AL-QADISIYAH JOURNAL FOR ENGINEERING SCIENCES

Vol. 10 , No. 3
ISSN: 1998-4456

SYNTHESIS AND CHARACTERIZATION OF NEW ALKYD RESINS OBTAINED FROM BITTER ALMOND OIL AND COCOANUT OIL AS BINDER FOR SURFACE COATING

Mohammed Ail Mutar,

Department of Chemical Engineering, College of Engineering , University of AL-Qadisiyah .E mail: mohammed.ail@qu.edu.iq

NOOR MOHAMMED ABDUL HASSAN,

Department of Chemistry , College of Education, University of AL-Qadisiyah

E mail: Nm045744@gmail.com

Received on 8 Jonuary 2016 *Accepted on 9 August 2017*

Abstract: *Alkyd resins constitute a very high proportion of conventional binders used in surface coating . A new alkyd resins were synthesized by reacting (Bitter almond oil or Coconut oil with propylene glycol or Ethylene glycol and phthalic anhydride) in the presence of lead oxide as a catalyst. synthesis of alkyd resins, two stages were involved. At the first stage, Bitter almond oil or Coconut oil was converted to monoglycerides as a polyol by alcoholysis. Esterification process was held at the second stage by adding phthalic anhydride and xylene in the mixture. Three different alkyd resins have been synthesized (Short , medium and long) from Bitter almond oil or Coconut oil by using different ratios of phthalic anhydride .The various physic-chemical properties of alkyd resins like acid value , saponification value , iodine value Density, viscosity, chemical resistance and volatile matter were studied . The resulted alkyd resins are readily soluble in aprotic polar solvents , such as (Toluene , Acetone , Benzene , xylene , DMF, DMSO , Methanol and ethanol) without need for heating. Thermal analysis of alkyd resins by Thermo Gravimetric Analysis (TGA) and thermal differential calorimeter (DSC) techniques. reveals that these Aromatic alkyd resins possess thermal stability. Alkyd resins were characterized by (FTIR and 1H-NMR) spectroscopies .*

Keywords: Alkyd, Bitter almond oil, Coconut oil , Paint, Binder

INTRODUCTION

Paints may possibly be described as a colloidal combination of chemical ingredients, when diffused on a surface in a thin layer they form a dense, consistent and adherent layer. They are used regularly in our life for ornamental purposes, and for preventing surfaces of being affected by different environmental influence as UV-radiation, chemical invasion and mechanical stresses. A binder, pigment, solvent, and additives are common ingredients of paint. The polymer-binding material (alkyd resin) is responsible in addition to wide range of variations for finding a continuous layer that adheres to the lower layers and binds other ingredients together (1) . Coating material through using Polyester or alkyd is commonly employed for surface covering as binders, adhesives and plasticizers. What is interesting about Alkyd is that it is the lowest materials in cost if compared with other coating materials and it is subject to give a covering that shows less layer faults during applications. Also, stability of alkyd layers, particularly for outdoors use, tends to be poorer than films, i.e., acrylics and polyurethanes (2,3). However, one of the factors affecting coating film properties is the type of fatty acid or oil used in the alkyd production (4,5) . Various types of oil can result in differences in film properties . The preparation of alkyd resins can be achieved by condensation polymerization of a polyhydric alcohol (e.g. glycerol) and polyfunctional acid or polybasic acids (e.g. phthalic anhydride and isophthalic acid) changed by oily acid or their triglyceride. The alkyd resins manufactured this way are known as oil-modified alkyd resins and form 70% of the common binders used in external coating (6). They define the performance quality of surface coatings such as the degree of drying, gloss, stability of the dry layer and resistance of the dry layer to scratch and chemicals . However, categorizing of alkyd resins is centered on the oil length and oil type (7) The vegetable oils, which used in oil-modified alkyd resins are typically extracted either by a mechanical press or solvent extraction(8) . The natural oil in the oil-modified alkyds reacts with atmospheric oxygen, which leads to the formation of a network of polymers cross-linked through the (C=C) bond. The oil oxidative drying brings about the formation of a layer that displays enhanced characteristics with drying time, hardness or water resistance(9). Alkyd resins have gained high significance due to their economy, availability of raw materials, durability, biodegradability, , good adhesion, flexibility and ease of application .In this work, two alkyd resin (AR1-AR2) have been synthesized in high yield by polycondensation between dicarboxlic acid and polyols with oils using lead oxide as catalyst . Qualitative structure analysis of the polymers have been carried out by the using of FT-IR, and 1H-NMR spectroscopy, thermal stability were systematically investigated .

1. OBJECTIVE OF STUDY

1- The objective of the study is to produce different types of alkyd resins containing the Ester group obtain high adhesion and dehydration without the addition of a dry material and high elasticity compared to alkyd resins used in the market and then used in the manufacture of dyes.

2- Alkyd resins are prepared by reacting vegetable oils or fatty acids with multiple carboxylic acid (anhydrous phthalic acid), hydroxyl hydrolyses (propylene glycol, triethanolamine etc) with catalysts such as lead oxide.

3- Study and diagnosis of polymers prepared spectrally by the techniques of (FTIR, 1H-NMR)

4- Studying and evaluating the thermal stability of the prepared polymers through two thermal analysis techniques (TGA) and differential thermal analysis (DSC).

5- Study the solubility of polymers prepared in a range of different organic solvents.

.

2. EXPERIMENTAL

2-1- MATERIALS

Bitter almond oil ($C_{14}H_{14}O_2$) , Cocoanut oil ($C_{41}H_{72}O_6$) , phthalicanhydride ($C_8H_4O_3$) , lead oxide (Pb0) , xylene($C_6H_4(CH_3)_2$, all from made in (MERCK) ; propylene glycol ($C_3H_6(OH)_2$, Ethanediol ($C_2H_6O_2$), Ethanol (C_2H_5OH),all from made in (Scharlab S.L) ; Tetrahydrofurane (THF)(C_4H_8O),Dimethyl sulphoxide (DMSO)($(CH_3)_2SO$,all from (MERCK) ; Methanol(CH_3OH), Acetone(C_3H_6O), Toluene(C_7H_8), Carbon tetrachloride(CCl_4), all form (BDH-chemicals) ; Sulfuric acid(H_2So_4) form (Sd fine-CHEM) ;Hydrochloric acid(HCl) , Sodium chloride(NaCl) , all form (Hi-media) ; potassium hydroxide(KOH) , potassium Iodide(KI), Sodium thiosulfate($Na_2S_3O_3$) all from (HIMEDIA) .

