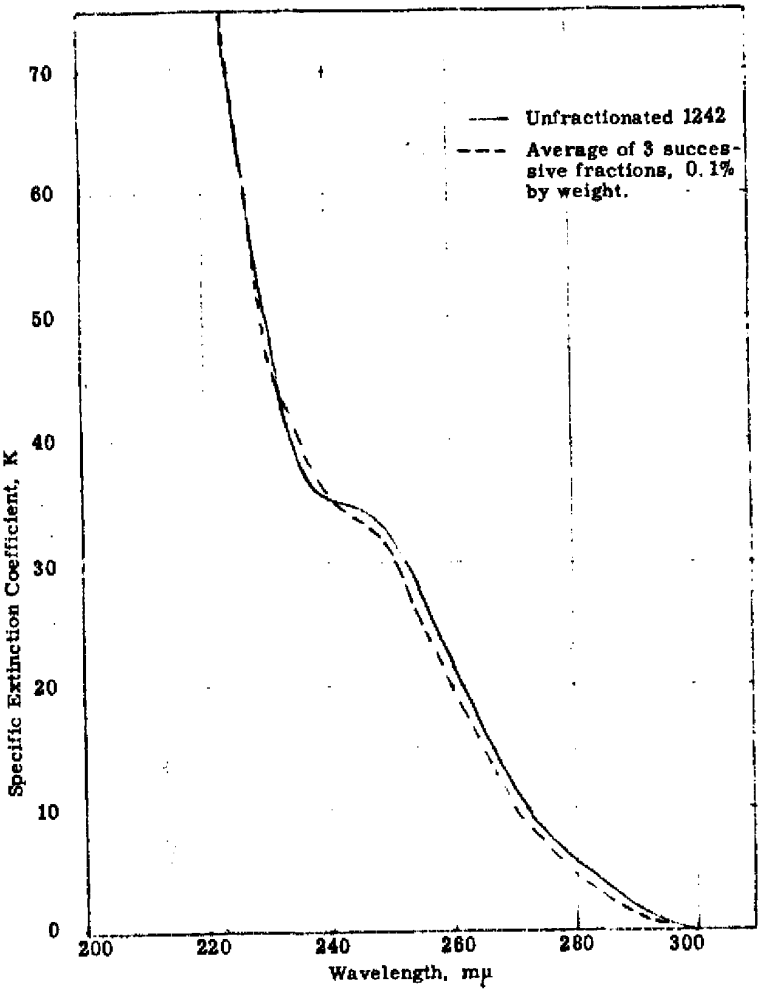

Figure 4

Spectra of Fractionated Aroclor 1242, lot 166

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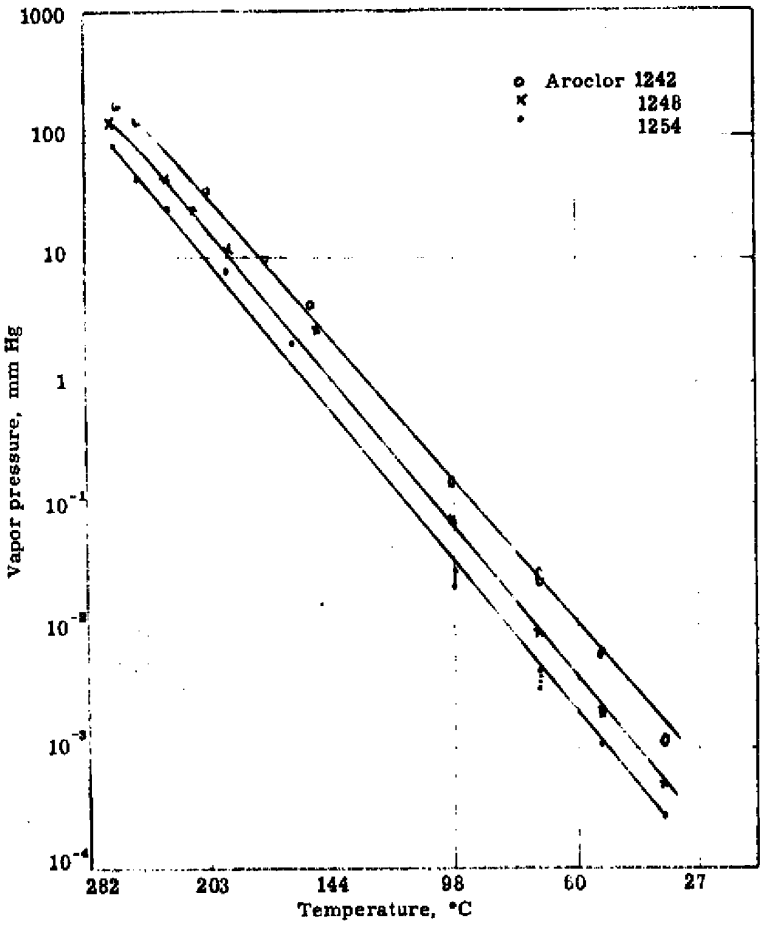

Figure 5
Comparison of Vapor Pressure Data

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It must be emphasized that the data recorded in this report are strictly valid only for the particular batches of Aroclor that were used in the determinations. These were Aroclor 1242, lot 166; 1248, lot E-5; and 1254, lot 1923. Since the manufacture of Aroclor is a batch process and the Aroclors are a mixture of many components there is no basis for assuming that the same vapor pressure is valid for all batches of the same type Aroclor unless all conditions of production are identical. However, the fact that Figure 5 showed such agreement between the vapor pressure determinations with different batches at different temperature intervals indicates that the differences in vapor pressure are probably small. Nevertheless to check the reliability of the data as being representative of all Aroclors of the same type the vapor pressure of several representative batches should be measured. It would probably be necessary to only check the vapor pressure at one temperature since the slope of the curve of log P vs. $\frac{1}{T}$ would be constant for all batches.

Submitted by William M. Nolan
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February 4, 1954
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