



Preparation of Alkyd Resins by using some Diacids with Dodecylbenzene and Study their Properties

Asaad F. Khattab, Yonis A. Ismail Alkikani

Mosul univ. / collage of science – chem. Dept., Iraq

Abstract Soya bean oil was used to prepare four type of alkyd resins. Phthalic anhydride, maleic anhydride, isophthalic acid, maleimide and phthalimide of dodecyl benzene have been used in preparing the alkyd resins. Acid value, Solid content, Viscosity and Gardner color are physical properties have been measured for the prepared alkyd resins. The results indicate that the physical properties of the prepared alkyd resin were depended on the type of the used diacid.

Keywords dodecyl benzene, alkyd resins, poly basic acid

Introduction

Alkyd resins are the most known raw materials used as a binder in coatings and paints industries [1]. The term alkyd is derived from two parts, (alk) derived from alcohol and (yd) which is referred to abbreviation of acid [2].

Many different attempts are used to define alkyd resins. One of such definitions is the reaction product of polyhydric alcohol and poly-functional acids modified by fatty acid or their triglyceride [3]. Igwe and Ogbobe [4] describe it as polyesters modified with unsaturated fatty acids. Aigbodin and Pillai [5] define it as a products of condensation between polyol, usually having greater than 3 functional groups, and poly basic acid, usually dibasic or its anhydride modified monofunctional acids. The definition given by [6] is a products of poly condensation reaction between poly basic acids and poly hydric alcohol modified with fatty acid or drying oil . Different vegetable oils are used for alkyd preparation including tall oil, soya oil and many others ; the useful properties of these oils are their high degree of unsaturation . The used poly hydric alcohol are glycerol , ethylene glycol and pentaerythritol [7]. The commonly used acids/anhydride are phthalic anhydride(PA), isophthalic,maleic anhydride [8], glutaric anhydride and succinic anhydride [9]. PA is the most prefer poly basic acid manufacturing because of its low melting point (131 °C) which falls below the reaction temperature(230-250 °C)for alkyd resin production . It also increase hardness and resistance to water [10]. In using isophthalic acid, the ester of isophthalic acid is more resistance to hydrolysis than that of PA in pH range 4-8. The uses of maleic anhydride as a partial replacement of phthalic anhydride improve the characteristic of the film of the paint, such as hardness and resistance against atmospheric and corrosion agent, and also decrease the condensation time of alkyd resin preparation [11]. In this paper four types of alkyd resins are prepared from soya bean oil modified with different poly basic acids like maleic anhydride, phthalic anhydride, isophthalic acid and mixture of maleimide and phthalimide that has been prepared from local dodecyl benzene.

Experimental

All chemicals used in the preparation of alkyd are purchased from different international companies and used without purification, Linear dodecyl benzene (LAB) was purchased from Arabian company for chemical detergent.



Preparation of dodecyl aniline

The pure LAB was nitrated by using nitration reaction with a mixture of nitric acid and sulfuric acid at 55°C [12]. The resulted nitro compound was reduced by hydrochloric acid and tin metal as catalyst.

Preparation of dodecyl maleimide and dodecyl phthalimide

Equivalent amounts of maleic anhydride or phthalic anhydride and dodecyl aniline have been mixed and warmed until the solid content are dissolved. After five minutes of heating the fused mixture a past material was directly formed.

Preparation of alkyd resins

Four types of alkyd resins have been prepared within the frame of this work. The amount of the used materials are elucidated in table (1).

The following procedure was used in preparing the alkyds types:

Soya bean oil, poly basic acid, pentaerythritol, glycerol and benzoic acid were mixed in three round bottom flask. Nitrogen gas tube was inlet through the mixture in order to expulsion the oxygen from the medium. The temperature of the mixture was raised to 200°C. Xylene was added to extract any water formed through the reaction period. The reaction was followed by measuring the acid number of the reaction mixture. When the acid number reach 10, xylene was distilled off, then the mixture was diluted with light naphtha.