Instruments

FTIR 8400S , Fourier Transform infrared spectrophotometer , SHIMADZU, Japan), (Oven ,Trivp International Crop .Italy) ,(Hot plate stir , Bibby Strlintd .UK) (Measurement of 1 HNMR Spectra : recorded NMR spectra using a type of Bruker ,Ultra shield 300 Mhz, Switzerl and using (DMSO-d6) as a solvent at the university's Educational teacher-Tehran Iran) ,(Thermogravimetry analysis (TGA) were performed on a polymer laboratories co England, Model PL-TG at Iran polymer & petrochemical institute , using a heating rate of 10ºC/min in Argon atmosphere within the temperature range of 25-800ºC)(differential thermal analysis (DSC) measurement using apparatus (DSC) type (DSC 131 Evo, SETARAM) is the origin (France) in the Department of Chemistry / Faculty of Education / University of Qadisiyah), (viscosity device The use of viscosity measurement device for measuring the viscosity of the alkyd resin models record in the Department of Chemistry / Faculty of Education / University of Qadisiyah / by a device from a company (Brookfield) type (RVDV- II + P 8500), (230 V~) and frequency (50/60 Hz) and strongly (30 VA). The machine is manufactured in (U.S.A) .

2-2- SYNTHESIS OF ALKYD RESIN

Two stages Preparation alkyd resins (10) :

Stage 1 (alcoholysis): In this stage, monoglyceride was first prepared by reacting (Bitter almond oil with propylene glycol or Coconut oil with Ethanediol), then added PbO as a catalyst. In alcoholysis reaction, the oil was heated with an agitation speed of (700 rpm) and N_2 sparging rate of about (0.06ft3/sec) to 230-240°C. Alcohol and selected catalyst were added and alcoholysis reaction was carried out at 230-240°C.The reaction of the mixture continued till the sample of the reaction mix became solvable in two to four volumes of anhydrous methanol. After completing alcoholysis reaction, the reaction mixture was cooled to 140°C.

Stage 2 (esterification): In this stage, phthalic anhydride was added to the monoglyceride mixture. The temperature was maintained at the range of 230-240°C and maintained at this temperature. The leakage amount of N2 was increased to (0.1ft3/sec). The reaction was observed by intermittent determination of the acid value of the mixture till acid value fell to nearly (9) .

Table (1) shows the proportions of the chemicals used in the reaction

Raw material	Short	Medium	long
Bitter almond oil Or Cocoanut oil	25-40 %	45-60 %	60-70 %
Phthalic anhydride	35 > gm	30-35 gm	20-30 gm
Glycerol	14.6 gm	14.6 gm	14.6 gm
Lead oxide	0.4 gm	0.4 gm	0.4 gm
Xylene	60 ml	60 ml	60 ml

2-3- PHYSICO – CHEMICAL TESTS

2-3-1- Acid value Test (11)

Acid value was determined according AOAC method and to standard 969.17 1997

2-3-2- Drying Test

Aluminum plates were cleaned by ethanol to make sure that there are no contaminants present to affect the result . A hand coater with different fixed thickness was used to evenly coat the resin on the surface of the testing plates (12) .

2-3-3- Saponification Number Test

Weight (1 gm) of sample into an Erlenmyer flask , in pipette 25 ml of (0.5 N) KOH put in the flask ,then add 4 ml of the solvent (ethanol-ether) to the flask , then reflux for (30) minutes, rinse the inside of the condensers with about (25) ml DI water allow the solvent to drain into the Erlenmeyer flask , and allow the solution to cool to room temperature , then add three to five drops of phenolphthalein indicator to the solution with moderate agitation , then add (0.5) HCl (titrant) to the burette , and not level , then add titrant from the burette to the solution until the faint pink color permanently (for at least thirty seconds) disappears, and not level of titrant in the burette (13) .

2-3-4- Iodine Number Test

Deliver (0.1) g sample to (300) ml conical flask with ground in stopper. Add 20 ml carbon tetrachloride and seal. Dissolve Sample in an ultrasonic washing machine , then add 25 ml Hanus solution, and seal. Shake for one minute , then keep it sealed and leave in a dark room (about 20 ºC) for 30 minutes , then add (10) ml of 15% potassium iodide and 100 ml water , and seal. Shake for (30) seconds, then titrate with (0.1) mol / L sodium thiosulfate to obtain iodine value then also perform blank test to obtain blank level(14) .

2-3-5- Density Test

The density was determined according to NF EN 1097-6 using analytical scale and pycnometer S9611826 (100 ccs)(15) .

2-3-6- Viscosity Test

rookfield rotary Viscometer Ku-2 model RVDV-II+ P8500 was used to measure the viscosity at 25 ºC, and using different spindle and speed (16) .

2-3-7- volatile matter Test

Three specimens were placed in the oven within (30) min after preparation of alkyd resin in previously weighed watch glass and heated for (2 h) at (135-140) ºC . The Nonvolatile matter was calculated from the difference in initial and final weights of the watch glass . The mean value of the three results was reported as the percentage nonvolatile matter .

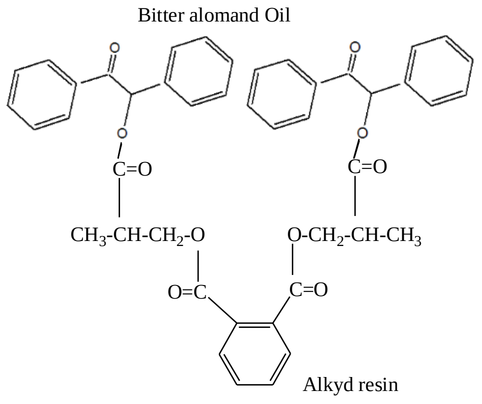


Figure (1) Structure of polymer (AR1)

