# CHAPTER III

# RESULTS AND DISCUSSION

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About forty-thousand years ago, water-soluble vehicles zoomed into prominence with cave-decorating craze that swept parts of Europe. Since that time, many kinds of water-thinned coatings have been used; but durable industrial types of today have come into existence only within our present generation.

The critical shortage of hydrocarbon solvents during the word war II spurred development of water-based industrial finishes in Europe. In the Unites States, the impetus was provided by postwar needs for automation of finishing methods and elimination of fire and health hazards.

The most rapide commercial adoption of water-based systems has been in continental Europe, where complete dipping of objects as large as auto bodies has become almost as common place as flow coating of small items. From the practical as well as the theoretical point of view, epoxy resins have not been described among the water-soluble industrial vehicles. This is attributed to the high functionality of the resin. However, epoxy resins can be water-solubilized by first reducing its functionality. The main technique adapted for this reason is through partial or complete esterification with mono basic acids.

The produced, epoxy ester are then subjected to either maleinization in case of completely defunctionalized epoxy esters or reaction with polybasic acid or anhydride in case of partial ester. The highly hydrophilic resins produced were then neutralized with organic volatile amine to produce the water-dilutable amine salt.

As has been mentioned above, the esterification concept constitute a main rule in the conversion of epoxy resin into the water-soluble form. For this reason, attention was directed towards the esterification of epoxy resins and also towards the various parameters affecting the formation of epoxy esters.

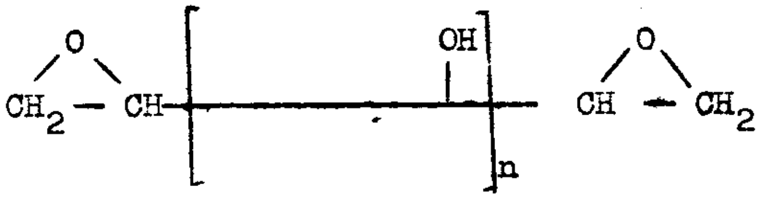
The formation of fatty acid esters is among the major outlets of epoxy resins. These possess most of the merits of the pure epoxy resins to a useful degree and in addition have the advantages of solubility in hydrocarbons and the ability to cure by air-drying or low temperature stoving.

The chemistry involved in the esterification of epoxy resins has been described in many papers and includes the following reactions:

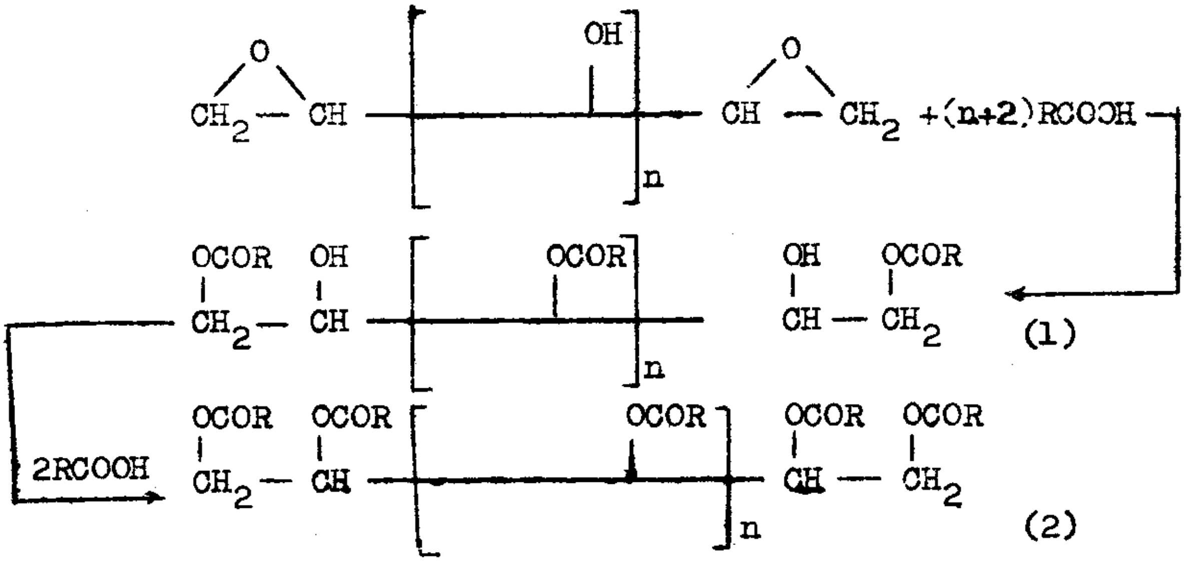
1- Carboxyl/hydroxy esterification
2- Carboxyl/epoxide
3- Epoxy/hydroxide etherification
4- Reaction occurred with the unsaturated fatty acid centers.

The reaction between epoxy and hydroxy groups has been proved to take place to a much greater extent during the esterification with fatty acids than usually encountered especially when using high molecular weight epoxy resins. This is attributed to the increased epoxy content of the base resin and thus resulting in lowering the epoxy content and consequently more water of esterification evolved than expected for reactions 1 and 2.

For simpelicity, the epoxy resin molecule can be represented by:



and reactions 1 and 2 can be illustrated by the following series of equations:

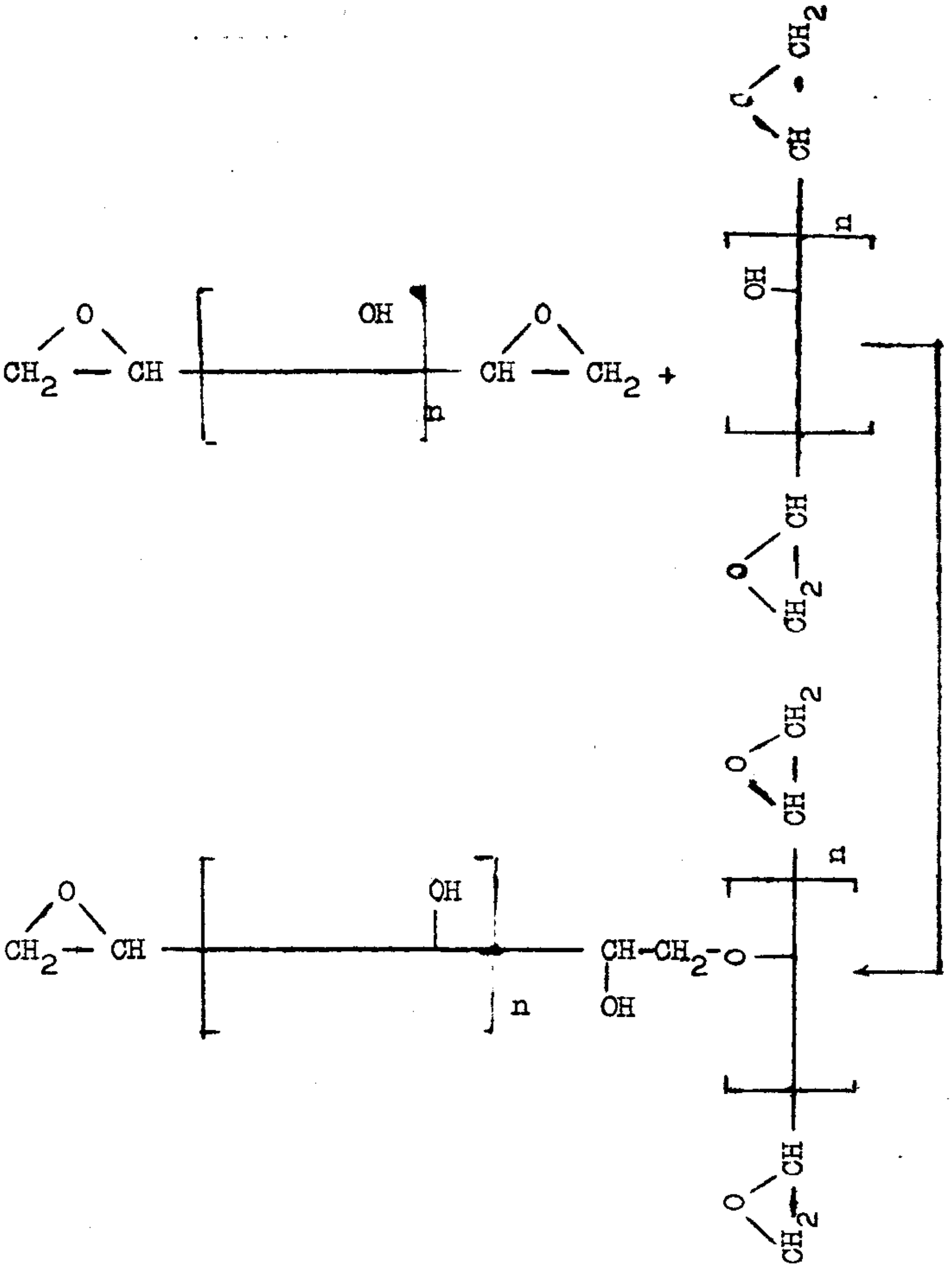


In the above reactions, the epoxy group is considered as equivalent to two hydroxyl groups.

The relative order of reactivity towards esterification of the epoxy and hydroxyl groups in the epoxy resin was a matter of interest especially in view of the possible preferential reaction of one type of grouping as might results in the formation of different type of products.

Coldblatt *et.al.*[182] studied the course of esterification and came to the concluded that epoxy and hydroxyl groups react in accordance with the relative number present. Consequently no significant differences in properties of epoxy esters obtained if mixed fatty acids are used.

The evolution of more water than expected for the esterification of both the epoxy and hydroxyl groups with the mono basic fatty acids can be explained by etherification of the epoxy groupes with the hydroxyl groups which proceeds as follows:



Disappearance of epoxy groups in this way means that for short-oil esters less fatty acids is able to react additively and consequantly more has to esterify with hydroxyl groups with liberation of water. This etherification reaction leads to higher molecular weight branched structures, higher ester viscosities and higher possibility of gelation during esterification.

During the course of esterification of high molecular weight epoxy resins, many trails attempted were failed in preparing linseed oil and dehydrated castor oil fatty acid esters due to premature gelation. For this reason it was felt of interest to forward the investigation towards decreasing the degree of etherification and cooking times.

The esterification was carried out quite simply by heating the epoxy resin with the fatty acids together under an inert gas blanket at 240°C. The progress of the reaction was followed by determining the acidity of samples removed periodically from the reaction mixture at different intervals. In order to carry out the esterification in a precise and quantitative manner, stearic acid was used at the begining before performing the trails on commercial oil fatty acids, for two reasons:

1- To eliminate any side chain reactions of the fatty acid skeleton since it contains no unsaturation center, and

2- it can be produced in a relatively pure grade.

## Esterification in Absence of Catalyst:

In order to prove that the presence of catalyst is effective in the esterification of epoxy resins with fatty acids, blank experiments were performed in which esterification was conducted for various periods of time but in absence of any added materials.

Attention was then directed towards the use of alkaline materials of similar nature to that use by Van Westrenen *et.al*.[127].

The catalysts studied are:

Lithium hydroxide
Zinc oxide
Sodium carbonate
Lead monoxide (Litharge)
Barium hydroxide
Calcium hydroxide

The catalyst concentration is the another parameter studied and the concentration range investigated included:

0.125 gram element/100 gram epoxy resin
0.250 gram element/100 gram epoxy resin

0.375 gram element/100 gram epoxy resin

0.500 gram element/100 gram epoxy resin.

It is noteworthy to mention that within each set of experiments, a blank experiment was conducted under similar experimental conditions.

The time-temperature programe for such epoxy/stearic acid esters are graphed in Figure (1)

Following the successful preparation of stearic esters of epoxy resin, the work was extended to include the esters of oleic acid.

The amount of fatty acids required to the complete esterification of the epoxy resin can be computed from the epoxy resin characteristics. For this reason, the constants of the resin were first determined according to well-known standard methods. The results obtained are given in Table (4).

