

RESULTS
AND
DISCUSSION

RESULT AND DISCUSSION

Alkyd resins are polyester-based materials that are normally modified with oils or fatty acids. These products are further modified with a variety of other chemical materials. Various polybasic acids, polyhydric alcohols, oils, fatty acids and modifying agents may be combined to produce alkyds with specifically designed properties.

Phthalic anhydride is the most important acid used in alkyd resin because of its low cost and the excellent properties. Isophthalic acid has become more extensively used. Its alkyd have the following characteristics, higher molecular weight, higher viscosity, better drying properties and harder and more durable films with better heat and chemical stability.

Also maleic and/or fumaric acids are used to replace part of the phthalic anhydride, these acids react with the unsaturation of the fatty acids, thus increase the molecular weight of alkyd resin. These alkyds dry more rapidly and gives harder films with better alkali resistance and better exterior durability.

The scope of the present investigation is the modification of alkyd by the partial replacement of the phthalic anhydride by tetrabromophthalic anhydride. This modification would expect to improve the performances of the dry films.

Although oil-modified alkyd resins have been known for quite along time, they have shown a remarkable ability to maintain their position as one of the major types of vehicles used in surface coating industry.

Another target of the present investigation is the formulation of long alkyds based on rice bran oil and evaluation of their varnish as a vehicle for surface coating.

Resin preparations:

Alkyds based on rice bran oil or fatty acid:

Glycerolysis of rice bran oil or fatty acids was carried out at 220°C in the presence of lead oxide as glycerolysis catalyst, the esterification reaction was conducted at 220°C to the end of the reaction. At the end of glycerolysis the reaction mixture was cooled to about 100°C, then phthalic anhydride and/or tetrabromophthalic anhydride were added. The replacement ratio of tetrabromophthalic anhydride are (0, 25, 50 and 100% respectively), without affecting the resin constant. The composition of different alkyd resins was listed in table (20).

Modification of long oil length from rice bran oil, linseed oil and its fatty acids:

In the following runs, a part of rice bran oil or its fatty acids was replaced by an equivalent amount of linseed oil or its fatty acids. Linseed oil was incorporated together with rice bran oil from the beginning of the glycerolysis reaction. The content of linseed oil in the oil mixture varied from Zero to 50 percent by weight. The reaction was followed by the method used previously for the unmodified rice bran oil.

The reaction was followed by measuring the acid value as shown in fig (1-12).

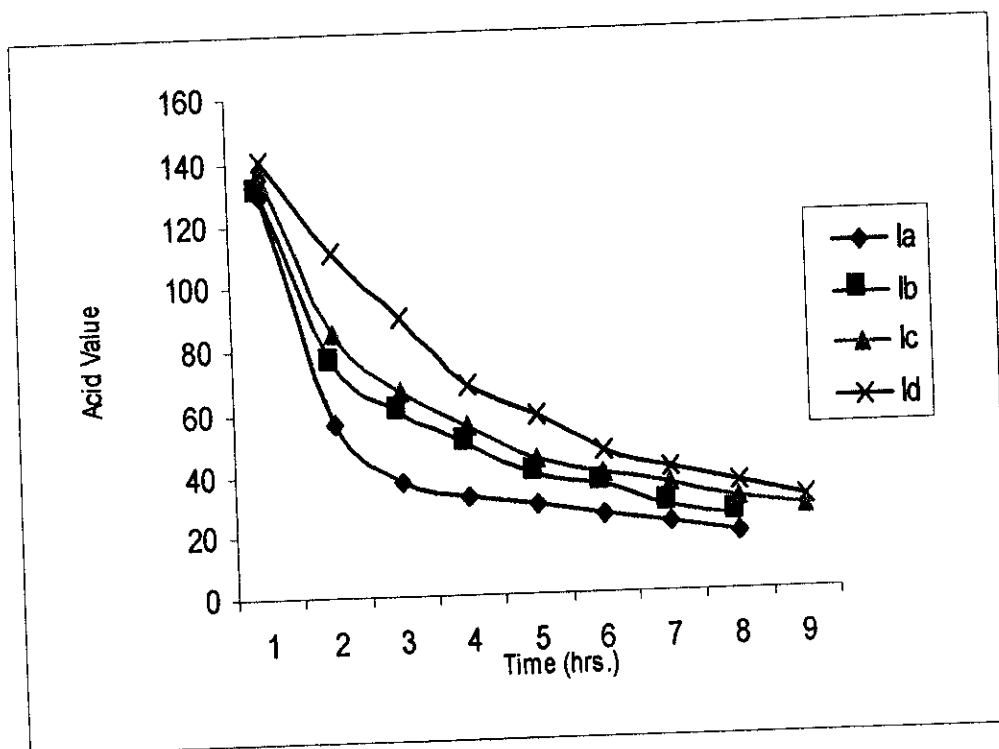


Fig. (1): Acid value of alkyd containing 100% RBO.

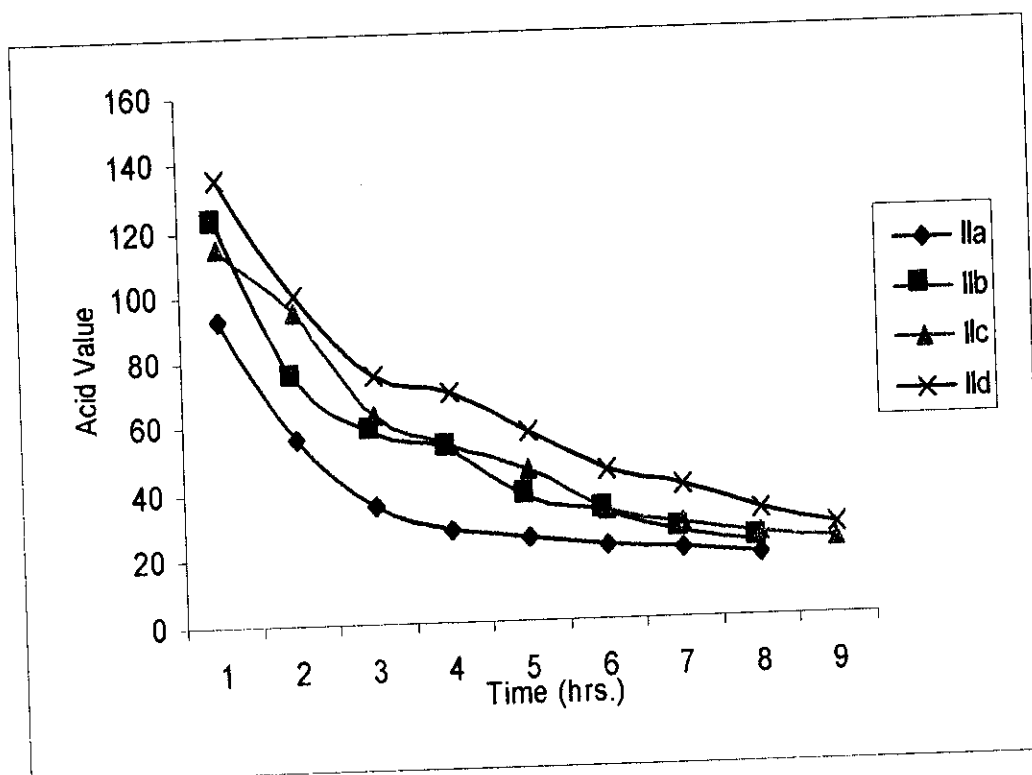


Fig. (2): Acid value of alkyd containing 90% RBO.

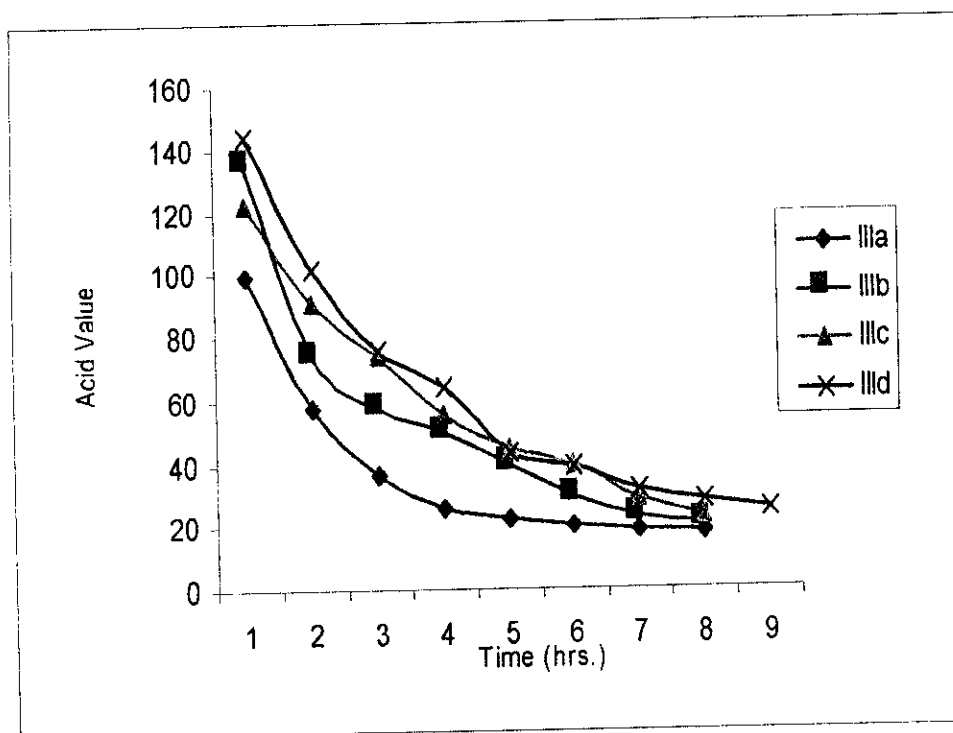


Fig. (3): Acid value of alkyd containing 80% RBO.

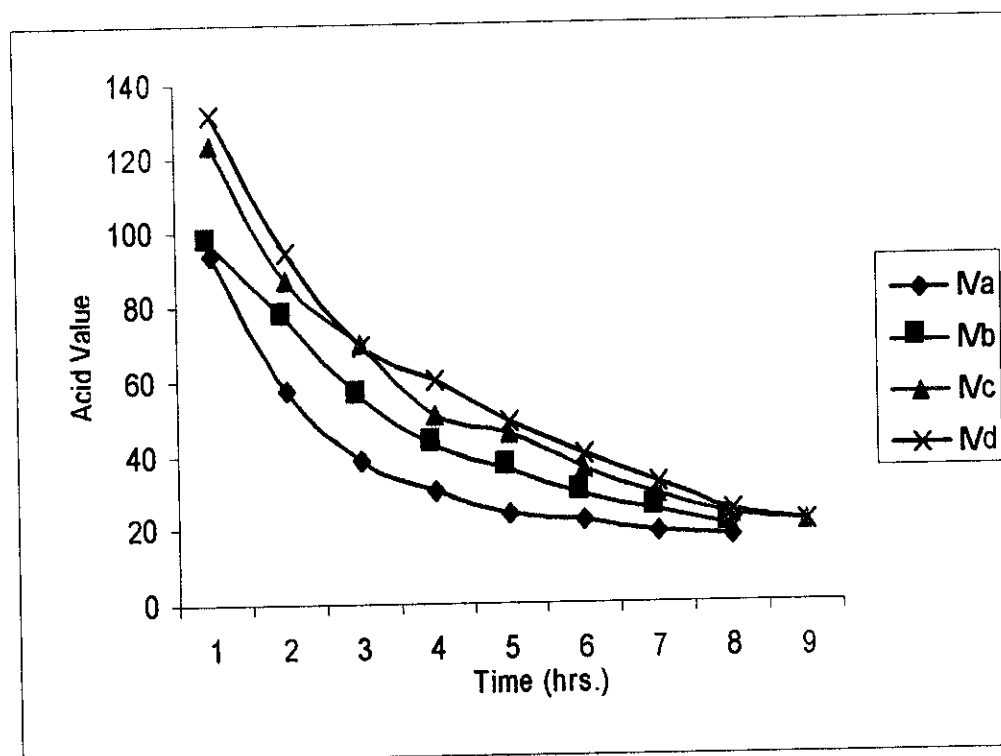


Fig. (4): Acid value of alkyd containing 70% RBO.

