

Epoxidation of linseed oil-Alkyd resins

By

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Abstract:

Three types of different linseed oil-alkyd resin (Alk (I), Alk (II), and Alk (III)) were prepared with the calculated amounts of monoglyceride and adipic acid (1:1, 1:2, and 2:1 Eq.Wt) respectively via monoglyceride method. The obtained alkyd resins were epoxidized via reaction with the calculated quantities of peracetic acid, which was prepared by the reaction of acetic anhydride with H₂O₂. Epoxidation occurred with the ratio (1:1, 1:3, and 1:6 Eq.Wt) of alkyd to peracetic acid. The effect of reaction time on the epoxy group content was measured during the epoxidation process. The prepared alkyd resins were analyzed by IR and H¹NMR. The metal coated film properties of epoxidized alkyd resins were compared with those of unmodified alkyd resins. It was observed that the coating films of epoxidized alkyd resins have better in drying properties, hardness, adhesion, impact and flexibility than those of unepoxidized alkyd resins. The flammability properties of the paper coated films for the prepared brominated epoxidized alkyd resins were found to be fire retardant.

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Key words:

Epoxidation of linseed oil, Alkyd resins, epoxidized alkyd resins, brominated epoxidized alkyd resins, metal coatings, paper coatings, coated film properties, flammability.

Introduction:

Alkyd resins have been used widely in the coating industry since they were invented in 1927. The alkyd resin was one of the first applications of synthetic polymer in surface coating technology. It was successful in chemically combining oil or oil derived fatty acids into a polyesters polymer structure, thus enhancing the mechanical properties, dry speed ⁽¹⁾, and durability ⁽²⁾. Which over and above those of the oils themselves and the oleoresinous vehicles than available.

Alkyd resins still represent the single largest quantity of solvent-soluble ⁽³⁾ resin produced for use in the surface coatings industry. This is due to a number of reasons such as:

- 1- They are a single-pack system that is stable for along period.
- 2- They are inexpensive on a cost/performance basis.
- 3- They can be modified to give properties ranging from fast, hard drying, low flexibility products to slow drying, soft, flexibility films.

Alkyds are prepared from polyols, dibasic acids and fatty acids. As such, they are polyesters, but in the coating field the term polyester is reserved for the “oil-free polyesters”. The term alkyd is derived from their preparation from alcohols and acids. Chronologically alkyds preceded polyesters by over 20 years⁽⁴⁾. As alkyd resins are polyesters, they are subject to normal ester hydrolysis; that is sensitivity to water, acid and alkali; particularly when they are dried by oxidation. On the other hand, the ester structure confers good ultra-violet and heat resistances. Adipic acid is one of the most frequently used linear

diacids since it gives an excellent compromise in terms of technical performance and price ⁽⁵⁾. The presence of the oil confers good pigment wetting and, when unsaturated, allows coherent films to be formed during drying. The polyester chain imparts hardness and durability and improves the drying rate. As the functionality of the polyol used is increased, the drying speeds increase.

The unsaturation gives reactive sites responsible for polymerization properties either thermal or oxidative ⁽⁶⁾. The position of the double bond can also have considerable effect on the properties of the fatty acid. Conjugated double bonds are more reactive than non-conjugated ⁽⁷⁾. Reactivity is also affected by the presence of functional groups such as hydroxyl groups. Alkyds with oil length greater than 60% are called long oil alkyds. Those with oil lengths from 40% to 60% are called medium oil alkyds and those with less than 40% are called short oil alkyds.

Paints based on epoxy modified alkyds show a strong tendency towards chalking and a resulting loss of gloss. Epoxy modified ⁽⁸⁾ alkyd resins are less expensive than epoxy resins and are used in low cost anticorrosion primers ⁽⁹⁾. The carbon-carbon unsaturation can be readily converted to oxiran (epoxy) groups by reaction with peracid or hydrogen peroxide ⁽¹⁰⁾. Because of economic and availability, the major epoxidized oils in common usage are based upon soybean and linseed oils, as well as the brominated compounds act as flame retardant coatings ^(11, 12). The aim of this work is to study the effect of the time on the epoxidation reaction of alkyd resins by measuring epoxy group content of the samples. The flammability properties of the prepared brominated epoxidized alkyd resins were studied. Epoxidized alkyd resins were compared with those of unepoxidized alkyd resins. It was observed that the epoxidized alkyd resins have better in drying properties, hardness, adhesion, impact and flexibility than the films of unepoxidized alkyd resins.

Experimental:

Chemicals Used and Their Characteristics:

1. **Linseed oil**, Tanta oil industry, M 876, Iodine value 178 mg I₂/ gm oil, Hydroxyl value 0 mg KOH/ gm oil, d 0.9271 g.cm⁻³,
- 2- **Glycerol**, El-Nasr Pharmaceutical Co. of Chemicals, C₃H₈O₃ content 98%, M 91.2, d 1.261 g.cm⁻³, bp 182⁰C, mp 20⁰C.
- 3- **Calcium Oxide**, FOB Sigma Co, CaO content 99.9 %, d 3.300 g.cm⁻³.
- 4- **Adipic Acid**, Fluka chemical. Co, HOOC (CH₂)₄COOH content 99%, M 146.14, mp 151-154 °C.
- 5- **Glacial Acetic Acid**, El-Nasr Pharmaceutical Co. of Chemicals, CH₃CO₂H content 96%, M 60.05, d 1.049 g.cm⁻³, bp 117-118 °C.
- 6- **Acetic Anhydride**, El-Nasr Pharmaceutical Co. of Chemicals, (CH₃CO₂)₂O content 99+%, M 102.09, mp -73 °C, bp 138-140 °C, n_D²⁰ 1.3900, d 1.082 g.cm⁻³.
- 7- **Hydrogen Peroxide**, El-Nasr Pharmaceutical Co. of Chemicals, 22.5% solution in water, H₂O₂ , M 34.02, mp -40 °C, bp 126 °C, d 1.100 g.cm⁻³.

1) Preparation of 100% solid Alkyd Resin via Monoglyceride process ^(13,14):

a) Monoglyceride formation:

The calculated amounts (2:1 molar ratio) of glycerol and linseed oil were introduced in three necked flask fitted with condenser, mechanical stirrer and nitrogen gas inlet tube. The mixture was heated to 200 °C and CaO (0.05% w/w based on oil) as catalyst was added. The temperature was then raised to 240 °C and maintained until satisfy the solubility in methanol. Characteristics of the prepared monoglyceride are as follows: total iodine value: 40 mg I₂/ mg oil, hydroxyl group value: 117 mgKOH/mg oil, acidvalue:6 mgKOH/mg oil.

b) Formation of Alkyd Resin:

The calculated amounts of the prepared monoglyceride and adipic acid were introduced in three necked flask fitted with condenser, mechanical stirrer and nitrogen gas inlet tube at 250 °C (1:1, 1:2, and 2:1 eq.wt.) to produce Alk (I), Alk (II), and Alk (III) respectively. The temperature was maintained till desired acid value.

2) Preparation of Peracetic Acid ⁽¹⁵⁾:

Glacial acetic acid 1.6 mol (96 g), hydrogen peroxide solution (22.5%) 4 mol (136 g) and sulfuric acid (2-3%) solution were introduced in three necked flask 500 ml fitted with condenser and mechanical stirrer, with continuous stirring at room temperature over a period 12-16 h. Such solutions contain some unconverted hydrogen peroxide and water, which was eliminated by the addition of small quantities (5-7 ml) of acetic anhydride, also shifts the equilibrium toward the formation of additional peracetic acid.

3) Preparation of Epoxidized Alkyd resin ^(16, 17):

The calculated amount of alkyd was introduced into three necked flask 500 ml fitted with reflux condenser, dropping funnel, thermometer and mechanical stirrer, followed by addition of 1, 3 or 6 equivalent of peracetic acid solution (concentration 21.5 %), with continuous stirring the peracetic acid solution was added drop-wise at 6 °C for one hour. Before further reaction with selected reagents was attempted, the remaining acid present in the reaction mixture was removed. To achieve this, the reaction mixture was dissolved in dichloromethane and the solution was washed with a dilute alkaline solution.