Table 4: Characteristics of Epoxy Resin

| | |
|---|---|
| Epoxy equivalent (epoxy groups/100 gm) | 0.22 |
| Softening temperature °C | 70-75 |
| Colour (Gardner) 40% solution in amyl alcohol | 6 |
| Hydroxyl content (OH/100 gm) | 0.28 |
| Spicific Gravity | 1,1938 |
| Epoxy equivalent (gm/mole of epoxy) | 526 |

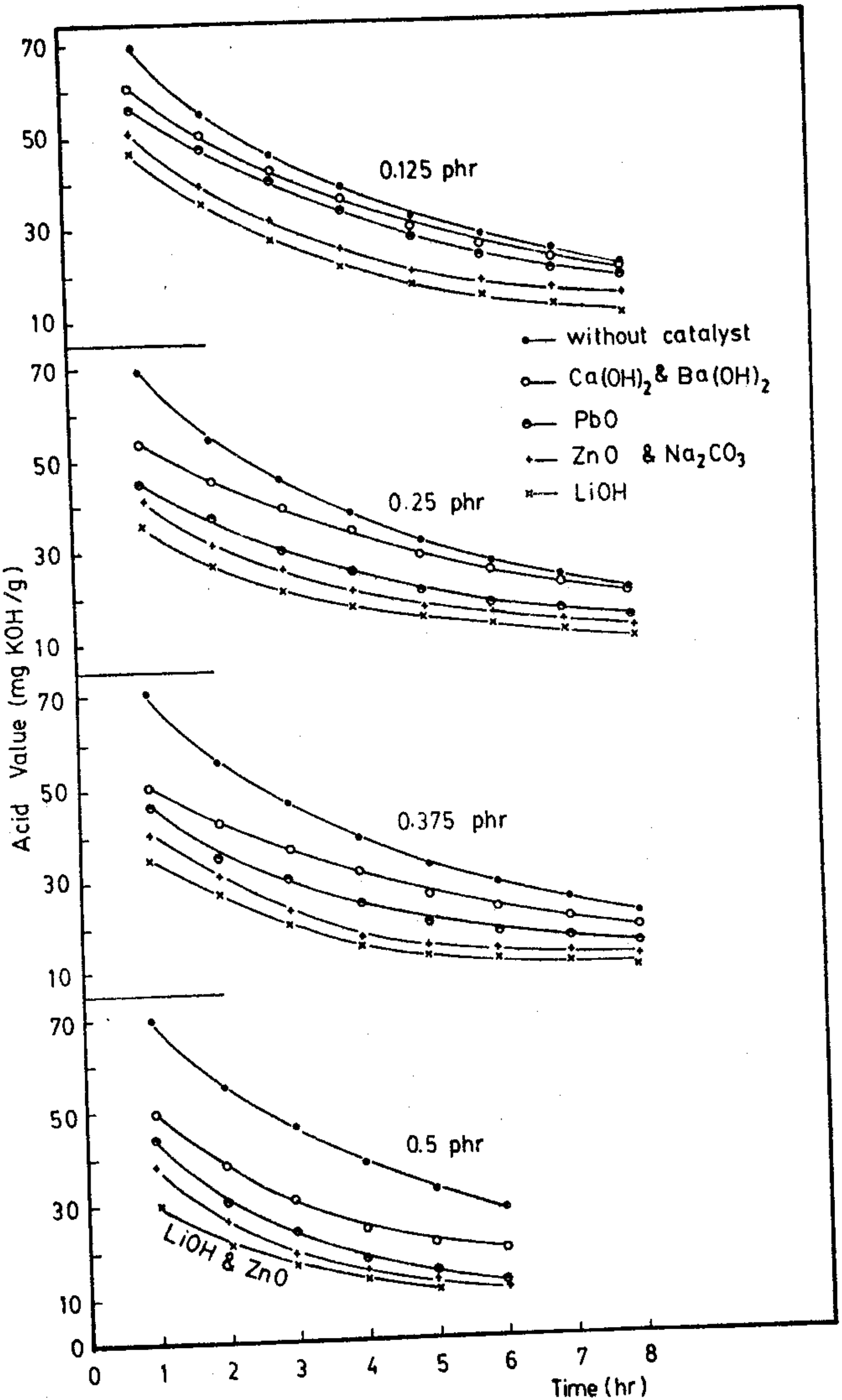


Fig.(1): Effect of Catalyst Concentration on the Esterification Reaction.

The ester equivalent weight which is defined as the grams required to complete esterification (complete defunctionalization) of one gram mole of a monobasic acid, can be calculated from both epoxy and hydroxyl equivalents as examplified below.

The total hydroxyl equivalents of the epoxy resin used is equal to:

$$2 \times 0.22 + 0.28 = 0.72$$

This means that:

each 100 grams of resin contains 0.72 hydroxy groups.

X grams of resin contains 1.0 hydroxy groups.

$$X = \frac{100 \times 1.0}{0.72} = 139 \text{ gm}$$

Thus 139 gm of the epoxy resin is required to esterify one mole of monobasic acid, such value is termed "ester equivalent weight".

On the bases described before, the equivalents of the materials studied are given in Table (5).

Table 5: Equivalent Weight (in gm) of Epoxy Resin and Fatty Acids.

| | Ester equivalent (wt. gm) |
|---|---|
| Epoxy resin | 139 |
| Stearic acid | 284 |
| Oleic acid | 282 |
| Linseed oil fatty acids (LOFA) | 280 |
| Dehydrated castor oil fatty acids | 284 |

To show the effect of the type and concentration upon the esterification rate, the following parameters were studied.

A- <u>Effect of the type of catalyst</u>:

From preliminary experiments, it was shown that 0.125 catalyst equivalent/100 gm epoxy resins (based on metal basis) is the most effective catalyst concentration taking into consideration the economic point of view. A set of experiments was performed for the esterification and differing in the type of catalyst present. In order to show such effect a blank experiment was included.

The course of esterification for each type of catalyst was followed and the data obtained are recorded in Figure (1).

The figure clearly indicate that the addition of the catalyst promotes esterification at the expense of etherification and hence reduces viscosity. Also reduction of the acid value of the product and the cooking time is among the observations noticed from the figure. According to the previous study, the catalyst investigated can be arranged on order of reactivity in the following Table (6).

Table 6: Esterification catalysts

| | |
|---|---|
| Highly effective catalysts | Lithium hydroxide,<br>Zinc oxid & sodium carbonate |
| Moderately effective catalyst | Lead oxide |
| Less effective catalysts | Barium & calcium hydroxides. |

B- Effect of catalyst concentration:

From the above paragraph, the importance of using a catalyst in the esterification of epoxy resins was shown. Experiments were then performed to define the most suitable catalyst concentration for producing the highest yield of epoxy esters. Based on four suitable concentrations of catalysts, experiments were performed under identical conditions.

The results are represented graphically in figure

(2A&"B)for 0.125, 0.250, 0.375 and 0.500 equivalent metal per 100 gm epoxy resin respectively. These figures show the effect of catalyst concentration on the rate of esterification. It can be seen from these figures that similar behaviour with respect to the catalyst reactivity are observed. Thus indicating that lithium and zinc catalyst are the most reactive. Also the increase in the amount of catalyst leads to a slight increase on the rate of esterification than would be expected.

As it is plausible that the concentration of the catalyst plays a role in the efficiency of esterification, the work was extended to employ zinc or lithium catalyst (0.25 element eq./100 gm epoxy resin) in the reaction for oleic or linseed oil fatty acids as the monobasic acid. The results obtained one represented in figure (3).

It can clearly seen from the figure thatincreasing the unsaturation of the mono basic acid leads to enhance the rate of estarification. This conclusion is in agreement with the theoretical basis since the relative reactivity values of the unsaturated fatty acids are in the order[183]:

Stearic < Oleic < Linoleic < Linolenic acids < Elestearic acid
0 : 1 : 20 : 40 : 80

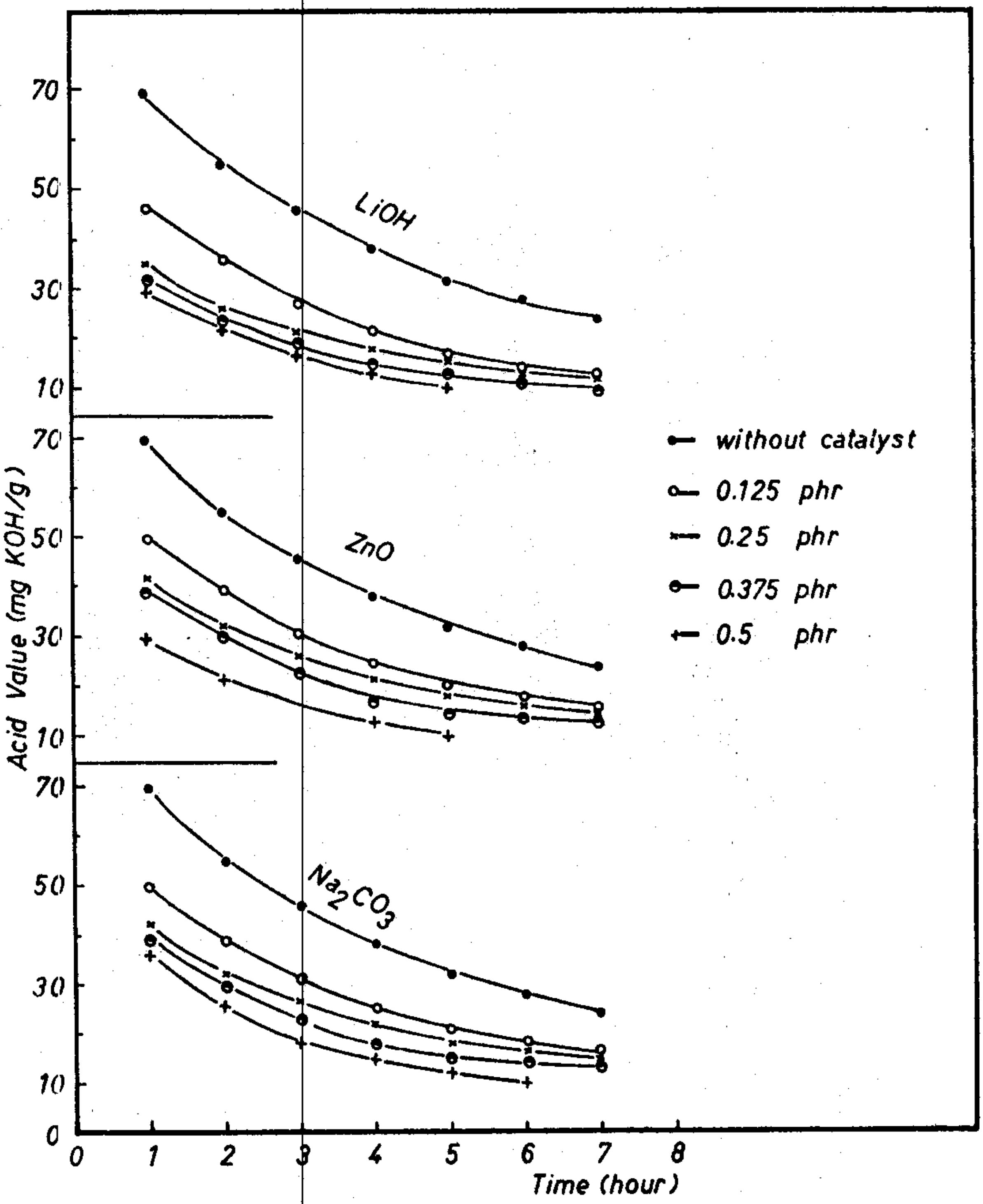


Fig.(2A): Effect of Different Catalysts on the Esterification Reaction.