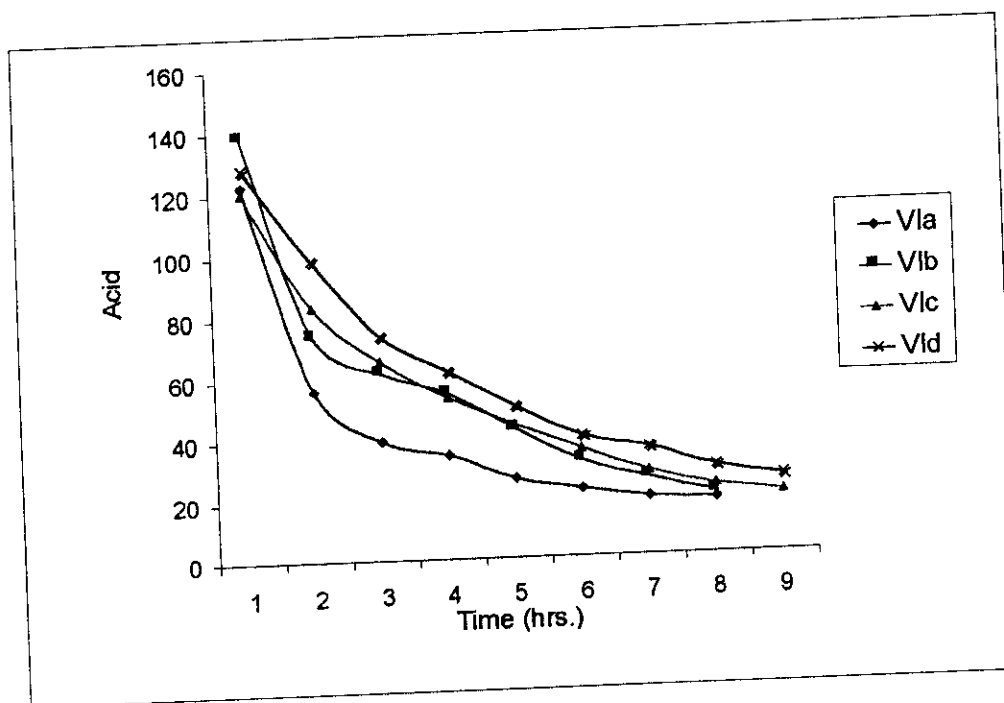


Fig. (5): Acid value of alkyd containing 60% RBO.

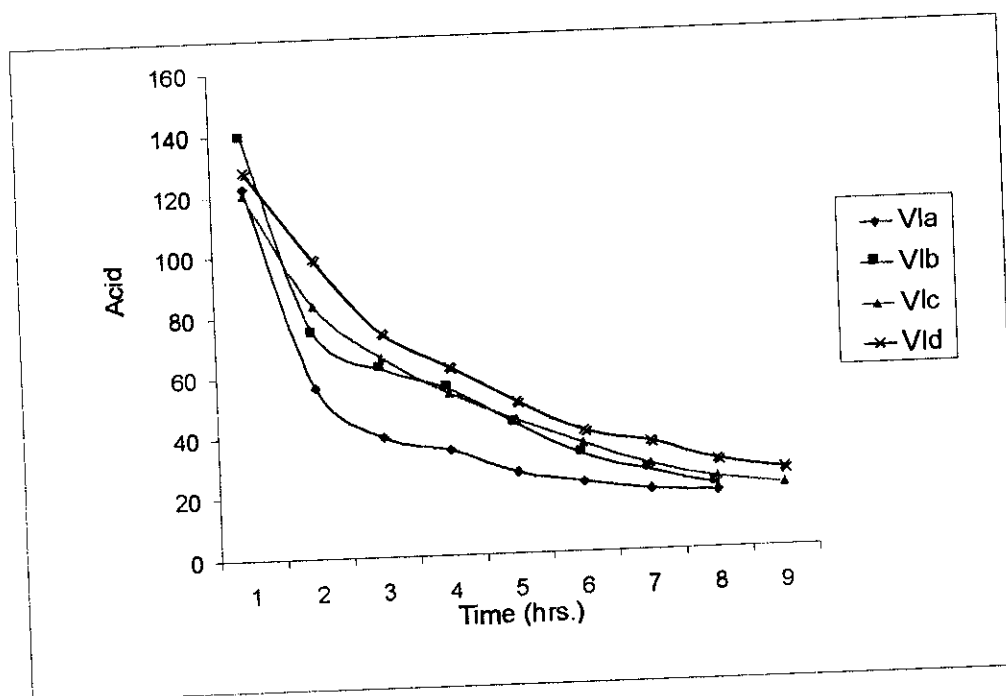


Fig. (6): Acid value of alkyd containing 50% RBO.

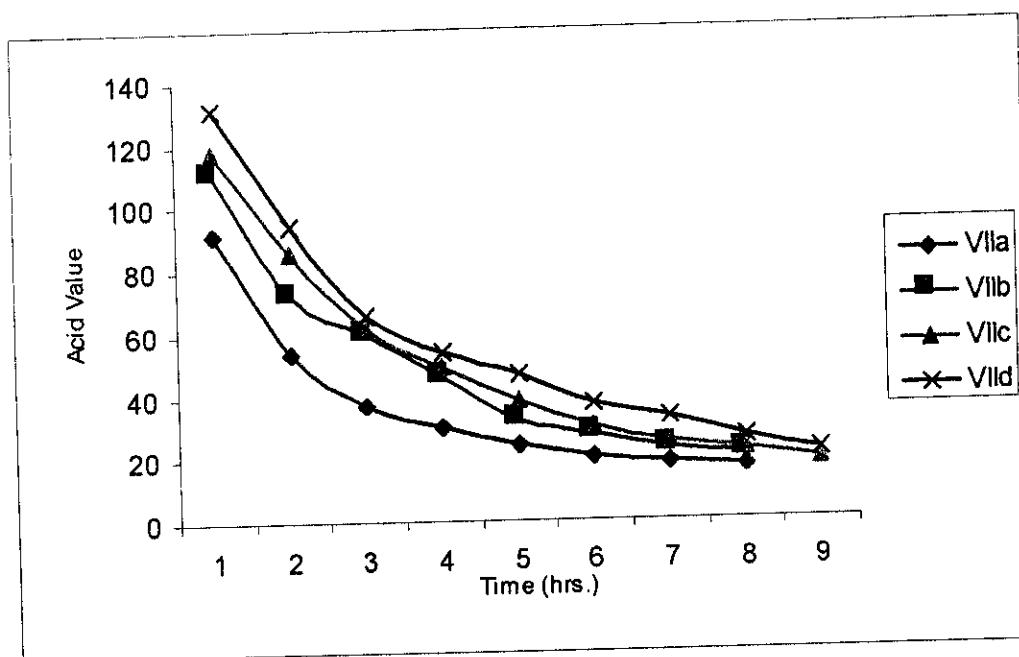


Fig. (7): Acid value of alkyd containing 100% LO

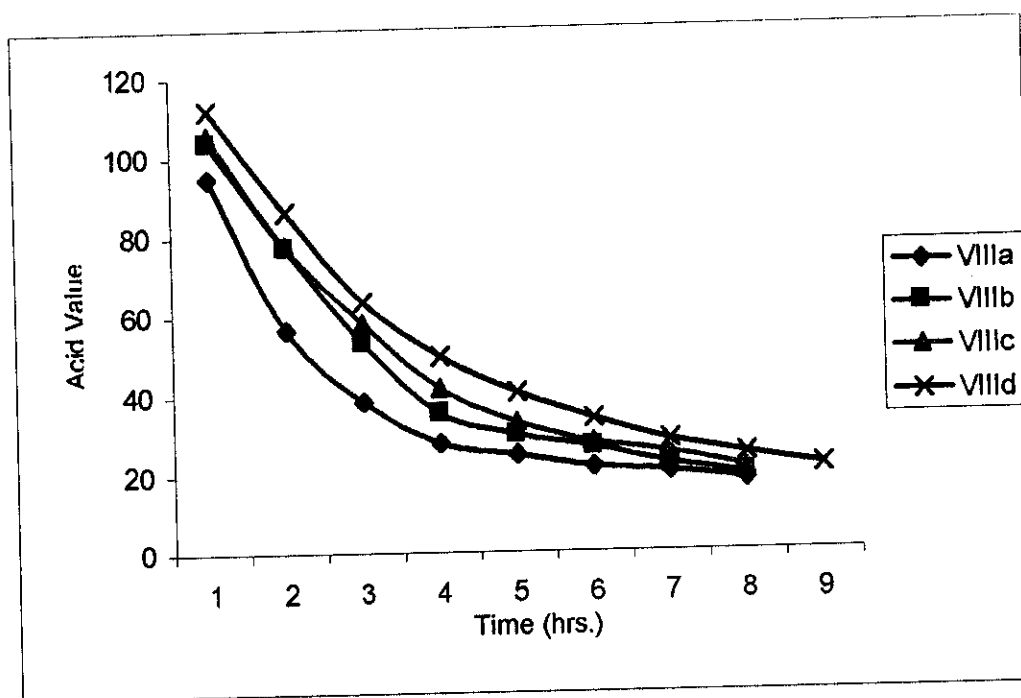


Fig. (8): Acid value of alkyd containing Oleic Acid.

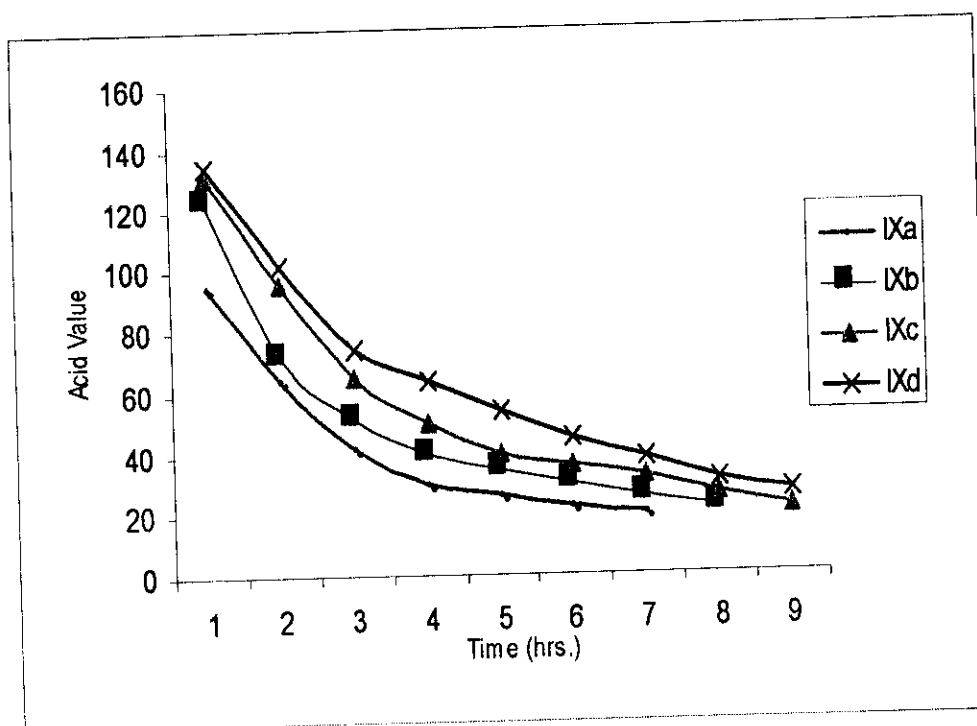


Fig. (9): Acid value of alkyd containing 100% RBFA.

