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SPECTROSCOPIC STUDY OF SILICONE-ALKYD COPOLYMERS

AND

THEIR DEGRADATION PRODUCTS

BY

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## ABSTRACT

Gabrielides has shown, in a previous work in this laboratory, that the use of strong monoprotic organic acids had deleterious side effects on the polyesterification reaction involved in the preparation of modified alkyd resins.

The aim of the present study was: first, to confirm the role of a strong acid on the above mentioned reaction. Second, to investigate the possibility of catalyzing commercial polycondensation reactions with the idea of reducing their processing time and temperature. Third, to prove through infrared study the existence of copolymerization between an alkyd resin and a silicone intermediate. Fourth, to use infrared spectroscopy in studying the degradation of the copolymers when heated to different temperatures and for different time intervals.

Alkyd resins were prepared by esterifying dibasic acids (isophthalic and phthalic acids) and benzoic acid with trimethylol ethane. The polymerization was run under an inert atmosphere ( $\text{CO}_2$ ) with agitation and azeotropic reflux in diisobutyl ketone until the acid number dropped below 10.

The effect of strong organic acids on the rate of

polymerization was studied by using p-nitrobenzoic acid, p-toluene sulfonic acid and trichloro-acetic acid in concentrations ranging from 1-3% by weight. It was found that the presence of a strong organic acid, up to about 2%, catalyzed the polymerization reaction and reduced the processing time from 4-5 hours to 50 minutes. This fact is of outstanding commercial importance from an economic point of view.

Strong organic acids, unlike weak organic acids such as benzoic, stearic, lauric etc., served only as catalysts and were not incorporated as telomers into the polymeric molecules.

The speed of the polymerization reaction increases with the increase in the strength and concentration of the acid up to a fixed value after which further increase resulted in appreciable decomposition and gave polymer masses of inferior colour.

Infrared study of the alkyd and silicone resins before and after processing confirmed the existence of copolymerization.

Infrared spectra of the cured copolymers after heating to various temperatures at different time intervals were difficult to interpret with reasonable certainty. However, it was shown that, on heating, the intensity of the phenyl carbon-hydrogen absorption band seemed to decrease relative to the alkyl carbon-hydrogen band. There were also some dif-

ferences in the intensity of the absorption bands of the phenyl group on heating.

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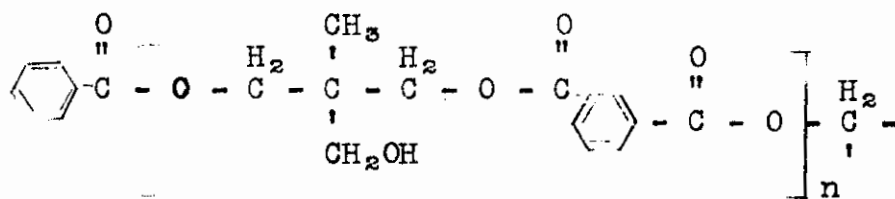
## INTRODUCTION

### Theoretical

Alkyds: Alkyds have been defined as polymeric condensation products of polyhydric alcohols and polybasic acids. Any polyfunctional acid or alcohol can be used as long as cyclization is not the predominant trend of the reaction.

Bifunctional acids and alcohols produce linear resins which are thermoplastic, soft, flexible and may possess fibrous character. When the functionality of either acid or alcohol exceeds two, three dimensional polymerization becomes possible and the products are hard, brittle and thermosetting. The properties of the products are thus a function of the average functionality of the reactants.

One of the alkyds used in the present investigation has the following structure:



In another formulation the isophthalic acid segment was replaced by phthalic acid.

Silicones: Silicones are the hydrolysis products of alkyl or aryl silicon halides. The high ionic character of the siloxane chain renders a protective effect on the



alkyd components on the properties of the copolymers, particularly as they bear on their thermal stability for high temperature surface coatings.

A statistically designed experiment was formulated using the three isomeric phthalic acid isomers at one level of concentration, benzoic acid (used as a telomer) at three levels of concentration, a silicone in three levels of composition and trimethylol ethane (T.M.E.) in stoichiometric quantity to react with the alkyd and silicone component.

It was found that:

- (1) The stability of the copolymer was independent of the levels of concentration of benzoic acid used.
- (2) Of the isomeric phthalic acids, isophthalic acid produced the more stable copolymer.
- (3) Of the three silicone intermediates studied, the aryl silicone, phenyl ethoxy polysiloxane (25% ethoxy) and the alkyl-aryl silicone, phenyl dimethyl ethoxy polysiloxane, showed no significant differentiation at temperatures below 250°C. At temperatures above 250°C, the aryl silicone showed superior thermal stability, good gloss and colour retention. Sylkyd-50 was the least stable of the three.
- (4) Of the different polyols used (1,2,6-hexanetriol, trimethylol propane, trimethylol ethane (T.M.E.), pentaerythritol, neopentyl glycol and 1,5-pentane diol) it was found that T.M.E. produced resins of overall superior

properties.

- (5) Of the monobasic acids used, (benzoic acid, p-tertiary butyl benzoic acid, caproic acid and trichloro-acetic acid) benzoic acid produced the more stable copolymers.
- (6) In processing alkyds containing strong acids, such as trichloro-acetic and p-nitrobenzoic acid, side reactions other than esterification resulted in excessive decomposition and the liberation of a yellow distillate.

The aim of the present study is: First, to confirm the role of a strong organic acid in the polymerization reaction involved in the preparation of an alkyd, Second, to investigate the possibility of catalyzing commercial polymerizations with the idea of reducing the processing time, and temperature of the reaction. Third, to prove, through the use of infrared spectroscopy, the existence of copolymerization between an alkyd resin and a silicone intermediate. Fourth, to use infrared spectroscopy in studying the degradation of the silicone-alkyd copolymer heated at different temperatures and for different time intervals.

Though a large number of patents were issued and articles published on silicones and alkyds during the years 1958 and 1959, practically nothing has been published on silicone-alkyds. The only patent related to the subject was issued to Midland Silicones Ltd.<sup>3</sup> concerning a method for the preparation of alkyd copolymers with diphenyl and

phenyl methyl siloxane.

Information regarding the absorption bands of silicon compounds have appeared in many articles. N. Wright and M.J. Hunter<sup>4</sup> examined open chain compounds ranging from hexamethyl disiloxane to octadecamethyl octasiloxane. J.F. Hyde, L.K. Frevel, H.S. Nutting, P.S. Petrie and M.A. Purcell<sup>5</sup> showed that polymorphic crystalline forms of alkyl silanes and siloxanes can exist and this would be expected to have a considerable influence on the absorption pattern. C.W. Young, P.C. Servais, C.C. Currie and M.J. Hunter<sup>6</sup> carried extensive studies in the silicon field. They employed solutions in carbon disulfide and carbon tetrachloride. R.E. Richards and H.W. Thompson<sup>7</sup> studied siloxy methyl silanes. In ten compounds examined as liquids, in which the methyl group is directly attached to silicon they find strong bands in the range  $1269 - 1256 \text{ cm}^{-1}$ , whereas in those containing ethyl groups the frequency falls to  $1250 - 1239 \text{ cm}^{-1}$ . H. A. Clark, A.F. Gordon and C. W. Young<sup>8</sup> examined the spectra of twelve aryl trimethyl silanes in solutions. All show absorption bands close to  $840 \text{ cm}^{-1}$ .

It is interesting to note that at least three books (9,10,11) in the English language have been published describing the Chemistry, properties, technology, and uses of silicones and their copolymers. Post's "Silicones and other Organic Silicon Compounds" is the oldest of the three. It emphasizes the chemistry and academic growth of the

silicones and organo-silicon compounds and contains an excellent bibliography of the published and patent literatures to 1947. Rochow's "An Introduction to the Chemistry of the Silicones" has been revised and includes a comprehensive survey of the field, making the new edition a suitable textbook on the subject. McGregor's "Silicones and Their Uses" is written in non-technical language and gives an over-all picture of what silicones are and the wide fields of uses to which they are applied.

## EQUIPMENT

The alkyds were prepared in a 500 mls. round bottom flask with four ground glass necks. To these were fitted a filling tube, an inert gas ( $\text{CO}_2$ ) delivery tube, a thermometer, a glass stirrer or collapsable double bladed stainless steel stirrer both of which were sealed with an adjustable graphite packing and driven by a variable speed motor, and a reflux condenser with a Stark and Dean trap. Heating was accomplished through the use of a heating mantle controlled by a Variac auto transformer. A flowmeter was inserted in the inert gas line to measure the rate of input of carbon dioxide (Fig. 1).

For copolymerization, a fractionating column was substituted for the reflux condenser and the Stark and Dean trap. A condenser was connected to the top of the column and the alcohol liberated was collected in a graduated cylinder fixed to the outlet of the condenser (Fig. 2).

Infrared spectra of the different polymeric compounds were taken using the single beam Perkin-Elmer Infrared Spectrometer (Model 112, Series 44) as well as the double beam Perkin-Elmer Infracord (Model 137).