Characterization**Acid value**

The acid value of the prepared alkyd resins was estimated by titration with solution of (0.1M) KOH as follows: (1-2) gm of the sample was dissolved in toluene/methanol mixed solvent (2/1) at 300°C. The mixture was titrated against alcoholic solution of (0.1M) KOH after cooling to room temperature. The acid value was calculated according to the following equation :

$$\text{Acid value} = \frac{V_{eq} * F_{KOH}}{W_t * SC\%}$$

V_{eq} = equivalent volume of KOH

F_{KOH} = coefficient factor of KOH = 5.3

W_t = mass of the sample

SC% = percent solid content which can be calculated by weighing out accuracy 1.5gm of the resin in small aluminum container, cover the sample with toluene and heat in oven at 150°C for 35min. The sample was weighted again. The solid content can be calculated from the equation :

$$SC\% = \frac{W_2 - W_0}{W_1 - W_0} * 100$$

W_1, W_2 is the weight of the container with the sample before and after heating

W_0 = weight of the empty container

Viscosity

The viscosity of alkyd resins samples were estimated by using Brookfield (VIII Black one) at 25°C in centy poise meter

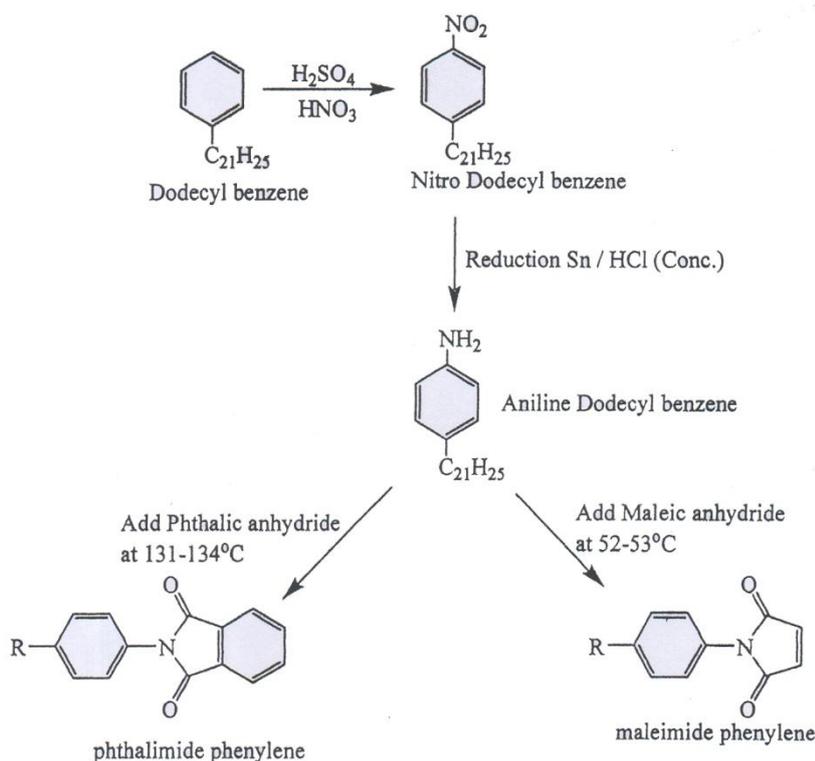
Gardner color

The Gardner color was measured by using Gardner color meter model DR /LANCE Company / Germany

Result and Discussion**Dodecyl maleimide and Dodecyl phthalimide**

Schame (1) outline the reaction route for preparation of dodecyl maleimide and dodecyl phthalimide compounds. The method includes the direct reaction of anhydride with amino dodecyl benzene without using any solvent. The resulted compounds have a putty phase. They have been characterized by IR spectroscopy. Figures 1 and 2 showed the FTIR spectra of these compounds. Table (2) indicates the absorption bands of the characteristic functional groups in these compounds.





Scheme 1: The reaction route for preparation of dodecyl maleimide and dodecyl phthalimide compounds

Alkyd resins

In order to improve the oil to be suitable in alkyd and paint industries, it was modified with some diacid derivative, like maleic, phthalic and isophthalic. The advantage of these added materials is to increase the double bond amount within the oil chain and also can be react with glyceride moieties of the oil by transesterification reaction [13].