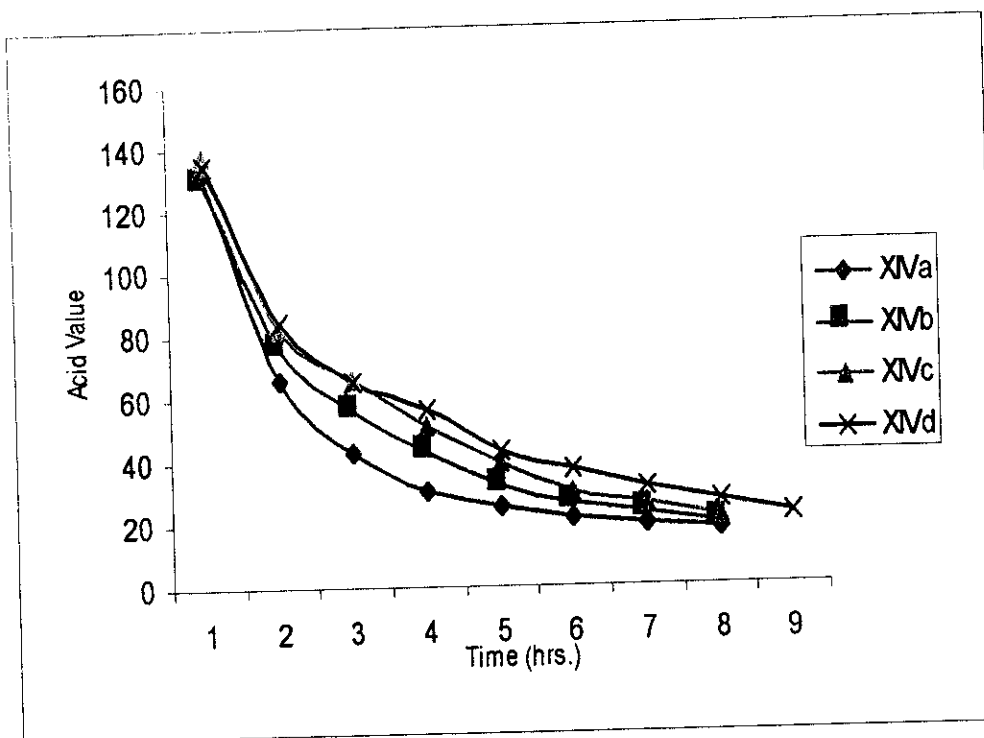


Fig. (10): Acid value of alkyd containing 50% RBFA.

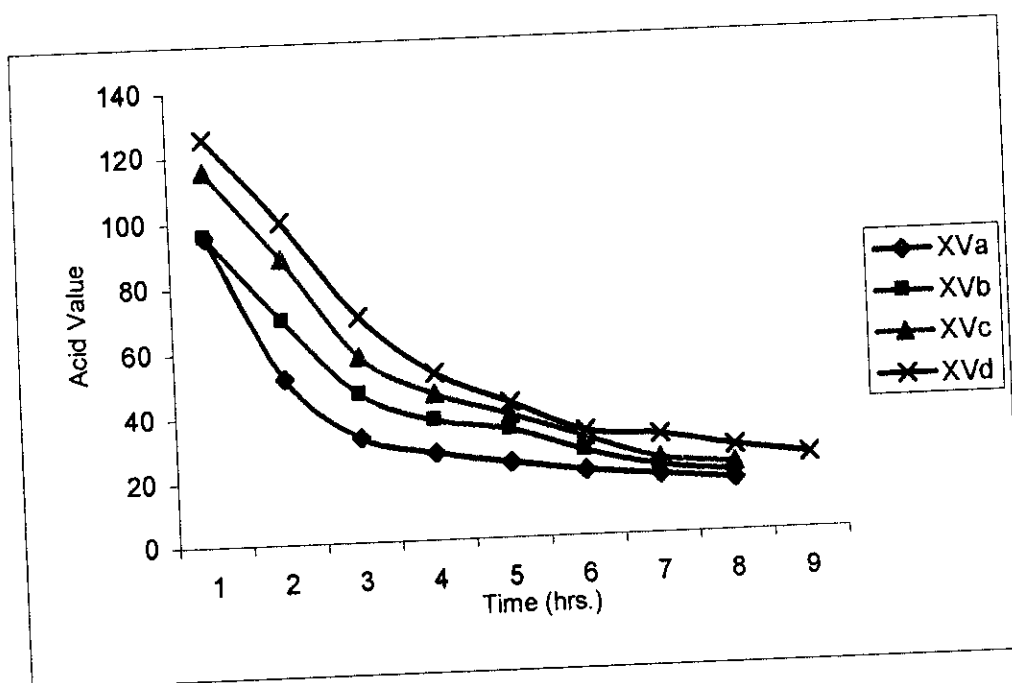


Fig. (11): Acid value of alkyd containing 100% LFA.

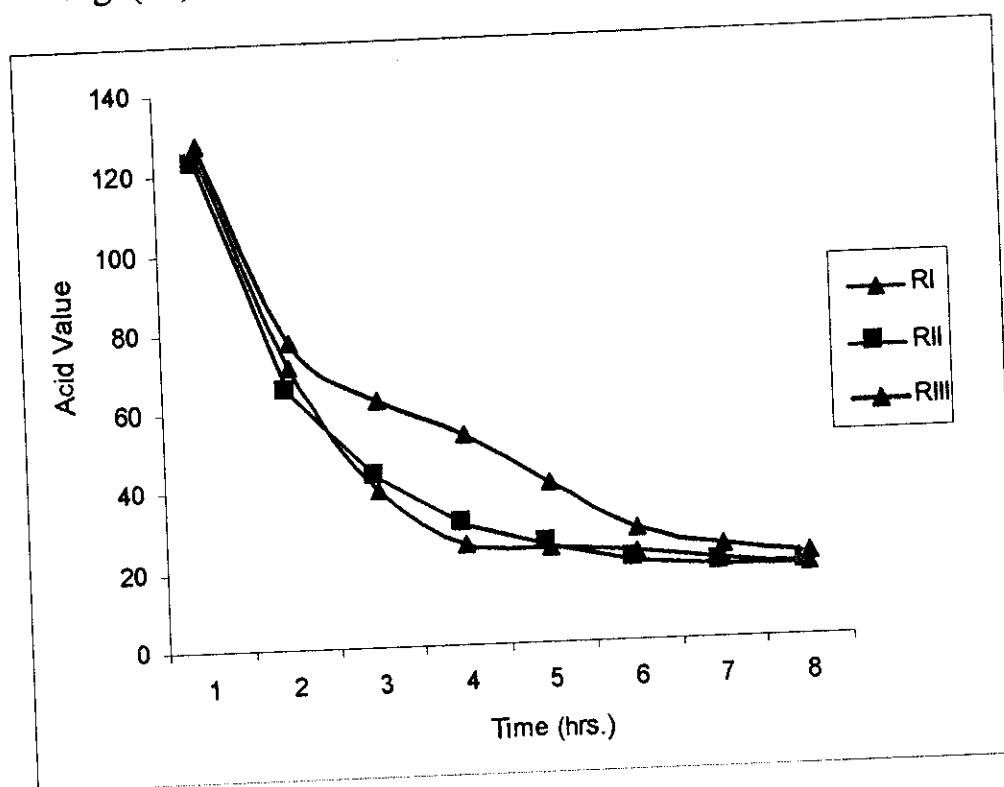


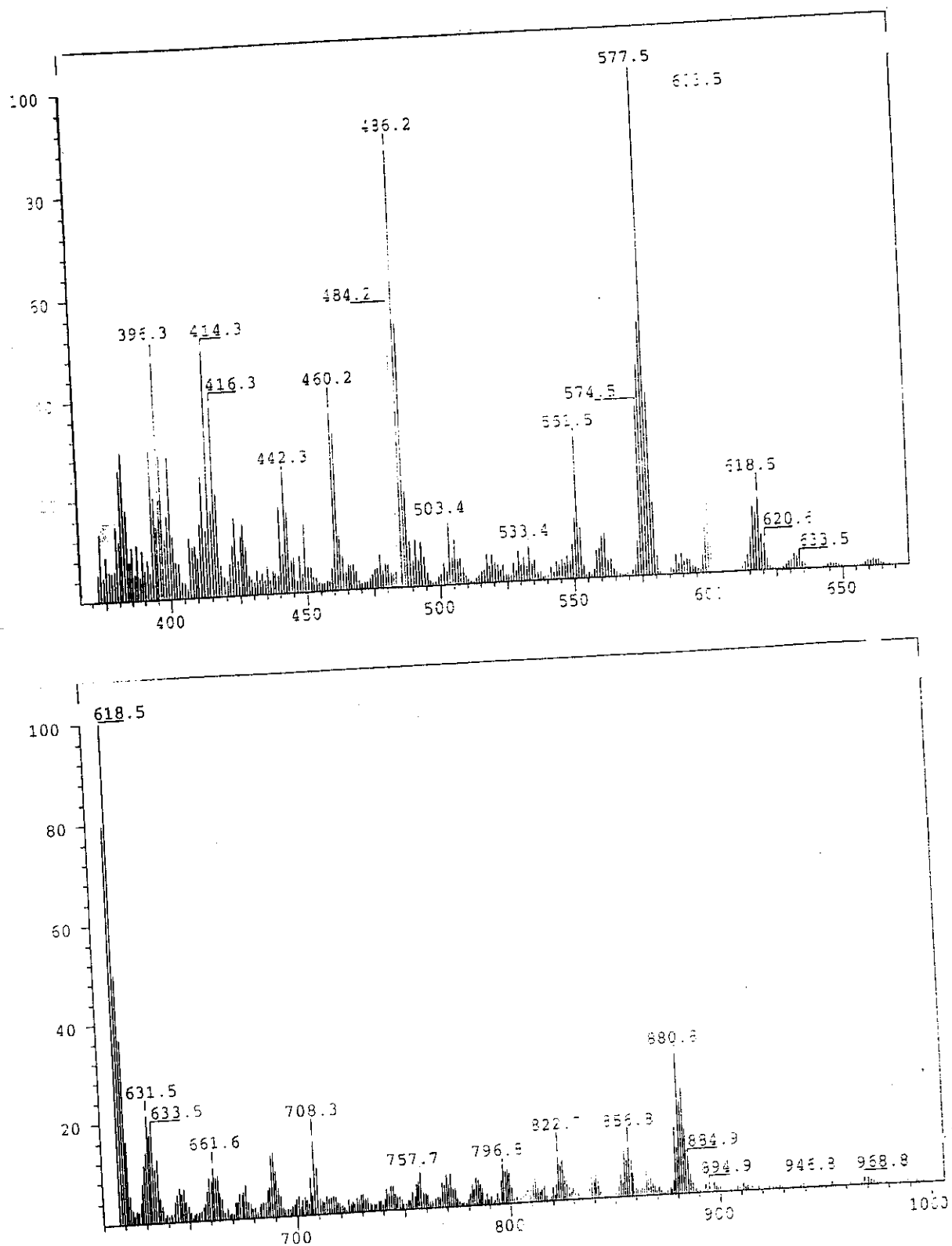
Fig. (12): Acid values of alkyd containing 50% RBO with Itaconic.

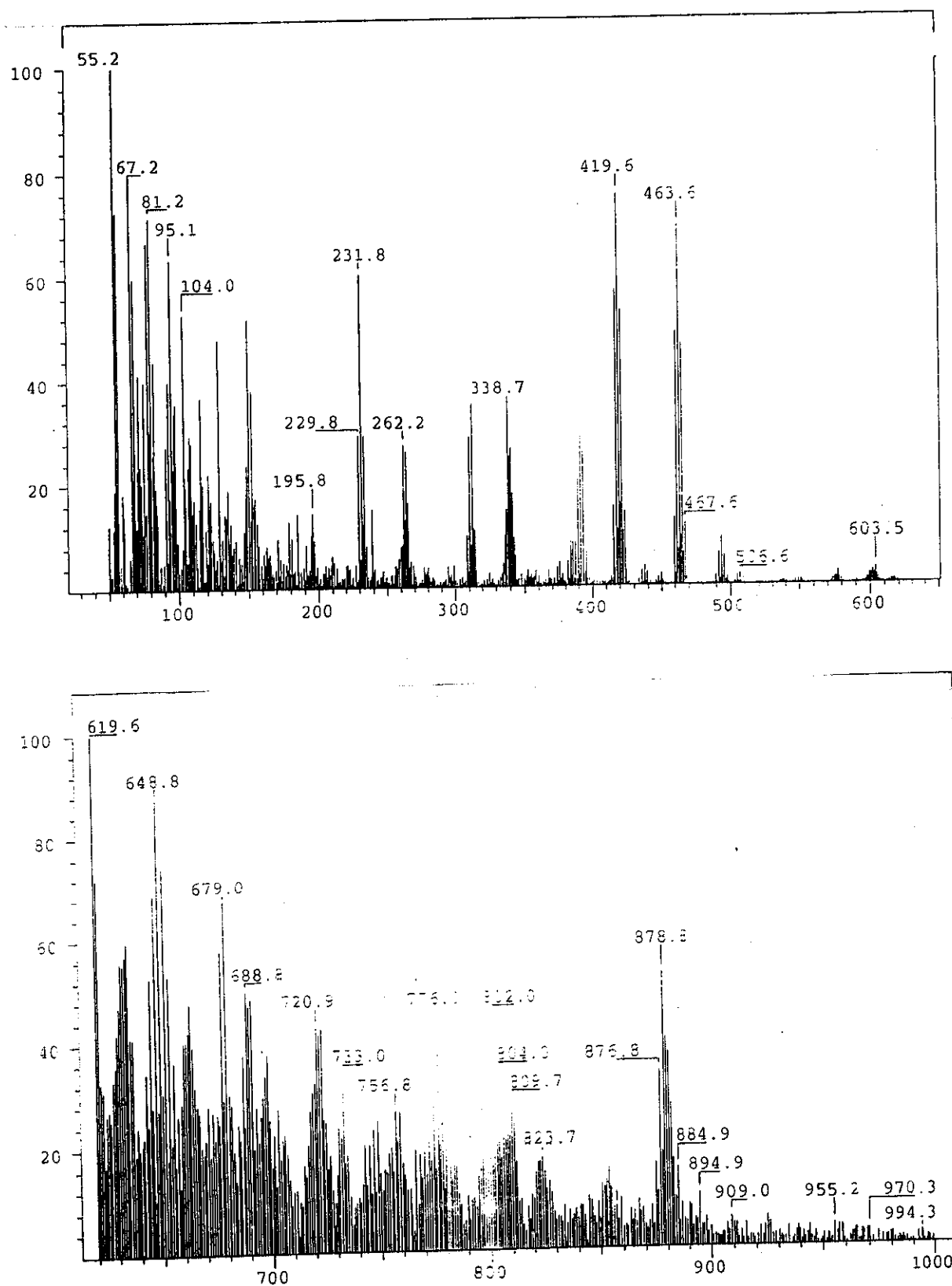
The following observations were noticed during the resin preparations:

- 1- The time of the esterification reaction increase by increasing the percent of rice bran oil and tetrabromophthalic anhydride. .
- 2- The colour of the prepared resin usually increases by increasing the percent of tetrabromophthalic anhydride in most cases.
- 3- As the percentage of tetrabromophthalic anhydride increases the acid value of final resin increased.