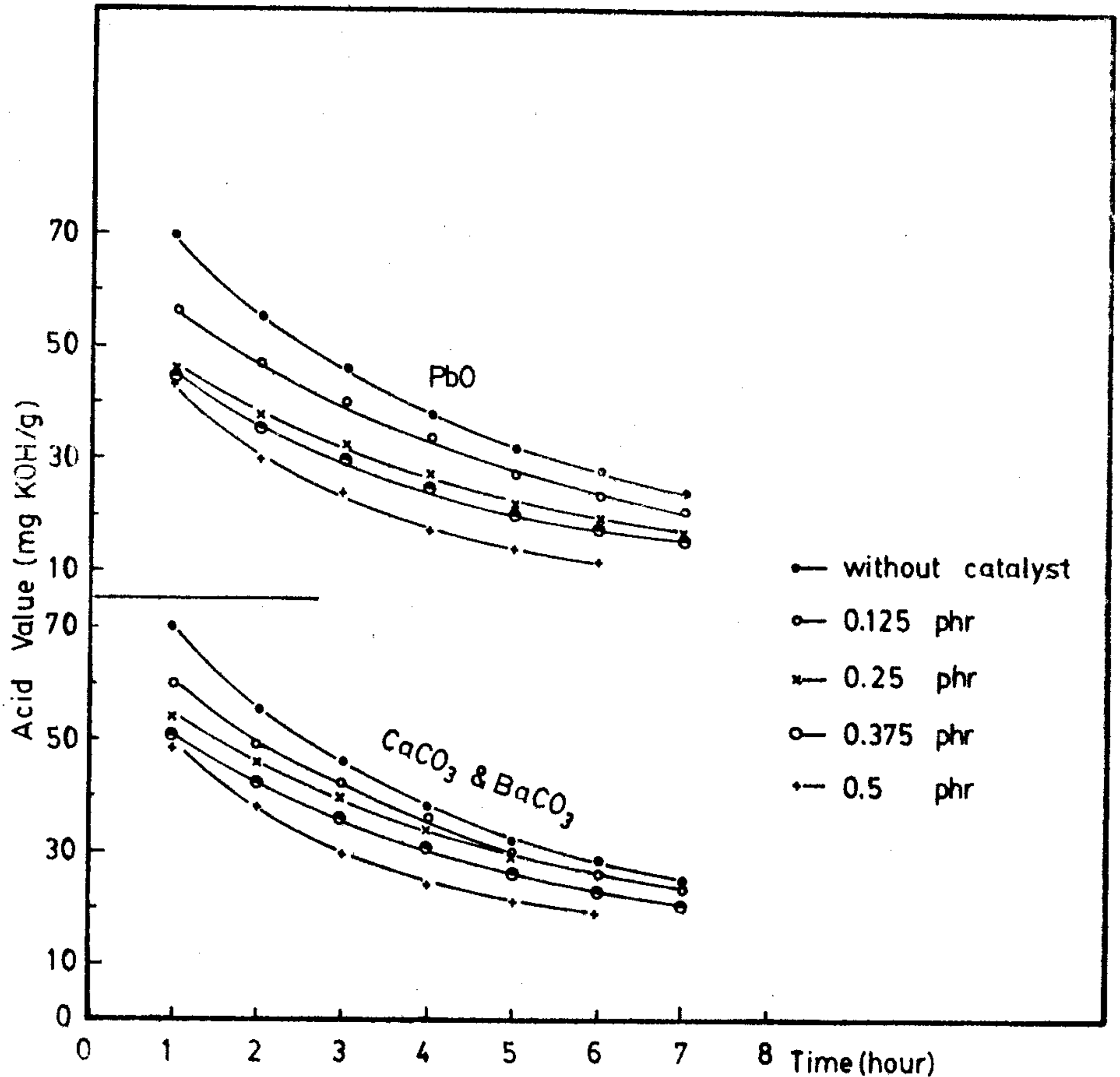


Fig (2 B): Effect of Different Catalysts upon the Esterification Reaction

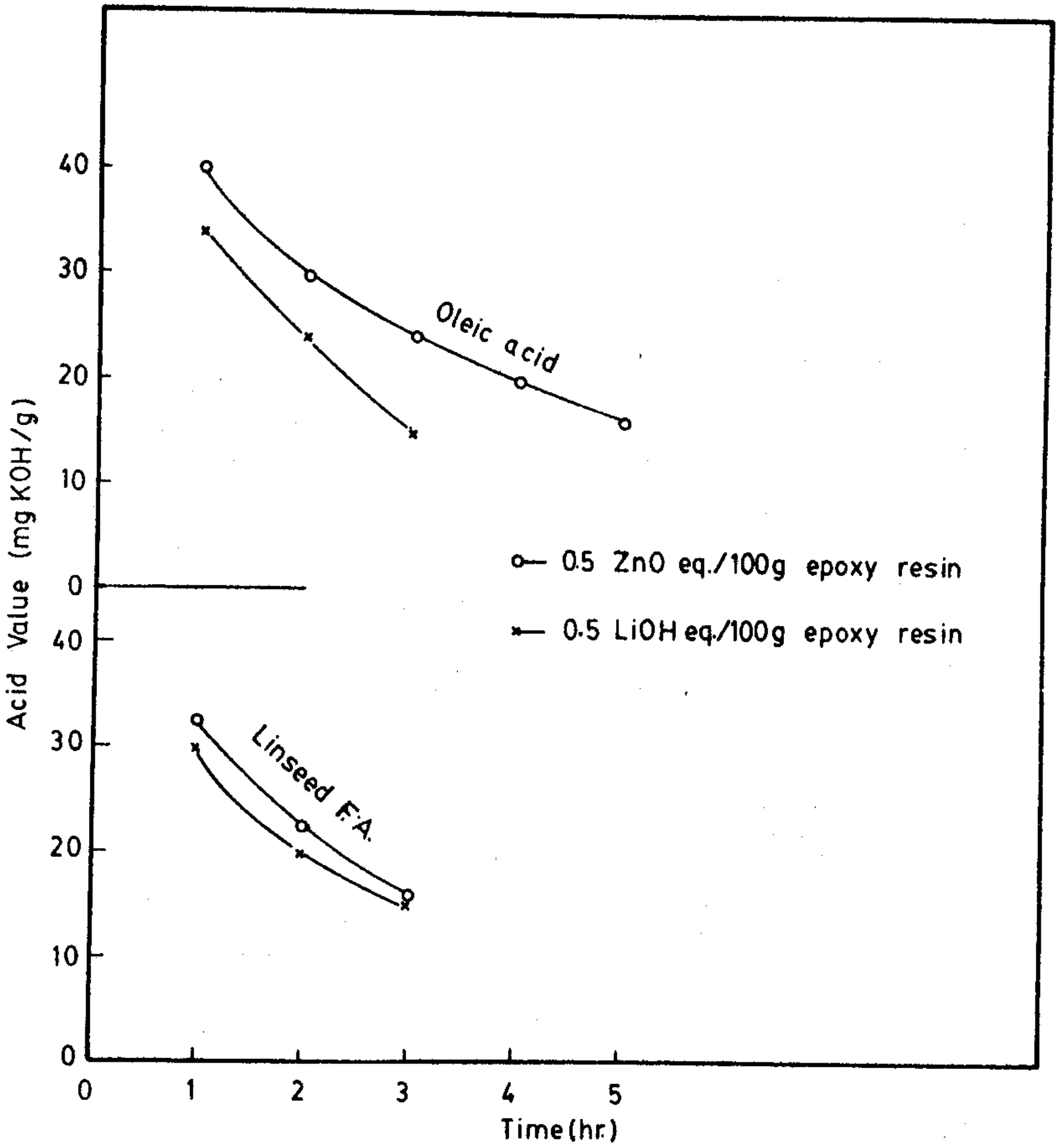
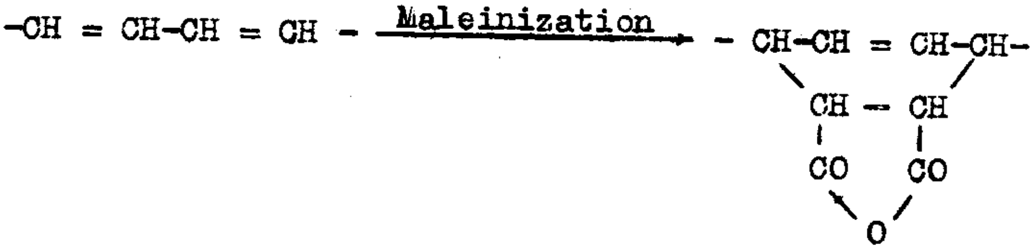


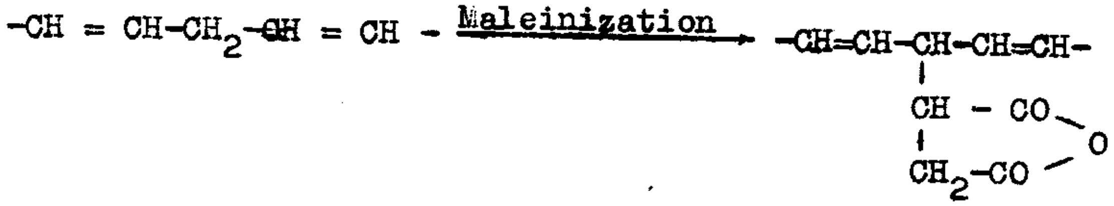
Fig.(3): Effect of Lithium & Zinc Catalysts upon Esterification of Epoxy Resin.

Maleinized Epoxy/Fatty Acid Esters:

The same technique adapted for water-solubilization of unsaturated oils was also applied for the completely defunctionalized epoxy esters. The term maleinization is frequently used for the reaction of maleic anhydride with the unsaturated centers of the fatty chain: The most interesting feature of maleinization is that one has a simple process for adding acidic groups in the molecule.

The addition of maleic anhydride to the oil portion of the epoxy ester molecule depends upon the type of unsaturation present. The following equations illustrates the possible reaction mechanisms for both the conjugated and nonconjugated systems:





Moreover in the later case, the reaction occurs at 200-250°C which is relatively high as compared with that required for conjugated fatty acids (80°C). The maleinization is carried out under nitrogen atmosphere and continuous stirring.

In order to explore any advantage performances of maleinized epoxy esters over maleinzed oils, comparitive study between them and other maleinized linseed and dehydrated castor adducts was introduced.

The reaction completion was performed through the anilic acid number and unreacted anhydride content determinations. It is noteworthy to mention that, all acidity determination of the maleinized adducts depends on the anilic acid number method. This method is preferable than the conventional following reasons:

1- The maleic adduct is not completely hydrolyzable.

2- The presence of any water traces interfers in the determination.

3- The possible formation of semi-esters of the dicarboxylic acid with alcohols present in the solvent and in the presence of alkali which acts as catalyst[184].

4- The formation of strong type of hydrogen bonding if non-aqueous solvents are used[185].

Preliminary trials were carried out to estimate the optimum maleic anhydride needed to provide water solubility for both L.O. and L.O/D.C.O. at mixture. 15% M.A. seemed to be the most suitable anhydride ratio. There is a great tendency for gelation when D.C.O. is maleinized. This is recently attributed to the residual hydroxyl groups left after the dehydration of castor oil, ~~This possibility~~ is eliminated by replacing the hydroxyl groups by chloride groups[188].

Three different oil formulations were prepared and were included among other formulations for the sake of comparison. These formulation are given in Table (7).

Table 7: 15% Maleinized Oil Formulations

| Oil Composition | | Temp. °C | Anilic Acid No. mg KOH/g | Unreacted mg KOH/g | Time min. | Solubility |
|---|---|---|---|---|---|---|
| L.O. | D.C.O. | | | | | |
| 100 | 00 | 250 | 80 | 8 | 180 | Sol. |
| 70 | 30 | 200 | 85 | 10 | 45 | Sol. |
| 60 | 40 | 200 | 75 | 3 | 45 (gel upon cooling) | Sol. |

It can be concluded from the data in table (7) that the incorporation of D.C.O. leads to reduction in both the reaction time and temperature. It would be expected that formulations based on high D.C.O. percentage (over 40%)

tend to converted to gel upon cooling. Moreover, the colour of the adduct tends to be paler as the percent of D.C.O. increases. This is attributed for the presence of linolenic acid in linseeed oil which responsible for the yellowing.

For the forgoing reasons, only the 15% maleinized L.O. and 15% maleinized L.O./D.C.O. (70:30 by wt.) were employed.

After the preparation of maleinized oils and assessting their suitability as a water-binedrs for paints, attention was drawn towards the adaptation of this technique for maleinization of completely defunctionalization epoxy resin. The maleinization was carriedout after the completion of the esterification of epoxy resin with fatty acids in the manner described before, and using the same apparatus assembly used.