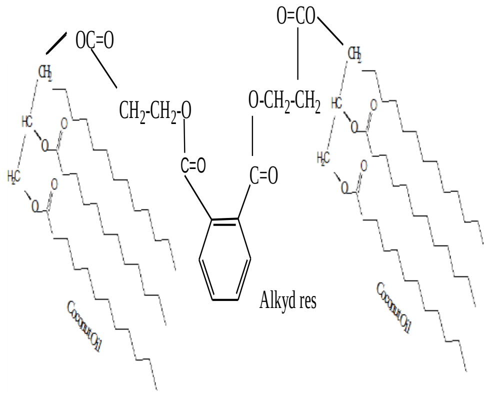


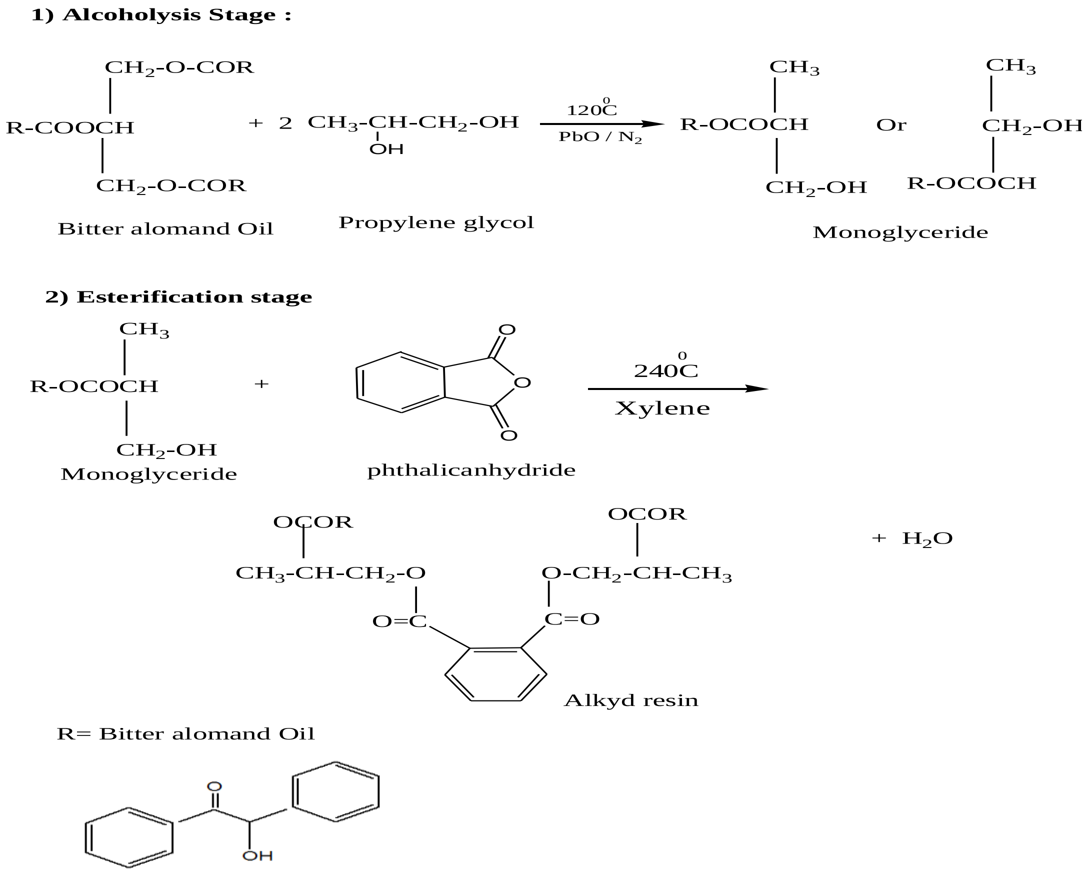
Figure (2) Structure of Polymer (AR2)

3- RESULT AND DISCUSSION

3-1- SYNTHESIS AND CHARACTERIZATION OF POLYMERS PREPARED

3-1-1- synthesis and characterization of (AR_1)

This polymer was synthesized by the condensation of Bitter almond oil with Propylene glycol and phthalic anhydride (17) in the presence of lead oxide as catalyst and temperature is (120-240 c º) for (6 hours) according to the equation in the reaction scheme (1) .



scheme (1) synthesis of (AR1)

Characterization of (AR_1)

FT-IR spectrum :

The FTIR spectra of (AR1) as show in (Figure 3) which indicates absorption band of (OH) Carboxylic at (3505 cm-1) ,(C-H) aromatic at (3002 cm-1) , (C-H) aliphatic at (2854, 2923 cm-1), (C=O) in the ester group at (1745 cm-1) , (C=C) aromatic at (1475 cm-1) , and (C-O) at (1220 cm-1) .

(^{1}H-NMR) Spectrum of (AR1) , is shown in (Figure 4) assigns the following chemical shifts ; (δ= 1.15-1.44 ppm) for methyl group, (δ= 1.89-1.96 ppm) for (CH_2) , (δ= 5.19-5.30 ppm) for (OH)in Bitter almond oil, (δ= 2.5 ppm) for (DMSO), (δ= 2.49 ppm)for (H_2O), (δ = 7.67 ppm) for Ar-H group .

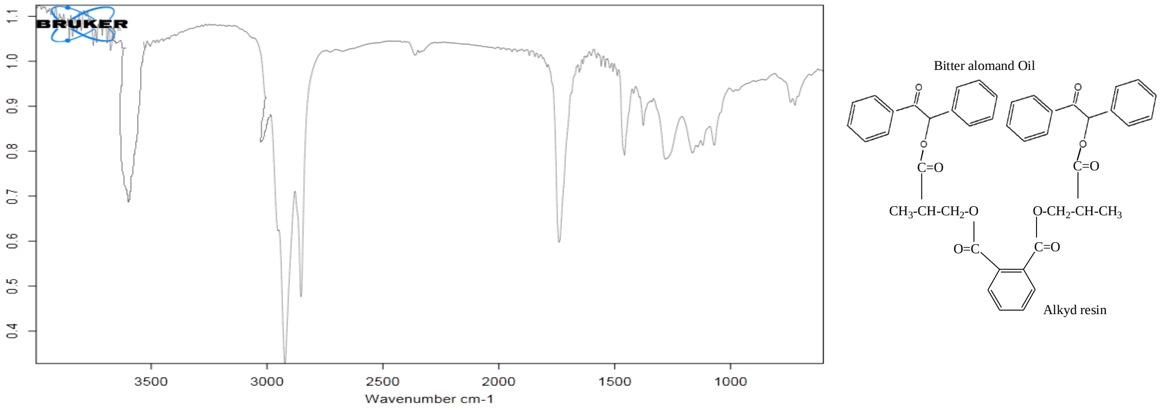


Figure (3) : FTIR spectra of (AR_1)