4) Preparation of Brominated Epoxidized Alkyd resin ⁽¹⁸⁾:

A solution of epoxy resins (10gm in 2 ml of toluene) was introduced into three necked round bottom flask fitted with a dropping funnel, thermometer and mechanical stirrer, the calculated amount of bromine 4 ml into the dropping funnel. Cool the flask in a mixture of ice and salt and, Set the stirrer in motion and when the temperature has fallen to -5°C , drop the bromine slowly in period 90 min at such a rate that the temperature does not rise above 0°C .

5) Methods of testing and evaluation:

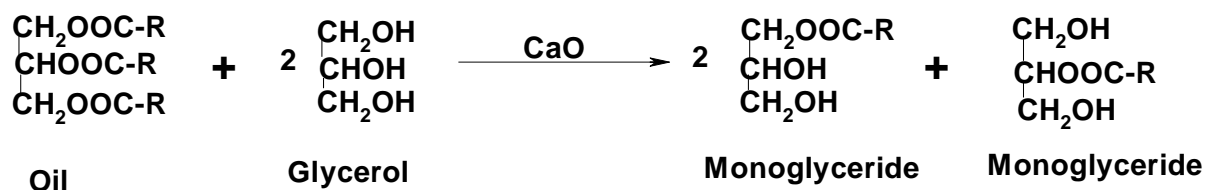
- IR ⁽¹⁹⁾ and H¹NMR ⁽²⁰⁾ Spectra.
- Determination of Film Thickness According to ASTM D4138-94.
- Determination of Drying Properties (Touch Dry) According to ASTM D1647-59.
- Adhesion by Tape Test According to ASTM D3359-95
- Scratch Hardness by Pencil Test According to ASTM D3363-92a
- Impact Test According to ASTM D2794-93.
- Mandrel Bend Test (Flexibility) According to ASTM D522-93a.
- Flammability Test According to ASTM D1433-66.

Results and Discussion:

Monoglyceride Formation:

By heating linseed oil and the requisite amount of glycerol together at 250-280⁰C in the presence of catalyst as CaO and under an inert atmosphere as N₂ to minimize discoloration and dimerization of oils. The reaction can be followed by a simple solubility test; glycerol is soluble in methanol but linseed oil is not. A dispersion of the reaction mixture in methanol during the initial heating period is therefore cloudy and separates into two phases. But as the reaction proceeds

better solubility is achieved and finally the product is quite easily soluble in methanol and gives a clear solution. With the following properties of the prepared monoglyceride such as: total iodine value:40 mgI₂/mg oil, hydroxyl group value: 117 mgKOH/mg oil and acid value:6 mgKOH/mg oil. This alcoholysis takes place quite rapidly and the new monoglyceride is formed according to the following equation:



(Where R: Fatty acid moiety)

The total iodine value of the prepared monoglyceride is (40 mgI₂/mg oil) lower than of linseed oil (178 mgI₂/mg oil), which indicated that the esters of oil are partial replaced with hydroxyl groups of glycerol. Also the hydroxyl value of the prepared monoglyceride is (117 mgKOH/mg oil) higher than of linseed oil (0 mgKOH/mg oil) due to achieve the total desired glycerol content.

IR spectra of the prepared monoglyceride was given in Fig(1).

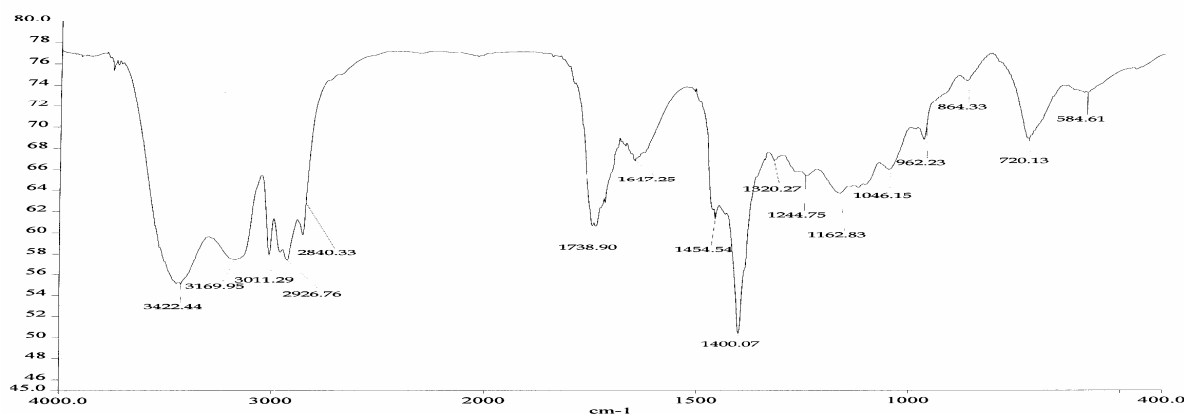


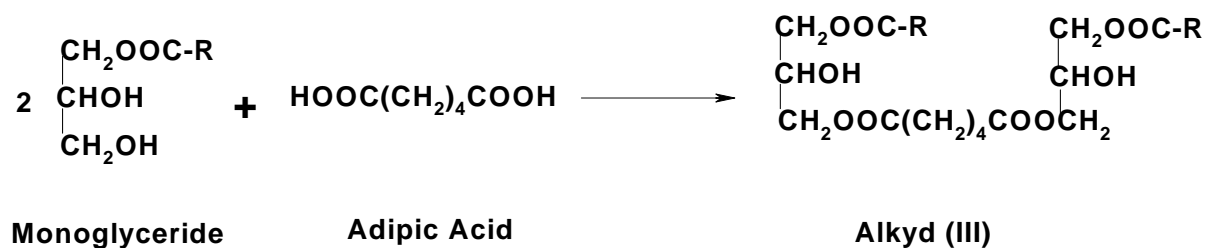
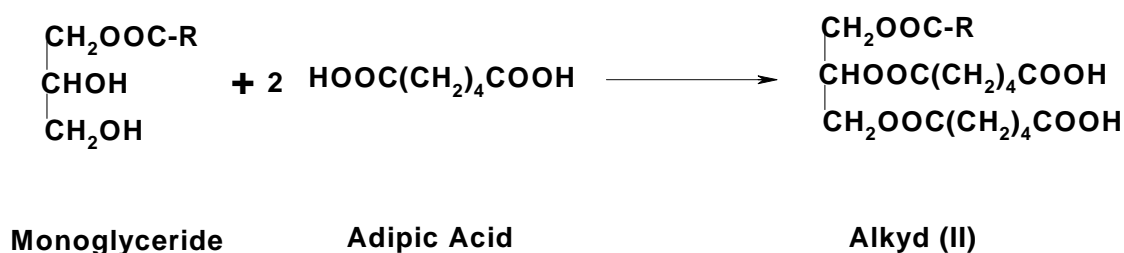
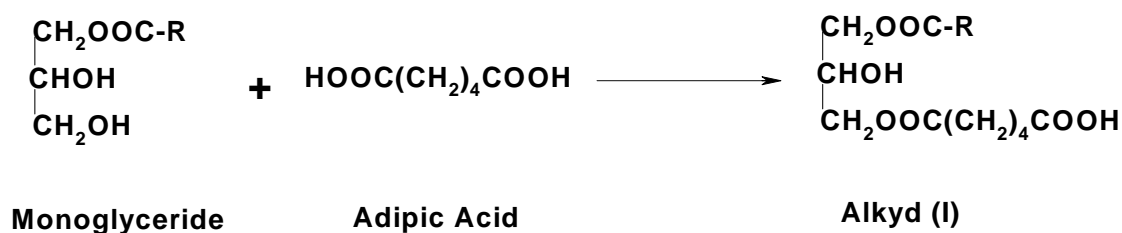
Fig. (1): IR Spectrum of Monoglyceride

From Fig(1) IR spectra of the prepared monoglyceride indicated that, absorption band of C=O appears at 1740 cm^{-1} , C-O at 1200 cm^{-1} , OH at 3400 cm^{-1} and C=C at 1640 cm^{-1} (19).