The parameters affecting the maleinization of epoxy esters of linseed oil fatty acids are discussed separately:

### 1- Effect of Maleic Anhydride Concentration and Temperature:

Three sets of experiments were conducted for the purpose of proving the effect of temperature and maleic anhydride ratio on the production of stable and water-soluble adducts. Each set consists of three runs belonging to 10, 15 and 20% by weight maleic anhydride. The temperatures investigated were 220, 200 and 150°C. The results obtained are collected in Table (8).

Table 8: Maleinization of Epoxy Esters of Linseed Oil Fatty Acids.

| Maleic Anhydride % | Temp. °C | Anilic Acid No. (mg KOH/g) | Unreacted (mg KOH/g) | Gel formation |
|---|---|---|---|---|
| 10 | 220 | — | — | Immediately |
| 10 | 200 | — | — | After 15 minutes |
| 10 | 150 | — | — | After 30 minutes |
| 15 | 220 | — | — | Immediately |
| 15 | 200 | — | — | After 15 minutes |
| 15 | 150 | 47 | 14 | — |
| 20 | 220 | — | — | Immediately |
| 20 | 200 | — | — | After 15 minutes |
| 20 | 150 | 100 | 56 | After 40 minutes |

The above data clearly illustrates, the effect of both anhydride concentration and temperature in promotion of gelation. Thus increasing the anhydride percentage or the reaction temperature lead to high possibility of gelation. This conclusion is in agreement with the previous observation and is analogous to the theoretical considerations. These findings, also indicate the unsuitability of this type of epoxy resins in producing water-soluble epoxy esters. As a matter of fact low molecular weight epoxy resins (370) gave promising results in producing water soluble varnishes[186].

However, it was thought of interest to incorporate oils in the reaction mixture just prior to the maleinization would expect to eliminate the possibility of gelation and thus produces adducts of suitable viscosities. For this purpose, a definite amount of linseed oil was added after the complete esterification of epoxy resins followed by the usual addition of maleic anhydride. These studies are gathered in Table (9).

Table 9: Maleinized Epoxy Ester/Linseed Oil Adduct.

| Adduct composition % | | | Temp. °C | Anilic AN ber mg KOH/g | Unreacted mg KOH/g | Time | Solubility |
|---|---|---|---|---|---|---|---|
| L.O. | Epoxy Ester | M.A. | | | | | |
| 24 | 56 | 20 | 200 | * | --- | < 1 hr | Sol. |
| 32 | 48 | 20 | 200 | * | --- | < 1 hr | Sol. |
| 33 | 49 | 18 | 200 | 30* | 3 | 2 hrs | Sol. |
| 33 | 49 | 18 | 180 | 75* | 9 | 1 hr | Sol. |
| 40 | 40 | 20 | 180 | 86 | 20 | 1 hr | Sol. |
| 34 | 51 | 15 | 150 | 89 | 12 | 1 hr | Sol. |
| 42.5 | 42.5 | 15 | 150 | 65 | 10 | 2½ hrs | insol. |
| 24 | 56 | 20 | 150 | 83 | 30 | 2 hrs | insol. |
| 32 | 48 | 20 | 150 | 81 | 43 | 3 hrs | Sol. |

* Gel upon cooling.

From the above data it can be concluded the following:

1- The addition of linseed oil in an amount to 24 percent of the reaction mixture or higher eliminates the possibility of gelation, when performed at temperatures less than 200°C, or at short maleinization periods.

2- Within the experimental limits tested, it seems that the shorter the maleinization period is, the better results obtained. This is achieved by using higher temperature; and 200°C seems to be the optimum maleinization temperature.

From the above record of experiments, 15% maleic anhydride adducts were prepared at 200°C in which drying oil was incorporated in mixture prior to maleinization. Their characteristics were determined and are given in Table (10).

Table 10: Maleinized Epoxy Ester/Drying Oil Adduct 15% Maleic Anhydride

| Adduct composition % | | | | Temp. °C | Anilic A.N. mg KOH/g | Unreated mg KOH/g | Time | Solubility |
|---|---|---|---|---|---|---|---|---|
| L.O. | D.C.O. | Epoxy Ester | M.A. | | | | | |
| 57 | —— | 28 | 15 | 200 | 85 | 5 | 1 hr* | Sol. |
| 64 | —— | 21 | 15 | 200 | 40 | 10 | 1½ hr | Sol. |
| 68 | —— | 17 | 15 | 200 | 75 | 8 | 1½ hr | Sol. |
| 43 | 21 | 21 | 15 | 200 | 65 | 10 | ½ hr | Sol. |

* Gel upon cooling

An important finding derived from the above study is the deviation of the acid value of the maleic adduct from the theoretical values. This deviation can be shown from the following Table (11).

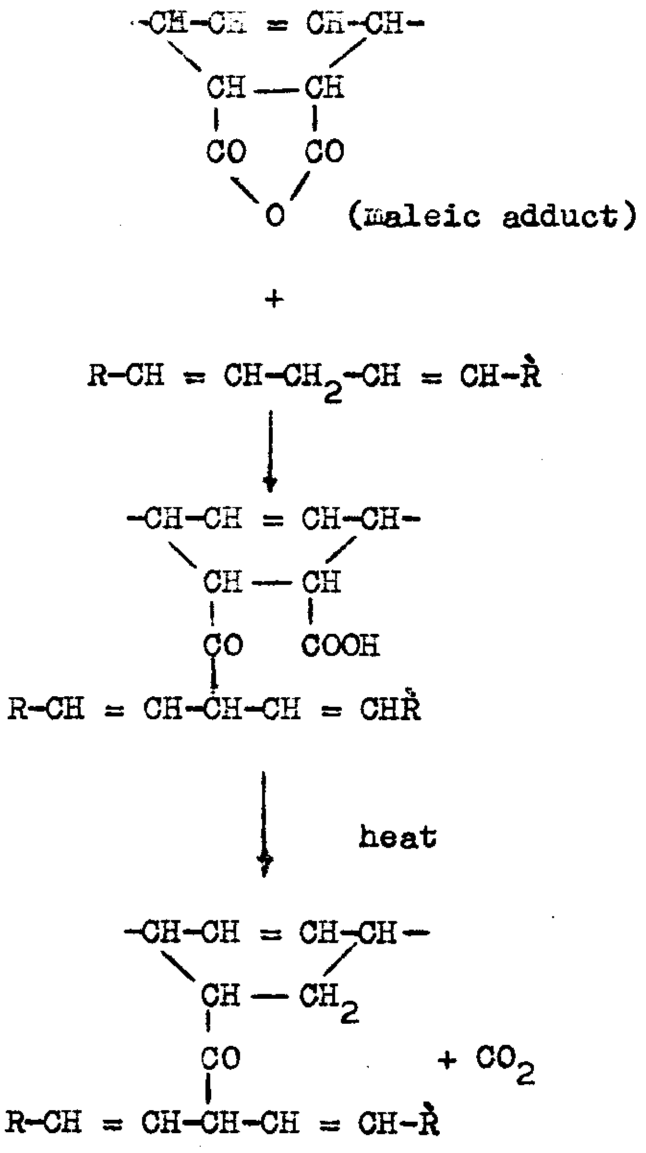
Table 11: Acid Value of the Maleic Adducts

| | Experimental Acidity mg KOH/g | Theoretical Acidity mg KOH/g | % Loss |
|---|---|---|---|
| 15% maleic adduct of 28% epoxy ester | 90 | 173 | 48 |
| 15% maleic adduct of 21% epoxy ester | 85 | 173 | 51 |
| 15%maleic adduct of 17% epoxy ester | 83 | 173 | 52 |
| 15% maleic adduct of 21% epoxy ester containting 21% D.C.O. | 75 | 173 | 62 |

The conclusion drawn from the data given in Table (11) clearly illustrates the dependance of the acid value of the adducts on the amount of oil incroporated in the resin.

The loss of acidity during maleinization is very important both fundamentally and economically since it might require the use of a high proportion of maleic ahhydride to ensure its solubility, thus the reactivety of the molecule being undueby reduced.

There are several suggestions and explanations for this loss of acidity. The probable explanation of this loss of acidity rests upon the fact that the adducts exhibit higher viscosities and gel-like apperance. In addition, carbon dioxide gas was detected during the maleinization reactions. For these reasons, the following series of reactions are suggested to explain the phenomena of lost acidity:



Where R = $CH_3(CH_2)_4$ & $\dot{R}$ = $-(CH_2)_7-COOH$

The work carried-out recently Ghanem __et.al__.[187] on the maleinization of drying oils proved that the acidity of the adducts equal to the anilic acid number plus twice the acidity due to carbon dioxide evolution.

Another observation seen from the above data is the presence of dehydrated castor oil among the oil portion used for the modification of epoxy esters leads to the formation of higher viscosity products and higher acidity loss. This is explained on the bases that the residual hydroxyl groups present condensed with the anhydride groups leading to the formation of products similar to the alkyds in nature, thus reduces potentially the carboxylic groups.

## Water-Soluble Epoxy-Modified Alkyd Resin:

Alkyd resins are used extensively in protective and decorative coatings and as a vehicle in automotive and industrial finishes, water-thinned paints lacquers, enamels and as a grinding vehicle. They are also used in adhesives, inks and in various compositions containing rubber. This wide usage range has resulted from the various desirable properties of the resins such as good colour retention, toughness, heat resistance, resistance to weather exposure, flexibility and ease of application. For these reasons, it has been though desirable to provide a water-soluble resin which combines the useful advantages of both alkyd and epoxy resins. A further desirable characteristic is that it becomes hydrophobic upon curing, that is, its resistance to water absorption is substantially increased after being cured.

Because of the high functionality characteristics of both epoxy and alkyd resins, most previous attempts to combine the two materials resulted in gelation before low acid values could be reached.

Epoxy-modified water-soluble alkyds have improved film forming properties, adhesion qualeties over unmodified alkyd resins. Also, they maintain their stabilities during cycles of freezing and thawing.

Solvent type alkyds are ordinarily prepared by the reaction of a polybasic acid or anhydride with a polyhydric alcohol to an acid number below 15 mg KOH. At the begining of the reaction, the acid value is relatively high. As the reaction proceeds, the acid value falls until the reaction reaches completion when the acid value is at its minimum value.

However, it is believed that the most common method of the production of water-soluble alkyds consists in interrupting the esterification reaction at some intermediate acid number, say in the range of 30 to 80 mg KOH during the cook. The resultant high acid value alkyds will become water-soluble upon blending with ammonia or some derived volatile amine (i.e. triethylamine) to produce a loosely reacted amine-alkyd polymer soluble in water.

Such high acid value alkyds exhibit properties similar to low acid value alkyds. However, there is a relationship between the acid number and stability and solubility, if the acid value is too high, i.e. above 80, the alkyds tends to be unstable and cannot be stored for periods sufficient for commercial use. On the other hand, if the acid value is too low, i.e. below 25, the resin is very difficult to solubilize by treatment with a base.

The technique adapted in this work for solubilizing the epoxy resins consists of:

<u>Stage A</u>: Involvesthe preparation of partial esters of epoxy resins with monobasic acids.

The term defunctionalization was given for this step. The technique involves formation of a partial ester of the epoxy resin with the fatty acid desired, through both the epoxy and hydroxyl groups present. The resultant product having a hydroxyl functionality between 1 and 4.

<u>Stage B</u>: Involvesthe addition of the alkyd ingredients and cooking was continued to the desired acid value. In this stage, the epoxy resin partial ester is introduced alkyd resins.

<u>Stage C</u>: Involves the neutralization of the modified alkyd resin with a base to obtaine the final water-solubl resin.

The weight of amine necessary to neutralize the acidity of a high acid alkyd resin can be computed from the following equation[189]:

$$W_{amine} = \frac{W_{alkyd}\ [AN]\quad E_{amine}}{56,100}$$

Where:

$W_{amine}$ is the weight of amine,

AN acid value of the alkyd,

$W_{alkyd}$ is the weight of alkyd; and

E is the equevalent weight of the amine.