Extenders are materials used in paint industry in order to aid the pigments to spread over a large area of substrate. To collect the advantageous of diacids and extender within one molecule we suggest to use the maleimides and phthalimides of dodecyl benzene as a diacids and extenders source. The long carbon chain moiety (C_{12}) within the dodecyl molecules have can be estimated as extender.

The method used for alkyd resins preparation is according to alcoholysis method combined with isotropic esterification with refluxing xylene which carries away the formed water [14].

The applied recipes are presented at table (1). The formula of the produced alkyd resins are accomplished according to MPCPROKIM company for paint industry method [15].

The characterized functional groups of alkyd resin (IV) are shown in figure (3). The spectrum revealed the presence of many functions of the recipes.

Straight chain alkane ($-CH$) was detected at 1376 cm^{-1} , 2853 cm^{-1} , 2922 cm^{-1} and 2954 cm^{-1} carbonyl group of benzoic acid was detected at 1718 cm^{-1} , while the absorptions at $(1718-1739)\text{ cm}^{-1}$ is belong to carbonyl groups of maleimides. The aliphatic ($-C=C-$) groups was detected at 1513 cm^{-1} and 1464 cm^{-1} .

The physical properties of the alkyd resins have been examined by the general methods. The viscosity was determined in a centy poise scale by a rotational viscometer. The result in table (3) and figure (4) show that the values have the order :

$$IV > III > II > I$$



The differences in viscosity number can be attributed to the variation in the composition of alkyd samples, since they were prepared from different poly basic acids, which also influenced the polymer back bone formed through synthesizing the alkyd resins. In all samples the values are within the acceptable limits.

The measured acid values are indicated in figure (5). The results show that the acid value increased from sample I to IV to III to II. Samples I, III and IV, which are produced mainly by phthalic anhydride, isophthalic acid and maleimide respectively, have lower acid value that of sample II which are prepared mainly from maleic anhydride. This variation in values can be attributed to variation in the acid values of the diacids type used in alkyd production.

Where the acid value of maleic anhydride is 1144.2 mg KOH/g, phthalic anhydride is 757.5mg KOH/g [16].

The solid content percent of the alkyd resins were shown in figure (6). The results indicate that sample IV had a higher value than that of the other samples. This implies that the dodecyl alkyd sample will be the more suitable in manufacturing paint with high solid contents in the other hand, phthalic anhydride, maleic anhydride and isophthalic alkyd samples will also produced paint with high solid content.

Gardner color is a measure of the transparency whiteness of the liquid. It can be account as a measure for the ability of the liquid to disperse the pigment through it. The rang of this type of scale is (1-18). The rang from (1-8) is belong to the color of potassium chloro palatinate, where the color is between yellow to red. The rang between (9-18) is compared to ferric chloride solution.

Figure (7) shows the results of gardner color measurements of the alkyd resins. The differences can be ultimate to the type of the diacids used which effect the viscosity and the solid content in comparison.

From the above results we can conclude that alkyd resin IV, which was prepared by using local dodecyl benzene is the more suitable material to use in paint manufacturing.

Table 1: Constituents of alkyd resins according to (MPCPROKIM) formula

(gm)	Raw material	I	II	III	III
	<i>Soya bean oil</i>	250	250	250	250
	<i>Pentarytritol</i>	120	120	120	120
	<i>Phthalic anhydride</i>	120	118	-	-
	<i>Maleic anhydride</i>	-	2	2	-
	<i>Isophthalic</i>	-	-	118	-
	<i>Glycerol</i>	30	30	30	30
	<i>Benzoic acid</i>	100	100	100	100
	<i>Light naphtha</i>	520	520	520	520
	<i>Phthalimide</i>	-	-	-	118
	<i>Maleimide</i>	-	-	-	2