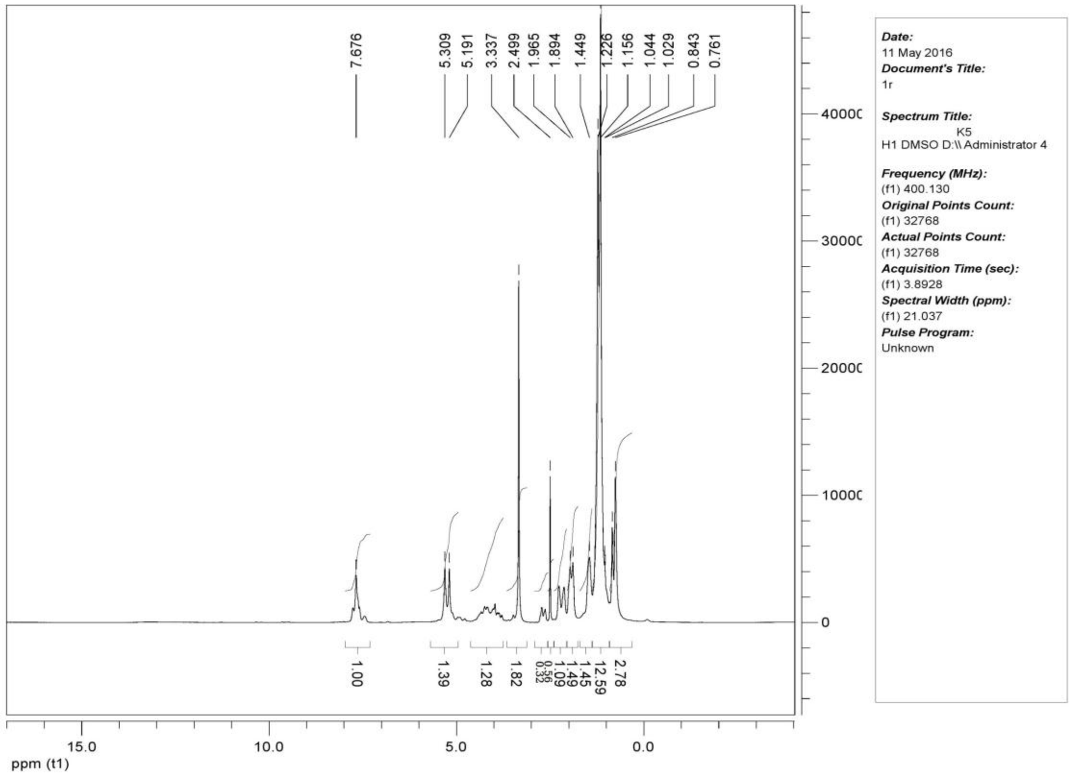
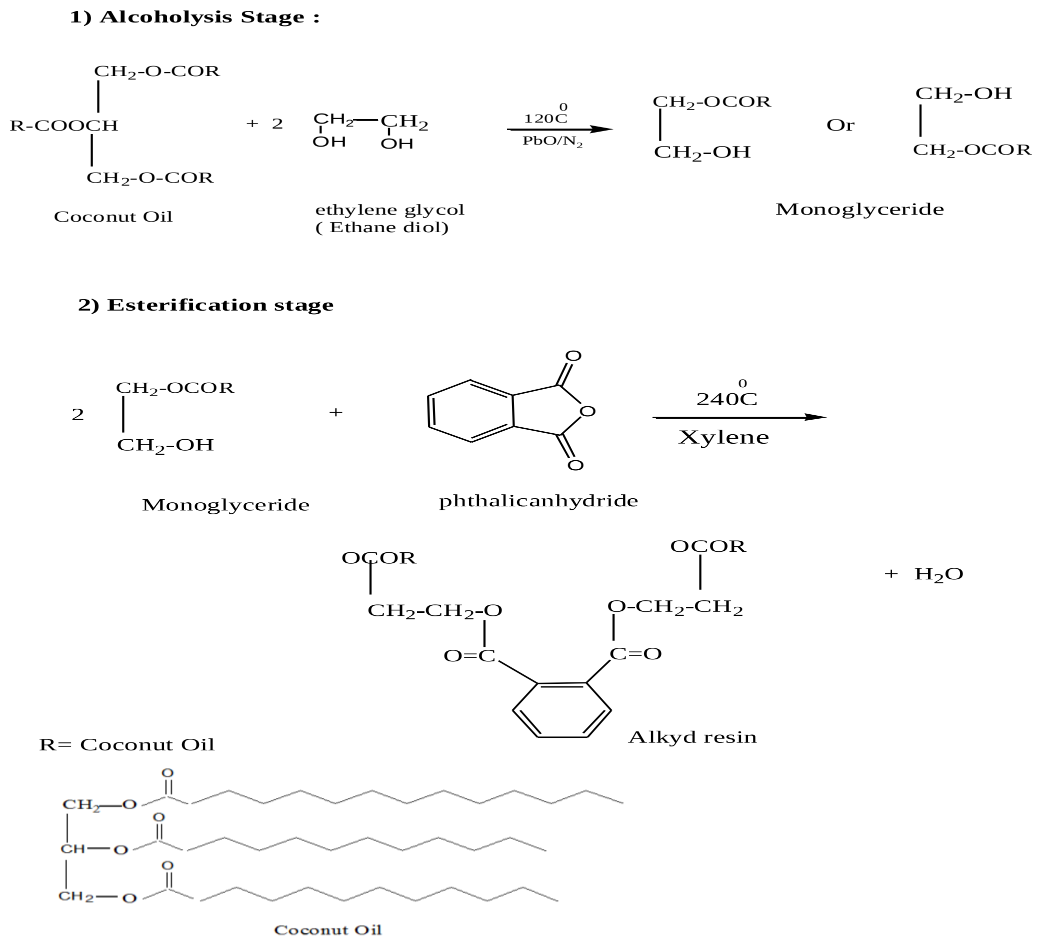


Figure (4) 1HNMR spectra of (AR1)

3-1-2- synthesis and characterization of (AR2)

This polymer was synthesized by Condensation of Cocoanut oil with Ethanediol phthalic anhydride in the presence of lead oxide as catalyst and temperature is (120-240 c º) for (6 hours) according to the equation in the reaction scheme (2) .



Scheme (2) synthesis of (AR2)

Characterization of (AR2)

FT-IR spectrum : The FTIR spectra of (AR2) as show in (Figure 5) which indicates absorption band of (C-H) aromatic at (3100 cm-1), (C-H) aliphatic at (2854, 2923 cm-1) , (C=O) in the ester group at (1681 cm-1) , (C=C) aromatic at (1445 cm-1) , and (C-O) at (1300 cm-1).

(^{1}H-NMR) Spectrum of (AR1) , is shown in (Figure 6) assigns the following chemical shifts ; (δ= 3.64-3.67 ppm) for methyl group, (δ= 4.21-4.23 ppm) for (OCH_2) , (δ= 2.5 ppm) for (DMSO), (= 3.39 ppm)for (H_2O), (δ= 7.58-7.67 ppm) for Ar-H group .

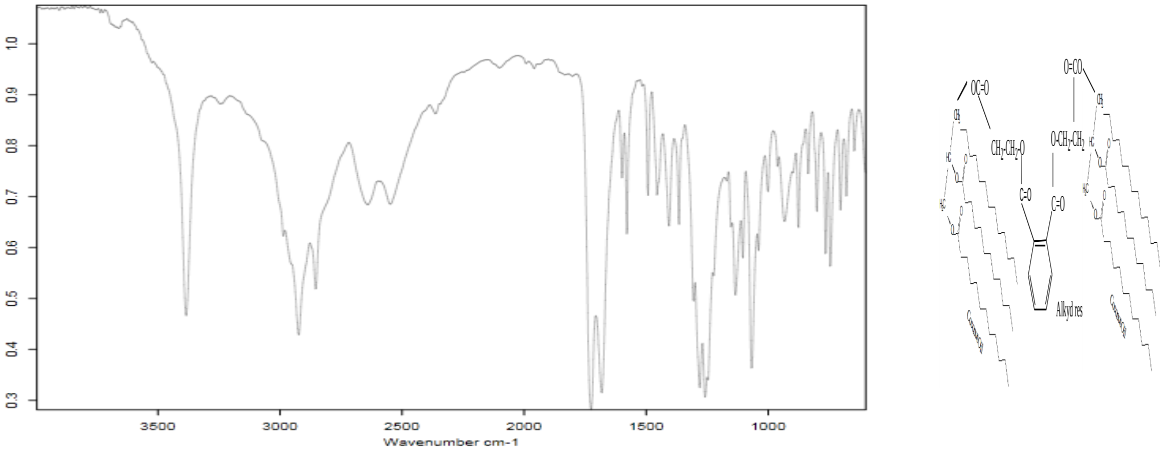


Figure (5) FTIR spectra (AR2)