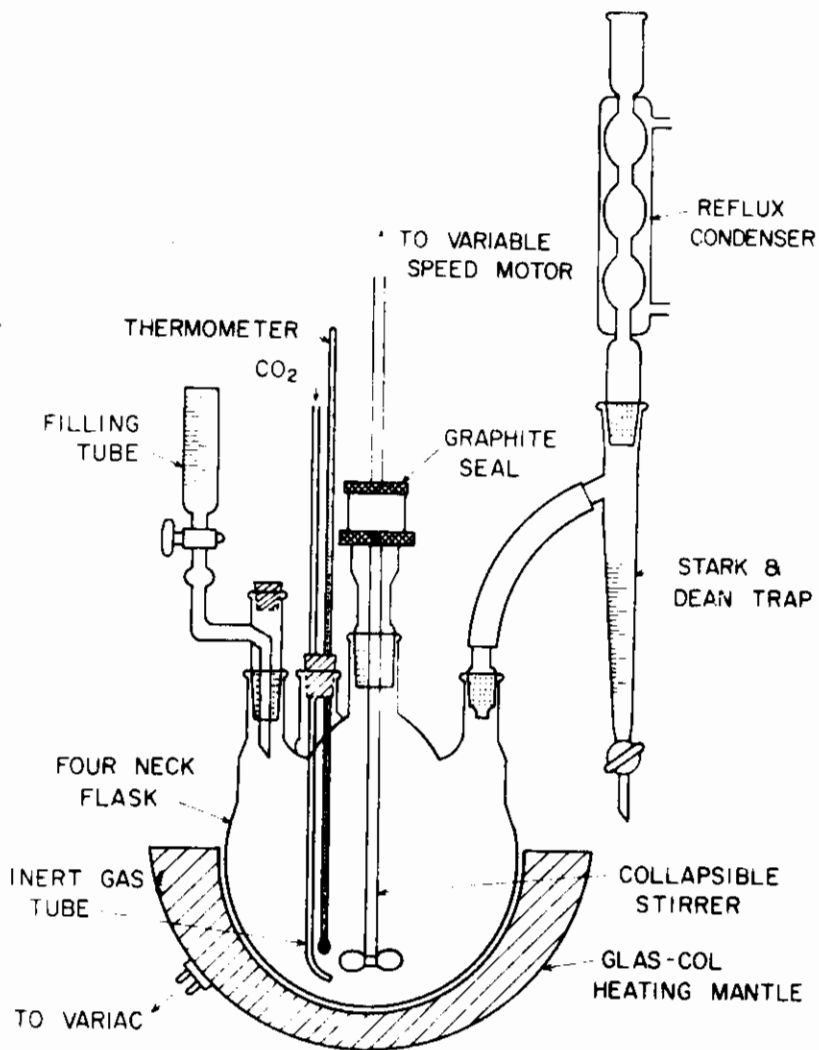


FIGURE 1  
 APPARATUS FOR PREPARATION OF RESINS

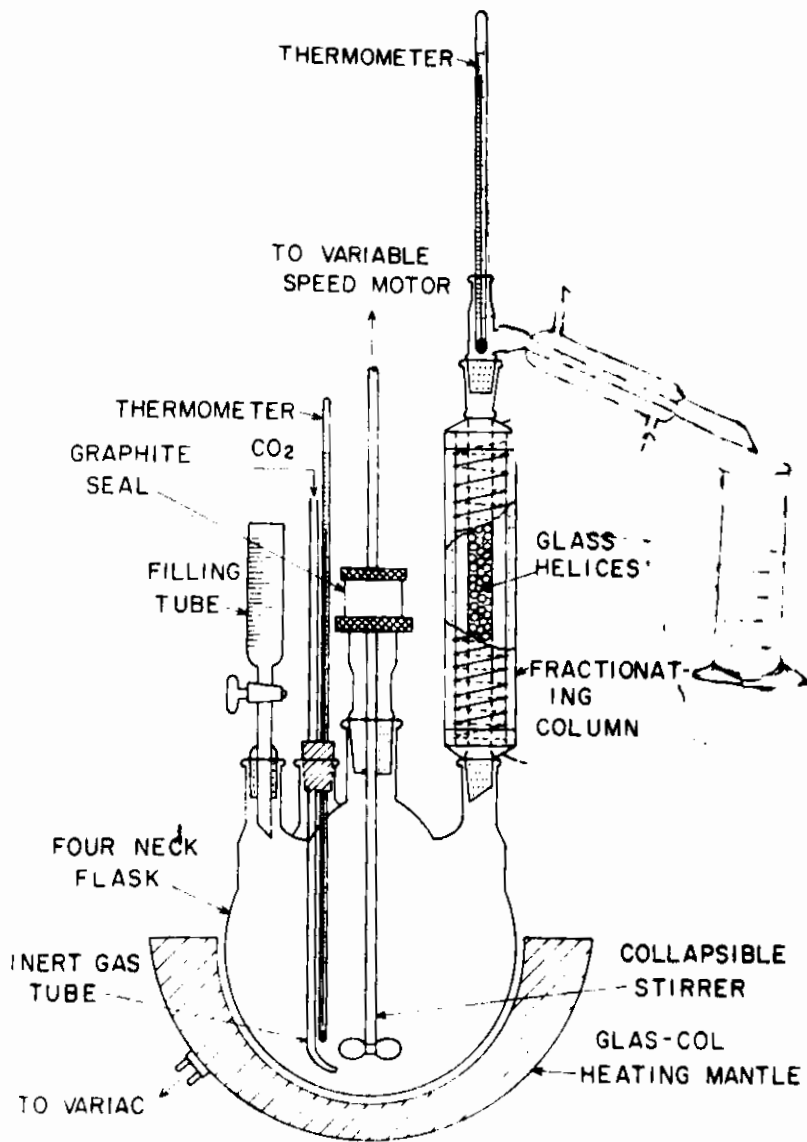


Figure 2

Apparatus for Copolymerization

## PROCEDURE

The required quantities of polyol, dibasic and monobasic acid were weighed and introduced into the reaction flask. Through the filling tube a quantity of solvent, amounting to 10 - 15% of the weight of the reactants, was added. The mixture was heated to a steady reflux at a temperature varying between 180 - 230°C.

Simultaneously the stirrer was started and a moderate rate of carbon dioxide was allowed to bubble through the molten mass at the rate of 100-200 cc/min. Once the mixture melted and became homogeneous, the stirring was adjusted to 600-900 r.p.m.

The water given off was collected in the Stark and Dean trap. In the case of acid catalyzed polymerization the temperature was allowed to reach a maximum of 210°C. In the case of the uncatalyzed polymerizations, a temperature of 230°C. was attained.

When the water collected was within 1.0 ml of the theoretically calculated value, a sample of the resin was withdrawn and titrated against alcoholic potassium hydroxide. When the acid number dropped below 10, the heating mantle was disconnected and the desired amount of solvent added to stop the reaction. In the cases where the silicone copolymer was to be prepared the temperature was lowered to 170°C. and the reflux condenser replaced by a

fractionating column. The desired amount of silicone was then added to the alkyd resin. An additional weight of solvent equal to 10-20% of the weight of the reactants was added, stirring resumed at 900 r.p.m. and the temperature raised and kept between 185 - 190°C. The thermometer at the top registered a temperature <sup>2-3 °C</sup> ~~a bit~~ lower than the boiling point of the specific alcohol liberated.

After 30-40 minutes, the reaction mixture, which seemed incompatible at the start, became clear and homogeneous. The reaction was allowed to proceed until imminent gelation. At this stage the reaction was stopped by lowering the heating mantle and enough solvent was added to make the total solid content of the copolymer 60-70%.

In alkyd preparations where a strong organic acid was used as a catalyst, the acids used were reagent grade chemicals. However, in the case of p-toluene sulfonic acid, the technical grade reagent was purified prior to its use according to the following procedure:

Preliminary study showed that an aqueous solution of p-toluene sulfonic acid containing 204 gms of the acid per hundred milliliters of water, gave the best yield of the pure crystalline acid on saturation with hydrogen chloride gas. Hence 204 gms of the commercial reagent was dissolved in water, the mixture filtered to remove suspended impurities and the filtrate decolorized with activated charcoal for fifteen minutes. The filtrate which was still slightly

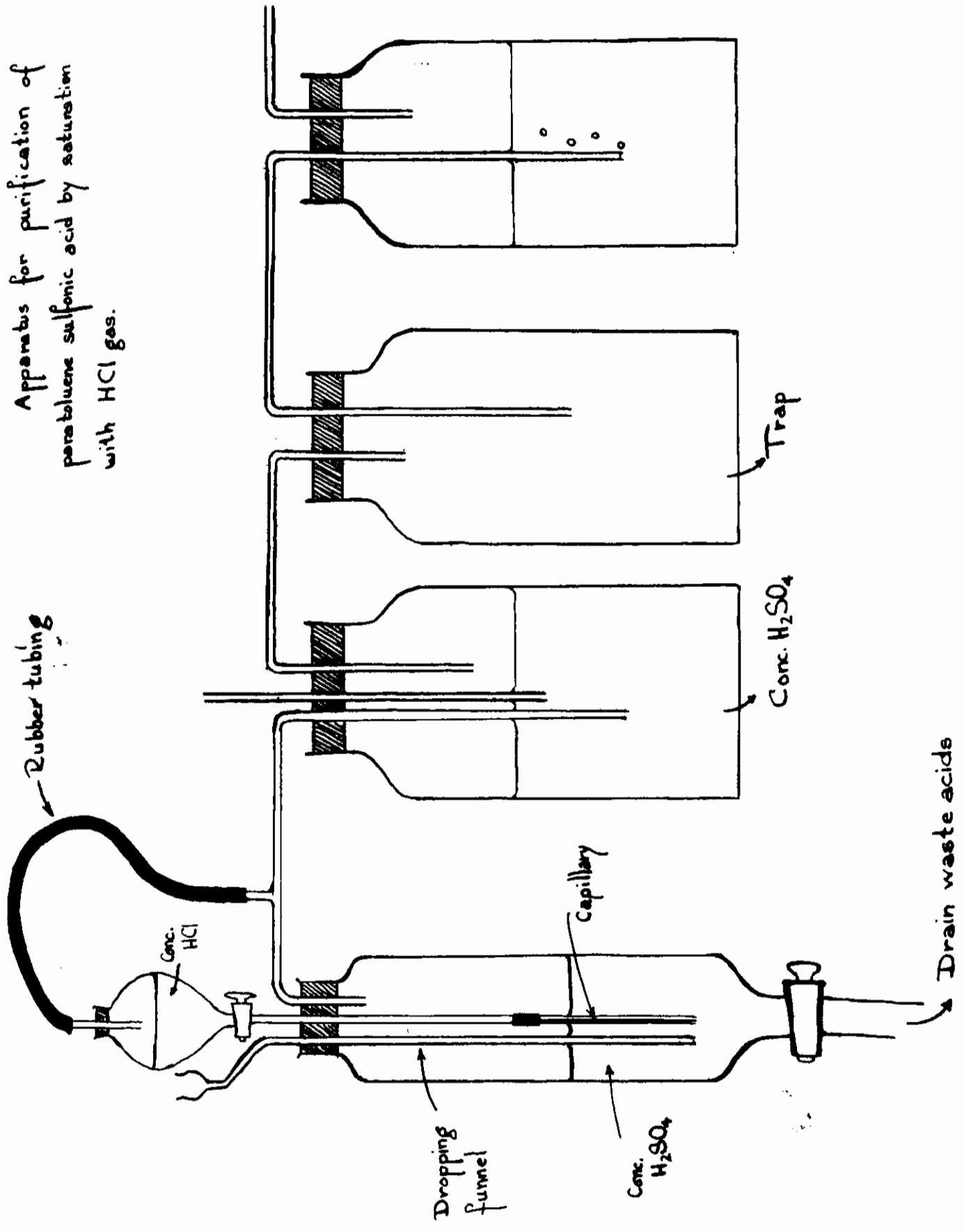
coloured was saturated with hydrogen chloride gas. The apparatus used for saturation is given in fig. 3, and has been adopted from a procedure given by Fieser<sup>12</sup>.

Dry hydrogen chloride gas bubbled through the solution. Crystals of the p-toluene sulfonic acid were immediately precipitated. The hydrogen chloride gas continued to be bubbled through until no further precipitation was seen. The flask was disconnected from the generator and the contents allowed to cool to room temperature. These were then put for a few hours in the refrigerator. The acid was filtered by suction and the crystals washed with cold concentrated hydrochloric acid. The acid produced was further purified by two more recrystallizations. The pure crystals were put in a vacuum desiccator charged with potassium hydroxide and allowed to dry.

Infrared spectra of the solvents used, alkyds, silicones and the silicone-alkyd copolymers were then taken using both spectrophotometers.

Thin films of the different copolymers prepared, were spread on thin aluminum foil by the dip method. The films were cured at 180°C. for one hour and then heated for specific intervals at different temperatures. The aluminum foil was then dissolved in hydrochloric acid and the film produced repeatedly washed with distilled water. After drying in a vacuum desiccator, (at a pressure of thirty millimeters of mercury) the spectrum of the film was taken.

Apparatus for purification of  
paratoluene sulfonic acid by saturation  
with HCl gas.



Rubber tubing

Conc. HCl

Dropping  
funnel

Capillary

Conc.  
 $H_2SO_4$

Conc.  $H_2SO_4$

Trap

Drain waste acids

## EXPERIMENTAL AND RESULTS

I- (A) The effect of strong organic acids on the polymerization reaction involved in the preparation of an alkyd.

The effect of strong acids on the polymerization reaction involved in the preparation of an alkyd was studied with a view to find out whether the acid acted catalytically (as it would in ordinary polyesterification reactions) or incorporated itself into the polymeric mass as a telomer (monobasic acids act as terminating blocks for polymeric macro molecules).