Table 2: IR absorption bands of derivatives dodecyl benzene

Compound	C=C	=C-H	C=O	-CH γ	-CH
	Aromatic	aromatic		aliphatic	Aliphatic
<i>Phthalimide</i>	1599-1466	3060	1785-1706	2954-2921-2852	1465-1377
<i>Maleimide</i>	1631	3029	1780-1702-1628	2955-2923-2853	1465-1407

Table 3: Physico-Chemical properties of alkyd resins

Property	Unit	I	II	III	IV
<i>Solid content</i>	%	51.27	52.7	51.7	54.4
<i>Viscosity</i>	CP	925	1400	2830	2912
<i>Acid value</i>	mg KOH/g	2.06	4.4	2.76	2.64
<i>Gardner color</i>	-	7.2	8.1	7.5	8.7



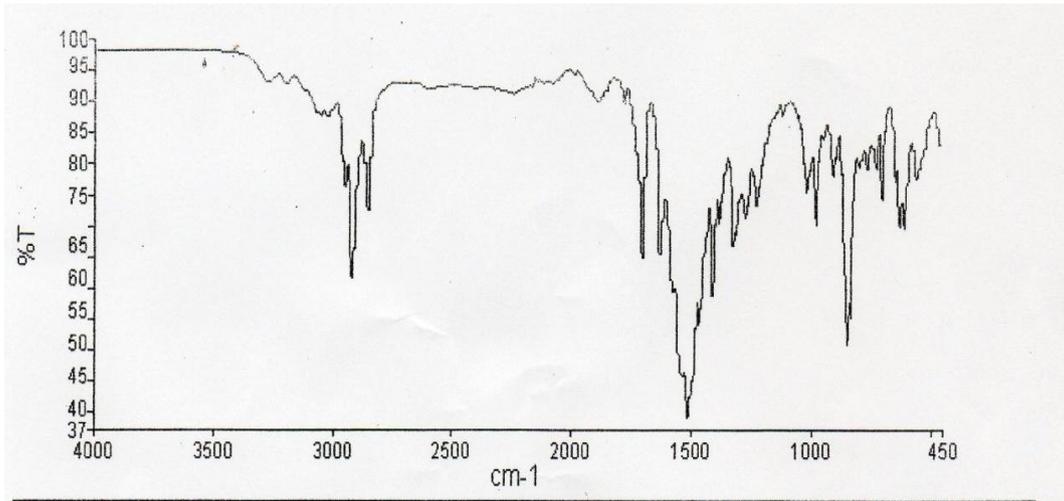


Figure 1: IR spectrum of dodecyl phenylenemaleimide

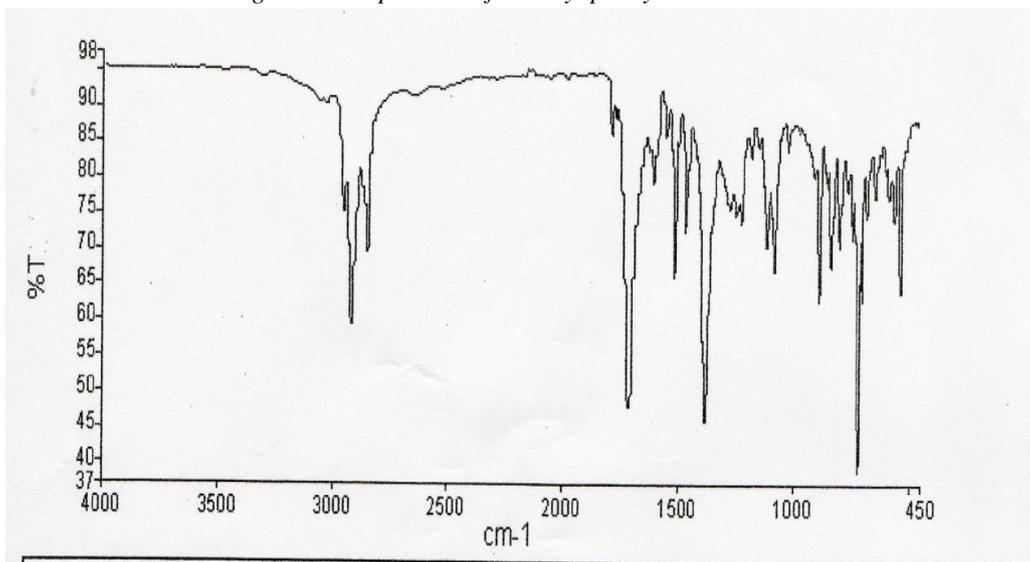


Figure 2: IR spectrum of dodecyl phenylenephthalimide

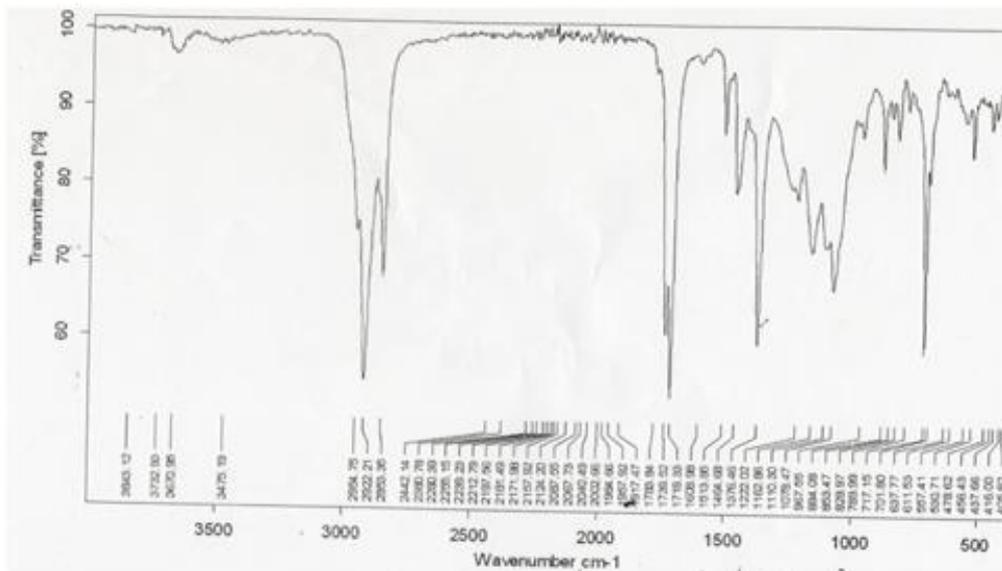


Figure 3: IR spectrum of Alkyd resin IV

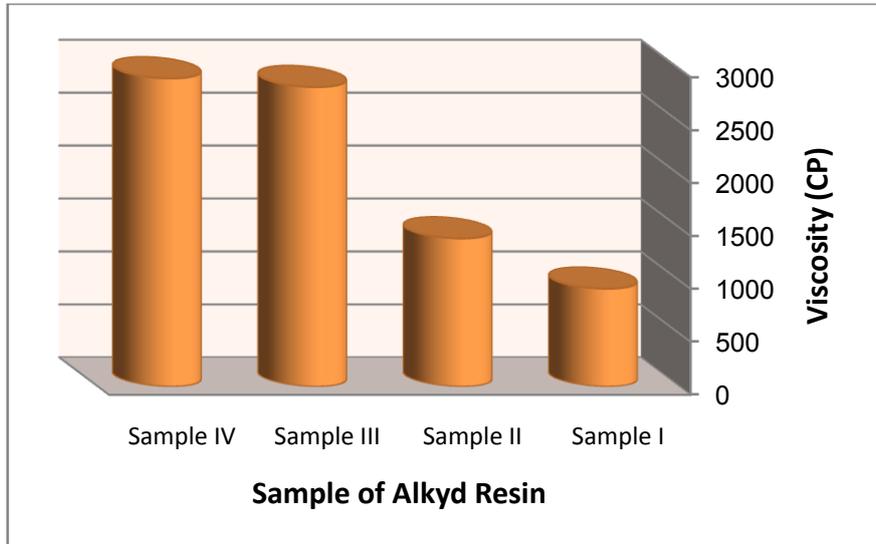


Figure 4: Viscosity of Alkyd Resins