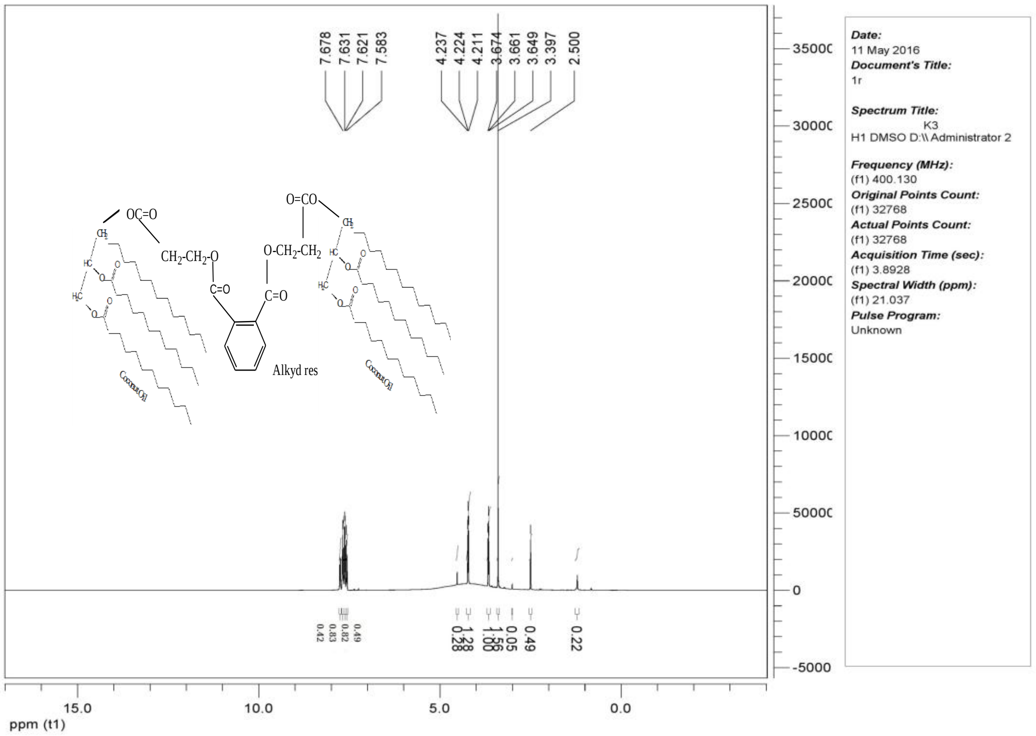


Figure (6) 1HNMR of (AR2)

3-2- PHYSICO – CHEMICAL TESTS

3-2-1- Acid value test

The acid value (AV) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid$^{(18)}$. It has been observed from the results shown in the (table 2), (AR2) prepared from Cocoanut oil showed an acid value higher than the (AR1) prepared from Bitter almond oil due to the length of the fatty acid chain component there of resin Cocoanut oil, containing (C_{41}) carbon atom and Bitter almond oil containing (C_{14}) .

Table (2) shows the values acidity of alkyd resins prepared

Alkyd resins	Acidity		
	Short	Medium	Long
AR1	7.01	7.29	7.57
AR2	8.41	8.69	8.97

3-2-2- Iodine number test

The value of Iodine in chemistry is calculated through the mass of Iodine in grams, which is used by 100 grams of a chemical substance. The numbers of Iodine are regularly employed to define the extent of unsaturation in oily acids. This unsaturation takes the form of double bonds that reacted with Iodine compounds. The higher the Iodine number, the more C=C bonds are present in the fat (note that the number of iodine saturated fatty acids equals zero). As well as the number of Iodine used in the to detect adulterated vegetable oils with oils constants. Whenever a high Iodine number, i.e. it contains high proportion of unsaturated fatty acid and iodine number and if Iodine number is low, i.e. fatty acids is saturated(19). The results of the prepared resins observed through the (table 3), The Iodine value is higher in (AR2) prepared from Cocoanut oil showed an acid value higher than the (AR1) prepared from Bitter almond oil due to the length of the fatty acid chain component there of resin Cocoanut oil, containing (C_{41}) carbon atom and Bitter almond oil containing (C_{14}) .

Table (3) shows the values iodine number of alkyd resins prepared

Alkyd resins	Iodine number		
	Short	Medium	long
AR1	100	98	96
AR2	140	133	27

3-2-3- Saponification value test

Saponification value represents the number of milligrams of potassium hydroxide required to saponify (1g) of fat under the conditions specified. This is to measure the average molecular weight of all the fatty acids presented in this process. Most of mass of fat /tri-ester is in the three fatty acids, it permits for comparison of the average fatty acid length chain. The long chain of fatty acids, which are found in fats have low saponification value due to their relative fewer number of carboxylic functional groups for each mass unit of the fat when compared to short chain fatty acids (20) . The results were observed from the (table 4) showed (AR2) prepared from Cocoanut oil (C_{41}) less saponification value than (AR1) prepared from vegetable oil short-chain Bitter almond oil (C_{14}) because of the saponification number proportional inversely to the length of chain fatty acid .

Table (4) shows the values Saponification number of alkyd resins prepared

Alkyd resins	Saponification		
	Short	Med.	long
AR1	263	258	252
AR2	195	192	189

3-2-4- Density test

A substance density and the volumetric mass density is its mass per unit volume. Mostly used symbol for density is ρ. And depends on temperature and pressure . The results were observed for the resins prepared in the (table 5), The density is less of alkyd resin increasing fatty acid chain length and vice versa, also due to the presence of a relatively less number of active carboxyl groups . Is observed (AR2) prepared from Cocoanut oil (C_{41}) showed the density is less than (AR1) prepared from vegetable oil short-chain Bitter almond oil (C_{14}) because of the saponification number proportional inversely to the length of chain fatty acid .

Table (5) shows the values density of resins

Alkyd resins	Density		
	Short	Med.	Long
AR1	0.935	0.930	0.925
AR2	0.804	0.798	0.793

3-2-5- Drying test

Drying rate of alkyd resin based on Bitter almond oil or Cocoanut oil of diverse applied thickness and employed certain amount of cobalt. These oils categorized as non-drying oil that contain fatty acid higher proportion in saturated chains than other types of oil. Non-drying oil alkyds do not produce layer without alteration(21) . However, alteration and addition of driers provide resins the form of film at regular atmospheric circumstance. Denser layers (120 µm) are in need for much more time to dry in comparison with thinner layers (30 µm).The thicker films drying mechanism necessitate a great deal of cobalt to cross-link between chains. When the catalyst concentration decreased, a less dense cross-linked network was formed. The thicker films alkyd drying time can radically increase the oxygen uptake either at the double bond or methylene group as the increasing presence of driers(22). It was noted that the resin ability to air dry is because phthalic anhydride modification in specific amount and drier that leads to resin to cross link. The higher the presence of phthalic anhydride and the driers, the longer chain length and a higher cross linked dense resin through condensation polymerization. The resin turns to be denser, viscous and more compact conferring self-curing feature. The results were observed from the (table 6) showed Higher oil content in long oil and medium oil alkyds gave slower initial drying , due to more thermosetting of long oil alkyd as compared to short oil alkyd. Subsequently, better thorough drying can be assigned to same thermosetting nature of oil present in long oil alkyd. Short oil alkyd thus has slower thorough drying due to less oil present .