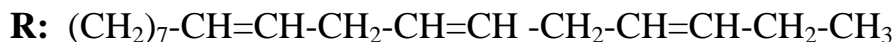
Alkyd Formation:

The monoglyceride product contains two free hydroxyl groups and can be regarded as a derivative of glycerol. As such it reacts quite easily with adipic acid in different equivalent ratio at the usual esterifying temperatures of $180\text{-}250\text{ }^{\circ}\text{C}$ to give alkyd resins.

The following equation represents the preparation of alkyd (I), alkyd (II), and alkyd (III):



Where:-



The characterization of the prepared alkyd resins given in Table (2).

Table (2): Characterization of prepared alkyd resins.

| Alkyd Type | Hydroxyl value mgKOH/ g oil | Acid value mgKOH/ g oil | Iodine value mgI₂/ g oil |
|-------------------|--|--|--|
| Alkyd (I) | 37.4 | 7 | 38 |
| Alkyd (II) | 14 | 10 | 38 |
| Alkyd (III) | 56.1 | 8 | 44.4 |

Data given in table (2) indicated that the unsaturation (Iodine value) of Alkyd (III) is the highest than for both Alkyd (I) and Alkyd (II) due to the incorporation in the reaction of Alkyd (III) by two moles of glycerides where Alkyd (I) and Alkyd (II) are have the same iodine value, due to incorporation by only one mole of glyceride. It was observed from the data that the hydroxyl value of Alkyd (III) is the highest than for both Alkyd (I) and Alkyd (II) , where Alkyd (III) have two hydroxyl groups ,Alkyd (I) have one hydroxyl group, and Alkyd (II) haven't hydroxyl group but due to the presence OH group in carboxylic acid. IR and NMR analysis of the prepared alkyd resin types as Alkyd (I, II and III) were given in Figs (2-8) respectively.

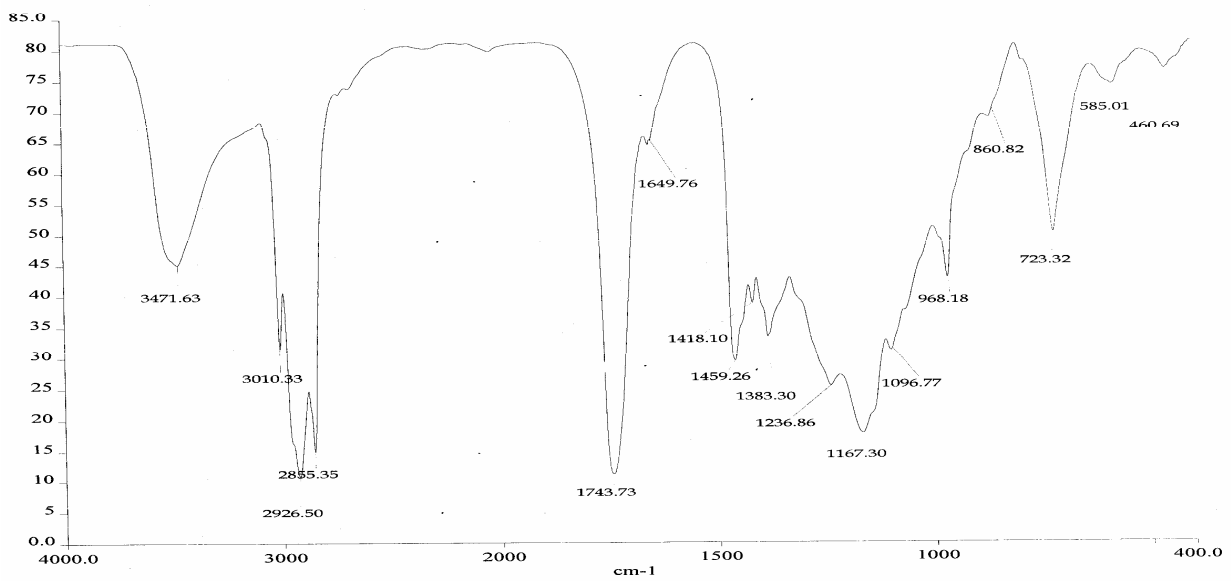


Fig. (2): IR Spectrum of Alkyd (I).

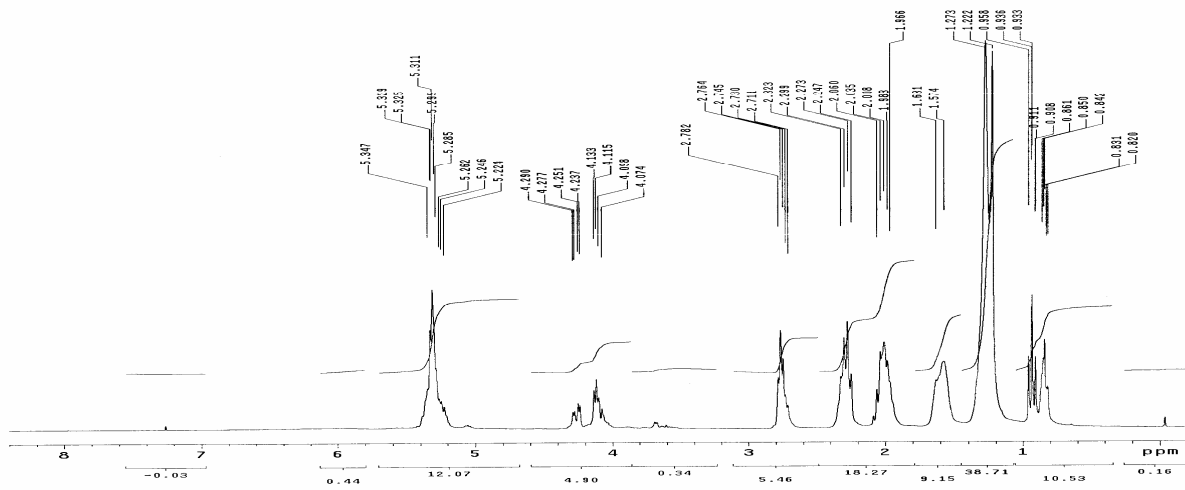


Fig. (3): ¹H NMR Spectrum of Alkyd (I).

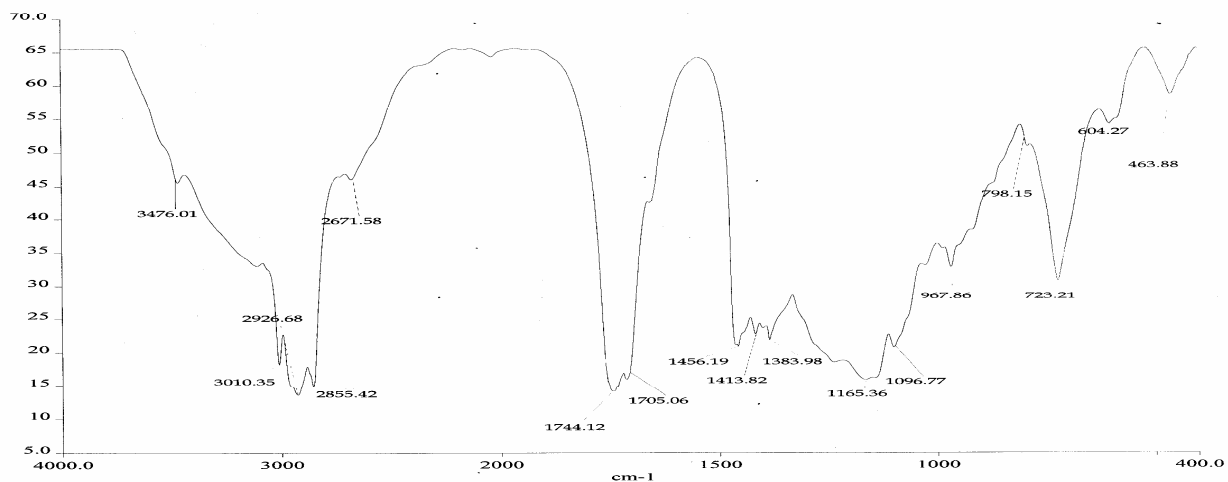


Fig. (4): IR Spectrum of Alkyd (II).