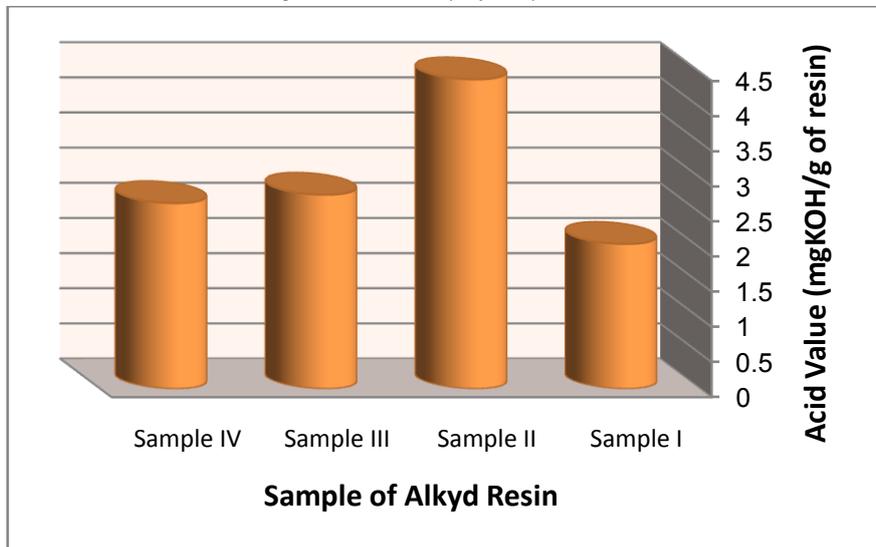


Figure 5: Acid Value of Alkyd Resins

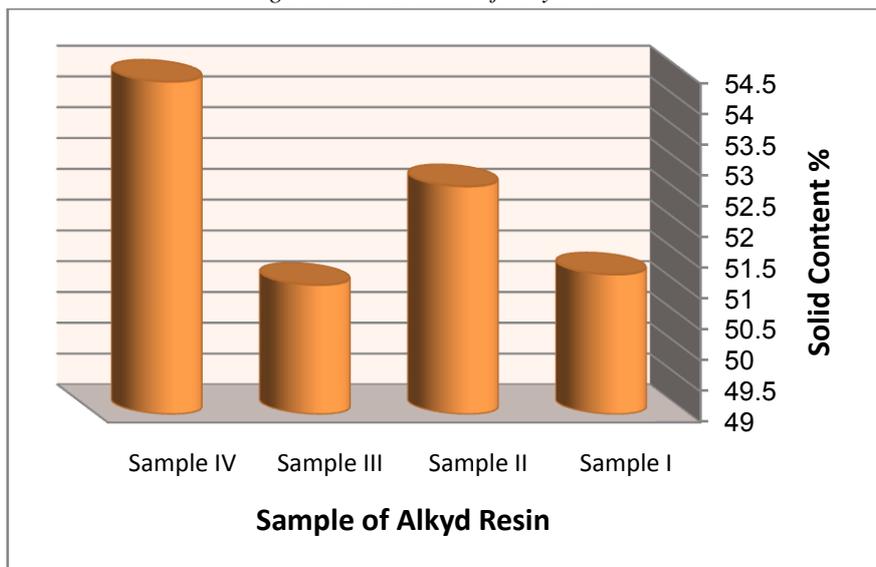


Figure 6: Solid content of Alkyd Resins

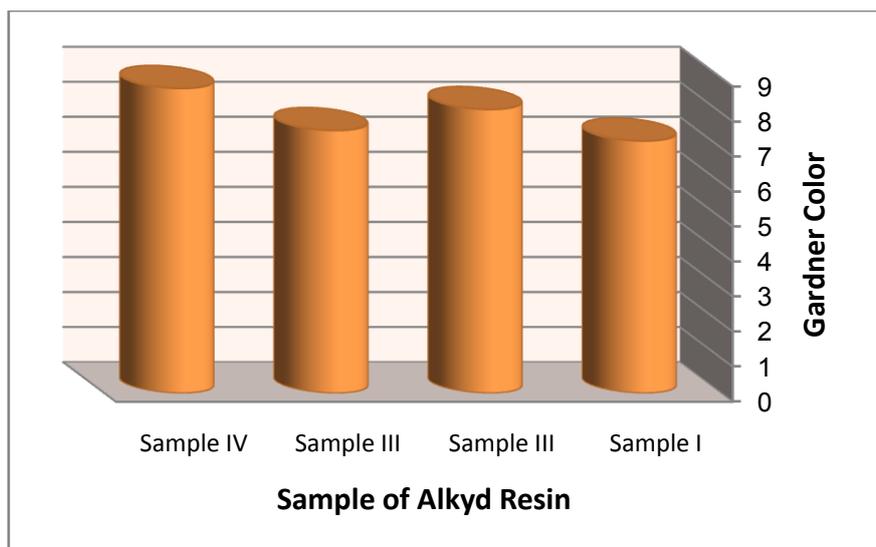


Figure 7: Gardner Color of Alkyd Resins

Reference

- [1]. M.A. Mazandarani, Paint and Resin Technology, Vol.12, 3rd ed, Pishro Publication, Iran,(1992) .
- [2]. A. Mukhtar, U. Habib and H. Mukhtar, Fatty acid composition of tobacco seed oil and synthesis of alkyd resin. Chinese J. of Chemistry, 25, 705-708, (2007).
- [3]. E.G. Bobaleck, E.R. Moore, S.S. Ivey and C.C. Lee. Some applications of gel point concept on the chemistry of alkyd resins .J of Applied Polymer science, 8, 625-657, (1964).
- [4]. I.O. Igwe, and O.A. Ogbobe. A study of the kinetics of Nigeria, 26(1), 75-80(2001).