Table (6) shows the values drying time of resins

Alkyd resins	Drying time		
	Short	Med.	long
AR1	10 min	15 min	20 min
AR2	20 min	25 min	33 min

3-2-6- Viscosity test

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress . For liquids, it corresponds to the informal concept of "thickness" .The viscosity of the solution is an important tool for characterization polymers are a measure of molecular weight of polymer as the viscosity of the solution is a measure of the size. The factors affecting viscosity:

a) pressure: pressure viscosity little importance but viscosity effect appears when the pressure increases (68 bar).

b) temperature: when temperatures decrease viscosity because at high temperature of liquid increase distances between molecules less friction and therefore less viscous.It is noted that the viscosity resins alkyd increases during reaction for all types of oils used in manufacturing, and also notes that the viscosity increase slowly during the hours (2-3) interaction. Then, it increases viscosity significantly in esterification reaction between mono glyceride and phthalic anhydride however after 5 or 6 hours ends interact very viscous alkyd resin consists of any strings are A gelatinous substance polymer (gelatin)(23).

c) The viscosity is highly dependent on amount of cross-linking in polymer. It was noted by the results shown in (table 7), showed (AR1) prepared from Cocoanut oil (C_{41}) higher viscosity than (AR2) prepared from vegetable oil short-chain Bitter almond (C_{14}) because of the viscosity proportional inversely to the length of chain fatty acid .

Table (7) shows the viscosity values of prepared resins

Alkyd resin	Short	Medium	Long	Speed	No. Spindle	Temper.
AR1	170	160	130	100	6	25
AR2	60	40	40			

3-2-7- Volatility matter test

It was noted by the results shown in (table 8), where the difference in the value of the volatility between each resin prepared (AR1) showed less value volatility due to the short chain fatty acid (Bitter almond oil) while (AR2) showed a high value volatility due to length chain fatty acid Cocoanut oil container in structure on the double bonds of the ability to interact with oxygen therefore volatility quickly .

Table (8) shows the values volatility of resins

Alkyd resins	Volatility
AR1	%40
AR2	%70

3-2-8- Chemical resistance test

The resistance of alkyd resins prepared for some chemicals was tested. The results indicated in (Table 9) show the difference in chemical resistance between each resin. The AR1 and AR2 resin prepared from bitter almond oil and coconut respectively are resistant (Insoluble) in water because the resin is made up of a chain of unsaturated fatty acid, i.e., non-polar organic compounds and water is a polar solvent. While it is not resistant to any (dissolved) in the solvent tetrahydrofuran (THF) because it is a non-polar organic solvent. The AR2 resin is also noted. The record of coconut oil is non-resistant (dissolved) in hydrochloric acid, sulfuric acid, sodium hydroxide and sodium chloride. While resin (AR1) is resistant to solvents above due to the different type of vegetable oils manufactured by alkyd resin according to their nature and their resistance to solvents.

Table (9) shows the chemical resistance values of prepared resins

Alkyd resin	THF	NaCl	KOH	H2SO4	HCl	Distilled water
AR1	–	+	+	+	+	–
AR2	–	–	–	–	–	–

3-2-9- Solubility test

Alkyd resins showed high solubility in different type of solvents .(table 10) described solubility of samples, was measured by taking the solubility (0.01 g) of the sample prepared resin and melted in (2 ml) of the solvent, The solvents used include (DMF, Acetone, Toluene, Xylene,) (Polar aprotic) non-polar solvents such as (Benzene, $CHCl_3$) and other solvents such as methanol, ethanol. The solvent molecules increase with the distance between the molecular chains of the resin. The spaces between long chains with pendant side group of resin are invaded by solvent molecules as they fill the space made available by chain movements. When movements bring two chains close to proximity, short range attractive forces are therefore established resulting in restricted chain movement and thus the formation of a viscous system (24 ,25). Solvent are added to deal with the problem of high viscous resin which is an obstacle in substrates wet ability .

Table (10) shows the solubility of alkyd resins

Alkyd Resin	Solvent							
	Xylene	DMF	Toluene	Acetone	DMSO	Benzene	Methanol	Ethanol
AR1	+	+	+	+	+	+	+	+
AR2	+	+	+	+	+	+	+	+

\+ soluble at room temperature , +- Partially Soluble

3-3- THERMO GRAVIMETRIC ANALYSIS (TGA) STUDY

Thermo gravimetric Analysis (TGA) involves determining changes in mass as a function of temperature . It is commonly used to search degradation temperatures, absorbed content of materials, levels of inorganic and organic parts contained in a material and analysis solvent residues (26) . It employs a sensitive electronic balance from which the sample is suspended in a furnace controlled by a temperature programmer . The thermal properties of two samples of these alkyd resins were investigated by means of thermo gravimetric analysis (TGA) in Argon atmosphere at heating rate of 10 ºC/ min . The results such as Ti , Top , Tf , T50% , % Residue at 300 ºC , and char yields at 200 ºC are summarized in (Table11) and (curve 7,8) . The temperatures of 50% weight loss of (AR1 , AR2) as a standard indication for thermal stability of polymers were all from 300 ºC, The char yields of (AR1) are 50% and (AR2) are 98% at 200 ºC in Argon atmosphere (27) , which indicate they could meet temperature resistant requirements, which can be used in surface coating application . weight residue of (AR1) are 20% and (AR2) are 65% at 300 ºC .

Table (11) Some properties of the thermal stability of the curves of thermal analysis (TGA)

Alkyd Resin	DT/°C				T50%	Residue at oC300	Char % At 200°C
	Ti	Top1	Top2	Tf			
AR1	260	200	288	>300	288	65	98
AR2	200	150	250	>300	295	20	50

DT : Decomposition temperature.درجة حرارة التفكك
Ti : Initial decomposition temperature.درجة حرارة التفكك الابتدائية
Top : Optimum decomposition temperature.درجة حرارة التفكك المثلى
Tf : Final decomposition temperature.درجة حرارة التفكك النهائية
T50% : Temperature of 50% weight loss, obtained from TGA درجة حرارة التفكك عند فقدان البوليمر 50% من وزنة
Char% at 200°C : Residual weight percentage at 200°C in Argon by TGA.
النسبة المئوية لتفحم العينة عند درجة