That the organic acid acted catalytically was proved by two different approaches:

1) Kinetic Approach: An alkyd was prepared using trimethylol ethane, benzoic acid and isophthalic acid in the proportions given below. This alkyd will henceforth be called alkyd A.

	<u>No. of equivts.</u>	<u>Equivt. weight</u>	<u>Total weight in grams</u>
Benzoic acid	0.535	122	65.4
Isophthalic acid	0.855	83	71
Trimethylol ethane (T.M.E.)	1.39	40	55.6
Solvent: diisobutyl ketone (75 cc.)			

The rate of polymerization was kinetically determined by the amount of water that distilled off at regular

intervals. Four polymerization reactions containing the above components were run. The first served as a control and contained no strong organic acid. The other three polymerizations were run using 0.06 equivalents of pure p-toluene sulfonic acid, ( $K_1$  determined by pH measurement and found to be  $2.134 \times 10^{-4}$ ) 0.03 equivalents of p-nitrobenzoic acid ( $K_1$  determined by pH measurement and found to be  $4 \times 10^{-4}$ ) and 0.04 equivalents of dichloro-acetic acid ( $K_1$  is  $5 \times 10^{-2}$ )<sup>13</sup>.

According to Flory<sup>14</sup> catalyzed polyesterifications are second-order reactions.

If in a polyesterification  $[\text{COOH}] = [\text{OH}] = c$  one can write  $-dc/dt = Kc^2$ .

Where the concentration of the catalyst is included in the second-order rate constant K.

It is convenient here, and for many other purposes to introduce a parameter called the extent of the reaction and designated by P, which represents the fraction of the functional groups initially present that have undergone reaction at time t. In the polyesterification process P represents the ratio of the volume of the water liberated at any time t to the theoretical volume expected when cross linking is complete (This is given in column six in all subsequent tables). Now  $c = c_0 (1-P)$  where  $c_0$  is the initial concentration of the functional groups.



$$\text{Therefore, } c_0Kt = \frac{1}{1-P} - \text{constant}$$

Thus the plot of  $\frac{1}{1-P}$  versus time for catalyzed polyesterifications should give a linear curve.

The results of the three polymerizations run in the presence of the strong organic acid are summarized in tables II, III and IV. The plots of  $\frac{1}{1-P}$  versus time for these three cases are given in figures 4, 5 and 6. The linear nature of the curves obtained confirm the belief that the strong organic acids acted catalytically.

In the case of the uncatalyzed polyesterification

$$-d \frac{[\text{COOH}]}{dt} = K [\text{COOH}]^2 [\text{OH}] .$$

If the hydroxyl and carbonyl group concentrations are equal, both given by  $c$ , the above equation may be replaced by the standard integrated expression for a third-order reaction.

$$2Kt = \frac{1}{c^2} - \text{constant,}$$

however  $c = c_0(1-P)$ ,

$$\text{therefore } 2c_0^2Kt = \frac{1}{(1-P)^2} - \text{constant.}$$

Thus the plot of  $\frac{1}{(1-P)^2}$  versus time for uncatalyzed polyesterifications should give linear curves.

The results obtained for the polymerization run in the absence of the strong acid are summarized in Table I.

Table I

Preparation of alkylid (A) in the absence of a strong organic acid (P represents the ratio of the volume of water liberated to the total volume of water expected when cross linking is complete)

Time in min.	Temp. °C	mls of H <sub>2</sub> O distilled	stirring r.p.m.	mls CO <sub>2</sub> per min.	P	1/(1-P) <sup>2</sup>
40	202	4.5	900	200	4.5/25	1.5
70	208	7.3	900	200	7.3/25	2.0
100	210	13.0	900	200	13.0/25	4.4
130	208	16.2	900	200	16.2/25	8.1
160	212	17.6	900	200	17.6/25	11.5
190	215	18.6	900	200	18.6/25	15.0
220	208	19.2	900	200	19.2/25	18.5
250	210	19.7	900	200	19.7/25	22.1
280	213	20.0	900	200	20.0/25	25.0

Table II

Preparation of alkyd (A) in the presence of 0.06 equivalents of p-toluene sulfonic acid

Time in min.	Temp. °C	mls of H <sub>2</sub> O distilled	Stirring r.p.m.	mls CO <sub>2</sub> per min.	P	l/l-P
25	147	5.0	900	200	5/25	1.25
30	157	10.6	900	200	10.6/25	1.73
35	164	14.0	900	200	14/25	2.30
37	168	15.0	900	200	15/25	2.55
40	192	16.0	900	200	16/25	2.80
45	210	18.0	900	200	18/25	3.57
50	212	22.5	900	200	22.5/25	10.0

Table III

Preparation of alkyd (A) in the presence of 0.03 equivalents of p-nitrobenzoic acid

Time in min.	Temp. °C	mls of H <sub>2</sub> O distilled	stirring r.p.m.	mls CO <sub>2</sub> per min.	P	1/1-P
30	183	0.5	900	200	0.5/25	1.02
35	185	1.5	900	200	1.5/25	1.05
40	185	1.7	900	200	1.7/25	1.07
45	191	2.7	900	200	2.7/25	1.10
50	198	3.1	900	200	3.1/25	1.18
55	200	4.1	900	200	4.1/25	1.20
60	202	5.7	900	200	5.7/25	1.30
65	203	7.2	900	200	7.2/25	1.40
70	205	8.5	900	200	8.5/25	1.50
90	196	12.0	900	200	12.0/25	1.90
110	204	14.3	900	200	14.3/25	2.30
125	205	16.0	900	200	16.0/25	2.70
140	207	17.8	900	200	17.8/25	3.55

Table IV

Preparation of alkyd (A) in the presence of 0.04 equivalents of dichloro-acetic acid

Time in min.	Temp. °C	mls of H <sub>2</sub> O distilled	Stirring r.p.m.	mls CO <sub>2</sub> per min.	P	l/l-P
30	190	-	900	200		
40	195	1.0	900	200	1/25	1.04
50	200	4.0	900	200	4/25	1.20
60	202	8.0	900	200	8/25	1.50
70	205	12.0	900	200	12/25	2.04
80	208	16.0	900	200	16/25	2.80
90	210	17.8	900	200	17.8/25	3.40
100	210	19.0	900	200	19/25	4.10
110	210	20.0	900	200	20/25	5.00

Fig.4. Preparation of alkyd (A) in the presence of 0.06 equivalents  
of p-toluene sulfonic acid.  
(data from table II)

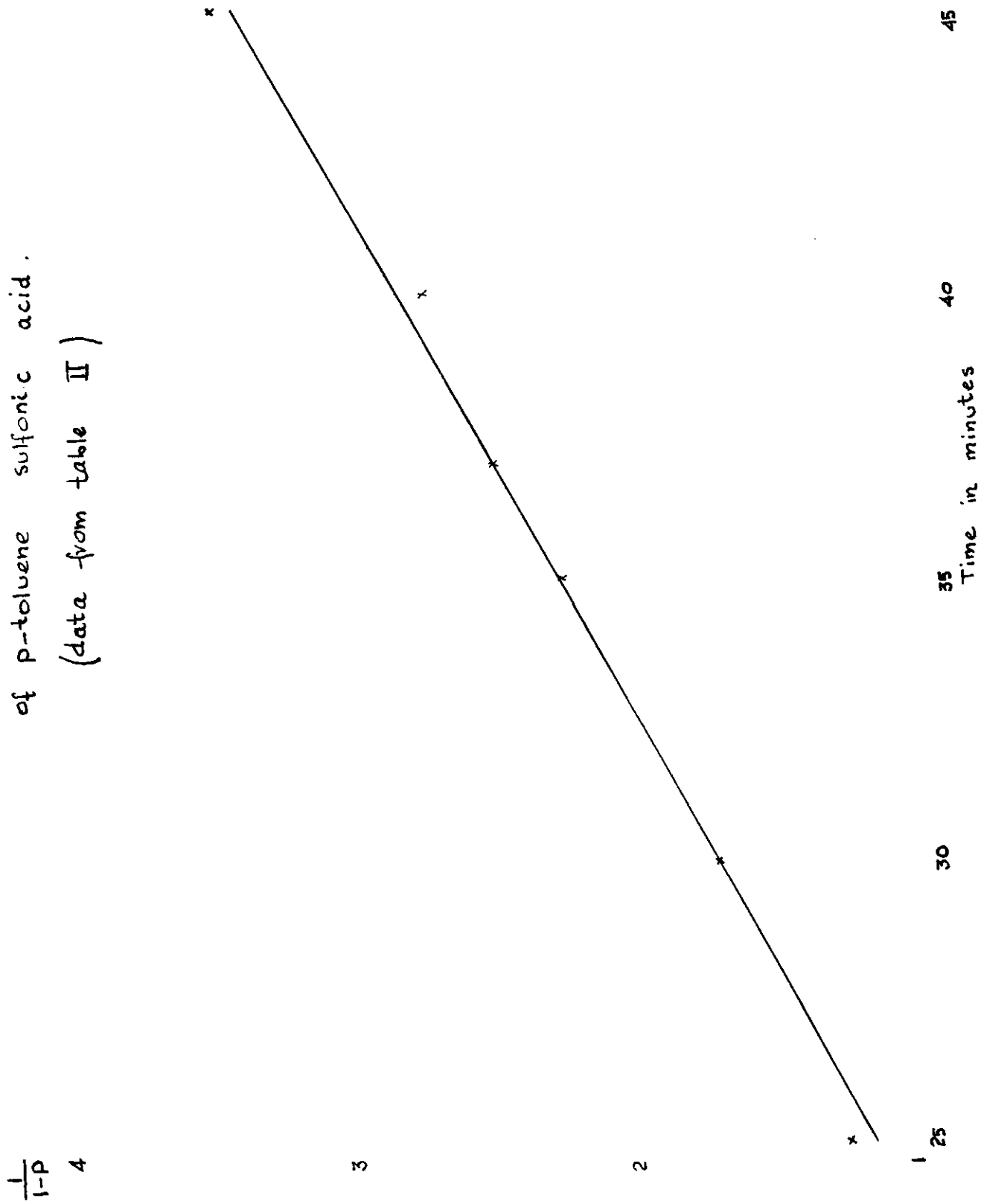


Fig.5. Preparation of alkyd (A) in the presence of 0.03 equivalents  
of p-nitrobenzoic acid.  
(data from table III)