- [5]. A.L. Aigbodin and C.K. Pillia, Synthesis and molecular weight characterization of rubber seed oil – modified alkyd resins, J. of Applied Polymer science, 79, 2431-2438, (2001) .
- [6]. E.U. Ikhoria, A.I. Aigbodion and F.E. Okeiemen, Enhance the quality of alkyd resins using methyl ester of rubber seed oil, Tropical J. of Pharmaceutical Research, 3(1), 311-317, (2004).
- [7]. N.O. Shaker, N.A. Alian and M.M. El-suwly Der Chemica Sinica, 3(5), 1157-1162, (2012).
- [8]. F.S. Guner, Y.Yusuf and A.T.Erciyas. Polymers from triglyceride oils progress in organic coatings, 31, 633-670, (2006).
- [9]. K.D.Weiss, paint and coatings. A progress in polymer science, 22, 203-245, (1997).
- [10]. I.O. Isaac and E.V. Nsi, Influence of poly basic and type on the physico-chemical and viscosity properties of cotton seed oil alkyd resins. The International J. of Engineering and Science, 23, 1-14, (2013).
- [11]. K. Vaso and Dema, Preparation of the anticorrosive paints with long oil alkyd resins modified with maleic anhydride and phthalic anhydride. Zastita Materijala, 51, 87-93, (2010).
- [12]. A.I. Vogel, Text book of practical organic chemistry, 3rd ed, Longman group limited, 526, (1972).
- [13]. K.Vaso and M. Dema. The improvement of the technology characteristics of semi drying oils through the thermo-chemical process of them "Pollution management and environmental protection", 154,(2009).
- [14]. M.W. Fomo, Ester reaction of fatty materials. J. of American Oil Chemists Society, 13(11),548-559, (1954).
- [15]. K. Bades, Adapted from MPCPROKIM Chemicals company.
- [16]. S. Aydin, H. Akcay, E. Ozkan, F. S. Gunner and A. T. Erciyas, the effects of anhydride type and amount on viscosity and film properties of alkyd resin, Progress in organic coatings, 51, 275-279, (2003).