Mass spectra studies:

The fatty acid composition effect of each component in the prepared alkyd resin was investigated by a comparative analysis of I_a , I_c , IV_c and V_c respectively (cf. Fg 13-16). For a given oil type, the relative abundance of high-molecular weight species, increases when the oil length decreases. The main fragmentation ions of the monomer pattern, showed in figures (13-16), were detected in all spectra. Ions with a loss of two, four or six protons corresponded to fragments that contained polyunsaturated fatty acids, for example, the molecular ion at $m/z = 881$ corresponding to oleic acid, ions at $m/z = 879$ ($R =$ linoleic acid), and $m/z = 877$ ($R =$ linolenic acid) ⁽⁵⁵⁾. The mass spectrum of (I_a) showed peaks at m/z (relative intensity %) 968 (0.01), 824 (0.07), 486 (5.45) and 338 (10.13). This resin contains rice bran oil, phthalic anhydride and glycerol, where the molecular ion at $m/z = 824$ ($R =$ oleic acid), molecular ion at $m/z = 822$ ($R =$ linoleic acid) and $m/z = 820$ ($R =$ linolenic acid). Where as the mass spectrum of (I_c, IV_c and V_c) these resin resins which containing rice bran oil, linseed oil, phthalic anhydride, tetrabromophthalic anhydride and glycerol, showed peaks at $m/z = 993.6$ with relative intensity (0.01), (0.01), and (0.01), 815.6 (0.01), (0.02), and (0.01) and 493.6 (2.51), (7.26), and (9.09) respectively.

Fig. (13): Mass spectra of I_a .

Fig. (15) : Mass spectra of IV_c.

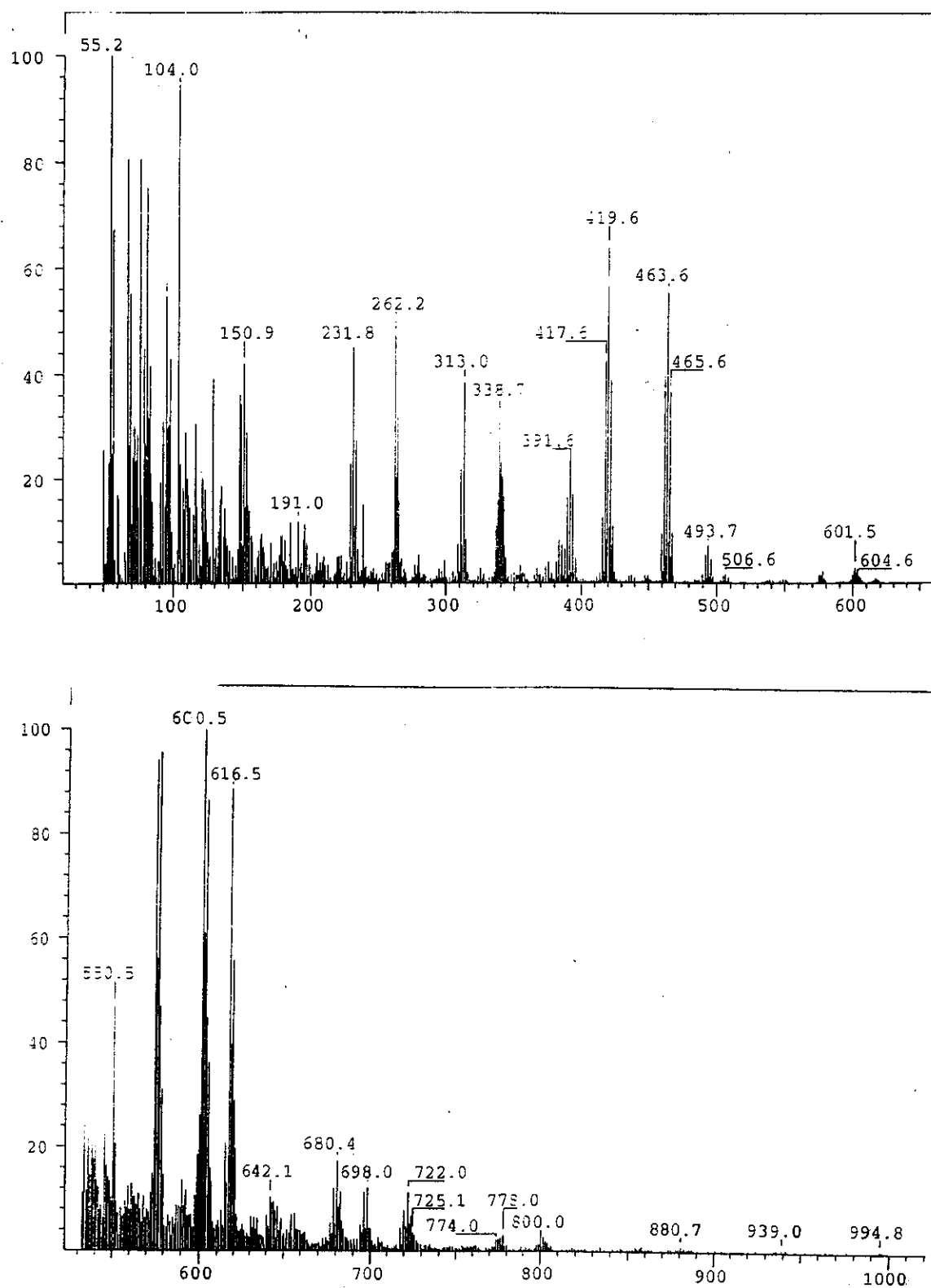
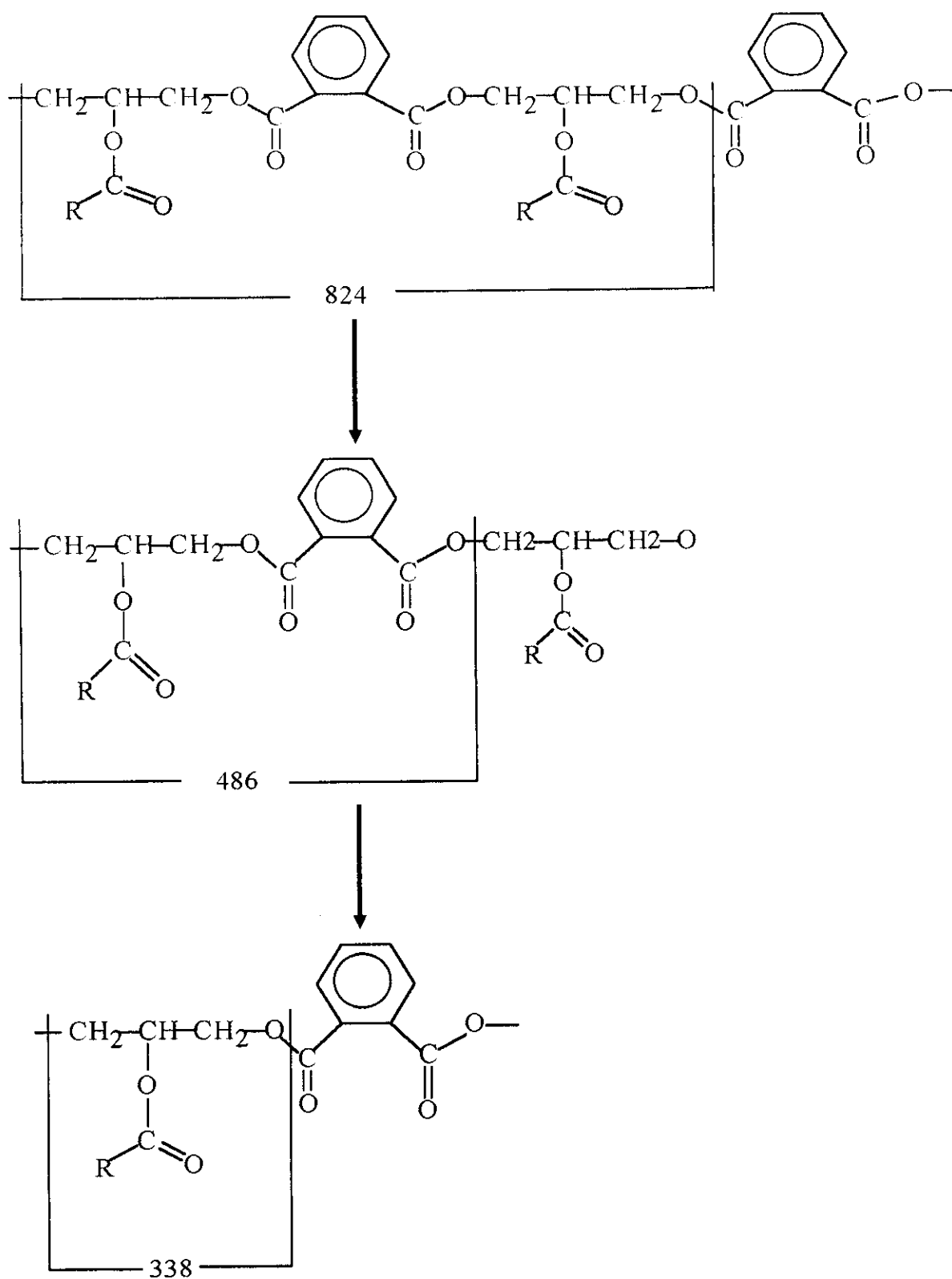
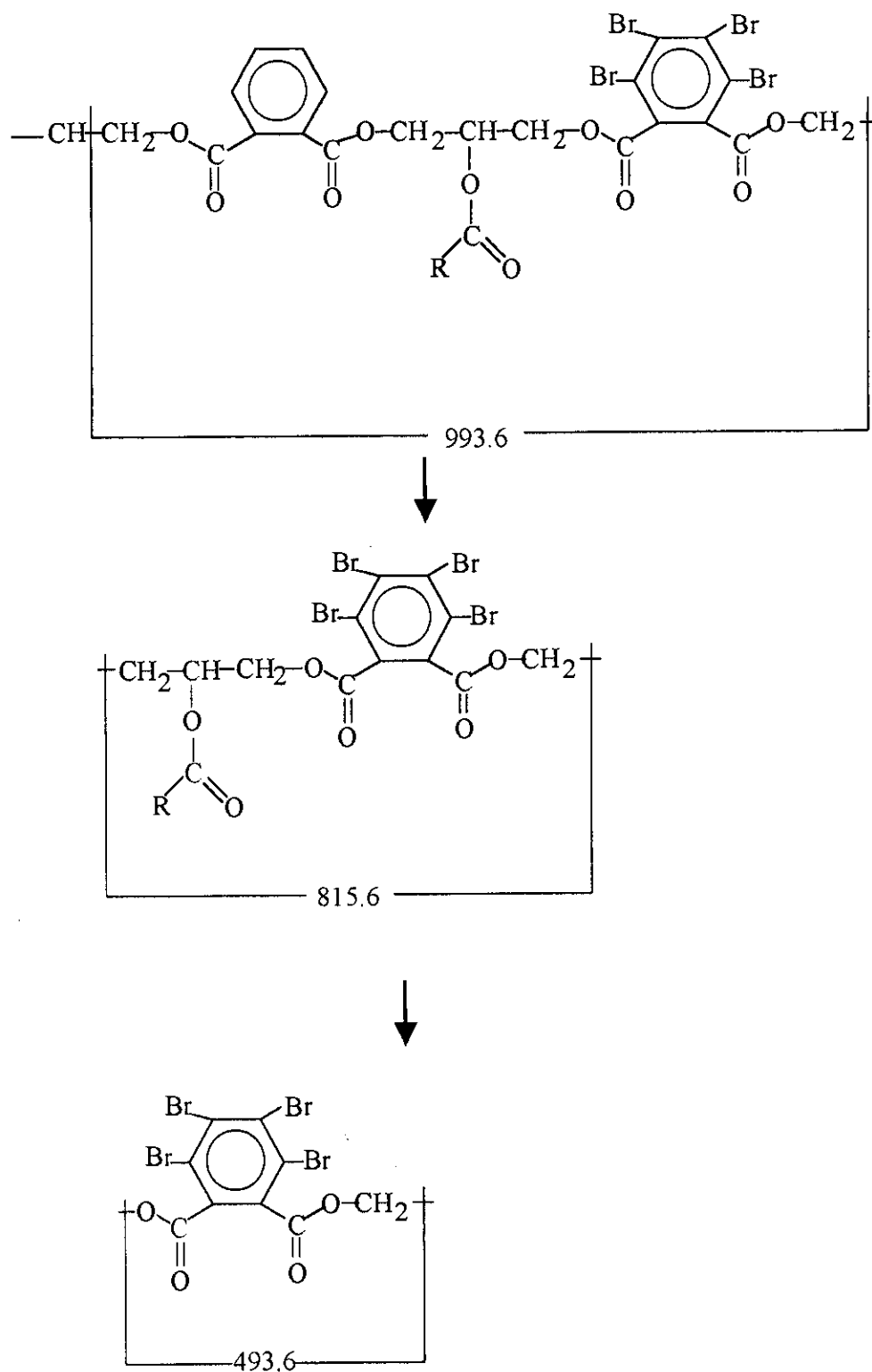