$\frac{1}{1-P}$   
3

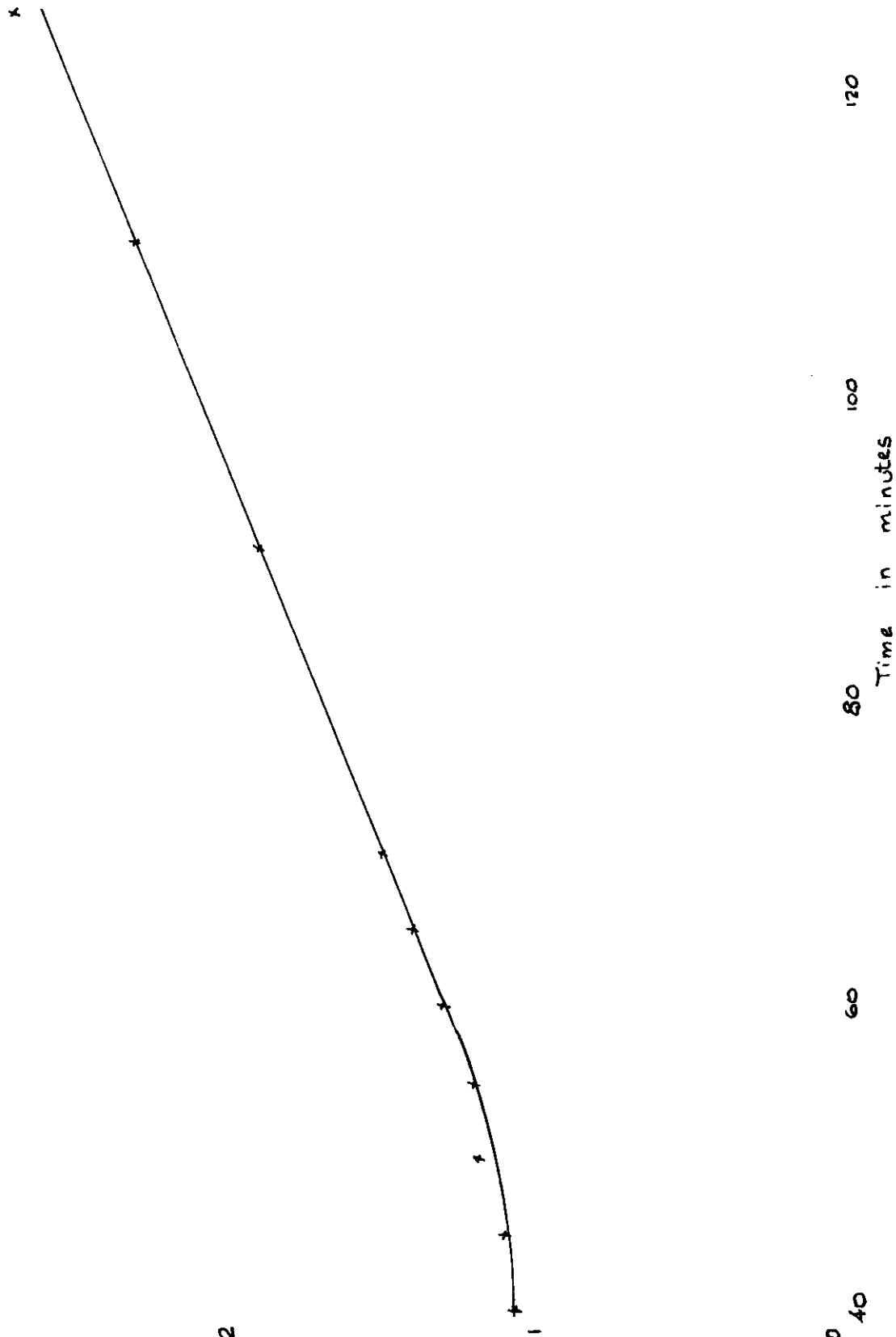
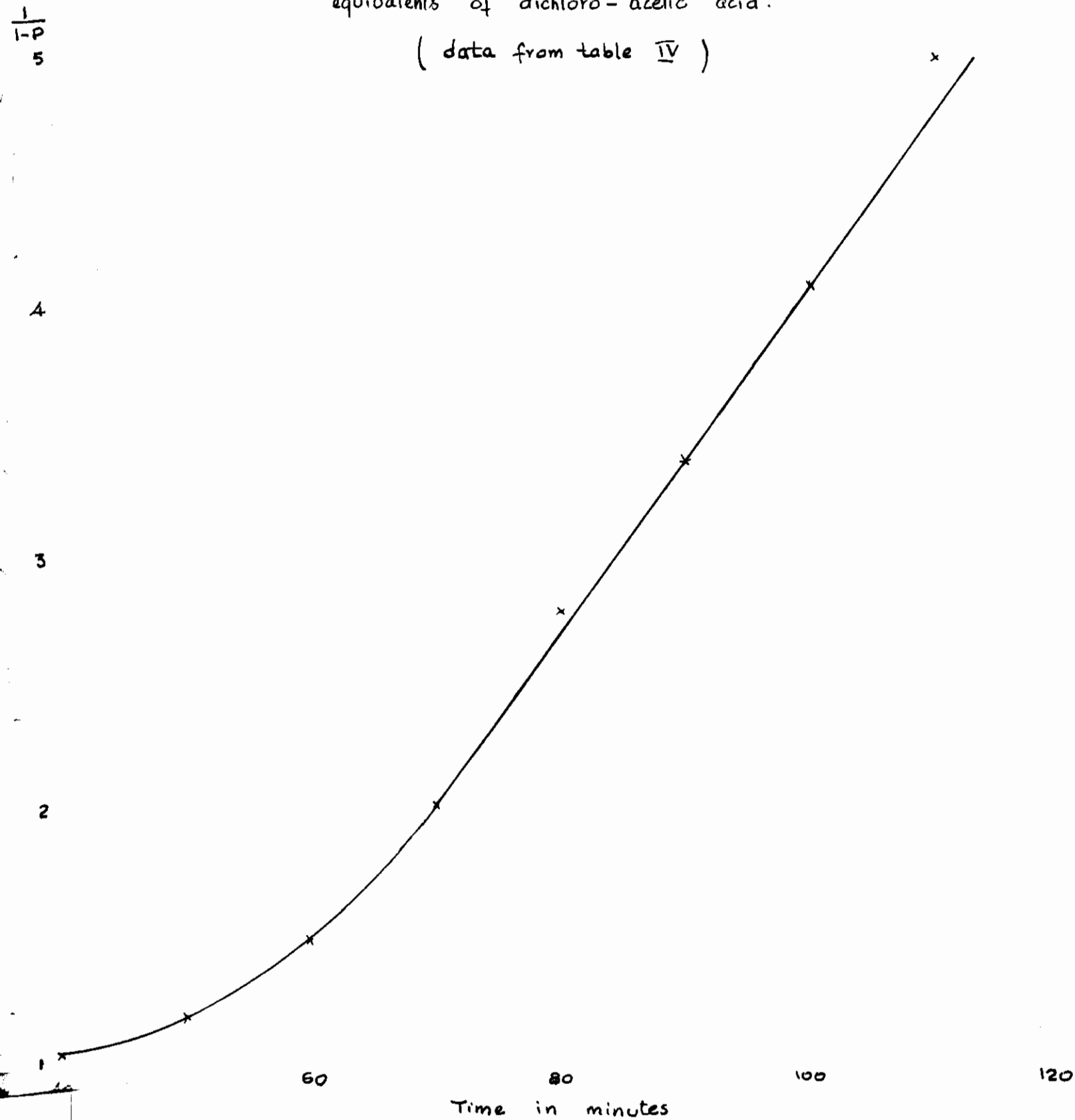


Fig. 6. Preparation of alkyd (A) in the presence of 0.04 equivalents of dichloro-acetic acid.

( data from table IV )

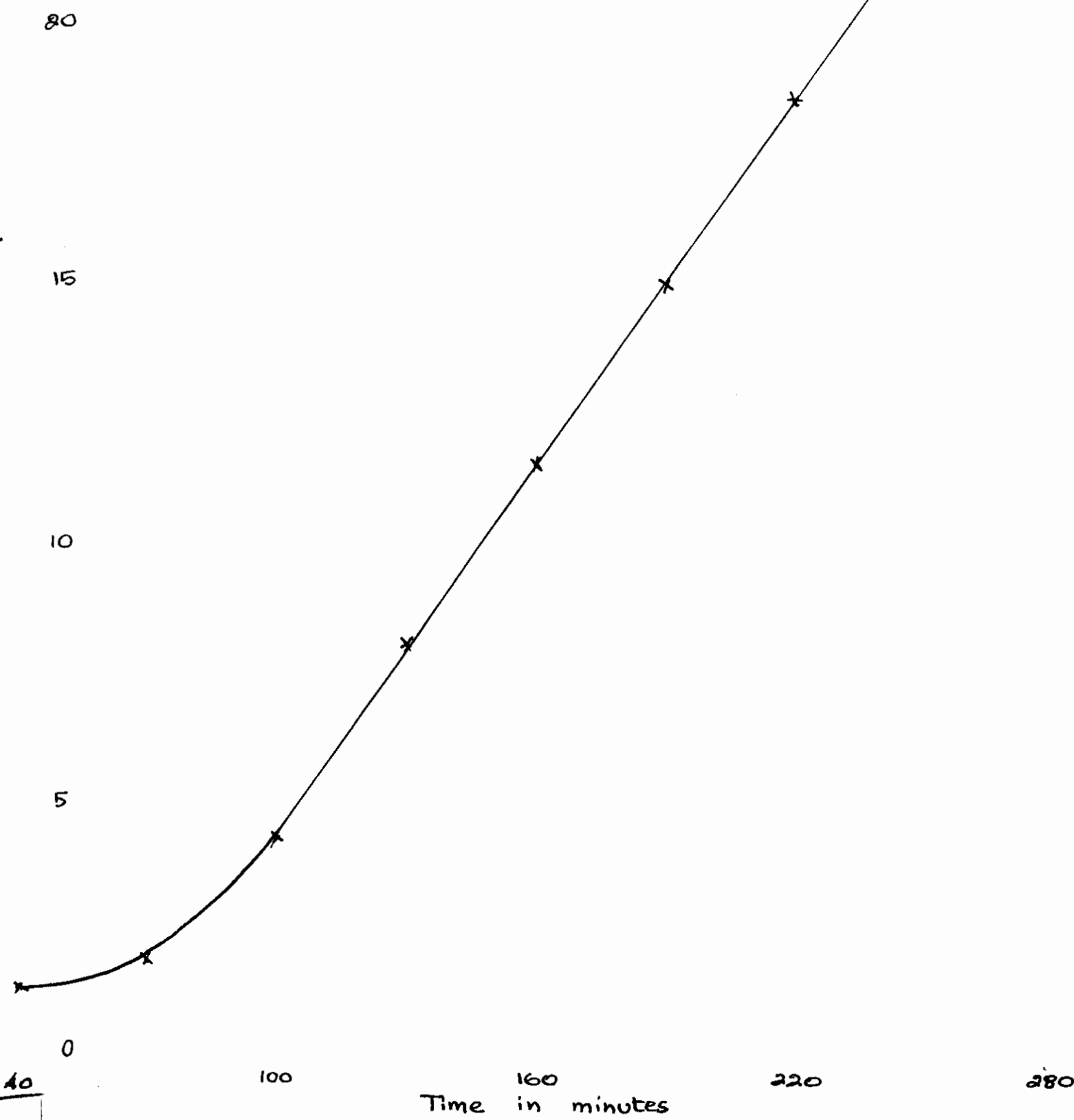




$$\frac{1}{(1-P)^2}$$

25

Fig. 7. Preparation of alkyd (A) in the absence of a catalyst.  
(data from table I)



The plot of  $\frac{1}{(1-P)^2}$  versus time (Fig. 7) gave a linear curve.

The non-linear nature of some of the curves over the earlier portion of the reaction has been attributed by Flory<sup>15</sup> to pronounced changes in the characteristics of the medium with the disappearance of so many hydroxyl and carboxyl groups.

(A)  
2) End-group analysis approach: Alkyds ~~of various formulations were~~<sup>was</sup> prepared in the normal way using different concentrations of p-toluene sulfonic acid. The polymers were dried and each was purified by repeated extraction with water. p-toluene sulfonic acid is water soluble and would be expected to be washed away unless it reacted as a telomer with the constituents of the alkyd. The purified polymer was tested for the presence of sulfur by different qualitative tests. These were all negative.