Basic Formulations:

Carothers equation relating the functionality of the alkyd systems to the extent of the reaction as the degree of polymerization is expressed as:

$$\frac{2 \times 100}{\text{average functionality}} = \%\text{ of reaction at gelation}$$

The average functionality can be calculated as follows:

$$= \frac{\text{Total functionality}}{\text{number of moles}}$$

The formulations of the epoxy modified alkyd were based on the constants method rather than the Carothers's method. The former was proved to be more precise and can be applied to the water-soluble systems.

Four different types of epoxy modified alkyd resins were formulated. These resins correspond to 0, 10, 20 and 30% excess hydroxyl content. These formulations were computed according to average functionality method and are given from Tables (13 to 20). Table (21) illustrates the collective constants drawn from the previous tables.

Table 13: Formulation of 30% Excess Hydroxyl Epoxy Modified Alkyd (Whole Charge).

| | Charge | | | | Break Down | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Epoxy resin | 160 | 130 | 1.23 | --- | 1.23 | 6 | 0.205 |
| LFA | 525 | 280 | 1.87 | 1.87 | --- | 1 | 1.870 |
| Glycerol | 316 | 30.7 | 10.29 | --- | 10.29 | 3 | 3.430 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | --- | 2 | 3.475 |
| | 1516 | | 20.34 | 8.82 | 11.52 | | 8.980 |
| Water loss - | 72 | | | | | | |
| | 1444 | | | | | | |

$$R = e_B/e_A = 11.52/8.82 = 1.3 = 30\% \text{ excess } -OH$$

$$K = m_o/e_A = 8.980/8.82 = 1.018$$

$$Y = 1 - \frac{e_{PA} \times 9}{\text{total wt}} = 1 - \frac{6.95 \times 9}{1444} = 1 - 0.043 = 0.957 = 95.7\%$$

$$\text{Acid value} = \frac{56.1 \times e_A \times 1000}{\text{wt of charge}} = \frac{56100 \times 8.82}{1444} = 342$$

$$P_{\text{gel point}} = \frac{\text{I.A.V. - Final}}{\text{I.A.V.}} = \frac{342-60}{342} = 0.824 = 82.4\%$$

extend of reaction

**Table 14: Formulation of 30% Excess Hydroxyl Epoxy Modified Alkyd.**

| | Charge | | | Break Down | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Def. epoxy ester | 387 | 557 | 0.69 | — | 0.69 | 3 | 0.230 |
| LFA | 283 | 280 | 1.0 | 1.0 | — | 1 | 1.000 |
| G. | 301 | 30.7 | 9.80 | — | 9.80 | 3 | 3.266 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | — | 2 | 3.475 |
| | 1486 | | 18.44 | 7.95 | 10.49 | | 7.971 |
| Water loss − | 72 | | | | | | |
| | 1414 | | | | | | |

$$R = e_B/e_A = 10.49/7.95 = 1.31 = 31\% \text{ excess } -OH$$

$$K = m_o/e_A = 7.971/7.95 = 1.00$$

$$Y = 1 - \frac{e_{P.A.} \times 9}{\text{total wt.}} = 1 - \frac{6.95 \times 9}{1414} = 1 - 0.045 = 0.955 = 95.5\%$$

$$\text{I.A.V.} = \frac{56.1 \times e_A \times 1000}{\text{wt of charge}} = \frac{56.1 \times 7.95 \times 1000}{1414} = 315$$

$$P_{\text{gel point}} = \frac{315 - 60}{315} = 84.1\ \%$$

extent of reaction

**Table 15: Formulation of 20% Excess Hydroxyl Epoxy Modified Alkyd (Whole Charge)**

| | Charge | | Break Down | | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Epoxy resin | 160 | 130 | 1.23 | —— | 1.23 | 6 | 0.205 |
| **LFA** | 525 | 280 | 1.87 | 1.87 | —— | 1 | 1.870 |
| **G.** | 287 | 30.7 | 9.354 | —— | 9.354 | 3 | 3.118 |
| **P.A.** | 515 | 74.1 | 6.950 | 6.95 | —— | 2 | 3.475 |
| | 1487 | | 19.404 | 8.82 | 10.584 | | 8.668 |
| **Water loss** | - 72 | | | | | | |
| | 1415 | | | | | | |

$$R = e_B/e_A = 10.584/8.82 = 1.2 = 20\% \text{ excess } -OH$$

$$K = m_o/e_A = 8.668/8.82 = 0.98$$

$$Y = 1 - \frac{e_{PA} \times 9}{\text{total wt}} = 1 - \frac{6.95 \times 9}{1415} = 1 - 0.045 = 0.955 = 95.5\%$$

$$I.A.V. = \frac{56.1 \times e_A \times 1000}{\text{wt of charge}} = \frac{56.1 \times 8.82 \times 1000}{1415} = 349$$

$P_{gel}$ point extent of reaction $= \frac{349 - 60}{349} = \frac{289}{349} = 82.8\ \%$

**Table 16:** Formulation of 20% Excess Hydroxyl Epoxy Modified Alkyd

| | Charge | | Break Down | | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $n_o$ |
| Def. epoxy ester | 387 | 557 | 0.69 | —— | 0.69 | 3 | 0.230 |
| LFA | 283 | 280 | 1.00 | 1.00 | —— | 1 | 1.000 |
| G. | 272 | 30.7 | 8.85 | —— | 8.85 | 3 | 2.950 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | —— | 2 | 3.475 |
| | 1457 | | 17.49 | 7.95 | 9.54 | | 7.655 |
| Water loss - | 72 | | | | | | |
| | 1385 | | | | | | |

$R = e_B/e_A = 9.54/7.95 = 1.2 = 20\%$ excess -OH

$K = n_o/e_A = 7.655/7.95 = 0.96$

$$Y = 1 - \frac{6.95 \times 9}{1375} = 1 - \frac{62.55}{1385} = 1 - 0.046 = 0.954 = 95.4\%$$

$$I.A.V. = \frac{56.1 \times e_A \times 1000}{\text{wt of charge}} = \frac{56.1 \times 7.95 \times 1000}{1385} = 324$$

$$P_{\text{gel point}} = \frac{324 - 60}{324} = \frac{264}{324} = 81.5\%$$

extent of reaction

**Table 17:** **Formulation of 10% Excess Hydroxyl Epoxy Modified Alkyd (Whole Charge).**

| | Charge | | Break Down | | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Epoxy resin | 160 | 130 | 1.23 | —— | 1.23 | 6 | 0.205 |
| LFA | 525 | 280 | 1.87 | 1.87 | —— | 1 | 1.870 |
| G. | 260 | 30.7 | 8.472 | —— | 8.472 | 3 | 2.824 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | —— | 2 | 3.475 |
| | 1460 | | 17.522 | 8.82 | 9.702 | | 8.374 |
| **Water loss-** | 72 | | | | | | |
| | 1388 | | | | | | |

$R = e_B/e_A = 9.702/8.82 = 1.1 = 10\%$ excess $-OH$

$K = m_o/e_A = 8.374/8.82 = 0.95$

$$Y = \frac{6.95 \times 9}{1388} = 1 - \frac{62.55}{1388} = 1 - 0.045 = 955 = 95.5\%$$

$$I.A.V. = \frac{56.1 \times 8.82 \times 1000}{1.388} = 356$$

$P_{gel\ point}$ extent of reaction $= \frac{356 - 60}{356} = \frac{296}{356} = 0.831 = 83.1\%$

Table 18: Formulation of 10% Excess Hydroxyl Epoxy Modified Alkyd

| | Charge | | Break Down | | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Def. epoxy ester | 387 | 557 | 0.70 | —— | 0.7 | 3 | 0.23 |
| LFA | 283 | 280 | 1.0 | 1.0 | —— | 1 | 1.00 |
| G. | 247 | 30.7 | 8.045 | —— | 8.045 | 3 | 2.681 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | —— | 2 | 3.475 |
| | 1432 | | 16.795 | 7.95 | 8.745 | | 7.386 |
| Water loss − | 72 | | | | | | |
| | 1360 | | | | | | |

$$R = e_B/e_A = 8.745/7.95 = 1.1 = 10\%\ \text{excess} -OH$$

$$K = m_o/e_A = 7.386/7.95 = 0.93$$

$$\dot{Y} = 1 - \frac{6.95 \times 9}{1360} = 1 - \frac{62.55}{1360} = 1 - 0.046 = 0.954 = 95.4\%$$

$$\text{I.A.V.} = \frac{56.1 \times 7.95 \times 1000}{1360} = 328$$

$P_{\text{gel point}}$ $= \dfrac{328 - 60}{328} = \dfrac{268}{328} = 81.7\ \%$

extent of reaction

**Table 19:** Formulation of 0% Excess Hydroxy Epoxy Modified Alkyd (Whole Charge)

| | Charge | | | Break Down | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Epoxy resin | 160 | 130 | 1.23 | —— | 1.23 | 6 | 0.205 |
| LFA | 525 | 280 | 1.87 | 1.87 | —— | 1 | 1.870 |
| G. | 233 | 30.7 | 7.59 | —— | 7.59 | 3 | 2.530 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | —— | 2 | 3.475 |
| | 1433 | | 17.64 | 8.82 | 8.82 | | 8.080 |
| Water loss - | 72 | | | | | | |
| | 1361 | | | | | | |

$R = e_B/e_A = \frac{8.82}{8.82} = 1.0$ = 0% excess -OH

$K = n_o/e_A = 8.08/8.82 = 0.916$

$Y = 1 - \frac{6.95 \times 9}{1361} = 1 - \frac{62.55}{1361} = 1 - 0.046 = 0.954 = 95.4\%$

$\text{I.A.V.} = \frac{56.1 \times 8.82 \times 1000}{1361} = 364$

$P_{\text{gel point}} = \frac{364-60}{364} = \frac{304}{364} = 0.835 = 83.5\%$

extent of reaction

Table 20: **Formulation of 0% Excess Hydroxyl Epoxy Modified Alkyd.**

| | Charge | | | Break Down | | | |
|---|---|---|---|---|---|---|---|
| | W | E | $e_o$ | $e_A$ | $e_B$ | F | $m_o$ |
| Def. Epoxy ester | 387 | 557 | 0.70 | —— | 0.70 | 3 | 0.230 |
| LFA | 283 | 280 | 1.0 | 1.0 | —— | 1 | 1.000 |
| G. | 223 | 30.7 | 7.25 | —— | 7.25 | 3 | 2.416 |
| P.A. | 515 | 74.1 | 6.95 | 6.95 | —— | 2 | 3.475 |
| | 1408 | | 15.90 | 7.95 | 7.95 | | 7.121 |
| Water loss - | 72 | | | | | | |
| | 1336 | | | | | | |

$$R = e_B/e_A = \frac{7.95}{7.95} = 1.0 = 0\% \text{ excess } -OH$$

$$K = n_o/e_A = 7.121/7.95 = 0.9 = 90\%$$

$$Y = 1 - \frac{6.95 \times 9}{1336} = 1 - \frac{62.55}{1336} = 1 - 0.046 = 95.4\%$$

$$I.A.V. = \frac{56.1 \times 7.95 \times 1000}{1336} = 333$$

$$P_{\text{gel point}} = \frac{333-60}{333} = \frac{273}{333} = 0.82 = 82\%$$

extent of reaction

Table 21: Alkyd Constants of Various Water-Soluble Epoxy modified Alkyd Formulations.

| Excess - OH | Charge based on epoxy resin | | | Charge based on epoxy ester | | |
|---|---|---|---|---|---|---|
| | K | Y | $P_{gel}$ | K | Y | $P_{gel}$ |
| 30% | 1.018 | 95.7 | 82.4 | 1.00 | 95.5 | 84.1 |
| 20% | 0.980 | 95.5 | 82.8 | 0.96 | 95.4 | 81.6 |
| 10% | 0.950 | 95.5 | 83.1 | 0.93 | 95.4 | 81.7 |
| 0% | 0.916 | 95.4 | 83.5 | 0.90 | 95.4 | 82.0 |

## Evaluation

Representative samples of the prepared water-soluble varnishes, covering a wide range of resin types and their mode of formation, were selected and evaluated as vehicles for paints. The evaluations were conducted according to well-known international standard specifications. These samples are listed in Table 22 together with their main compositions.