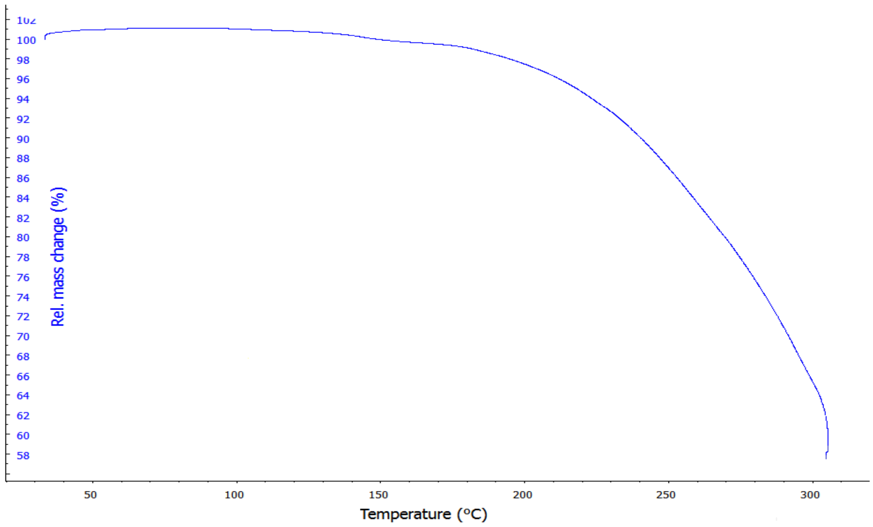


Figure (7) TGA cure of AR1

3-4- DIFFERENTIAL SCANNING CALORIMETER ANALYSIS (DSC) STUDY

Differential Scanning Calorimetry,is a technique of thermal analysis that investigates how material's heat capacity (Cp) is transformed by temperature. A known mass sample is heated or cooled and the variations in its heat capacity are observed as alterations in the heat flow. This allows to reveal transitions such as melts glass transitions (Tg), and the melting point (Tm) the degree of crystallization (Tc) (28). this test was applied to the prepared samples , Shows the(table 12)and (curve 9) for the sample came from reaction Bitter almond oil with Propylene glycol The results showed the value of the glass transition (Tg) of the mixture (35c º), referring to obtain the flow temperature and then increases endothermic the sample to reach the melting point (Tm) at (295 c º) . It also shows a (curve 10) for the sample came from reaction Cocoanut oil with Ethanediol and the results showed the value of the glass transition (Tg) of the combination (36.4cº) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (297 c º) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (85.1 cº).

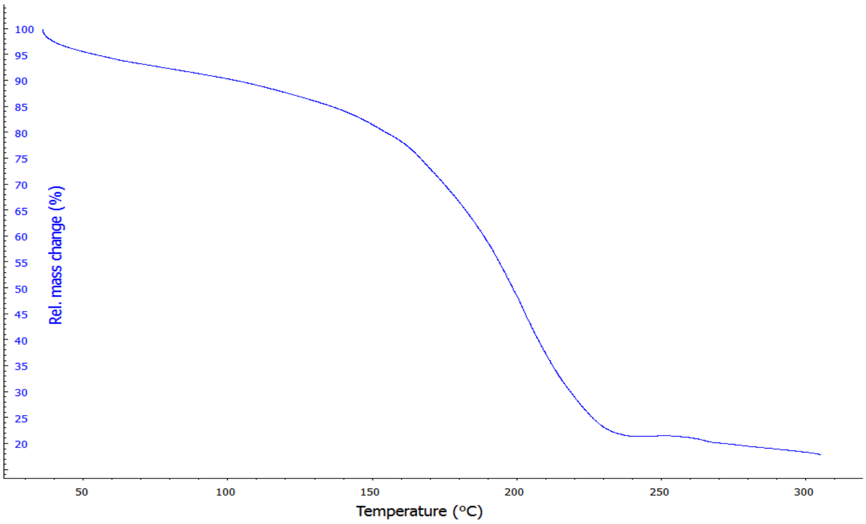


Figure (8) TGA cure of AR2

Table 12: Shows the Degree of Glass Transition, Melting Point and the Degree of Crystallization in the Differential Thermal Analysis

Samples	Tg (cº)	Tm (cº)	Tc (cº)
AR1	35	295	165.1
AR2	36.4	297	85.1

Tg : Degree glass transition , Tm : Melting Point , Tc : Degree of crystallization

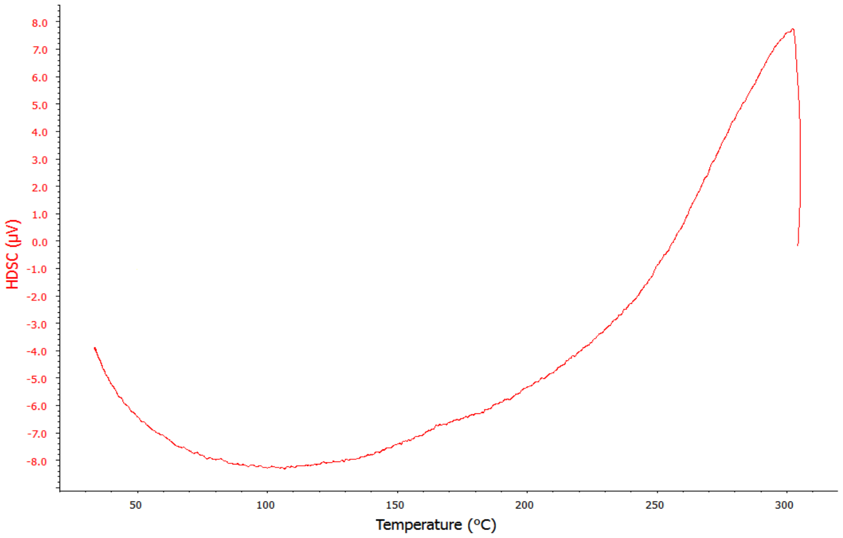


Figure (9) DSC cure of (AR1)

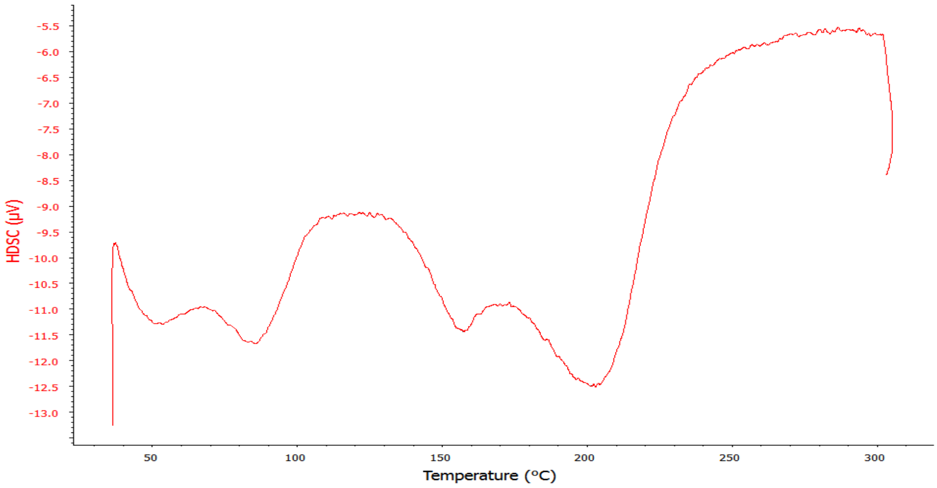


Figure (10) DSC cure of (AR2)