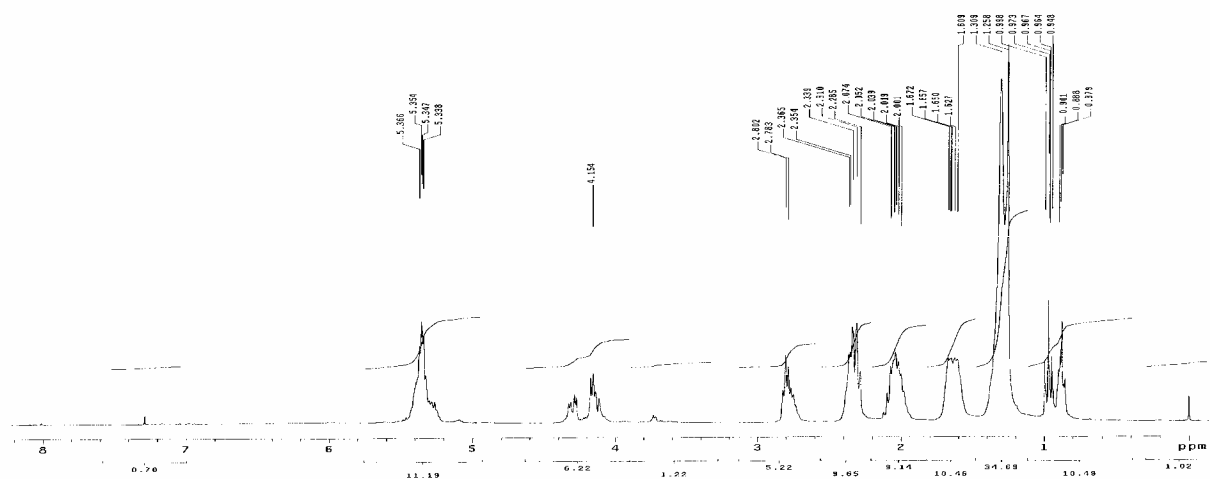


Fig. (5): HNMR Spectrum of Alkyd (II).

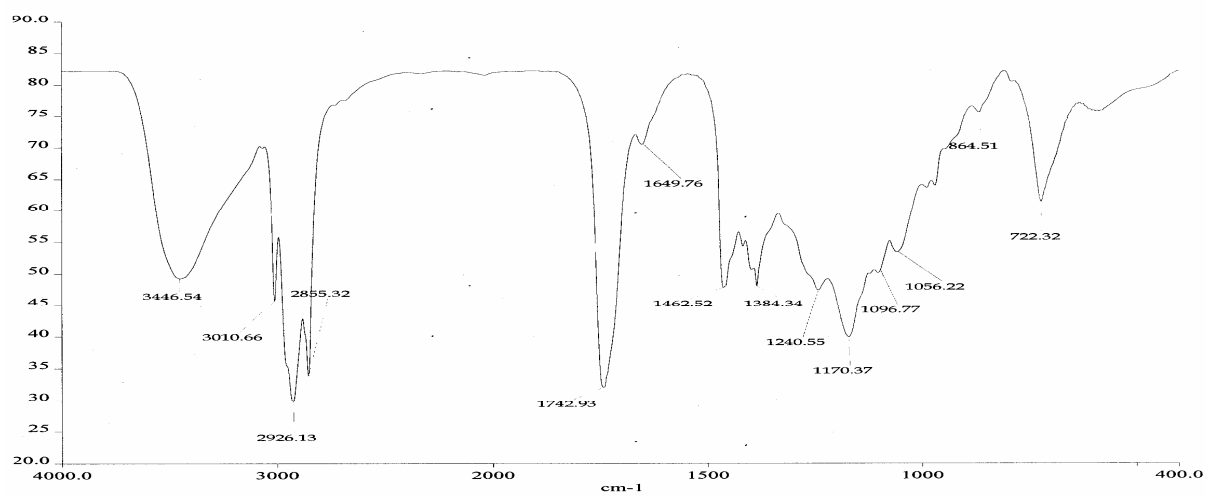


Fig. (6): IR Spectrum of Alkyd (III).

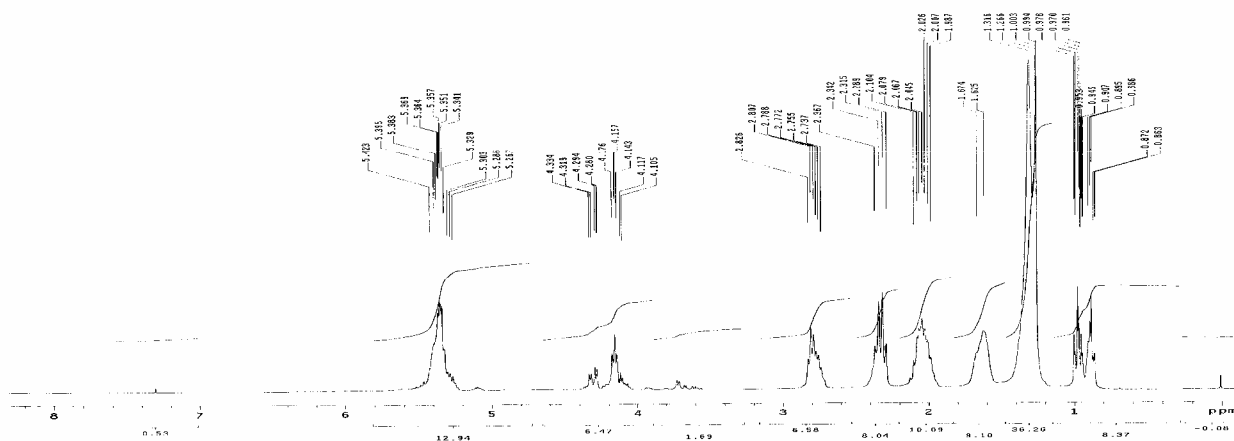


Fig. (7): ¹H NMR Spectrum of Alkyd (III).

It was observed from Figs (2, 4, 6) that in IR spectra⁽¹⁹⁾ group C=O appears near 1740 cm^{-1} , C-O near 1200 cm^{-1} , OH near 3400 cm^{-1} , and C=C near 1640 cm^{-1}

While from Figs (3, 5, 7) in ¹H NMR⁽²⁰⁾ spectra observed that OH group near 1.5 ppm, =CH near 5.4 ppm, CH₃ near 1.2 ppm, CH₂ near .8 ppm.

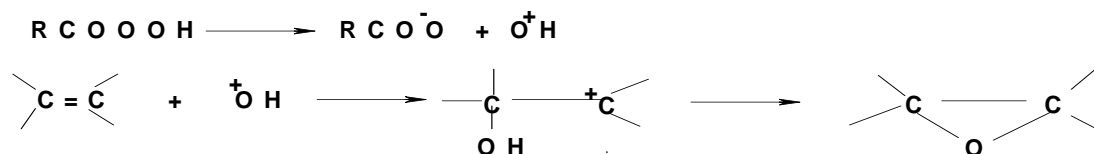
Data which given from IR and ¹H NMR spectra confirmed the structure of the prepared alkyd resins.

The prepared alkyds resins have many advantages due to the presence of functional groups. Those alkyd resins can modify to achieve their chemical and physical properties such as Double bonds, which can react with peracetic acid to give epoxidized alkyd resins.