Table 22: List of Varnishes Evaluated

| Sample No. | Composition |
|---|---|
| I | 15% Maleinized linseed oil. |
| II | 15% Maleinized linseed/D.C. oils (70:30 by wt.) |
| III | 15% Maleinized linseed oil/epoxy ester (3:1 by wt.) |
| IV | 15% Maleinized linseed oil/D.C.O./epoxy ester (2:1:1 by wt.) |
| V | 30% Excess-OH epoxy modified alkyd resin based on LFA made by fatty acid method. |
| VI | 20% Excess-OH epoxy modified alkyd resin based on LFA made by fatty acid method. |
| VII | 10% Excess-OH epoxy modified alkyd resin based on LFA made by fatty acid method. |
| IIX | 0% Excess-OH epoxy modified alkyd resin based on LFA made by fatty acid method. |
| IX | 30% Excess-OH epoxy modified alkyd resin based on LFA produced by monoglyceride method. |
| X | 30% Excess-OH epoxy modified alkyd resin based on LSO./D.C.O. (1:1 by wt.) produced by monoglyceride method. |
| XI | 30% Excess-OH epoxy modified alkyd resin based on D.C.F.A. produced by monoglyceride method. |

The percent compositions of the resin employed are given in Table 23. These composition percentages were computed from the data given from the alkyd resin constant calculations and the charged weights.

**Table 23:** Percentage Composition of the Resins

| Ingredient | I | II | III | IV | V | VI | VII | IIX | IX | X | XI |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Defunctionalized Epoxy Resin | | | 21 | 21 | 26 | 26 | 27 | 27 | 25 | 25 | 25 |
| L.O. | 85 | 60 | 64 | 43 | | | | | 20 | 10 | |
| L.O.F.A. | | | | | 20 | 20 | 20 | 20 | | | |
| D.C.O. | | 25 | | 21 | | | | | | 10 | 20 |
| Glycerol | | | | | 20 | 19 | 17 | 16 | 20 | 20 | 20 |
| Phthalic Anhydride | | | | | 35 | 35 | 36 | 37 | 35 | 35 | 35 |
| Maleic Anhydride | 15 | 15 | 15 | 15 | | | | | | | |

The selected varnishes were in the form of aqueous solutions. Their composition formules are given in Table 24.

Table 24: Varnish Compositions

| Ingredient | Percent Composition | |
|---|---|---|
| | Maleinized adduct | Epoxy-modefied alkyd |
| Resin | 30 | 30 |
| Amm. hydroxide or triethylamine | till pH 8 | till pH 8 |
| Water | 55 | 35 |
| Ethanol | 15 | 35 |

The selected resin formulations were tested for the following vehicle properties:

A- <u>Colour and viscosity measurements of the resin solution</u>:

The selected resin solutionswere subjected to colour measurement using the colour comparator adapted by Gardner. On the other hand the viscosity of there solutions was measured by using Ford Cup No. 4 and is expressed in seconds. The results obtained are shown in Table 25.

Table 25: Vehicle Characteristics.

| Resin No. | Colour (Gardner)at 15% solid content | Viscosity (second)at 30% solid content |
|---|---|---|
| I | 14 - 15 | 60 |
| II | 12 - 13 | 40 |
| III | 16 17 | 90 |
| IV | 16 - 17 | 210 |
| V | 14 - 15 | 40 |
| VI | 14 - 15 | 40 |
| VII | 14 - 15 | 40 |
| IIX | 14 - 15 | 40 |
| IX | 14 - 15 | 175 |
| X | 14 - 15 | 120 |
| XI | 13 - 14 | 70 |

It can be clearly shown from the data given in Table 25 that resins containing the dehydrated fatty acid as the main or partial constituent of the oil-portion exhibit paler colours than others. This is attributed to the absence of linolenic acid which has an influential effect upon the yellowing tendencies.

## B- Parameters affecting the viscosity of the solutions:

The aqueous solutions of the neutralized resins are viscous and gel-like materials. Therefore, their ease of application is not practical and hence alcohols are introduced into the formulations to reduce this viscosity to the workable limits. They also improve the transperancy of the solutions and prevents foaming. For there reasons, it was thought of interest to extend the work for further investigation to show the parameters affecting the viscosity flacuations.

### i-The effect of the solid content on the viscosity.

In order to show the effect of solid content on the varnishes's viscosity, a known weight of the resin was neutralized with the suitable base till pH 8 reached. The neutralized mass was then thinned with water/alcohol mixture of definite ratio until 50% resin content by weight reached. The viscosity was then measured using FordCup No. 4 as described in the experimental section.

More water/alcohol diluent was added to adjust the solid contents to 40, 30, 20 and 10% and the corresponding viscosity of each was measured. The data obtained was graphically represented in figure (4).

It can be concluded from figure 4 that increasing the alcohol percent leads to more reduction in viscosity. It is also concluded that at low solid contents, the viscosity was slightly affected by the alcohol percentage. As a matter fact, the viscosity of these resins at 5% solid or less is the same. Also there is a sudden drop in the viscosity reduction curve at solid content between 20-30%.

Another important finding noticed from the reduction curve is that resins containing the epoxy esters exhibit highest viscosities. This is beleived that such resins are of higher molecular weight than the others. Exception from this generalization was observed for resins containing the dehydrated castor fatty chain. This is attributed to the presence of the residial hydroxyl groups which are hydrophilic in nature.

It is also noteworthy to mention that the 50% solids show higher viscosities which were difficult to measure. For this reason, viscosity measurements were performed first on 30% solid and not 50% solids as planned.

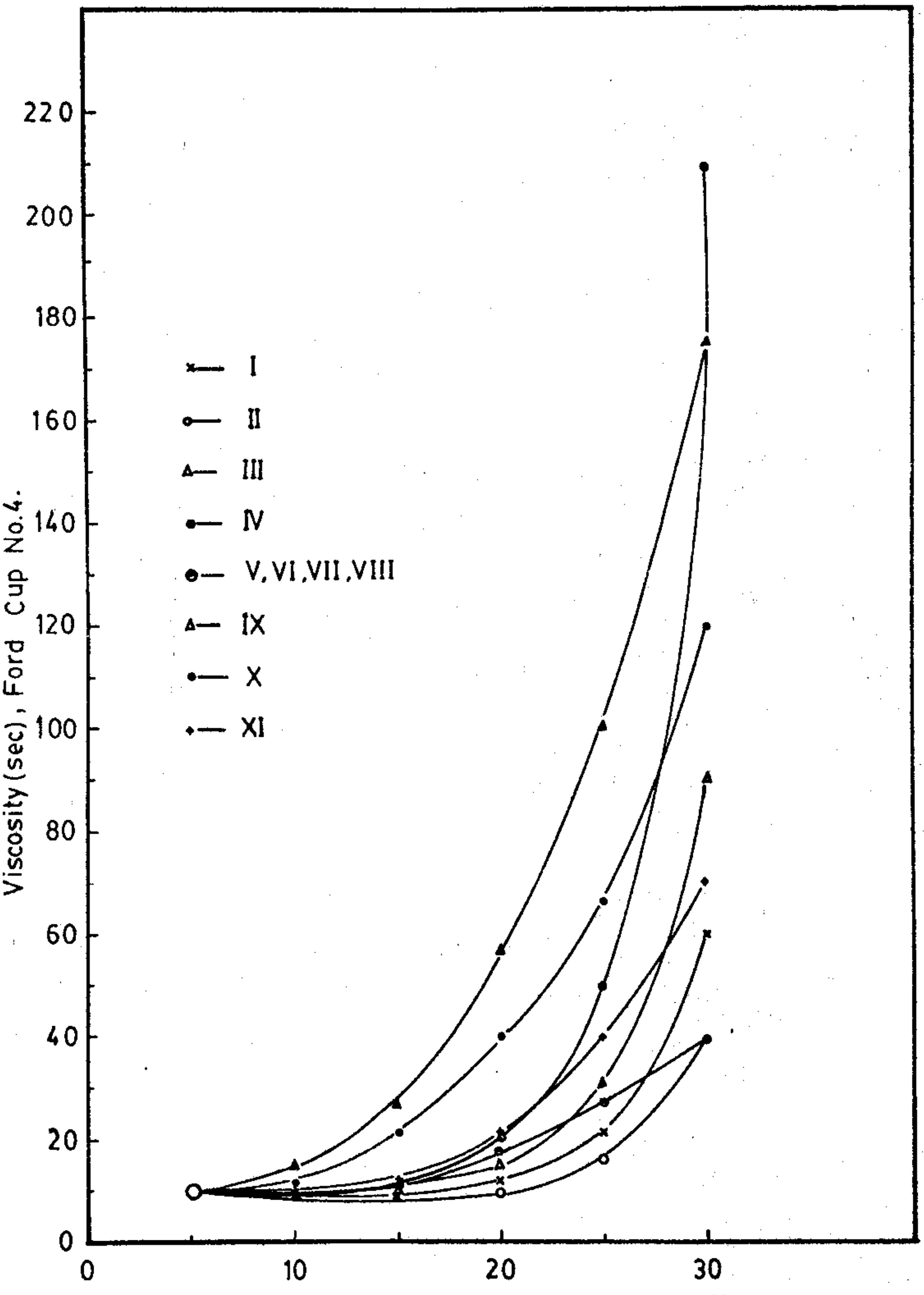


Fig. (4): Effect of Solid Content on the Viscosity of the Varnish.

### ii- The effect of ethyl alcohol on the reduction of viscosity:

As has been pointed before, the importance of the presence of ethanol among the diluent constituents is shown. For this reason, set of experiments were performed in which 30% aqueous solutions of the resins were treated with a definite alcohol ratio and the corresponding viscosities were measured. The resins selected were those corresponding to 30% excess hydroxyl contents (V, IX, X and XI). The data obtained are plotted in figure 5.

Similar behaviour to those of the previous item, was also regarding the effect of alcohol on the viscosity reduction. All the viscosity of resins tested greatly affected by the presence of ethanol. These observations are in agreement with the previous work of Ghanem & Naser(187). Their work mainly concered with 20% maleic adduct of linseed oil and linseed/D.C. oil mixture (60:40 by weight).

### iii- The effect of pH of the varnish solution on the viscosity:

Another set of experiments was conducted to show the effect of pH on the viscosity of the vehicle. For this reason, 30% resin solution were prepared according to the method described before and the pH values were measured using a pH meter. The resins employed in this study are 30% excess hydroxyl epoxy modified alkyd resin based on L.O./D.C.O. (X) and 15% maleic