Hence, end-group analysis adds another conclusive evidence that p-toluene sulfonic acid acted in a catalytic capacity.

(B) Effect of acid concentration on the speed of the polymerization reaction involved in the preparation of an alkyd.

The effect of the acid concentration on the speed of the polymerization reaction was studied using p-toluene sulfonic acid at four levels of concentration, namely 0.018, 0.03, 0.06 and 0.09 equivalents. The results obtained are

tabulated in Tables V, VI, II and VII respectively.

The plot of  $1/1-P$  versus time for the first three cases are given in fig. 8. The results show that the speed of the polymerization, increases with the increase of the catalyst concentration. This is true until a certain limit after which further increase in concentration results in side reactions which are characterized by appreciable decomposition and discoloration of the polymeric mass. This was clearly shown in the case where 0.09 equivalents of the acid was used, hence, the reason for the absence of a fourth curve.

(C) Effect of the strength of an acid on the speed of the polymerization reaction involved in the preparation of an alkyd.

Two similar formulations were polymerized, the first catalyzed with 0.03 equivalents of p-nitrobenzoic acid and the second with 0.03 equivalents of p-toluene sulfonic acid. The results are given in fig. 9. p-toluene sulfonic acid is stronger than p-nitrobenzoic acid. The difference in slope between the two curves justifies the belief, that stronger acids are more effective in so far as the speed of the polymerization is concerned.

(D) Side effect of strong organic acids on the alkyd polymerization reaction.

Strong organic acids when used in catalyzing alkyd preparations, in concentrations above certain fixed values,

Table V

Preparation of alkyd (A) in the presence of 0.018 equivalents of p-toluene sulfonic acid

Time in min.	Temp. °C.	mls of H <sub>2</sub> O distilled	Stirring r.p.m.	mls CO <sub>2</sub> per min.	P	l/l-P
25	180	2.3	900	200	2.3/25	1.10
30	185	7.8	900	200	7.8/25	1.45
35	192	9.8	900	200	9.8/25	1.65
40	200	12.5	900	200	12.5/25	2.00
45	210	13.8	900	200	13.8/25	2.25
50	215	15.0	900	200	15.0/25	2.50

Table VI

Preparation of alkyd (A) in the presence of 0.03 equivalents of p-toluene sulfonic acid

Time in min.	Temp. °C.	mls of H <sub>2</sub> O distilled	Stirring r.p.m.	mls CO <sub>2</sub> per min.	P	l/l-P
25	149	3.3	900	200	3.3/25	1.15
30	157	9.8	900	200	9.8/25	1.65
35	168	13.5	900	200	13.5/25	2.20
40	182	15.8	900	200	15.8/25	2.70
45	190	17.0	900	200	17.0/25	3.20
50	200	20.0	900	200	20.0/25	5.00

Table VII

Preparation of alkyd (A) in the presence of 0.09 equivalents of p-toluene sulfonic acid

Time in min.	Temp. °C	mls of H <sub>2</sub> O distilled	stirring r.p.m.	mls CO <sub>2</sub> per min.	P	l/l-P
25	150	5.0	900	200	5/25	1.25
30	160	11.0	900	200	11/25	1.80
35	165	14.0	900	200	14/25	2.30

1  
29  
1

The reaction was discontinued due to the fact that the dark colour of the polymer makes it useless for any practical purpose.

Fig. 8. Preparation of allyds using p-toluene sulfonic acid at 3 levels of concentration.

(data from tables II, V & VI)

$\frac{1}{1-p}$   
4

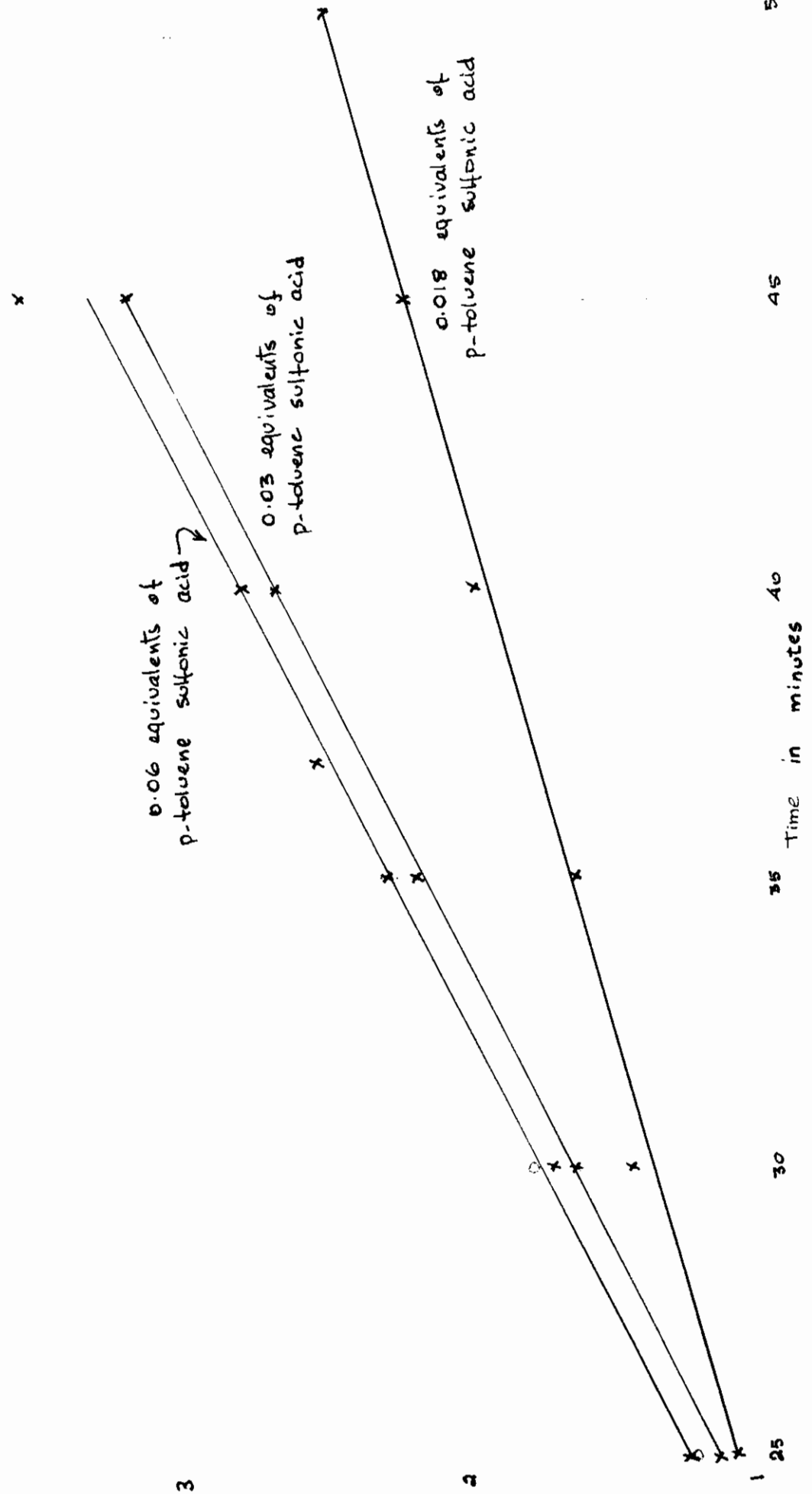
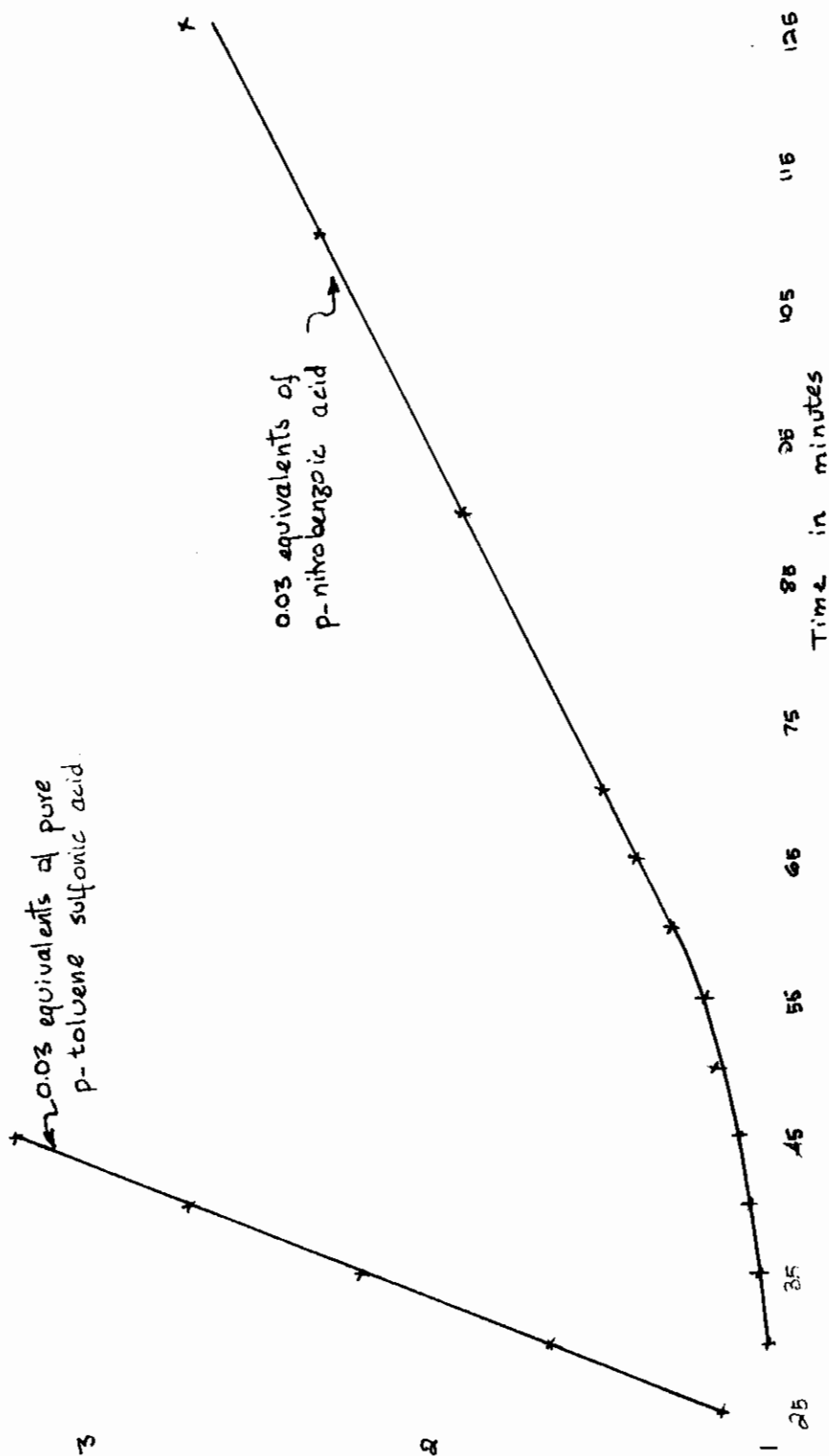


Fig. 9a. Preparation of alkyds in the presence of similar concentrations of two acids having different  $k_1$ 's.

data from tables III & VI

$\frac{1}{1-P}$   
4

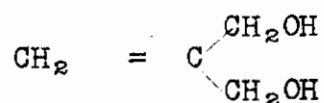




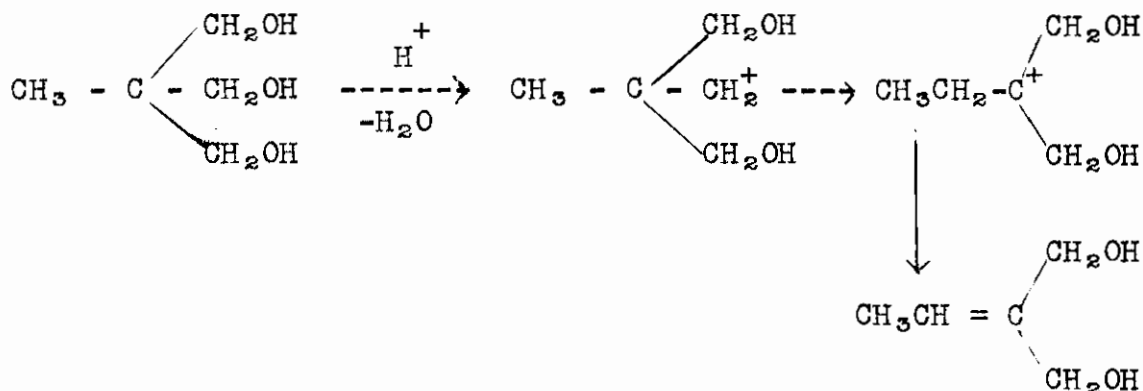
result in side reactions. These manifest themselves in appreciable discoloration of the polymeric mass and the appearance of coloured distillate by-products.