Fig. (16) : Mass spectra of V_c .

The possible fragmentation for I_a shown as the following scheme:



The possible fragmentation for I_c , IV_c and V_c can be shown as the following scheme:



Thermal analysis :

Thermal analysis is the measurement of changes in physical properties of substance as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Thermogravimetry (TG) measures the changes in sample mass with temperature. The TGA curves give information about the various unexpected phenomena observed during heat treatment. It is important to take into account that the TGA is concerned with calorific phenomena which often occur with no detectable weight change ⁽⁸³⁾.

The present investigation included the thermogravimetric behavior of some selected compounds under study.

The thermogravimetric (TG) analysis of the prepared alkyd resins (**I_a** and **I_c**) are represented in (fig.17) in nitrogen atmosphere, heating rate of 15°C.m⁻¹ . From the figure, it is clear that, the alkyd resin (**I_a**) with fragment of molecular ion (968.8) loses its weight in two steps, while the alkyd resin (**I_c**) with fragment of molecular ion (993) loses its weight in three steps . From the above data it is clear that the polymers have no stability over 150°C.

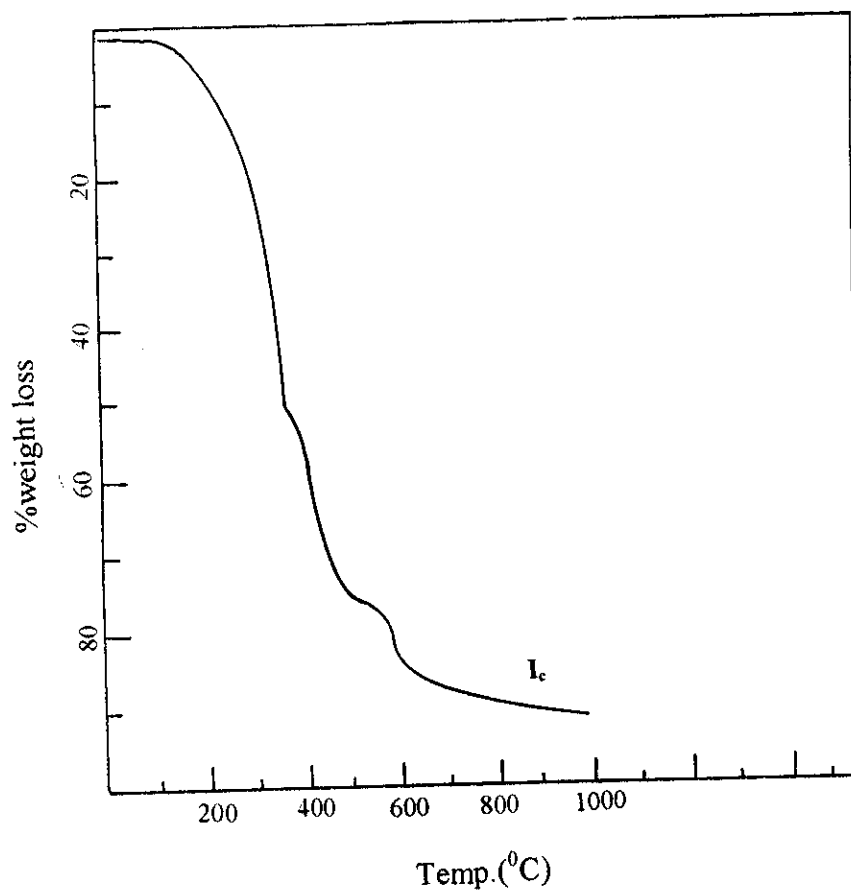
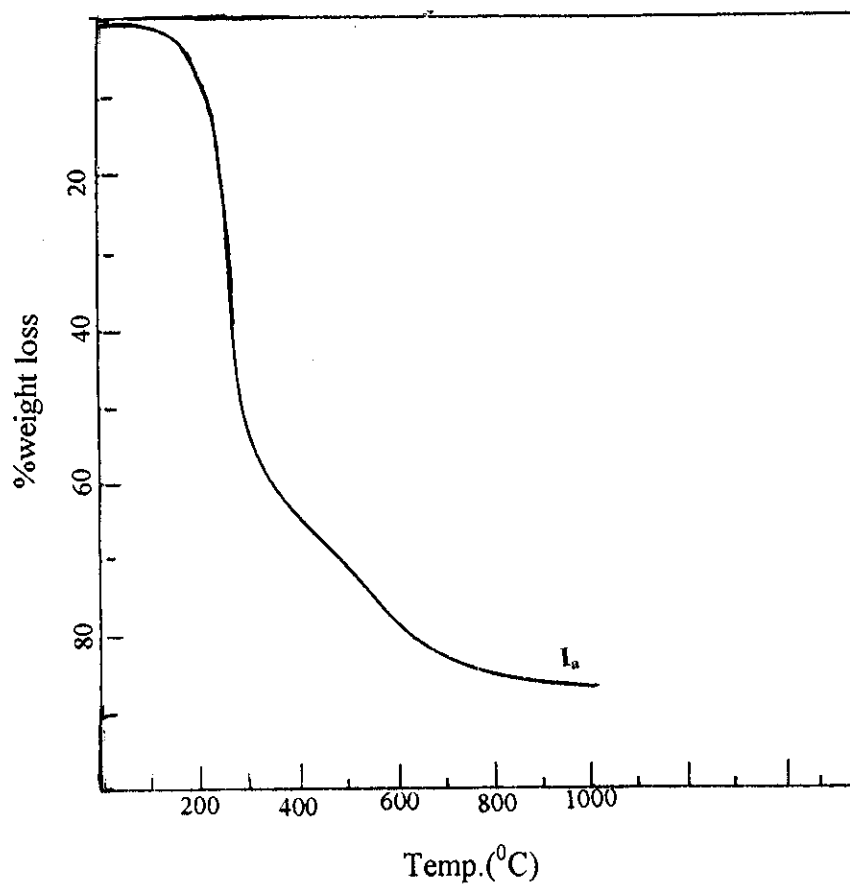


Fig.(17)

Evaluation studies:

The solid content of the prepared resins was diluted by xylene to 60% solids. The following driers combination were added to resins solution:

Cobalt octoate 0.05% (metal/resin)

Zirconium octoate 0.10% (metal/resin)

Manganese octoate 0.02% (metal/resin)

Varnishes characteristics:

The characteristics of various varnishes were evaluated and were recorded in tables (21,22) .

From the tables it is clear that :

The colour of varnish increases by increasing the amount of tetrabromophthalic anhydride and rice bran oil or its fatty acids, the viscosity of the prepared alkyds slightly increased by increasing the percentage of tetrabromophthalic anhydride .Finally the acid value of resins prepared by tetrabromophthalic anhydride are higher than those prepared by phthalic anhydride.

Table (21) Varnish characteristic data of various modified alkyd resins from oils:

<i>Resin NO.</i>	<i>Acid Value (mg KOH/g)</i>	<i>Colour "Gardener"</i>	<i>Viscosity "Gardener"</i>
<i>I_a</i>	18.9	15	<D
<i>I_b</i>	23.3	16	>D
<i>I_c</i>	27.1	17	>D
<i>I_d</i>	28.6	>18	>E
<i>II_a</i>	18.1	15	<D
<i>II_b</i>	20.5	-17	>D
<i>II_c</i>	22.4	17	<E
<i>II_d</i>	25.3	>18	>E
<i>III_a</i>	18.0	14	<D
<i>III_b</i>	20.7	16	<D
<i>III_c</i>	21.9	-17	>D
<i>III_d</i>	24.9	18	>E
<i>IV_a</i>	17.6	+15	>C
<i>IV_b</i>	20.2	-16	<D
<i>IV_c</i>	21.6	-17	>D
<i>IV_d</i>	21.3	18	E
<i>V_a</i>	19.0	13	>C
<i>V_b</i>	20.3	15	>C
<i>V_c</i>	20.7	17	>D
<i>V_d</i>	27.1	-18	<E
<i>VI_a</i>	18.1	13	<C
<i>VI_b</i>	19.6	-15	>C
<i>VI_c</i>	19.4	16	<D
<i>VI_d</i>	24.9	17	<E
<i>VII_a</i>	17.1	12	<C
<i>VII_b</i>	19.1	13	C
<i>VII_c</i>	19.0	-15	<D
<i>VII_d</i>	20.1	17	<E
<i>R_I</i>	18.5	16	>C
<i>R_{II}</i>	18.0	16	C
<i>R_{III}</i>	20.9	-17	D

Where: (C= 0.85, D=1.00, E= 1.25)

Table (22) Varnish characteristic data of various modified alkyd resins from fatty acids:

<i>Resin NO.</i>	<i>Acid Value (mg KOH/g)</i>	<i>Colour "Gardener"</i>	<i>Viscosity "Gardener"</i>
VIII _a	18.0	12	<C
VIII _b	19.1	-13	C
VIII _c	20.3	15	<D
VIII _d	21.3	16	<E
IX _a	18.1	14	C
IX _b	20.6	-16	>C
IX _c	21.6	17	>C
IX _d	26.9	>18	<E
X _a	17.4	15	<D
X _b	18.0	16	>D
X _c	19.7	17	>D
X _d	22.9	>18	>E
XI _a	18.0	-15	>C
XI _b	18.5	16	D
XI _c	19.7	17	>D
XI _d	23.1	>18	E
XII _a	17.9	14	>C
XII _b	18.7	-16	>C
XII _c	19.5	-17	>D
XII _d	23.1	18	<E
XIII _a	18.0	13	<D
XIII _b	19.0	+16	<D
XIII _c	21.5	-17	D
XIII _d	23.0	17	<E
XIV _a	17.9	13	<C
XIV _b	19.1	15	>C
XIV _c	20.8	+16	>C
XIV _d	23.3	17	<E
XV _a	16.1	12	C
XV _b	18.6	13	C
XV _c	20.1	15	>D
XV _d	22.6	17	<E

Film Performance

A- Drying characteristics :

The drying reactivity of drying oil is determined by linoleic and linolenic acid content, and thereby can be quantified from the drying index.

$$\text{D.I} = \text{linoleic \%} + 2 \text{ linolenic \%}$$

Where D.I is the drying index, linoleic % and linolenic % are expressed in weight percentage ⁽⁸⁴⁾.