Epoxidation of Alkyd Resins:

Peracid oxidation of olefins in non-polar solvents gives excellent yields of the corresponding epoxides⁽²¹⁾. Swern⁽²²⁾ indicated that the peracids are electrophilic reagents, it had been suggested that the peracid act by the provision of free hydroxyl cations⁽²³⁾, where the double bond between the two

carbon atoms consists of a strong sigma bond and a weak pi-bond, which is broken:



The carbon-carbon double bond acts as a source of electrons (nucleophilic agent) and it acts as a base. The compound with which it reacts are those that are deficient in electron called electrophilic reagents. However, Epoxidation always results in cis addition, thus precluding formation of a free carbonium ion ⁽²⁴⁾. Swern et al ⁽²⁵⁾ proposed a modified mechanism which is analogous to that of addition of halogen to olefins; and suggested a mechanism involving acid catalysis giving a transition state.

Representative structures of epoxidized alkyd resins which are prepared from alkyd (I), alkyd (II), and alkyd (III) in the presence of peracetic acid given in Fig (8).

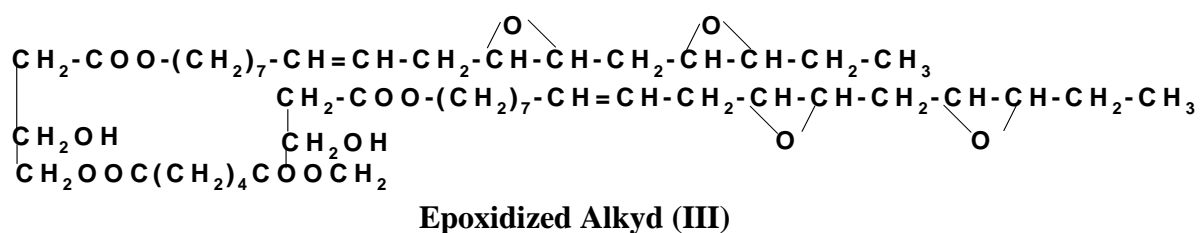
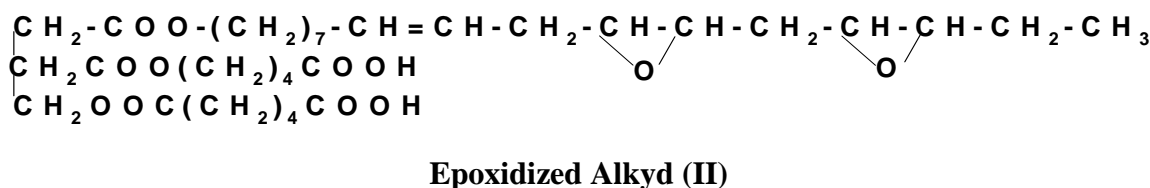
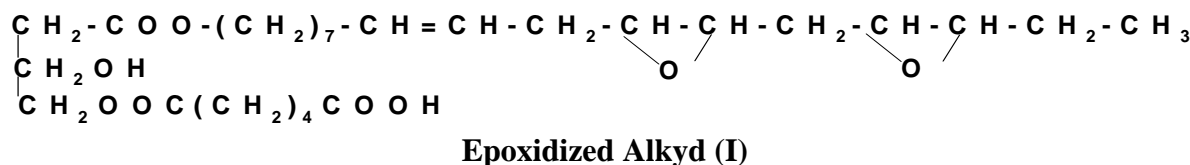


Fig (8)

IR analysis of the prepared epoxidized alkyd resins (I, II and III) with different equivalent ratios (1:1, 1:3 and 1:6) for each type were given in Figs (9-17) respectively.