A mechanism explaining the polymer decomposition, with the appearance of unsaturated by-products, has been suggested in a previous work by Gabrielides<sup>16</sup>.

It is known that compounds containing the following configuration



Reduce  $\text{KMnO}_4$  but do not add free bromine. The mechanism given for the formation of the unsaturated diol (refer to Table VIII) is as follows:



This partly decomposes, partly polymerizes by addition and partly by condensation.

(E) Summary.

It was found possible to catalyze the polymerization reaction involved in the preparation of an alkyd through the use of strong organic acids.

Table VIII

Acid catalyst used	Concentration in moles/batch	Colour of distillate	Reaction towards addition of $\text{KMnO}_4$ solution	Reaction towards addition of free bromine
No catalyst	----	colorless	does not discolor $\text{KMnO}_4$	does not add Br
p-toluene sulfonic acid	0.018	colorless	does not discolor $\text{KMnO}_4$	does not add Br
p-toluene sulfonic acid	0.03	slightly yellow	discolors $\text{KMnO}_4$	does not add Br
p-toluene sulfonic acid	0.06	yellow	discolors $\text{KMnO}_4$	does not add Br
p-nitrobenzoic acid	0.03	slightly yellow	discolors $\text{KMnO}_4$	does not add Br
p-nitrobenzoic acid	0.06	yellow	discolors $\text{KMnO}_4$	does not add Br
dichloro-acetic acid	0.04	yellow	discolors $\text{KMnO}_4$	does not add Br

The addition of p-toluene sulfonic acid in small amounts (2.1% by weight) to a reaction mixture, reduced the time required for polymerization from 4-5 hours (in the case of the uncatalyzed polymerization to 50 minutes.

In the polyesterification reaction involved in the preparation of alkyds, the temperature was continually changing within a range of 50°C. The fact that the plot of

$\frac{1}{1-P}$  (or  $\frac{1}{(1-P)^2}$ ) versus time remains linear, inspite of

these temperature variations strongly suggests that the activation energy of the polyesterification reaction is very close to zero.

## II- Infrared study of silicone-alkyd copolymers.

Infrared study of silicone-alkyd copolymers aimed at:

- A) Proving the existence of copolymerization between the alkyd resin and silicone intermediate.
- B) Finding out which of the components of the silicone-alkyd macromolecules is responsible for degradation at different service temperatures.

The two formulations mentioned below were used for all the infrared studies undertaken.

The following is a sample calculation showing how these formulations were obtained:

	<u>No. of equivts.</u>	<u>Eqivt.Wt.</u>	<u>Total weight in grams</u>
Benzoic acid	0.5	122	61
Isophthalic acid	0.66	83	55.4
Trimethylol ethane	1.16	40	<u>46.4</u>
			162.8
less of 1.16 moles of water liberated .....			<u>20.8</u>
weight of alkyd component .....			142.0
weight of silicone component in the product = $142 \times \frac{55}{45} = 173.5g.$			

equivalents of silicone needed =  $\frac{173.5}{180} = 0.96$

Hence total number of equivalents of T.M.E. needed =

$$0.96 + 1.16 = 2.12 \text{ equivalents.}$$

weight of T.M.E. needed =  $2.12 \times 40 = 84.8$  grams.

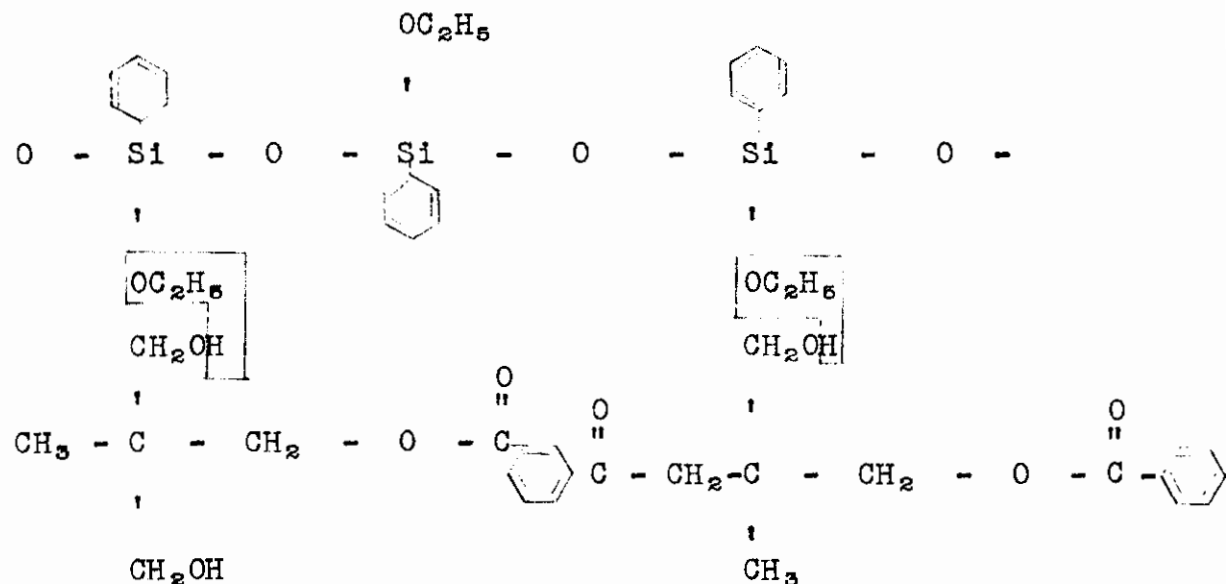
FORMULATION 1.

	<u>No. of Equivts.</u>	<u>Total Wt.</u>
Benzoic acid	0.5	61 grs.
Isophthalic acid	0.66	55.4 grs.
T.M.E.	2.12	85 grs.
Phenyl ethoxy (25%) polysiloxane	0.96	173.5 grs.

FORMULATION 2.

	<u>No. of Equivts.</u>	<u>Total Wt.</u>
Benzoic acid	0.5	61.0 grs.
Phthalic anhydride	0.66	49.4 grs.
T.M.E.	1.69	70.3 grs.
Phenyl ethoxy (25%) polysiloxane	0.87	158.0 grs.

In the next section, a proposal of the way in which copolymers are synthesized is given. The silicone intermediate is phenyl ethoxy (25%) polysiloxane, the polyol is trimethylol ethane, the dibasic acid is isophthalic acid and the monobasic acid is benzoic.



(A) Confirmation of the fact that copolymerization does take place between an alkyd resin and a silicone intermediate through infrared studies.

Infrared spectra of the alkyd resin and the silicone intermediate were taken separately for both formulations using both infrared instruments. The alkyd and silicone were then allowed to react together until imminent gelation. Spectra of the resulting resin in solution as well as in film form were taken. The changes in the bands characteristic of alkyd resin and the silicone intermediate were noted.

In the case of the two formulations under discussion, it is expected that copolymerization of the alkyd with the silicone is a co-condensation between the hydroxyl group of the alkyd and the ethoxy group of the silicone.

The evolution of ethyl alcohol during the co-condensation coupled with the fact that the hydroxyl band ( $3400\text{ cm}^{-1}$ ) which was very distinct in the spectrum of the alkyd and which was markedly decreased in intensity in the spectrum of the cured silicone-alkyd (fig. 11, 12 and 13) lent strong evidence that co-condensation involves the hydroxyl group of the alkyd and the ethoxy group of the silicone. The changes in the ethoxy band could not be detected as this group absorbs in a region of complete absorption (due to the influence of other groups which absorb in this same region).

Thus through the aid of chemical as well as instrumental methods, the belief that copolymerization is a co-condensation between the hydroxyl group of the alkyd and the alkoxy group of the silicone, was confirmed.

(B) Degradation of the silicone-alkyd copolymers.

Thin films of the copolymers made from the two previously mentioned formulations, were made by the dip method on glass panels covered with thin aluminum foil.

These films were degraded at  $220^{\circ}\text{C}$  for 25 hours, 50 hours and 75 hours; and at  $250^{\circ}\text{C}$  for 25 and 50 hours. To act as references films of the alkyd-silicones were given the less rigorous treatment of curing at  $180^{\circ}\text{C}$  for 1 hour.

After curing at the different temperatures the aluminum foil with the film was peeled off the glass panel and put on a Buchner funnel. Hydrochloric acid was added to dissolve the aluminum foil. After the aluminum was completely dissolved, the remaining film was repeatedly washed with distilled water. The film was then dried in a vacuum desiccator for twenty four hours at a pressure of 30 mms. of mercury.

The spectrum of the dried film was then taken using the double beam Perkin-Elmer Infracord.

The interpretation of the spectra of the cured and degraded films did not provide any conclusive information about the groups responsible for early degradation of the silicone-alkyd copolymers, at the different service temperature. The complexity of the molecular structure, resulting in an overlap of many bands, made the assignment of certain bands to specific groups difficult. Many of the regions of the spectra were regions of complete absorption where interpretation was not possible. Attempts at working with thinner films failed. Films made from very dilute solutions broke on subsequent curing and treatment. Thus, only regions where absorption was not intense could be studied.

Another of the problems confronting the tackling of this problem was the fact that the films made were not uniform in thickness. Thus, differences in the intensity of the absorption of certain bands, could not be used as a

conclusive criterion of changes in molecular structure, but could be attributed in some cases to differences in film thickness.

Fig. 9 is the spectrum of 25% ethoxy phenyl polysiloxane. Fig. 10, 11 and 12 show the spectra of silicone-alkyd films made from formulation 1. Fig. 10 shows the spectrum of the film cured for one hour at 180°C.; fig. 11 that of the film degraded at 250°C. for 50 hours and fig. 12 is the spectrum of the film degraded at 220°C. for 75 hours. Fig. 13 is the spectrum of a silicone alkyd film made from formulation 2. This film was degraded at 250°C. for 50 hours.