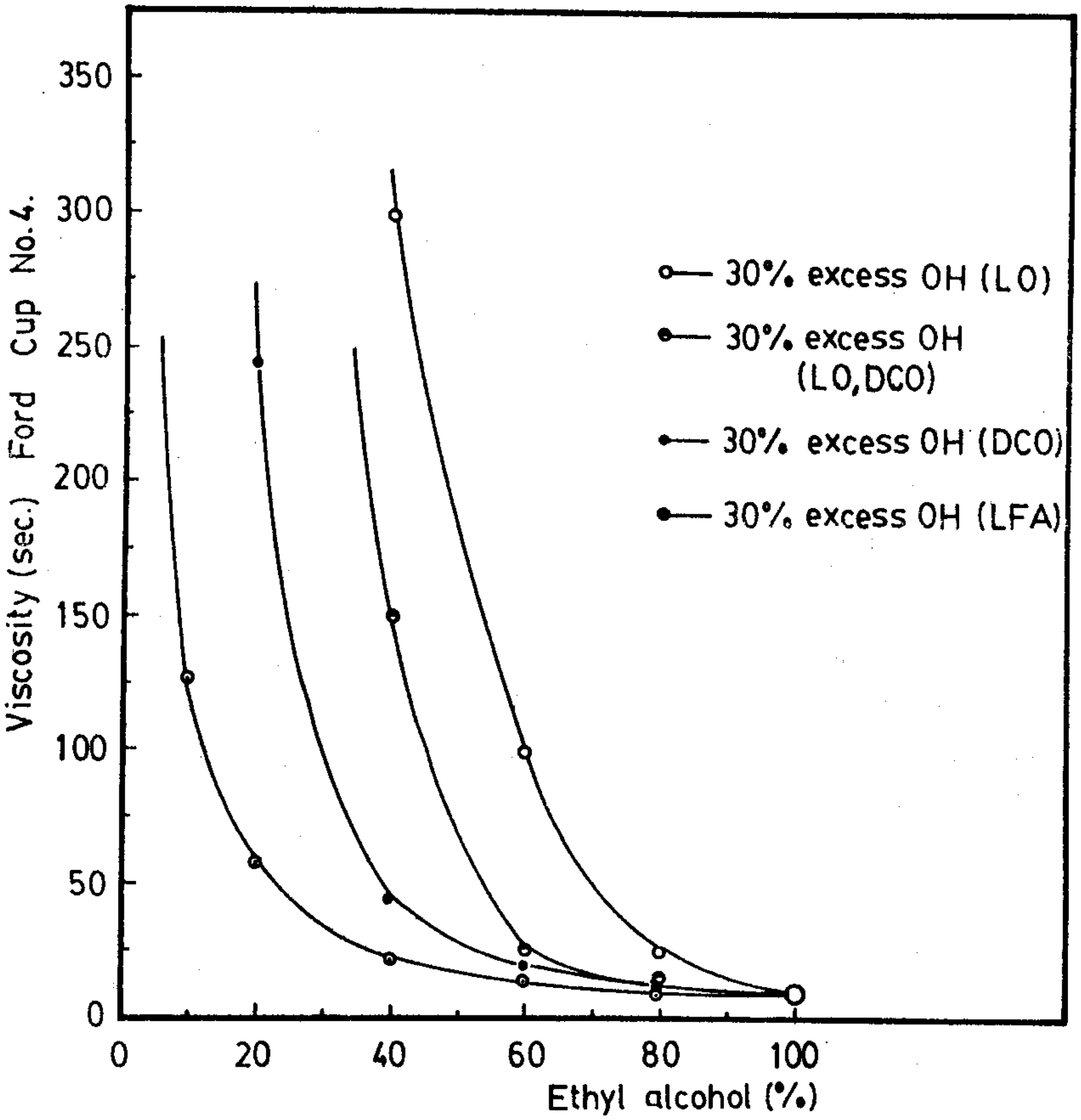


Fig.(5): Effect of Alcohol on the Varnish's Viscosity.

adduct of epoxy esters modified by L.O./D.C.O. (IV). Then more triethylamine was added in case of (X) and ammonium hydroxyde solution in case of (IV) with imediate measurement of pH. The results obtained are graphically represented in figure 6.

From figure 6, it can clearly seen that the pH of the medium has substantial effect on their viscosities, As the pH increases, the viscosity of the varnish decreases. The epoxy modified alkyd type of resin response sharply to pH variations where as the maleinized type of resin response gently.

### G- Drying Characteristics:

Films of the 30% resin solutions were applied over glass panels (5 x 15 cm$^2$) and placed in a well ventillated cabinet and checked every 6 hours for drying. the results obtained are given in Table 26.

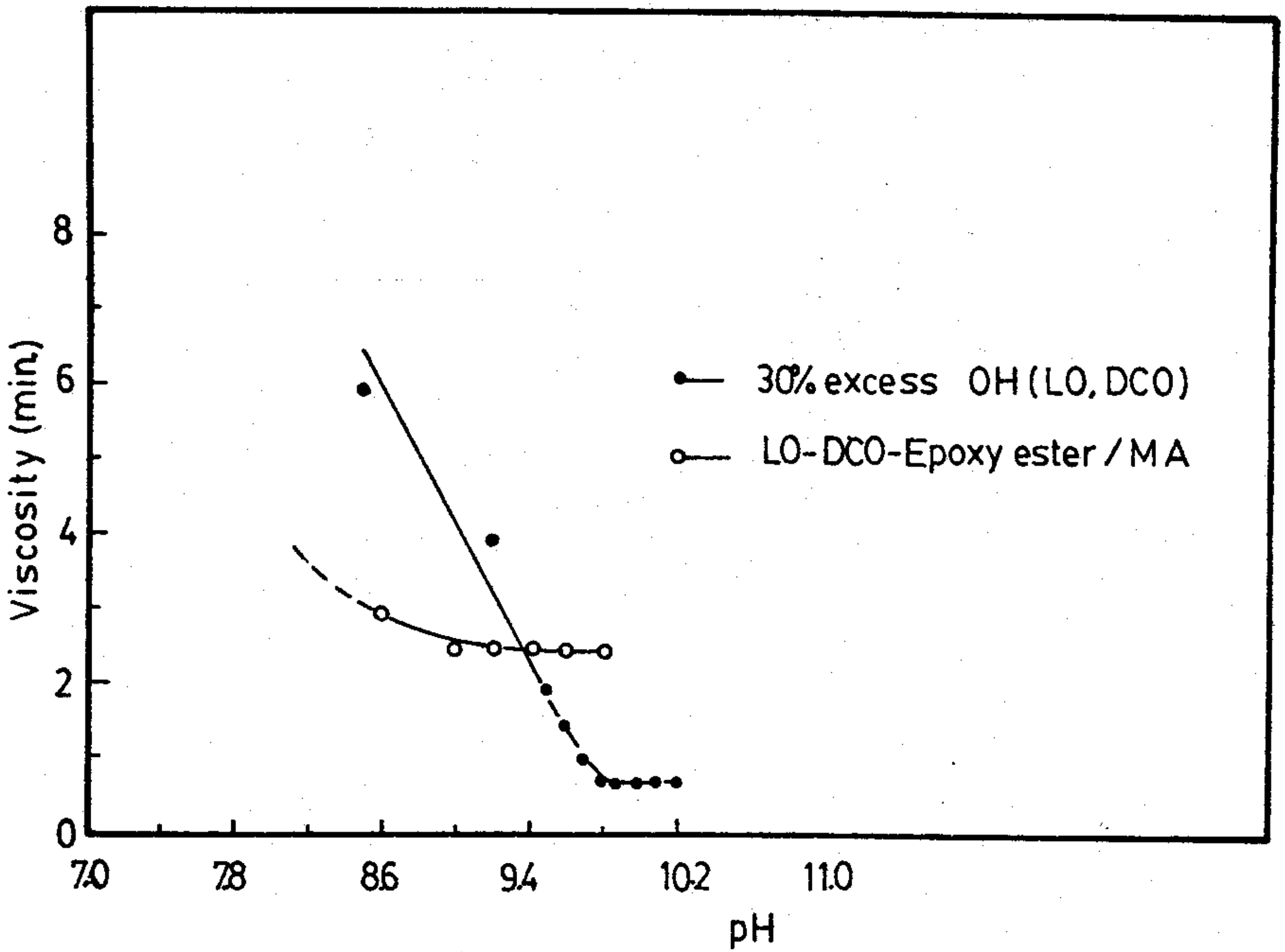


Fig.(6): Effect of pH on Varnish's Viscosity.

Table 26: Drying Characteristics Without Driers.

| Resins No. | Touch Dry (hrs.) | Hard Dry (hrs.) |
|---|---|---|
| I | 24 | > 24 |
| II | 24 | > 24 |
| III | 24 | > 24 |
| IV | 24 | > 24 |
| V | 24 | > 24 |
| VI | 48 | > 48 |
| VII | 48 | > 48 |
| IIX | 48 | > 48 |
| IX | 48 | > 48 |
| X | 72 | > 72 |
| XI | 72 | > 72 |

It can be clearly shown from the data given in table 26 that the drying times of the epoxy modified alkyds are more than 24 hours, which is not practical. For this reason, it was felt desirable to extend the work to include the effect of the presence of certain water-soluble salts. The salts selected as driers are manganese, cobalt and lead acetates. For preleminary trials, they are used in amounts of 0.01% based on metal resin.

Table 27: Drying Characteristics Including Driers.

| Resin No. | Touch Dry (hrs.) | Hard Dry (hrs.) |
|---|---|---|
| I | 18 | 24 |
| II | 18 | 24 |
| III | 18 | 24 |
| IV | 18 | 24 |
| V | 12 | 24 |
| VI | 12 | 24 |
| VII | 12 | 24 |
| IIX | 12 | 24 |
| IX | 12 | 24 |
| X | 12 | 24 |
| XI | 18 | 24<br>(with slight tackness) |

The most important finding drawn from the data given in table 27 is that the presence of driers is important in improving the drying of the films.

D- <u>Driers Effect</u>:

After the successful estimation of the role of catalyst on the drying of the water-soluble vehicles, attention was directed towards the determination of the most suitable catalysts concentrations. For this reason, a uniform film thickness coat was applied over (10 x 15 cm$^2$) glass panels using the spinner coater type. The resin selected for this study was resin (X) based on epoxy modified alkyds of L.O./D.C.O. (1:1 by weight). The film thickness of the coats was 20 ($\mu$). (After the film had been stoved for 2 hours in a well-ventillated drying oven at 150°C), the hardness was measured using the Rocker Hardness Pendulum (Persoz type). The results obtained are shown in Table 28. It should be noted that each reading represents the mean value of three readings.

Table 28: Effect of Drier Concentration upon Film Hardness.

| Catalyst concentration Percent metal/resin | Hardness in Seconds | | |
|---|---|---|---|
| | Mn acetate | Cobalt acetate | Lead acetate |
| 0.01 | 165 | 140 | 120 |
| 0.02 | 180 | 165 | 140 |
| 0.03 | 195 | 180 | 165 |
| 0.04 | pptn. | pptn. | pptn. |

It can be clearly seen from the data given in table 28 that the manganese drier is the most effective catalyst. On the other hand, lead acetate driers is the least effective one. Also hardness of the dried films increased by increasing the drier concentrations. Higher catalyst concentration , higher than 0.03% metal/resin,causes resin percipitation.

After determining the most effective catalyst concentration (0.03% metal/resin), the work was extended to include catalysts combination. Films of uniform thickness 20 (μ) were prepared using the same apparatus. In this case, more than drier are present. The hardness values of the dried films were taken as an indication of the function of the catalyst. The results obtained are given in Table 29.

Table 29: The Effect of Catalyst Combination on Hardness of Dried Films.

| Catalyst combination | Concentration ratio % metal/resin | Hardness seconds |
|---|---|---|
| Mn : Co | 1:1 | 160 |
| Mn : Pb | 1:1 | 160 |
| Mn : Co : Pb | 1:1:1 | 195 |
| Mn : Co | 2:1 | 180 |
| Mn : Pb | 2:1 | 175 |

The most important conclusion drawn from the above study is that the manganese acetate drier as effective catalyst as any other catalyst combination. For this reason, manganese acetate was used as the driers employed in further film evaluation. 0.03% concentration (metal/resin) was the optimum concentration used.

E- Hardness & Gloss Measurements:

Films of uniform thickness (20 μ) were applied over (10 x 15 $cm^2$) glass panels and allowed to dry at 150°C for two hours before measurements conducted. The results obtained are given in Table 30, and represented in figure 7.