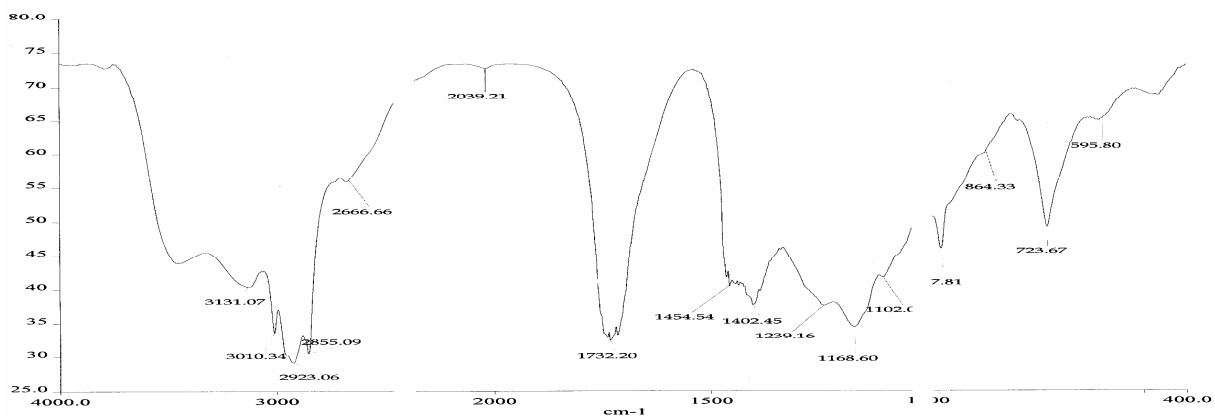


Fig. (9): IR Spectrum of Epoxidized Alkyd (I) 1:1

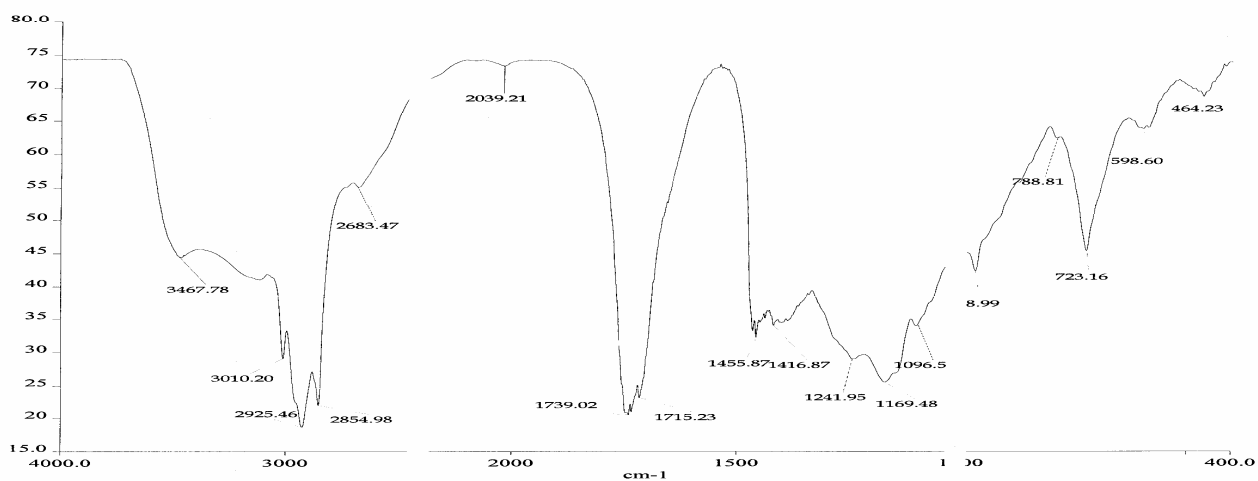


Fig. (10): IR Spectrum of Epoxidized Alkyd (II) 1:1

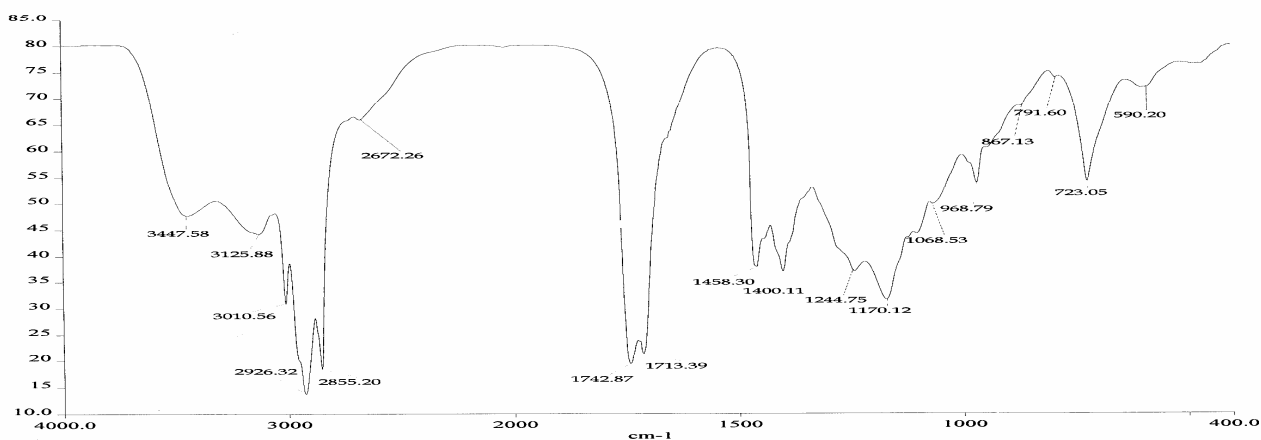


Fig. (11): IR Spectrum of Epoxidized Alkyd (III) 1:1

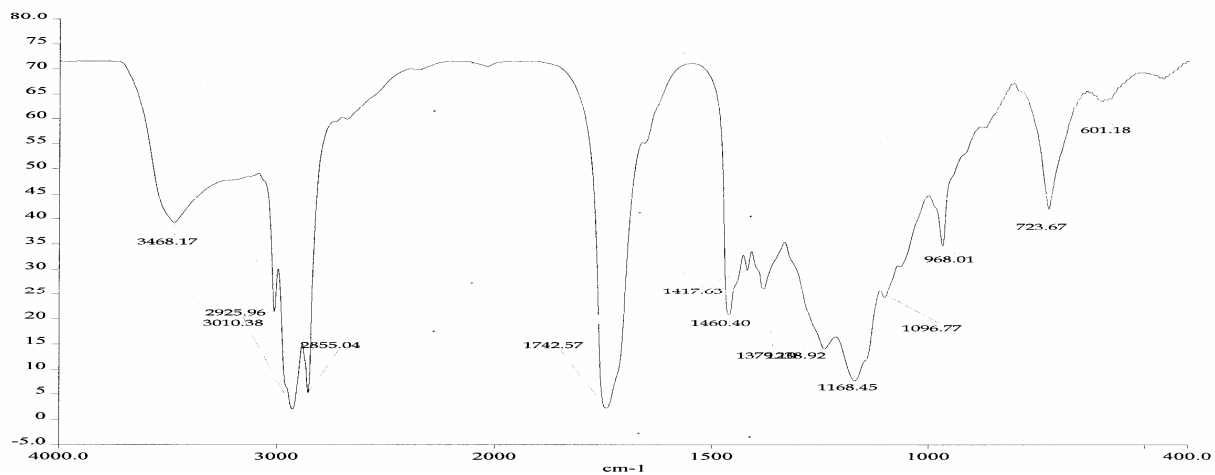


Fig. (12): IR Spectrum of Epoxidized Alkyd (I) 1:3

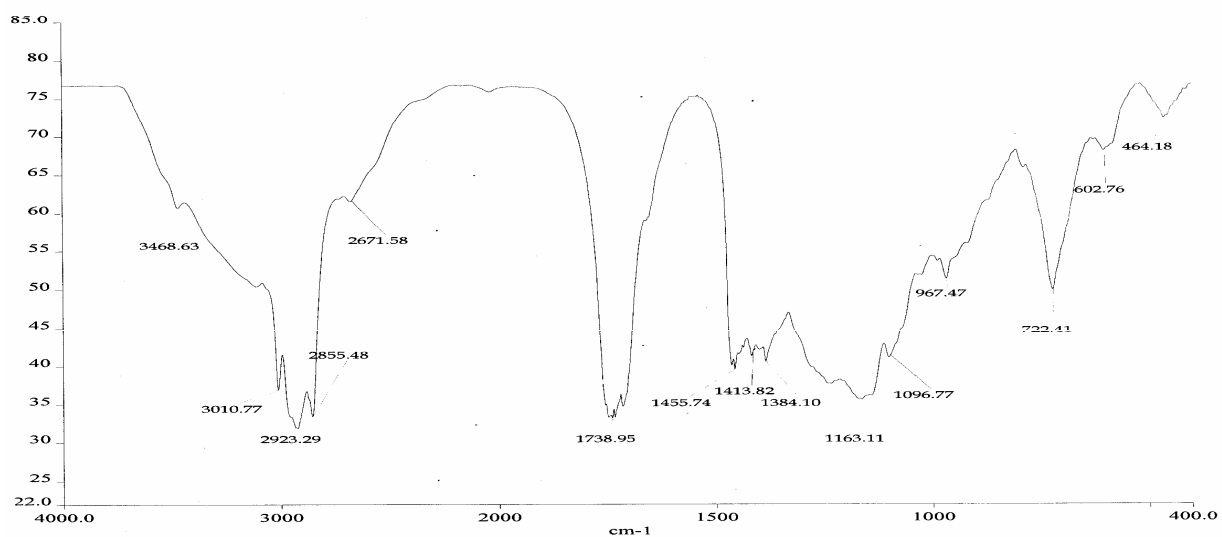


Fig. (13): IR Spectrum of Epoxidized Alkyd (II) 1:3

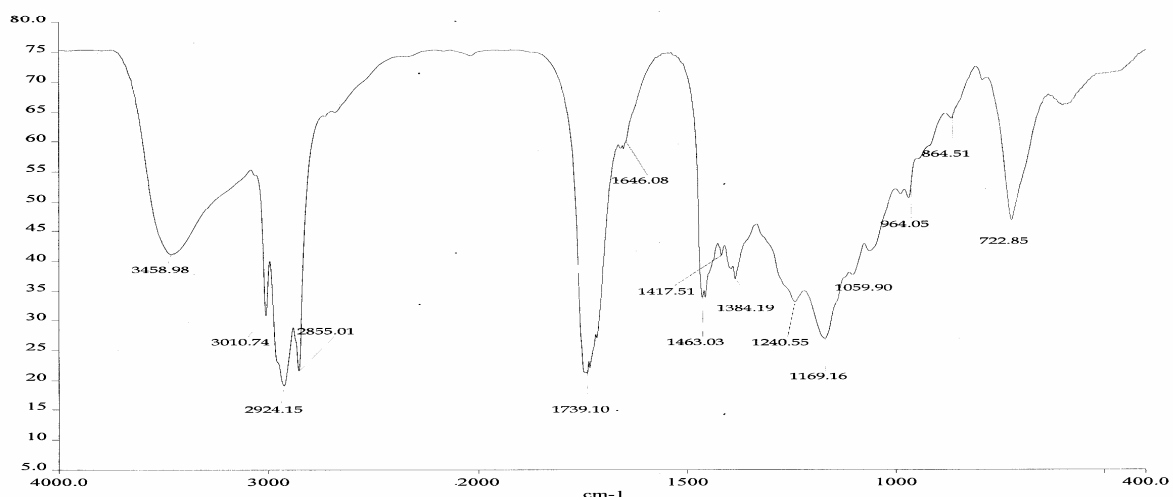


Fig. (14): IR Spectrum of Epoxidized Alkyd (III) 1:3

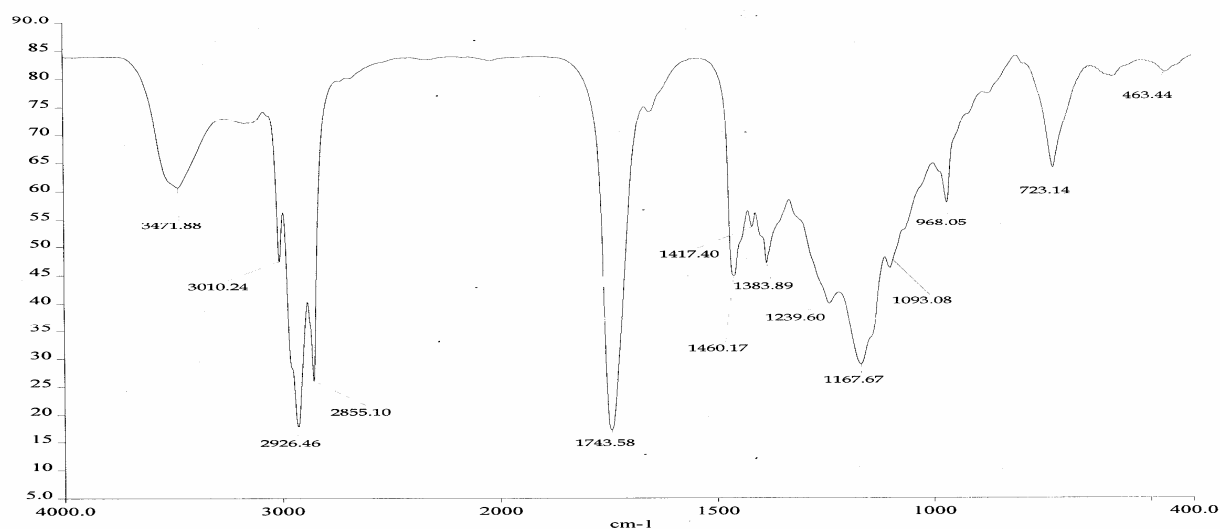


Fig. (15): IR Spectrum of Epoxidized Alkyd (I) 1:6

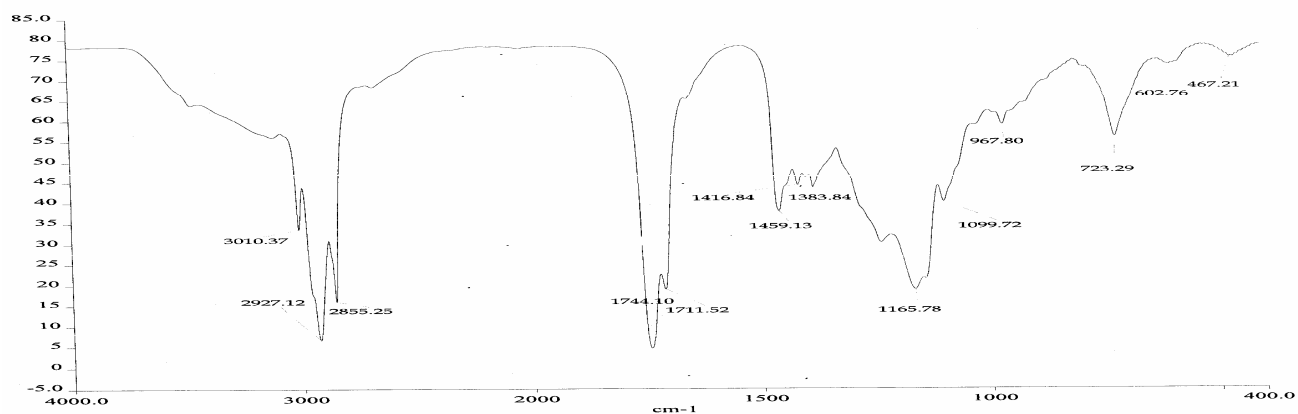


Fig. (16): IR Spectrum of Epoxidized Alkyd (II) 1:6

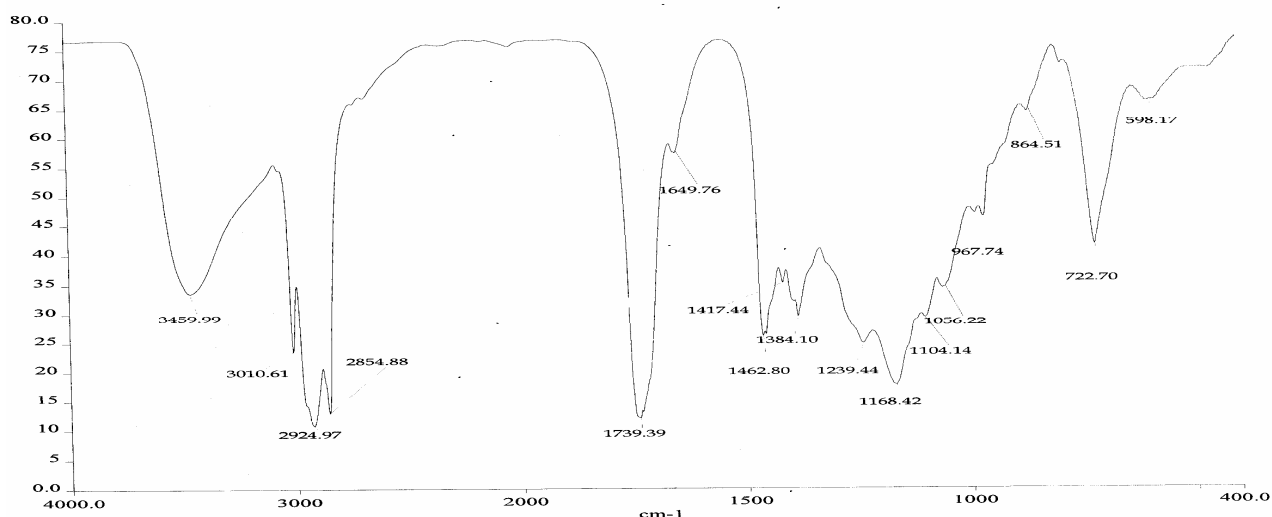


Fig. (17): IR Spectrum of Epoxidized Alkyd (III) 1:6

It was observed from Figs (9-17) that in IR spectrums absorption band group of C=O appears at 1740 cm^{-1} , C-O at 1200 cm^{-1} , OH at 3400 cm^{-1} and epoxy group at $950\text{ cm}^{-1(19)}$.

The Effect of Reaction Time:

The effect of reaction time of the epoxidation process on the three types of alkyds (Alk I, Alk II, Alk III) was studied over range till 5 hr. on addition of

three different molar ratio of alkyd to peracetic acid (1:1, 1:3, 1:6) at temperature 6⁰C and tabulated in table (3)

Table (3): Effect of reaction time on the epoxy group content

| Equivalent Ratio of Alkyd:Peracetic acid | Time (hr) | Epoxy group content | | |
|---|--------------|---------------------|---------------|----------------|