The drying characteristics of various varnishes were determined after the preparation of its films. These films were subjected to dry in air and also for stoved dry. The data are given in tables (23,24).

The main conclusion derived from drying characteristics data of various alkyd resins are:

- 1- Modification by either tetrabromophthalic anhydride or linseed oil or its fatty acids decreases the air drying time.
- 2- The alkyds based on linseed oil and its fatty acids are air dried.
- 3- Formulations containing rice bran oil and its fatty acids give air dried film only when the phthalic anhydride is totally replaced by tetrabromophthalic anhydride.
- 4- The stoved films improved by increasing the amount of tetrabromophthalic anhydride and linseed oil or its fatty acids.
- 5- The presence of rice bran oil or its fatty acids increases the air and stoved drying times, which may be due to the high percentage of saturated fatty acids in the oil composition ⁽⁵³⁾.

Table (23) Drying characteristic data of various modified alkyd resins from oils:

Resin No	Air drying time (hr)	Stoving			
		90°C		110°C	
		1hr	2hr	1hr	2hr
<i>I_a</i>	-	T	VST	VST	HD
<i>I_b</i>	-	T	VST	HD	-
<i>I_c</i>	-	T	VST	HD	-
<i>I_d</i>	48	VST	HD	-	-
<i>II_a</i>	-	T	VST	HD	-
<i>II_b</i>	-	VST	HD	-	-
<i>II_c</i>	-	VST	HD	-	-
<i>II_d</i>	17	VST	HD	-	-
<i>III_a</i>	-	T	VST	HD	-
<i>III_b</i>	-	VST	HD	-	-
<i>III_c</i>	-	VST	HD	-	-
<i>III_d</i>	11	VST	HD	-	-
<i>IV_a</i>	-	T	VST	HD	-
<i>IV_b</i>	-	VST	HD	-	-
<i>IV_c</i>	-	VST	HD	-	-
<i>IV_d</i>	11	VST	HD	-	-
<i>V_a</i>	-	T	VST	HD	-
<i>V_b</i>	-	VST	HD	-	-
<i>V_c</i>	-	VST	HD	-	-
<i>V_d</i>	9hr	HD	-	-	-
<i>VI_a</i>	-	ST	VST	HD	-
<i>VI_b</i>	-	VST	HD	-	-
<i>VI_c</i>	-	VST	HD	-	-
<i>VI_d</i>	5hr	HD	-	-	-
<i>VII_a</i>	6	VST	HD	-	-
<i>VII_b</i>	5	VST	HD	-	-
<i>VII_c</i>	4	HD	-	-	-
<i>VII_d</i>	2: 30	HD	-	-	-
<i>R_I</i>	-	ST	VST	HD	-
<i>R_{II}</i>	-	ST	VST	HD	-
<i>R_{III}</i>	-	VST	D	-	-

Table (24) Drying characteristic data of various modified alkyd resins from fatty acids:

Resin No	Air drying time (hr)	Stoving			
		90°C		110°C	
		1hr	2hr	1hr	2hr
VIII _a	-	T	T	ST	HD
VIII _b	-	T	ST	VST	HD
VIII _c	-	T	ST	HD	-
VIII _d	-	ST	VST	HD	-
IX _a	-	T	T	VST	HD
IX _b	-	T	ST	HD	-
IX _c	-	T	ST	HD	-
IX _d	46	ST	VST	HD	-
X _a	-	T	VST	HD	-
X _b	-	VST	HD	-	-
X _c	-	VST	HD	-	-
X _d	17	VST	HD	-	-
XI _a	-	ST	VST	HD	-
XI _b	-	VST	HD	-	-
XI _c	-	VST	HD	-	-
XI _d	12	VST	HD	-	-
XII _a	-	T	ST	HD	-
XII _b	-	VST	HD	-	-
XII _c	-	VST	HD	-	-
XII _d	10	VST	HD	-	-
XIII _a	-	ST	VST	HD	-
XIII _b	-	VST	HD	-	-
XIII _c	-	VST	HD	-	-
XIII _d	8	VST	HD	-	-
XIV _a	-	ST	VST	HD	-
XIV _b	-	VST	HD	-	-
XIV _c	-	VST	HD	-	-
XIV _d	5	HD	-	-	-
XV _a	5	VST	HD	-	-
XV _b	4.5	HD	-	-	-
XV _c	4	HD	-	-	-
XV _d	2:30	HD	-	-	-

B- Acid, Solvent, Water and Alkali Resistance :

The resistance of various modified alkyd resins towards acid, solvent, water and alkali were conducted according to standard methods on actual coated films.

To determine the extent to which the film breaks down and to show how far the film will withstand various chemical effects, stored and air dried films were subjected to acid and alkali resistance for 30 days or until complete film failure occurred. The data obtained are shown in tables (25-32).

From the data listed in tables (25-32) we can conclude that:

- 1- Acid and solvent resistance tests for all films examined showed excellent performance within experimental conditions employed, So it can not predict the effect of the modification on acid and solvent resistance.
- 2- The modification of resins using tetrabromophthalic anhydride are affected by water than those made by phthalic anhydride, where loss of gloss values were observed in case of tetrabromophthalic anhydride.
- 3- Films prepared from oleic acid give excellent resistance to water except those modified by tetrabromophthalic anhydride which were affected by water and least resistance to alkali than other resins.
- 4- The alkali resistance is highly improved by modification with tetrabromophthalic anhydride and linseed oil or its fatty acids, where films of the resins prepared from linseed oil or its fatty acids gives the best resistance to alkali.

- 5- Stoved films showed improved chemical resistance when compared to the air dried films of the same resin content.
- 6- Rice bran oil and its fatty acids produced alkyds with lower alkali resistance than that of linseed oil and linseed oil fatty acids, which may be due to the saturation nature of rice bran fatty acids.

From this data, we can note that the introduction of tetrabromophthalic anhydride in the resin preparation improves the chemical resistance of its films.

Table (33) shows the chemical resistance for the varnish's films in which itaconic acid was used in its composition.

From the data it is obvious that the films give better resistance to water, acid and solvent, where the alkali resistance of these films was satisfactory, and also showed the increasing percent of tetrabromophthalic anhydride improved the alkali resistance.

Immersion period "days"

[illegible]

[illegible]

[illegible]

Immersion period “days”

[illegible]

[illegible]

[illegible]

Table (30): Water resistance data of modified alkyd resins from fatty acids

[illegible]

Table (31) Alkali resistance data of modified alkyd resins from oils

Immersion period "days"																																							
Resin No.	Air dried film																							Stoved film															
	1	3	5	7	9	11	13	15	19	23	1	2	3	4	5	6	7	8	9	11	13	15	20	21	23	25	27	29	30										
I _a I _b I _c I _d	- - - Ex	- - - Ex	- - - G	- - - F	- - - P	- - - -	- - - -	- - - -	- - - -	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G G G Ex	F G G Ex	F F G Ex	F F G Ex	P P G Ex	- - F Ex	- - F G	- - F G	- - P F	- - F F	- - - P	- - - -	- - - -											
II _a II _b II _c II _d	- - - Ex	- - - Ex	- - - Ex	- - - G	- - - F	- - - F	- - - P	- - - -	- - - -	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G G G Ex	F G G Ex	F F G Ex	P F G Ex	- F G Ex	- F Ex	- F G	- - P G	- - F F	- - F F	- - - P	- - - -	- - - -											
III _a III _b III _c III _d	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - G	- - - G	- - - G	- - - F	- - - P	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G G G Ex	G G G Ex	F F G Ex	F F G Ex	P P G Ex	- - G Ex	- - F G	- - F G	- - P F	- - F F	- - - P	- - - -	- - - -											
IV _a IV _b IV _c IV _d	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - G	- - - F	- - - P	- - - -	- - - -	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G G G Ex	G G G Ex	F F G Ex	F F G Ex	P P G Ex	- P G Ex	- - F G	- - F G	- - P G	- - F F	- - - F	- - - F											

Immersion period "days"																													
Resi n	Air dried film															Stoved film													
No.																													
	1	3	5	7	9	15	19	21	25	30	1	2	3	4	5	6	7	8	9	11	13	15	19	21	23	25	27	29	30
V _a V _b V _c V _d	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - G	- - - F	- - - P	- - - -	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	F G Ex Ex	F G Ex Ex	F F G Ex	P F G Ex	- F G Ex	- P F Ex	- - P G	- - G	- - F	- - F	- - P	
VL _a VL _b VL _c VL _d	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - Ex	- - - G	- - - G	- - - F	- - - P	- - - -	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G G Ex Ex	F F Ex Ex	F F G G	P P G G	- - F G	- - F F	- - P F	- - P	- - -	- - -	
VII _a VII _b VII _c VII _d	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G G G Ex	F G G Ex	P P P Ex	- - - G	- - - G	- - - G	- - - F	Ex Ex Ex Ex	Ex Ex Ex Ex	Ex Ex Ex Ex	G Ex Ex Ex	G Ex Ex Ex	G G Ex Ex	F G Ex Ex	F G Ex Ex	P G Ex Ex	- G Ex Ex	- G G Ex	- F F G	- P F G	- - P G	- - F	- - F	- - F	- - F	

Resin No.	Air dried film														Stoved film													
	1	3	5	7	9	13	19	21	23	25	30	1	3	5	7	8	9	11	13	15	20	21	23	25	27	29	30	
XII, XII _a , XII _b , XII _c , XII _d	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	G	G	G	F	F	P	-	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	-	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	-	-	-	-	-	
	Ex	Ex	Ex	Ex	G	G	G	F	F	P	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	P	F	-	
XIII, XIII _a , XIII _b , XIII _c , XIII _d	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	G	G	G	F	P	-	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	Ex	Ex	Ex	Ex	Ex	G	G	F	F	P	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	P	P	-	
XIV, XIV _a , XIV _b , XIV _c , XIV _d	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	G	G	G	F	P	-	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	Ex	Ex	Ex	Ex	Ex	G	G	G	F	F	P	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	P	P	-	
XV, XV _a , XV _b , XV _c , XV _d	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	G	G	G	F	P	-	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	-	-	-	-	-	-	-	-	-	-	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	F	F	-	-	-	-	
	Ex	Ex	Ex	Ex	G	G	G	F	F	P	-	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	F	P	P	-	
XI _a																												

Table (33) Chemical resistant for alkyd containing itaconic acid

Resin No.	Immersion period "Days"													
	Stoved film													
	1	3	5	7	9	13	15	19	21	23	25	27	29	30
Acid res.														
RI	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RIII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
Solvent res.														
RI	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RIII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
Water res.														
RI	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
RIII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
Alkali res.														
RI	Ex	Ex	Ex	Ex	G	G	G	G	F	F	P	-	-	-
RII	Ex	Ex	Ex	Ex	G	G	G	F	F	F	P	-	-	-
RIII	Ex	Ex	Ex	Ex	Ex	Ex	Ex	G	G	G	F	F	P	-

C- Mechanical properties of dried films:

In the present investigation, films were applied over glass or tin panels and allowed to dry in both air and oven to prepare air-dried and stoved films. Film thickness, hardness, gloss, scratch hardness and adhesion, were measured according to the standard methods and the results are given in tables (34,35) and figures (18-21)..

Hardness:

Hardness is a conceptual term, and means different things when used to describe different materials. When organic coatings are examined for hardness, several variables must be considered. One of them is the substrate to which the coating has been applied. The second is the film thickness of the coating itself. The hardness of organic coating cannot be defined quantitatively as mass, length and gravity. The measurement of hardness of organic coating is based on practical concepts. Hardness then can be defined as a resistance to indentation and scratching ⁽⁸⁵⁾. From tables (34,35), we noticed that:

- 1- The hardness of dry films improved by increasing the percentage of linseed oil or its fatty acids and tetrabromophthalic anhydride.
- 2- The film hardness decreases as the percentage of rice bran oil or its fatty acids increases. This behaviour is due to the low degree of unsaturation of rice bran oil ⁽⁵³⁾.
- 3- Modification of alkyd by either linseed oil or its fatty acids or tetrabromophthalic anhydride improves the scratch hardness.

Adhesion:

Adhesion is the state in which two surfaces are held together by forces, which may be consisted of valence attraction, or interfacial forces or a combination of both. Interfacial forces could be defined as physical bonds, where as valence attractions are chemical in nature. The interfacial forces are too small to be measured by any mechanical device and if they could be measured, it would be found that most "adhesive" failures are cohesive failures of the film tested ⁽⁸⁵⁾. From tables (34,35), we can observe that the adhesion of modified alkyds showed outstanding performance similar to that of unmodified alkyds.