Table 30: Gloss and Hardness Measurements

| Resin No. | Gloss % | Hardness (seconds) |
|---|---|---|
| I | 100 | 80 |
| II | 100 | 50 |
| III | 100 | 95 |
| IV | 100 | 60 |
| V | 100 | 230 |
| VI | 95 | 230 |
| VII | 95 | 230 |
| IIX | 95 | 230 |
| IX | 100 | 210 |
| X | 100 | 195 |
| XI | 100 | 130 |

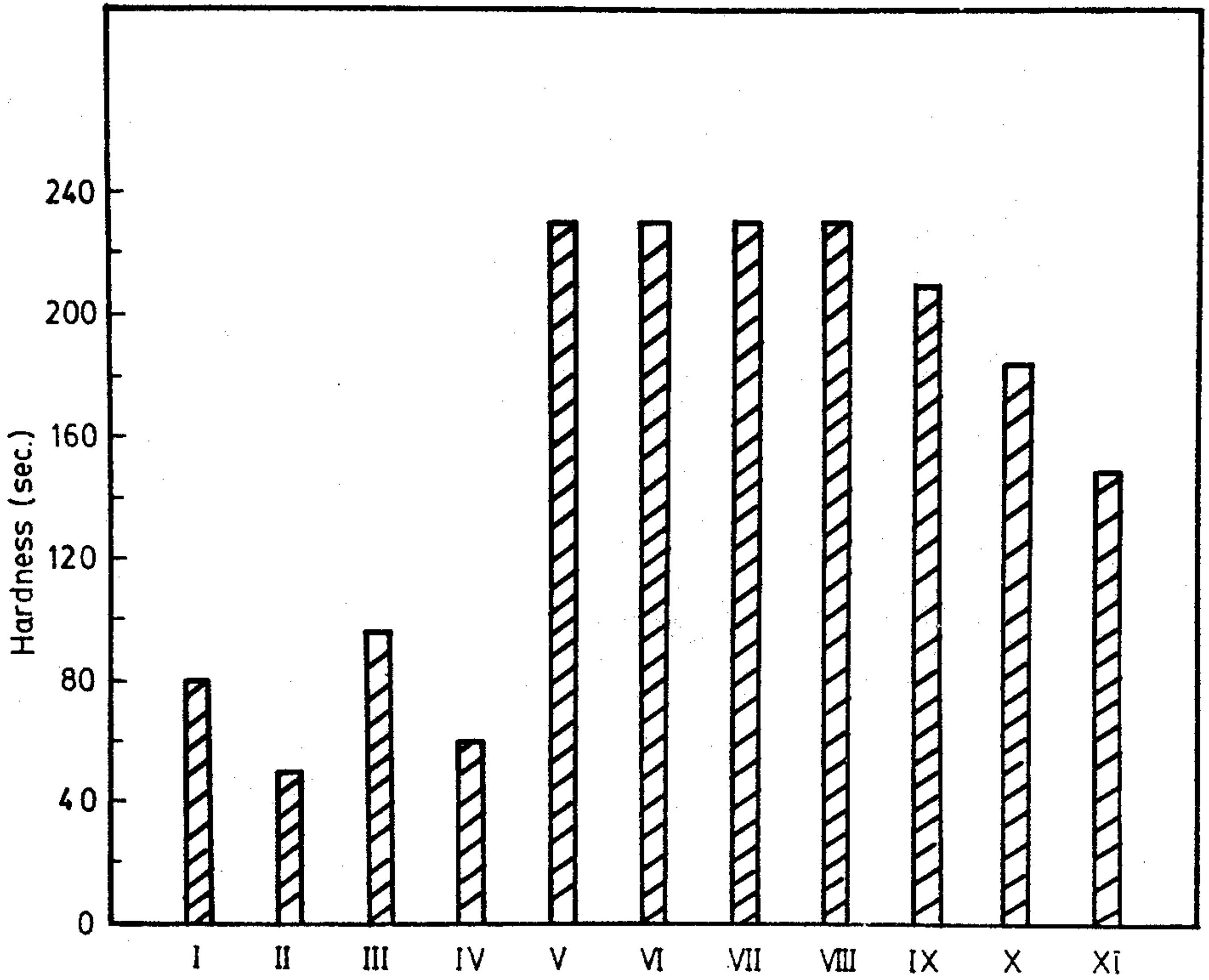


Fig. (7): Graphic Represintation of the Hardness of the Dry Films ($20\mu$) Versus Type of Resins

The conclusions drawn from the data of table 30 indicate that all films posses high gloss. Also the presence of the epoxy ester in the resin formulation improves the hardness of the dried films. The presence of dehydrated castor oil fatty chain reduces the hardness considerably due to their tackness properties.

The dependance of film hardness on the curing of the resin can be illustrated by allowing the films to be baked for two hours but at various time intervals. The results obtained are given in Table 31 and represented in fiure 8.

Table 31: Effect of Temperature on Film Hardness Baked for 2 hours.

| Temperature $^{0}C$ | Hardness (Seconds) |
|---|---|
| 100 | 30 |
| 125 | 105 |
| 150 | 195 |
| 175 | 235 |
| 200 | 300 |

It is notoworthy to mention that the resin empolyed was resin X and the film thickness was 20 $\mu$.

It can be concluded from the data of table 31 that the hardness of the films increased by increasing the

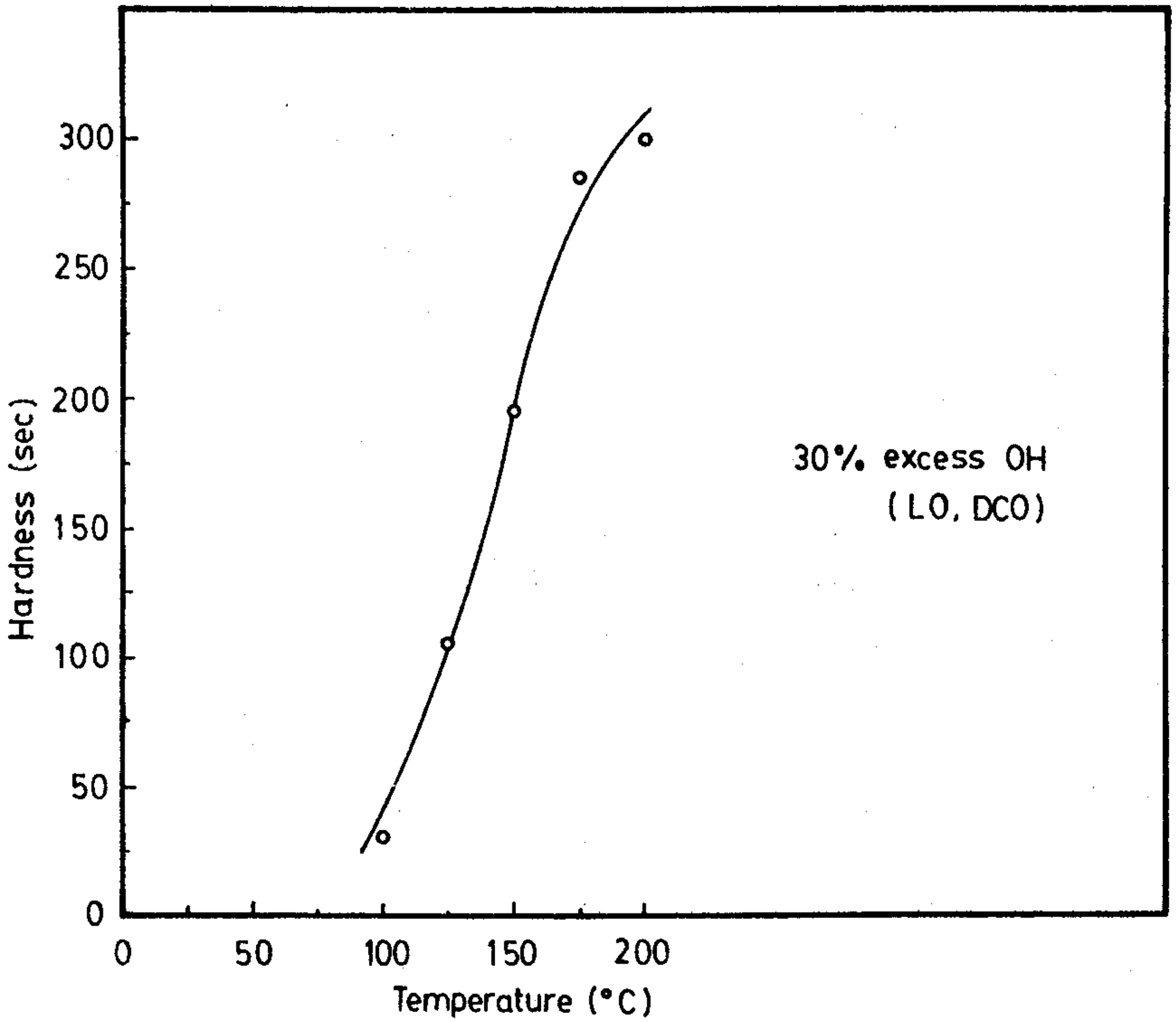


Fig.(8): Effect of Temperature upon the Film Hardness at Constant Thickness (20 µ) the baking temperature. It should also noticed that this possibility of the yellowing tendency is increased by increasing the stoving temperature.

From figure 7, the following generalizations were noticed.

1- Formulations based on epoxy modified alkyds prepared by fatty acid method show better film hardness than these made by glycerolysis method.

2- Formulations containing triglycerides show slightly lower film hardness than these containing no glycerides molecules.

3- The addition of epoxy esters to the oil systems greatly improves the hardness of the dried films.

4- Formulations containing dehydrated castor fatty chain show lower hardness values than others.

F- Water, Alkali and Acid Resistances

Films of the various resin formulations were applied over (5 x 15 $cm^2$) glass panels. The films were allowed to dry at air for 7 days or at $150^o$ for two hours. The edges of both set of panels were sealed by dipping in hot molten paraffin wax. The dried panels were then immersed in the test solution for the specified period of time. The results obtained are given in table 32.

Table 32: Water, Alkali and Acid Resistance Measurements.

| Resin No. | Water Resistance |  | Alkali Resistance |  | Acid Resistance |  |
|---|---|---|---|---|---|---|
|  | Air dry | Stoved | Air dry | Stoved | Air dry | Stoved |
| I | P | $E_x$ | P | $E_x$ | F | $E_x$ |
| II | P | $E_x$ | P | $E_x$ | F | $E_x$ |
| III | P | $E_x$ | P | $E_x$ | $E_x$ | $E_x$ |
| IV | P | $E_x$ | P | $E_x$ | $E_x$ | $E_x$ |
| VI | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |
| VII | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |
| IIX | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |
| IX | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |
| X | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |
| XI | F | $E_x$ | F | $E_x$ | $E_x$ | $E_x$ |

Rating of the above data was conducted according to the following:

| | | |
|---|---|---|
| $E_x$ | ; excellent | ; almost no change |
| G | ; good | ; no significant change |
| F | ; fair | ; slightly affected, and |
| P | ; poor | ; almost complete failure. |

In order to examine the extent after which the film break down; to show how far the film with-stand various chemical and physical effects, baked and air dried films were subjected to water, alkali and acid resistance tests. This method provide a quantitative mean for estimating the degree of effectivness towards the attacking reagent. The results obtained are given in Table 33.

Table 33: Degree of Effectivness towards Water, Alkali and Acids Solutions.

| Resin No. | Water Resistance |  | Alksli Resistance |  | Acid Resistance |  |
|---|---|---|---|---|---|---|
|  | Air dry | Stoved | Air dry | Stoved | Air dry | Stoved |
| I | < 2 hrs | 10 days | < 2 hrs | 1 day | <10 hrs | 25 days |
| II | < 2 hrs | 12 days | < 2 hrs | 1 day | <10 hrs | 25 days |
| III | < 2 hrs | 14 days | < 2 hrs | 2 days | 8 day | 25 days |
| IV | < 2 hrs | 35 days | < 2 hrs | 5 days | 28 day | 43 days |
| V | < 10 hrs | >60 days | < 3 hrs | 13 days | >60 days | >60 days |
| VI | <10 hrs | >60 days | < 3 hrs | 13 days | >60 days | >60 days |
| VII | < 10 hrs | >60 days | < 2 hrs | 10 days | 15 days | >60 days |
| IIX | < 10 hrs | >60 days | < 2 hrs | 10 days | 15 days | >60 days |
| IX | < 10 hrs | >60 days | < 3 hrs | 13 days | > 60 days | >60 days |
| X | < 10 hrs | >60 days | < 3 hrs | 13 days | >60 days | >60 days |
| XI | < 10 hrs | >60 days | < 3 hrs | 13 days | > 60 days | >60 days |

The conclusions drawn from the data given in Table 33 are:

1- The presence of epoxy ester improves considerably the water, alkali and acid resistances.

2- Maleinized epoxy esters system lies between the maleinized oils and epoxy-modified alkyds with respect to their water, alkali and acid resistances.

G- Flexibility and Adhesion Measurements:

Films were applied over (5 x 15 $cm^2$) tin plates by brushing. Two sets of panels were prepared; the first dried upon air exposure for 7 days; the second were stoved for 2 hours at 150°C. The test panels were subject to the flexibility and adhesion bending a apparatus over 3 mm rod diameter.

All films examined pass successfuly the test.