| | | Alkyd (I) | Alkyd (II) | Alkyd (III) |
| 1:1 | 1 | 0.75 | 0.9 | 1.2 |
| | 2 | 0.92 | 1.5 | 1.8 |
| | 3 | 1.1 | 1.3 | 2.1 |
| | 4 | 0.90 | 1.2 | 1.9 |
| | 5 | 0.85 | 0.95 | 1.5 |
| 1:3 | 1 | 0.89 | 1.5 | 1.5 |
| | 2 | 1.4 | 1.9 | 2.8 |
| | 3 | 1.1 | 2.2 | 2.5 |
| | 4 | 0.95 | 2.6 | 2.3 |
| | 5 | 0.89 | 2.3 | 1.8 |
| 1:6 | 1 | 1.5 | 1.2 | 1.4 |
| | 2 | 2.4 | 2.5 | 2.1 |
| | 3 | 2.8 | 3.4 | 2.5 |
| | 4 | 2.6 | 2.9 | 3.6 |
| | 5 | 2.1 | 2.2 | 3.4 |

The obtained results given in Table (3) show that with increasing the reaction time the epoxy group content increased at first until certain time, where the epoxidized alkyd have maximum epoxy group content, and after that time the epoxy group content decreased slowly. This can be attributed to the

Table (4): The times related to maximum values of epoxy group content

| Epoxy group content | Time (hr) | Equivalent Ratio of | Alkyd Sample |
|----------------------------|------------------|----------------------------|---------------------|
| 1.1 | 3 | (1:1) | Alkyd (I) |
| 1.4 | 2 | (1:3) | |
| 2.8 | 3 | (1:6) | |
| 1.3 | 3 | (1:1) | Alkyd (II) |
| 2.6 | 4 | (1:3) | |
| 3.4 | 3 | (1:6) | |
| 2.1 | 3 | (1:1) | Alkyd (III) |
| 2.8 | 2 | (1:3) | |
| 3.6 | 4 | (1:6) | |

The resins which have maximum epoxy group content are taken and measure their properties and compared to the unepoxidized alkyd resins. The drying time of the coated films applied on iron steel panale of epoxidized alkyd resins and unepoxidized alkyd resins were measuring by touch dry method given in Table (5).