Gloss:

Gloss is often described as giving the lustrous or shiny appearance to an object. *Specular gloss* or *Specular reflectance* is the fraction of the incident light reflected from a surface in the mirror direction within a specified angular tolerance. The aspect gloss is the most widely used and numerous instruments have been constructed for this purpose. The *ASTM method D523, Specular Gloss*, provides for measurements at three different angles of incidence, namely 20, 60 and 85 degree from the perpendicular to the specimen surface. The 85-degree reading is used for the low-gloss specimens, 60-degree gloss reading is used for the evaluation of specimens over the entire range and 20-degree angle is employed when a higher differentiation is required such as automotive finishes or other specimens having readings over 70 when 60 degree geometry is used ⁽⁸⁵⁾. From the collected results in tables (34,35), the gloss of dried films

investigated were satisfactory. However, it slightly increases by increasing the amount of tetrabromophthalic anhydride.

From the above mentioned results, we can observe that the presence of tetrabromophthalic anhydride improve the mechanical properties of the dried film, also increasing the percentage of linseed oil or its fatty acids improves these properties. Moreover, the stoved films showed better performance than the air dried films of the same resin content.

On the other hand, we tried to improve the character of some prepared alkyds by using itaconic acid. The introduction of itaconic in the alkyd resins doesn't give the predicted results, where all samples give less hardness compared to the prepared alkyds, but the gloss, scratching and adhesion are satisfactory.

Table (34) Film characteristics of modified alkyd resins from oils

Resin no.	Film thickness (μ)		Film hardness (Sec)		Film gloss at 20°		Film scratch (Kg)		Film adhesion	
	a	s	a	s	a	s	a	s	a	s
I _a	-	25	-	35	-	88	-	>1/2	-	Gt ₁
I _b	-	30	-	48	-	86	-	>1/2	-	Gt ₀
I _c	-	30	-	54	-	91	-	>1	-	Gt ₀
I _d	35	35	97	109	95	92	>2	>2	Gt ₀	Gt ₀
II _a	-	25	-	38	-	91	-	>1/2	-	Gt ₀
II _b	-	26	-	50	-	93	-	>1	-	Gt ₀
II _c	-	30	-	95	-	98	-	>2	-	Gt ₀
II _d	34	35	110	112	97	100	>2	>2	Gt ₀	Gt ₀
III _a	-	24	-	40	-	93	-	>1/2	-	Gt ₀
III _b	-	26	-	48	-	92	-	>1	-	Gt ₀
III _c	-	29	-	90	-	96	-	>2	-	Gt ₀
III _d	33	31	112	116	97	97	>2	>2	Gt ₀	Gt ₀
IV _a	-	27	-	45	-	88	-	>1/2	-	Gt ₀
IV _b	-	30	-	50	-	93	-	>1	-	Gt ₀
IV _c	-	32	-	94	-	93	-	>2	-	Gt ₀
IV _d	35	35	120	133	97	96	-	>2	Gt ₀	Gt ₀

Resin no.	Film thickness (μ)		Film hardness (Sec)		Film gloss at 20°		Film scratch (Kg)		Film adhesion	
	a	s	a	s	a	s	a	s	a	s
V _a	-	25	-	49	-	86	-	>1	-	Gt ₀
V _b	-	27	-	57	-	92	-	>1	-	Gt ₀
V _c	-	31	-	95	-	96	-	>2	-	Gt ₀
V _d	33	33	118	135	96	97	>2	>2	Gt ₀	Gt ₀
VI _a	-	25	-	46	-	91	-	>1	-	Gt ₀
VI _b	-	27	-	48	-	93	-	>1	-	Gt ₀
VI _c	-	30	-	105	-	96	-	>2	-	Gt ₀
VI _d	35	32	139	144	96	100	>2	>2	Gt ₀	Gt ₀
VII _a	25	20	49	55	92	92	>1	>1	Gt ₀	Gt ₀
VII _b	25	25	56	89	93	95	>1	>1	Gt ₀	Gt ₀
VII _c	27	35	116	122	95	96	>2	>2	Gt ₀	Gt ₀
VII _d	30	32	120	134	97	98	>2	>2	Gt ₀	Gt ₀
R _I	-	25	-	41	-	82	-	>1	-	GT ₀
R _{II}	-	25	-	40	-	76	-	>1	-	GT ₀
R _{III}	-	25	-	72	-	86	-	>1	-	GT ₀

Table (35) Film characteristics of modified alkyds from fatty acids.

Resin no.	Film thickness (μ)		Film hardness (Sec)		Film gloss at 20°		Film scratch (Kg)		Film adhesion	
	a	s	a	s	a	s	a	s	a	s
VIII _a	-	20	-	39	-	96	-	>1	-	Gt ₀
VIII _b	-	20	-	42	-	93	-	>1	-	Gt ₁
VIII _c	-	25	-	89	-	95	-	>1	-	Gt ₀
VIII _d	-	30	-	105	-	97	-	>2	-	Gt ₀
IX _a	-	20	-	40	-	86	-	>1/2	-	Gt ₀
IX _b	-	22	-	50	-	93	-	>1/2	-	Gt ₀
IX _c	-	25	-	58	-	92	-	>1	-	Gt ₀
IX _d	27	30	97	109	94	95	-	>2	Gt ₀	Gt ₀
X _a	-	23	-	47	-	88	-	>1/2	-	Gt ₁
X _b	-	25	-	49	-	90	-	>1	-	Gt ₀
X _c	-	30	-	93	-	92	-	>2	-	Gt ₀
X _d	34	33	103	115	96	97	>2	>2	Gt ₀	Gt ₀
XI _a	-	25	-	41	-	83	-	>1/2	-	Gt ₀
XI _b	-	25	-	50	-	84	-	>1	-	Gt ₀
XI _c	-	27	-	89	-	92	-	>2	-	Gt ₀
XI _d	32	30	108	110	95	97	>2	>2	Gt ₀	Gt ₀

Resin no.	Film thickness (μ)		Film hardness (Sec)		Film gloss at 20°		Film scratch (Kg)		Film adhesion	
	a	s	a	s	a	s	a	s	a	s
XII _a	-	25	-	43	-	84	-	>1/2	-	Gt ₀
XII _b	-	30	-	53	-	82	-	>1	-	Gt ₀
XII _c	-	30	-	92	-	88	-	>2	-	Gt ₀
XII _d	35	33	131	140	91	93	>2	>2	Gt ₀	Gt ₀
XIII _a	-	25	-	45	-	85	-	>1	-	Gt ₀
XIII _b	-	28	-	60	-	86	-	>1	-	Gt ₀
XIII _c	-	32	-	98	-	95	-	>2	-	Gt ₀
XIII _d	33	33	122	139	98	97	-	>2	Gt ₀	Gt ₀
XIV _a	-	20	-	44	-	91	-	>1	-	Gt ₀
XIV _b	-	25	-	56	-	92	-	>1	-	Gt ₀
XIV _c	-	30	-	101	-	94	-	>2	-	Gt ₀
XIV _d	35	33	134	148	96	99	>2	>2	Gt ₀	Gt ₀
XIV _a	22	20	50	57	93	95	>1	>1	Gt ₀	Gt ₀
XIV _b	25	20	56	85	94	96	>1	>1	Gt ₀	Gt ₀
XIV _c	30	27	110	120	95	97	>2	>2	Gt ₀	Gt ₀
XIV _d	30	33	120	130	99	98	>2	>2	Gt ₀	Gt ₀

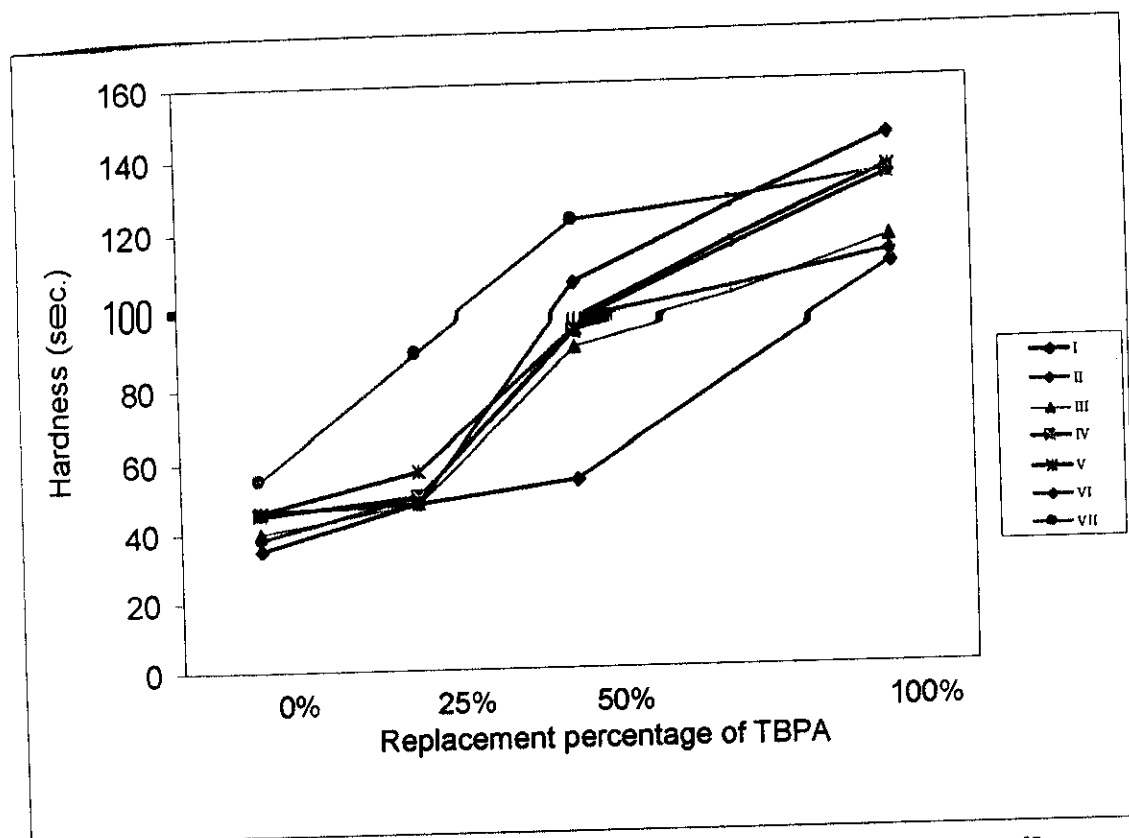


Fig. (18): Hardness of Alkyd Resin prepared from oils

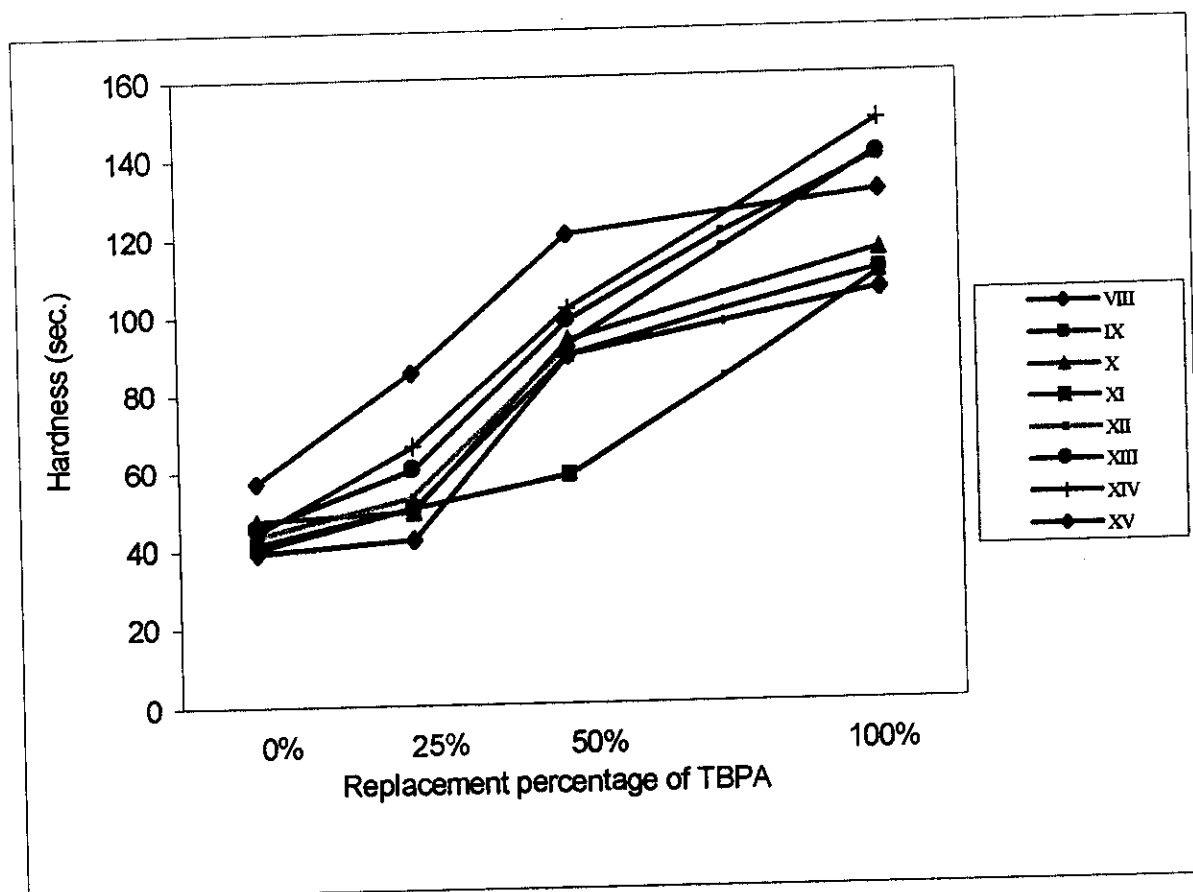


Fig. (19): Hardness of Alkyd Resin prepared from FA.