The only band which undergoes change and could be assigned to a definite group, is the band due to the hydroxyl group ( $3400\text{ cm}^{-1}$ ). This can be seen in the spectrum of the film cured at 180°C. for one hour, (fig. 10). This is within expectation as in this case the resin still has free hydroxyl groups. However, on curing at higher temperatures for longer time intervals, further cross linking takes place as witnessed by the practical disappearance of this band in the spectra given in fig. 11, 12 and 13. This has been used as one of the arguments for confirming the existence of copolymerization.

In the region between  $3000 - 2700\text{ cm}^{-1}$ , changes could be detected on degradation of resins at 250°C. The intensity of the sharp band near  $3000\text{ cm}^{-1}$  seemed to



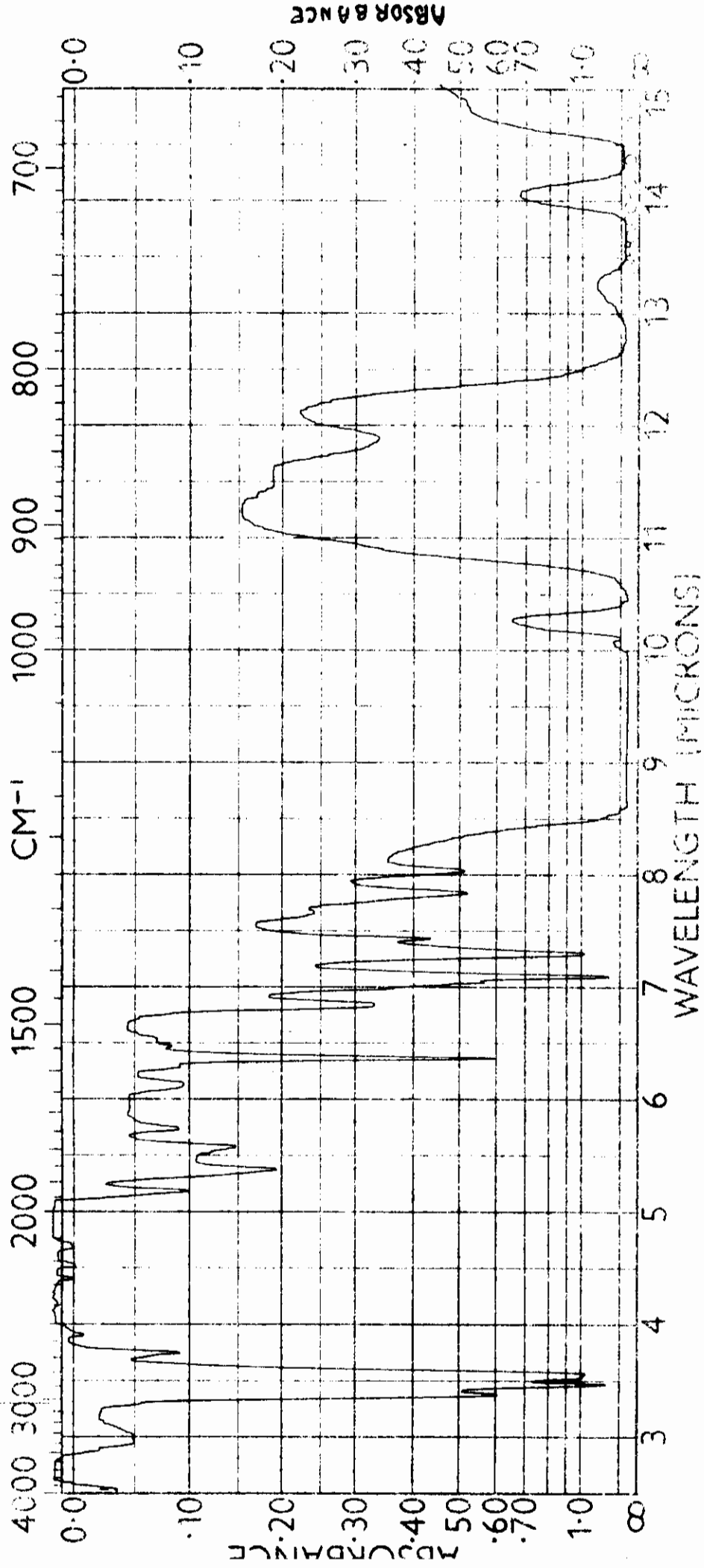


Figure 9. Spectrum of 25% Ethoxy phenyl polysiloxane

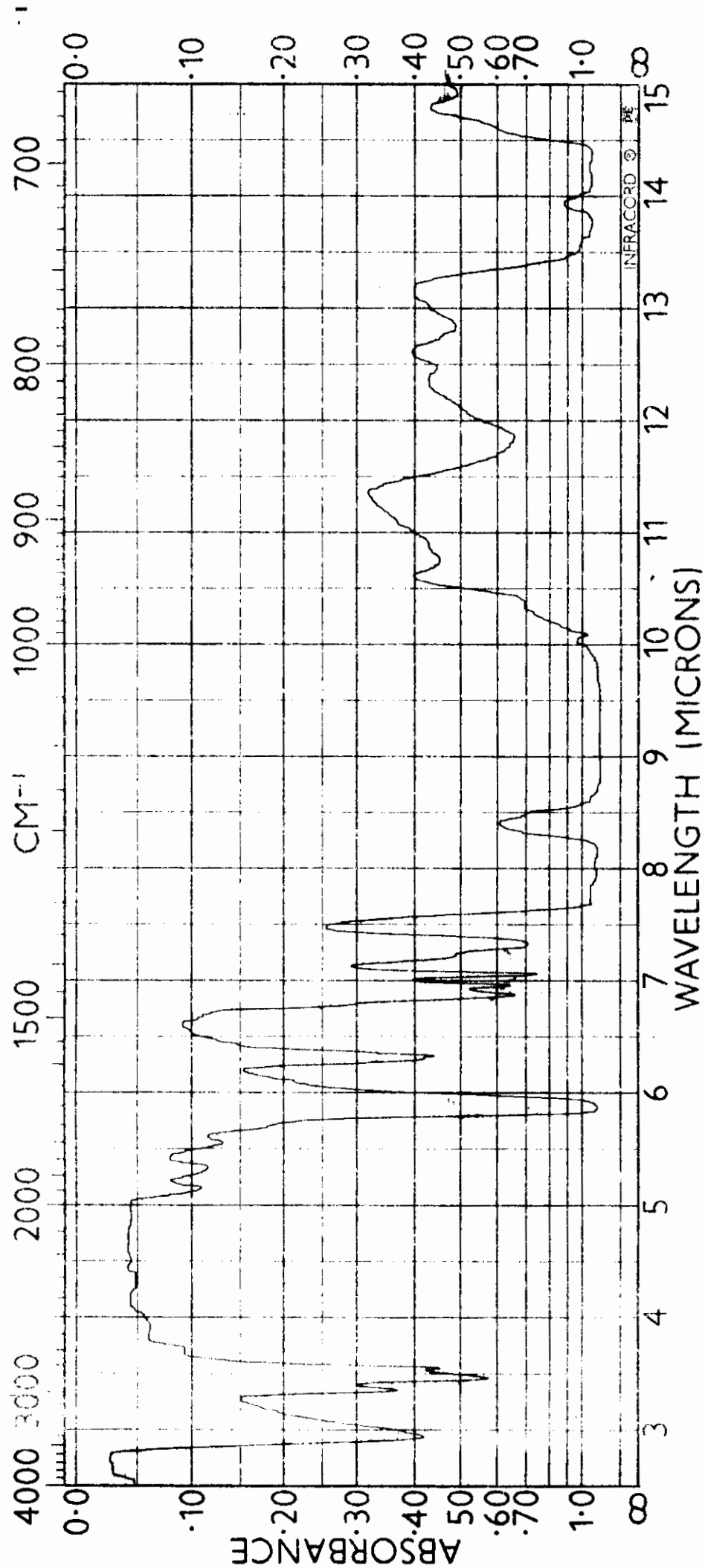


Figure 10 - Silicone - Alkyd (formulation I) Cured at 150°C for 1 hr

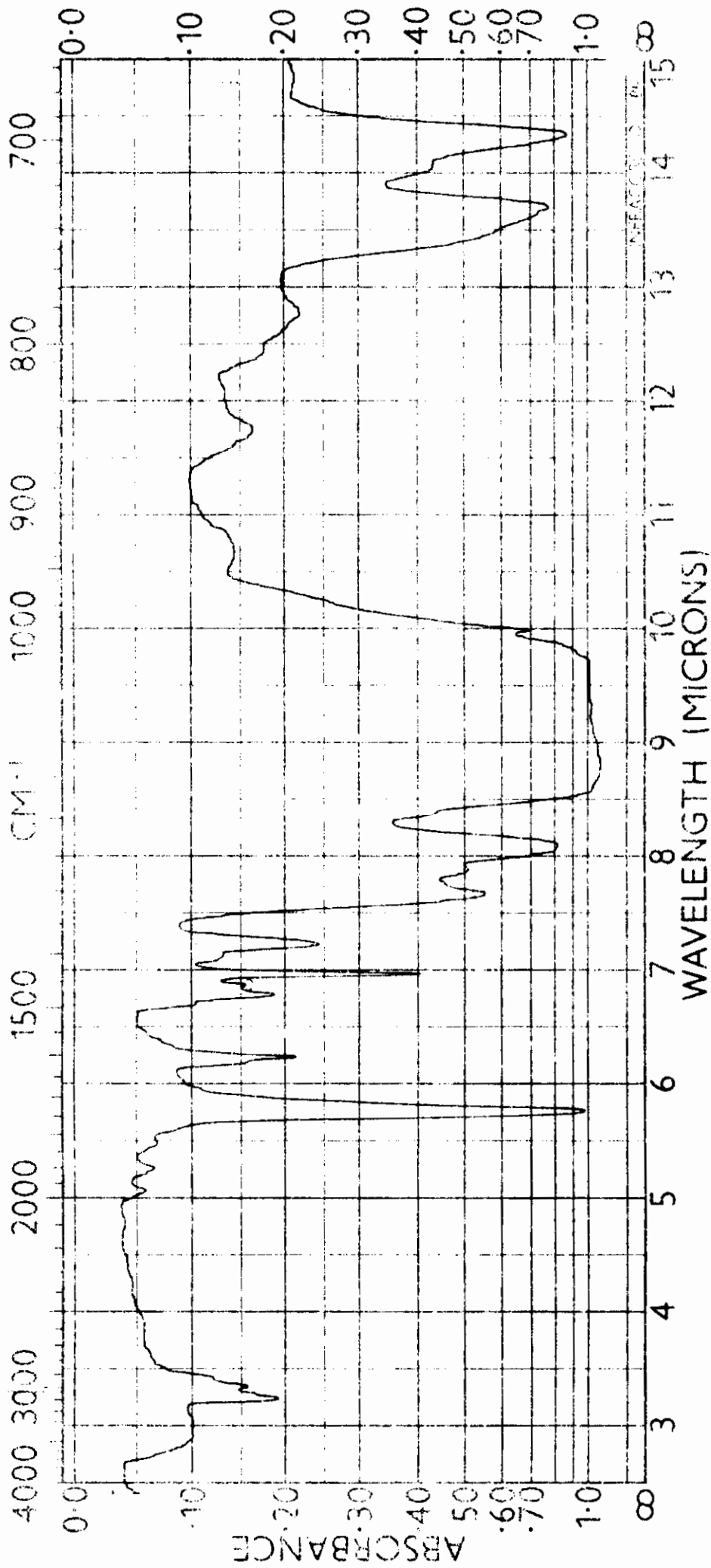


Figure 11 - Silicone-alkyd (formulation I) degraded at 250°C for 50 hrs.