Table (5): Drying time of coated films

| Hard (Day) | Slightly Tacky (Day) | Tacky (Day) | Sample |
|-----------------------|-------------------------------------|-------------------------|-----------------------|
| 19 | 14 | 6 | Alkyd (I) |
| 16 | 10 | 4 | Alkyd (II) |
| 23 | 17 | 10 | Alkyd (III) |
| 6 | 3 | 1 | Epox.Alk (I)(1:1) |
| 5 | 2.5 | 2 | Epox.Alk (I)(1:3) |
| 3 | 2 | 1 | Epox.Alk (I)(1:6) |
| 6 | 4 | 2 | Epox.Alk (II)(1:1) |
| 8 | 5 | 2 | Epox.Alk (II)(1:3) |
| 4 | 2 | 1 | Epox.Alk (II)(1:6) |
| 8 | 4 | 2 | Epox.Alk (III)(1:1) |
| 6.5 | 3 | 2 | Epox.Alk (III) (1:3) |
| 6 | 3 | 1 | Epox.Alk (III)(1:6) |

From the data shown in the table (5) obvious that the drying time for curing the epoxidized alkyd resins are less than the drying time for curing unepoxidized alkyd resins, due to the presence of epoxy rings in the epoxidized alkyd resins which decrease the drying time than the presence of double bonds in the unepoxidized alkyd resins.

The properties of coating films of the epoxidized alkyd resins and unmodified alkyd resins were measuring (with thickness approximately 20-30 μm) and applied on iron steel panale and tabulated in Table (6)

Table (6): Properties of coated films.

| Flexibility | Impact | Hardness | Adhesion | Sample |
|--------------------|---------------|-----------------|-----------------|-------------------------------|
| P | P | 1N | 1B | Alkyd (I) |
| P | P | 2N | 3B | Alkyd (II) |
| P | P | 2N | 4B | Alkyd (III) |
| P | P | 1N | 4B | Epoxidized Alk (I) (1:1) |
| P | P | 1N | 5B | Epoxidized Alk (I) (1:3) |
| P | P | 1.5N | 5B | Epoxidized Alk (I) (1:6) |
| P | P | 1N | 4B | Epoxidized Alk (II) (1:1) |
| P | P | 2N | 5B | Epoxidized Alk (II) (1:3) |
| P | P | 2.5N | 5B | Epoxidized Alk (II) (1:6) |
| P | P | 2N | 4B | Epoxidized Alk (III) (1:1) |
| P | P | 3N | 5B | Epoxidized Alk (III) (1:3) |
| P | P | 3N | 5B | Epoxidized Alk (III) (1:6) |

Where:-

5B: No peeling or removal,

4B: Trace peeling or removal along incisions or at their intersection,

3B: Jagger removal along incisions upto 1/16 in. (1.6mm) on either side,

2B: Jagger removal along most incisions upto 1/8in. (3.2mm) on either side,

1B: Removal from most of the area under the tape, and

0B: Removal beyond the area.

N: Newton force

P: Pass

From the data shown in the table (6) it is obvious that the properties of the coating films for the epoxidized alkyd resins are better than unmodified alkyd resins, due to the presence of epoxy rings in the epoxidized alkyd resins than the presence of double bonds in the unmodified alkyd resins.

The flammability properties of coating films of the brominated epoxidized alkyd resins and epoxidized alkyd resins were measuring and applied on paper samples 10 x 2.5 cm with thickness 1mm and tabulated in Table (7).

Table (7): Flammability of coating films applied on paper surface.

| Rating | Burned length (cm) | Burning time (sec) | Sample |
|---------------|-------------------------------|-------------------------------|-------------------------------|
| B | 8 | 7 | Epoxidized Alk (I) (1:6) |
| SE | 4.5 | 5 | Br-Epoxidized Alk (I) (1:6) |
| B | 7.5 | 6 | Epoxidized Alk (II) (1:6) |
| SE | 4 | 4 | Br-Epoxidized Alk (II) (1:6) |
| B | 7 | 5 | Epoxidized Alk (III) (1:6) |
| SE | 4 | 3 | Br-Epoxidized Alk (III) (1:6) |

Where:-

B: burning

SE: self exting.

From the data shown in the table (7) it is obvious that the flammability properties of the coating films for the brominated epoxidized alkyd resins are better than unmodified epoxidized alkyd resins, due to the presence of bromine which act as flame retarder in the epoxidized alkyd resins.

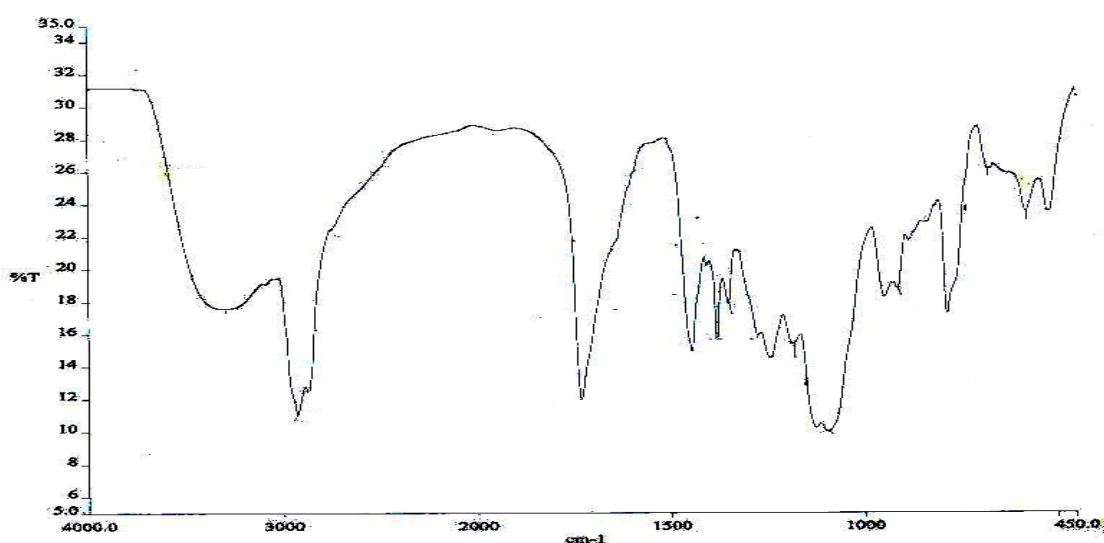


Fig. (18): IR spectrum of Br-Epoxidized Alkyd (III) (1:6)

It was observed from IR-spectrum⁽¹⁸⁾ Fig (18) that absorption band of C-Br group appear at 650^{-1}cm .

Conclusion:

- The preparation 100%high solids alkyd paints is the most useful method for decreasing of organic solvent contents (VOC). The simplest way of synthesizing high solids alkyd resins is decreasing of their molecular weight by increasing of fatty acids contents or increasing the ratio of OH/COOH groups. But, alkyd resins obtained in this way have insufficient properties; its drying times are very slowly and give coatings of weak performance.

-An epoxidized alkyd resin can be prepared from the reaction with peracetic acid and the time of reaction play an important role in determine the epoxy group content of the epoxidized samples, with increasing the reaction time the epoxy group content increased at first until certain time where the epoxidized alkyd have maximum epoxy group content and after that time the epoxy group content decreased slowly, at constant of concentration of peracetic acid and temperature of the reaction.

-The epoxidized alkyd resins with higher ratio of alkyd: peracetic (1:6), which have higher in epoxy group content, gives better properties in drying time and surface coating films than the epoxidized alkyd resins with lower ratio of alkyd: peracetic (1:1)

-The epoxidized alkyd resins have better in drying properties, hardness, adhesion, impact and flexibility than the unepoxidized alkyd resins.

- The flammability properties of the paper coated films for the prepared brominated epoxidized alkyd resins were found to be fire retardant.

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