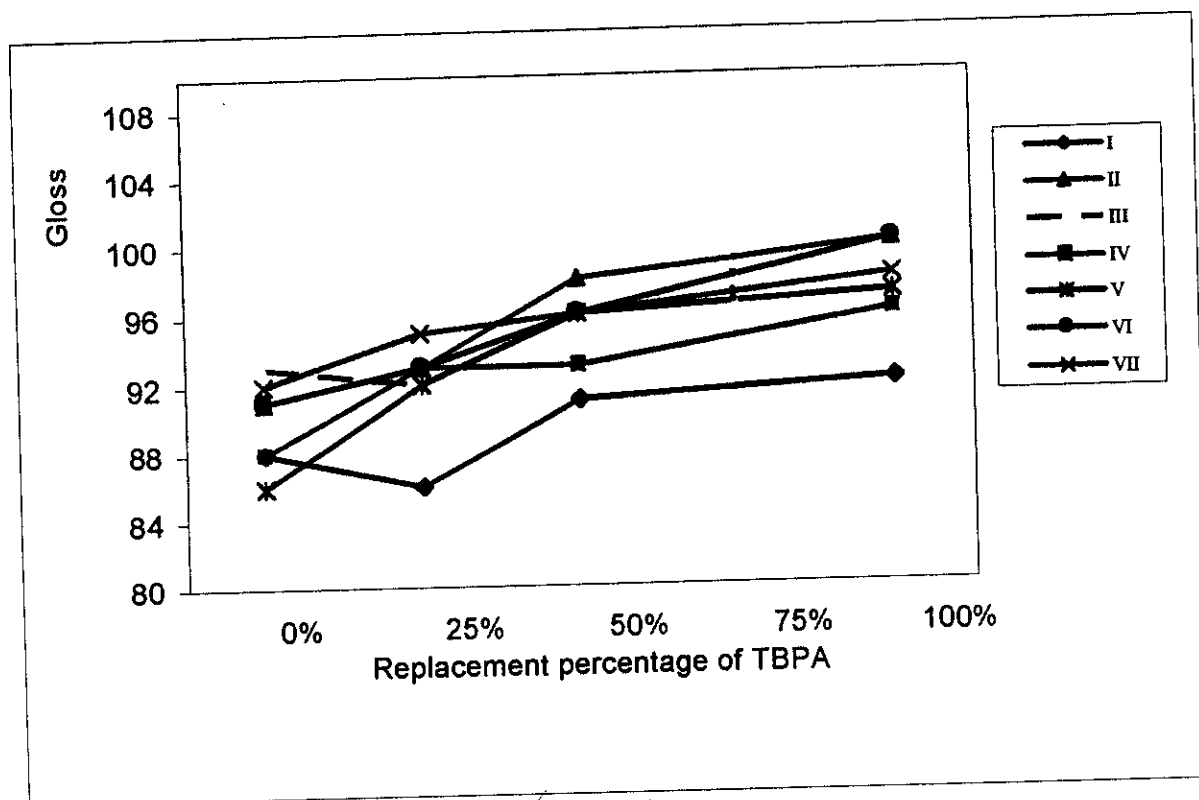


Fig. (20): Gloss of Alkyd Resin prepared from oils.

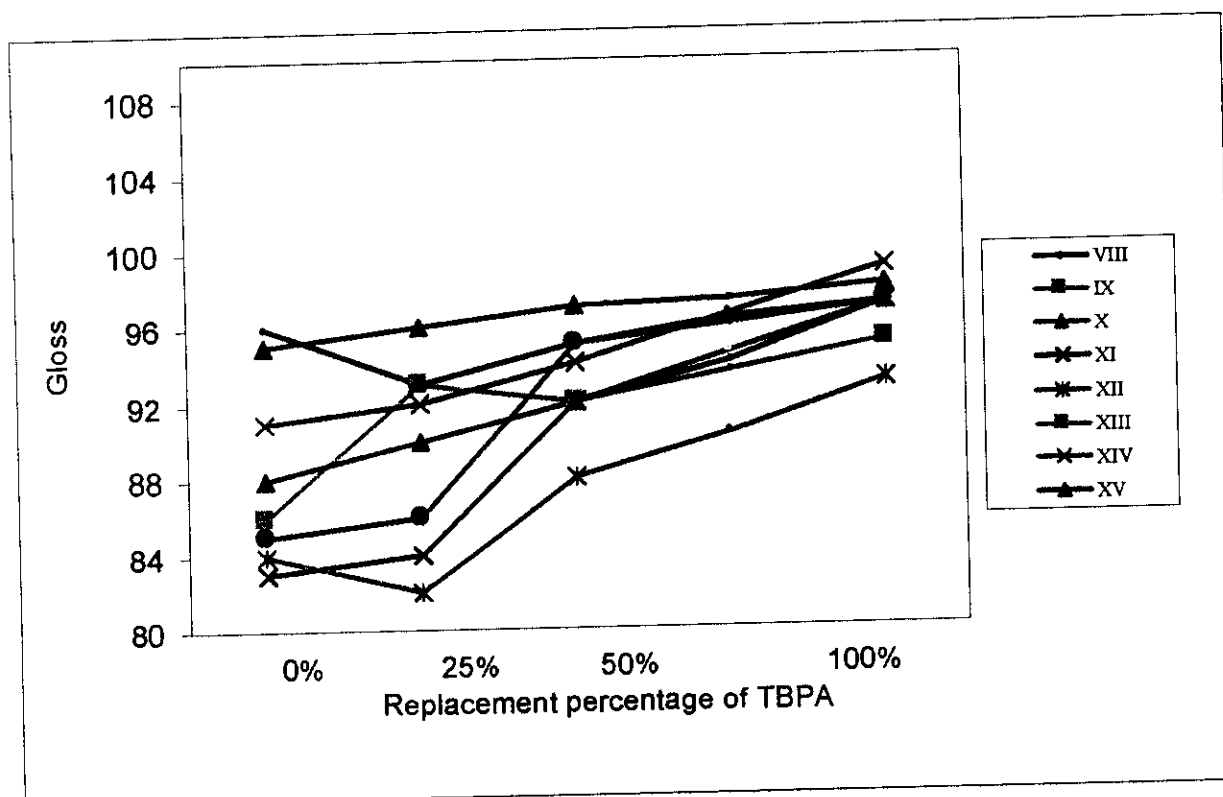


Fig. (21): Gloss of Alkyd Resin prepared from fatty acid.

Water soluble alkyd resins

A water-dispersible or emulsifiable alkyd to serve as a basis for water-thinned paints was obtained by cooking a surfactant into the alkyd so that it will disperse readily when water is added (86,87).

The most common method for producing water-soluble alkyds consists of interrupting the esterification reaction of a conventional alkyd at some intermediate acid value in the range of 30-80 followed by addition of ammonia or a volatile amine to produce a soluble polymer soap. On application of this water vehicle to a substrate, the amine gradually volatilizes, leaving behind, the high acidity alkyd polymer. Drying is effected either by air drying or heat curing (88).

Water-dispersible resins may be prepared by the introduction of polyethylene glycol into an otherwise conventional oil-modified alkyd resin. A typical formulation (89) consists of linseed fatty acid, 1605 parts, pentaerythritol 555, polyethylene glycol of approximately 1500 molecular weight 336, phthalic anhydride 711, styrene 336.

A modified alkyd resin (Z_I , Z_{II} , Z_{III} and Z_{IV}) was prepared by introduction of polyethylene glycol of approximately 600 molecular weight to the alkyd resins.

Where:

Z_I : 50% RBO + 50% LO + 50% PA + 50% TBPA + 75% G + 25% PEG.

Z_{II} : 50% RBO + 50% LO + 50% PA + 50% TBPA + 50% G + 50% PEG.

Z_{III} : 50% RBO + 50% LO + 50% PA + 50% TBPA + 25% G + 75% PEG.

Z_{IV} : 50% RBO + 50% LO + 50% PA + 50% TBPA + 100% PEG.

The surface active properties of the prepared water soluble alkyd resin were evaluated to estimate the suitable application and tabulated in table (36,37).

Table (36): The surface properties of water soluble alkylid resins :

Comp. no.	S.T. 0.1% (dyne/cm)	I.F.T 0.1% (dyne/cm)	Emul. Stab. 20 mmol min sec	Cloud point (1%) °C	Foam height 0.1% (mm)	Wetting time 0.1% (sec)
Z _I	35	12	25 : 30	29	48	19
Z _{II}	36	20	13 : 27	32	100	15
Z _{III}	36	21	10 : 15	47	180	13
Z _{IV}	38	24	4 : 35	56	200	11

Surface and interfacial tensions:-

Surface and interfacial tension ⁽⁹⁰⁾ of the prepared water soluble alkyd resin are recorded in table (36). The surface and interfacial tension of the synthesized water soluble alkyd resin (Z_I , Z_{II} , Z_{III} and Z_{IV}) were measured using a Du-Nouy tensiometer ⁽⁹⁰⁾ [Kruss Type 8451] at 25°C. These values are in the range (35-38 dyne/cm); and (12-24 dyne/cm), respectively. It is evident that; the surface and interfacial tensions increase with increasing the % of PEG (600 M.wt.) unit, on the other hand, the solubility increases by increasing the % of PEG in the formulation of water-soluble alkyd resin.

$$Z_{IV} > Z_{III} > Z_{II}$$

Also Z_I has the lower solubility, surface and interfacial values.

Cloud point ⁽⁹¹⁾ :-

The cloud point resulting data cited in table (36). It is clear that, the cloud point increases with increasing the % of PEG (hydrophile) unit in the formulation of the prepared alkyd resin. So, Z_{IV} afforded the higher cloud point than all prepared water soluble alkyd resins.

Foam height ⁽⁹²⁾ and Wetting time ⁽⁹³⁾:-

On the other hand, the foam height increases and wetting time decreases with increasing the percentage of PEG unit.

Emulsion stabilities ⁽⁹⁴⁾ :-

Emulsion stabilities were measured using standard procedures. The data tabulated in the table (36) revealed that Z_{IV} showed lower emulsifying stabilities than those of Z_{III} , Z_{II} and Z_I respectively.

Biodegradability⁽⁹⁵⁾ :-

Finally; the biodegradation data of the prepared water-soluble alkyd resins are recorded in table (37).

Table (37): Biodegradability of water soluble alkyd resins :-

Compd. No.	1st day	2nd day	3rd day	4th day	5th day	6th day	7th day
Z_I	48.27	53.80	57.93	66.20	67.57	75.86	77.24
Z_{II}	49.65	53.10	55.86	66.90	67.59	74.48	75.17
Z_{III}	49.65	55.17	56.55	66.90	71.03	77.24	78.62
Z_{IV}	51.03	56.55	63.45	69.66	71.72	73.10	80.00

The biodegradation was expressed by increasing the surface tension values by days. From the data shown in table (37) we can notice that, the biodegradability percentage increases by increasing the percentage of PEG in their molecules.