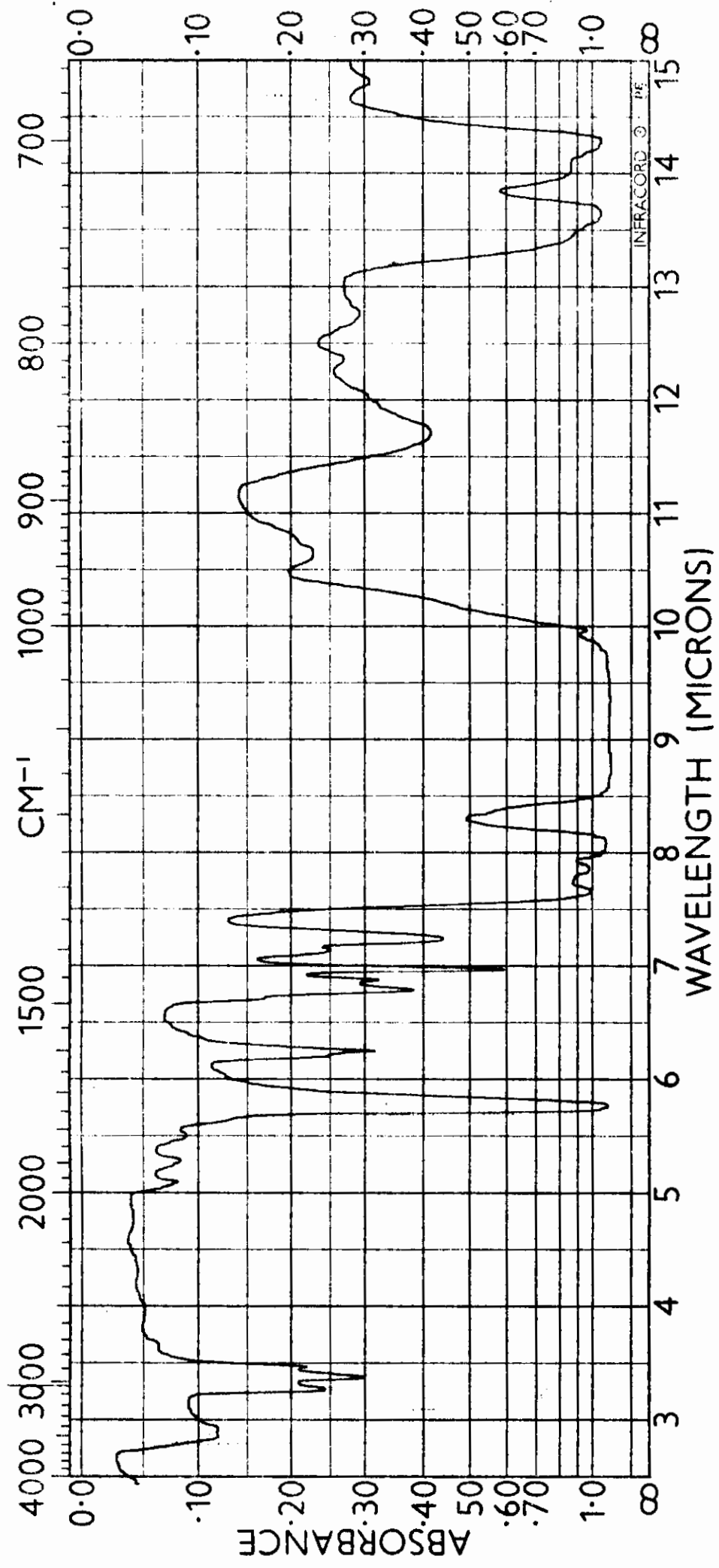


Figure 12 - Silicone-alkyd (formulation I) degraded at 220°C for 75 hrs

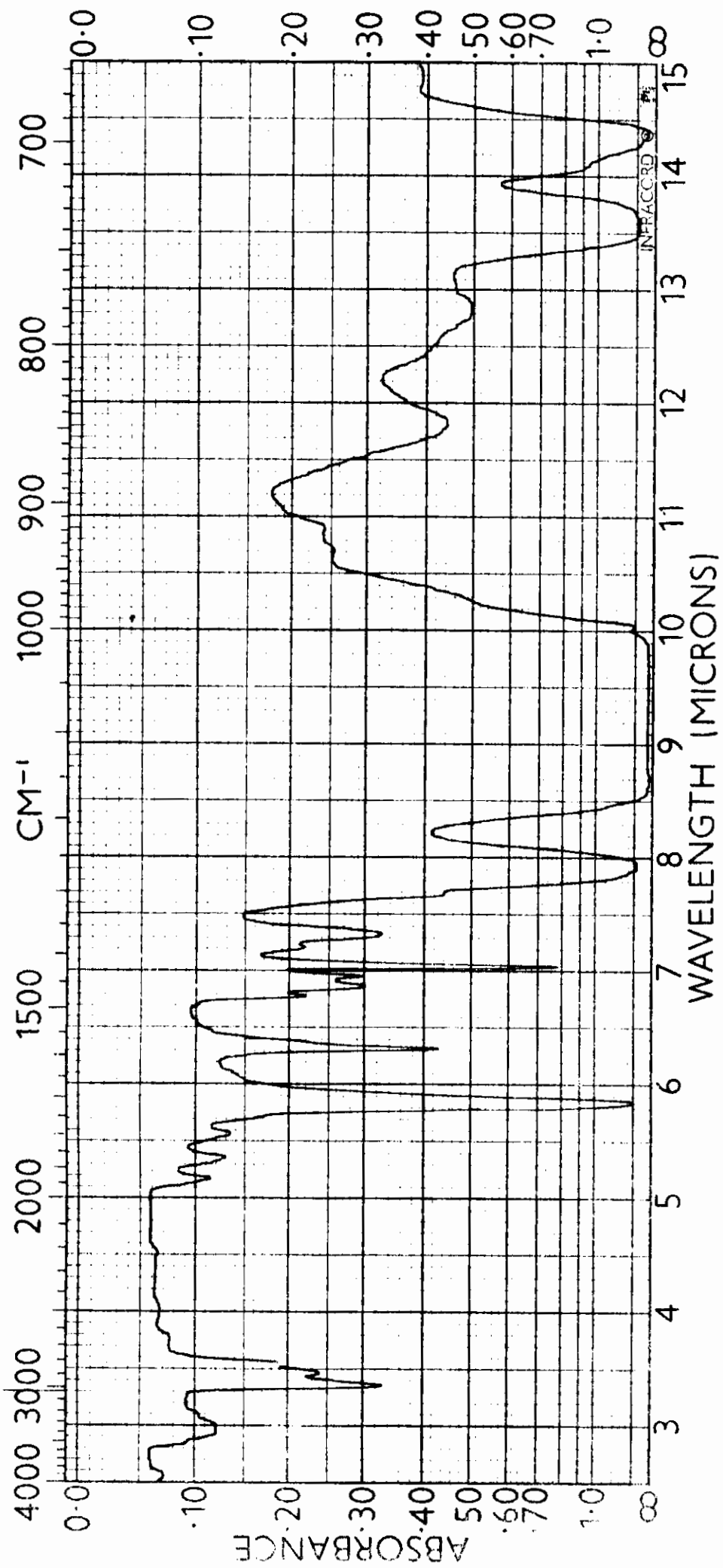


Figure 13 - Silicone alkylid (formulation 2) degraded at 250°C for 50 hrs.

decrease relative to the other two bands in this region (refer to fig. 10 and 13). The sharp band is attributed to aryl carbon-hydrogen vibrations (from the phenyl groups in the silicone), while the other two are alkyl carbon-hydrogen absorption bands<sup>17</sup>. The only conclusion one can draw is that on degradation at 250°C., the intensity of the phenyl carbon-hydrogen absorption band decreases relative to the alkyl carbon-hydrogen absorption band.

In the case of films made from formulation 1, another change was noted on degradation. The band at 1429 cm<sup>-1</sup> which was distinct in the spectrum of the film cured at 180°C. for one hour (fig. 10) seemed to decrease in intensity (relative to the sharp band at 1600 cm<sup>-1</sup>) on degradation at higher temperatures and for longer intervals of time (fig. 11 and 12). This band was not found in the spectrum of the silicone and could be attributed to the meta substituted phenyl group present in the alkyd<sup>18</sup>.

Another band which appeared to be changing in intensity on degradation was the one at 850 cm<sup>-1</sup> (refer to fi. 10 and 11). This could be the phenyl group absorption band<sup>19</sup>.

## BIBLIOGRAPHY

1. Abdul Karim, A., (Purdue University), Dissertation Ab.,  
17, 581 (1957).
2. Gabrielides, J., "Silicone-Alkyds", M.S. Thesis,  
American University of Beirut, (1958).
3. Midland Silicones Ltd., "Organosiloxane Copolymers",  
Brit. Patent 790, 182 (1950).
4. Wright, N., and Hunter, M.J., J. Am. Chem. Soc., 69,  
803 (1947).
5. Hyde, J.F., Frevel, L.K., Nutting, H.S., and Petrie, P.S.,  
J. Am. Chem. Soc., 69, 488 (1947).
6. Young, C.W., Servais, P.C., Currie, C.C., and Hunter, M.  
J., J. Am. Chem. Soc., 70, 3758 (1948).
7. Richards, R.E., and Thompson, H.W., J. Am. Chem. Soc.,  
124, (1949).
8. Clark, H.A., Gordon, A.F., and Young, C.W., J. Am. Chem.  
Soc., 73, 3798 (1951).
9. Post, H.W., "Silicones and Other Organic Silicon  
Compounds", Reinhold Publishing Corp., New York,  
(1949).
10. Rochow, E.G., "An Introduction to the Chemistry of the  
Silicones", Wiley and Sons, Inc., New York, 1951.
11. McGregor, R.R., "Silicones and Their Uses", McGraw-Hill  
Book Company, Inc., New York (1954).

12. Fieser, L., "Experiments in Organic Chemistry", D.C. Heath and Company, Boston (1955) p. 298.
13. Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland Ohio (1953-54) p. 1637.
14. Flory, P.J., "Principles of Polymer Chemistry", Cornell University Press, New York (1953) p. 81.
15. Flory, P.J., J. Am. Chem. Soc., 61, 3334 (1939); 62, 2261.
16. See Ref. 2, p. 46.
17. Bellamy, L.J., "The Infrared Spectra of Complex Molecules", John Wiley and Sons, Inc., New York p. 13 + p. 65.
18. See Ref. 17, p. 73.
19. See Ref. 17, p. 78.



RAW MATERIALS

Benzoic Acid: C.P., Merck.

Isophthalic Acid: Technical, Oronite Chemical Company.

Phthalic Anhydride: Technical, Monsanto Chemical and  
Plastics.

p-Nitrobenzoic Acid: C.P. Merck.

Dichloro-acetic Acid: C.P. Fisher Scientific Company.

T. M. E.: Technical, Hayden Chemical Corporation.

Phenyl-ethoxy-poly-  
siloxane (25% ethoxy): Union Carbide and Carbon Corporation.

Diisobutyl Ketone: Technical, Eastman Kodak.

p-Toluene sulfonic  
Acid: Technical, Eastman Kodak.