CONCLUSIONS

In this work, new alkyd resin used in many industries like paints and surface coatings because of their properties such as friction resistance, humidity, scalability high adhesion, high dry without addition a drying agent, and high flexibility. And It shows that through the study of their properties such as drying times, the volatility, saponification number, iodine number, acid value, and density of these resins all of the tests depends on the fatty acid chain length or type of vegetable oil used in the manufacture of these resins. Alkyd resins show high solubility in various solvents because their structures contain chemical groups such as (hydroxide, and links ethers) alkyd resins showed curves thermal gravimetric analysis (TGA) high increase in thermal stability because of the different types of vegetable oils used in alkyd resins industry and structural diversity of the structures of the new alkyd resins.

REFERENCES

1- **Wicks , Z. W., Jones**, F.N., & paappas, S.P. **(1994).** *Organic coatings* : science and technologe Vol. 1., John Wiley & Sons .

2- **Zeno, W.W.,Frank, N.J. and peter**, S.p., *Organic Coatings Science & Technology*, 2nd Ed., Wiley – Interscience, pp.135 and pp.142**(1996).**

3- **Kim, D. and Kim, S.W.,** ,,*Barrier property and morphology of polypropylene* / pol-yamide blend film,, Korean J. Chem. Eng., 20,776 **(2003).**

4- **Kabasakal, O.S., Guner, F.S.,** Erciyes, A.T. and Yagci, Y., ,,*Styrenation of oils based on secondary* esters of caster oil,,, J. Coating Technol., 67,47 **(1995)** .

5- **Kabasakal, O.S., Guner, F.S., Arslan, A., Ergan, A., Erciyes**, A.T. and Yagci, Y., ,,Use of caster oil in *the preparation of various oil-based binders*,, J. Coating Technol., 68,57 **(1996)** .

6- **Bajpai, M., & Seth, S. (2000)** . *Use of unconventional oils in surface coating blends of alkyd resins with epoxy esters. Pigment Resins Technol*., 29,82-87. http://dx.doi.org/ 10. 1108/03699420010317825 .

7- **Micciche, F. (2005).** *The combination of ascorbic acid derivative/iron salts as catalyst for the oxidative* drying of alkyd-paints : A Biomimetic approach. Technische Universiteit Eindhoven. http ://Alexandria.tue.nl/extra2/200512801.pdf

8- **Abulude, F.O., Ogunkoya, M.O., & Ogunleye, R.F**. **(2007)**. *Storage properties of oils of two Nigeria oil seeds Jatropha curcas* (physic nut) and Helianthus annuus. Amer. J. Food Tech., 2, 207-211. http://dx.doi.org/10.3923/ajft.2007.207. 211 .

9- **Akintayo, C.O. (2004).** *Synthesis and Characterization of AIbizia benth medium oil modification of alkyd resin and its chemically modified derivatives*. phD thesis . University of Ibadan, Nigeria.

10- **Ogunniyi D.S. & Odetoye T.E**, *Preparation and evaluation of seed oil –modified alkyd resins,* Biores Technol, 99. Pg: 1300-1304**,(2008).**

11 - **Ceirwyn S. J.,** *Analytical Chemistry of Foods, Blackie Academic and Professional*, Chapman and Hall, London, **(1995)** .

12- **R. S. Abiev**, I. V. Lavretsov, Chem. Eng. Sci., pg:74, 59– 68.

http://dx.doi.org/10.1016/j.ces.2012.02.024, **(2012).**

13- **A.O.A.C.** 17th edn, *Official method 920. 160- Saponification number of oils and fats* / IUPAC 2. 202 /I.S.I. Handbook of Food Analysis (Part XIII) – 1984, page 78**,(2000)** .

14- **A.O.A.C.** 17th edn*, Official method 920. 159- Iodine absorption number of oils and fats* / I.S.I. Handbook of Food Analysis (Part XIII) – 1984, page 76**,(2000)** .

15- *Density definition in Oil Gas Glossary*". Oilgasglossary.com. Retrieved -09-14 Pg: 18-19, **(2010).**

16- **M.I. Ojovan, K.P. Travis and R.J. Hand** "*Thermodynamic parameters of bonds in glassy materials from viscosity-temperature relationships"*. J. Phys.: Condensed matter 19 (41): 415107. doi:10.1088/0953-8984/19/41/415107. Pg: 237**,(2000).**

17- **rahimi, a. and farhangzadeh, s.** *"kinetics study of bisphenol a synthesis by condensation reaction",* iranian polymer journal. 10 (1) : 29–32 Pg: 38-39**,(2001)**.

18- **I.SI. Handbook of Food Analysis** (Part XIII)-1984 Page 67/ IUPAC 2.201/ I.S: 548 (Part 1) – 1964, Methods of Sampling and Test for Oils and Fats / ISO 660:1996 Determination of acid value and acidityPP:428-430, **(1979).**

19- **A.O.A.C.** 17th edn, *Official method 920. 159- Iodine absorption number of oils and fats* / I.S.I. Handbook of Food Analysis (Part XIII) – 1984, page 76 **(2000).**

20- **Multon J. L.,** *Analysis of Food Constituents,* Wiley-VCH, New,York Pg: 16, (1997) .

21- **Issam A.M., Cheun C.Y., (2009)**. *A study of the effect of oils on the properties of a new alkyd resin. Malaysian polymer Journal*, 4(1), 42-49.

22- **Akintayo, C.O., and Adebowale, K.O.,** (**2004**), *Syntheses Characterization and Evaluation of Chlorinated Albizia benth medium oil Alkyds, progress in Organic Coatings*. 2 pp 138-143.

23- **Glenn Elert**. "*The Physics Hypertextbook-Viscosity*" (http://physics.info/viscosity/). Physics.info. . Retrieved -09-14 Pg:24 **(2010).**

24- **Boxall ,J. and Von Fraunhofer, J.A., (1977).** Concise paint Technology, Elek Science London .

25- **Boxall ,J. and Von Fraunhofer, J.A., (1980**). Concise paint Formulation, principleand practice, George Godwin Limited London .

26- **andrey tarasov**.” *thermal analysis: methods, principles,applicason.*” lecture on thermal analysis 26.16.Pg: 76**,(2012).**

27- **K. B. Cantre, J. H. Martin and K. S. Ro** " *Application of Thermogravimetric Analysis for the Proximate Analysis of Livestock Wastes*", Journal of ASTM International. 7 (3)Pg:2-13**(2009).**

28- **Bernhard wunderlich** . *Thermal Analysis, text for an audio course*. ATHAS, Advanced Thermal Analysis, Alaboratory for Research and Instruction **(1981)**