



## RESEARCH ARTICLE

### PREPARATION OF ROSINATED MEDIUM ALKYD RESIN AS A BINDER FOR PAINT AND COATING TECHNOLOGY

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#### ABSTRACT

Alcoholysis-polyesterification method was used in the study of consumption of dehydrated castor oil and linseed oil in the formulation of rosinated medium alkyd resins. The extracted oil with the iodine number for castor oil is 86-90 and for linseed oil is 175-180 were applied in the preparation of middle alkyd resins and the physicochemical characterization indicated it is semi-drying in nature. Three grades of alkyds were formulated at 40% (I)-short alkyd resins, 45% (II)-middle alkyd resin and 55% (III)-long alkyds. The present work deal with the conventional method for the preparation of middle alkyd resin of dehydrated castor oil and linseed oil rosinated medium alkyd resins with 52% solid. The prepared resin was extensively used as a binder in the field of solvent based enamels and paints coating technology.

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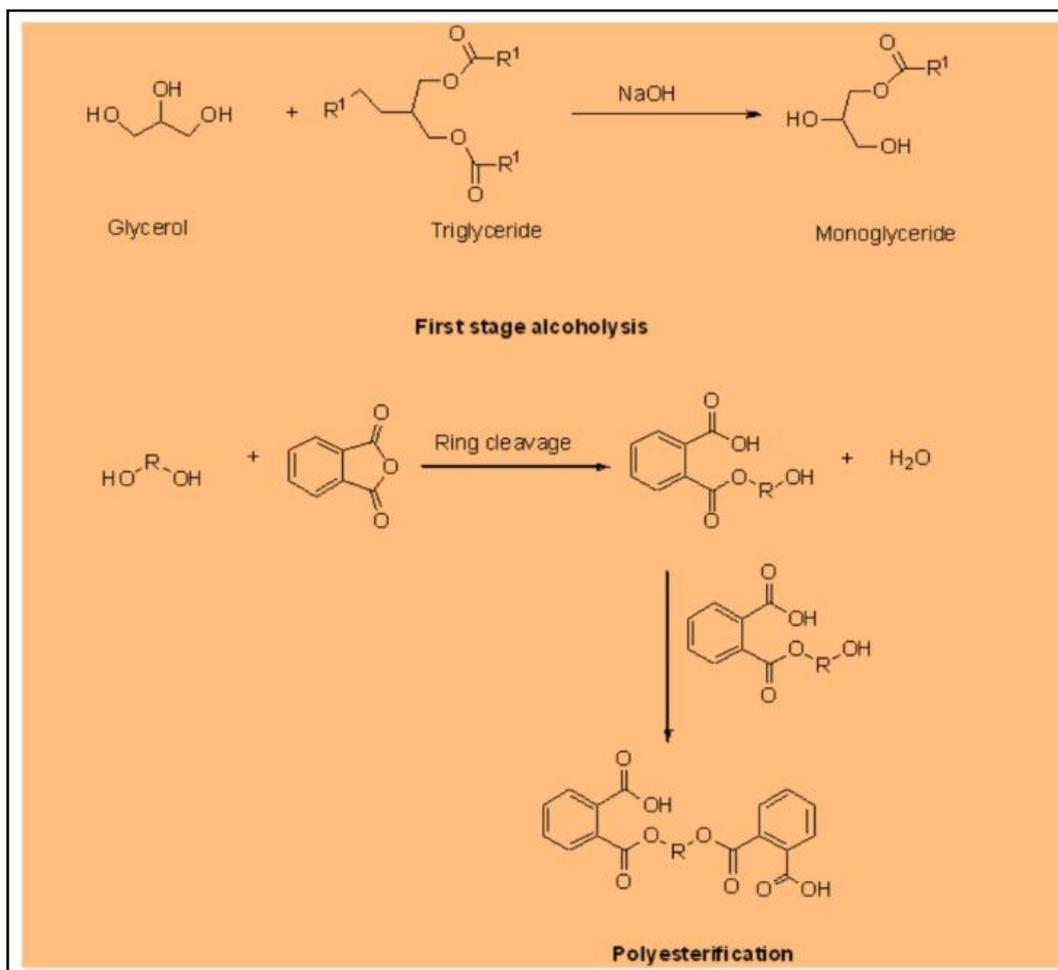
## INTRODUCTION

Vegetable oils have freshly achieved a lot of benefit due to the fact that, they are renewable resources and have high ecological benefits. Vegetable oils such as castor oil, linseed oil, soybean oil, rapeseed, olive, cotton seed and rubber seed are used in chemical industries for the manufacturing of coatings, surfactants, soaps, cosmetic products, lubricants, and paints (Aigbodion, 2011; Can, 2002 and Ramamurthi, 1998). Castor oil is viscous, pale yellow and non-drying oil with a bland taste and one of the low-priced renewable resources for manufacture of eco-friendly resins. Castor oil is achieved from seeds of plant, which belong to the family Euphorbiaceae. Castor oil consisting of triglycerides containing 90% ricinoleic acid (12-hydroxy-9-octadecenoic acid), and 10% non-functional acid residues (Nayak, 2000). Castor oil is also illustrious as of further vegetable oils by its high specific gravity and hydroxyl value. consequently, a lot of research work is being carried out towards the manufacture of vegetable oil based polymeric materials possessing good physical and chemical properties (Alam and Al-Andis, 2013; Li *et al.*, 2000; Nimbalkar and Athawale, 2010). Furthermore, castor oil based polymers are biodegradable, cheap, easy to modify, and easily available in large quantities (Thakur and Karak, 2013). Vegetable oils based biopolymers such as alkyd (Chaudhari, 2013), polyurethane (Sharmin, 2007), epoxy (Ahmad, 2002),

polyester amide (Meshram, 2013) and polyether amide (Alam, 2013 and Alam *et al.*, 2014) are used in the area of paint and coatings. These polymers are biodegradable, less volatile content, environmental friendly, non-toxic, and low-priced materials. Therefore several biopolymers have been prepared using various vegetable oils. Previously, castor oil is mainly used for synthesis of polyester amide, interpenetrating polymer network (IPN), polyurethane, epoxy, are blending with commercial poly methyl methacrylate, polystyrene, polyvinyl alcohol, and so forth (Sharma, 2007). The antimicrobial coating property is undoubtedly main concern for investigators of material science in the world. The nanoparticles in surface coatings can be used to improve gloss, impact resistance, scratch hardness, pencil hardness, and antimicrobial properties (Toker, 2013). Nanoparticle dimensions of less than 100 nm are adequate to reinforce polymer matrix without disturbing the transparency and other properties of the coatings. In the field of surface coatings frequently used nanoparticles are TiO<sub>2</sub>, Ag<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, and others (Behzadnasab, 2011; Yabuki *et al.*, 2011; Dutta and Karak, 2005; Alam and Al-Andis, 2012; Zafar *et al.*, 2004; Knothe *et al.*, 2012). Polymers containing TiO<sub>2</sub> (Nanoparticles) had attracted major attention owing to their executive biocidal properties with their less volatile nature (Guo, 2013; Asiagwu *et al.*, 2008; Aigbodion, 2001; Ogunniyi, 2000; Kildiran, 1996 and Majumder, 1999). Ambiguity in the prospect eases of use and contribution of petroleum products as the major basis of raw materials in diverse manufacturing field (Asiagwu, 2008).

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As a result, there has been an amplified attention in the research and development of renewable resources that would stand out as precious choice. However, in spite of evident reputation of fuel products as raw materials in diverse vicinity of application, fats and oils are being deeply favored for use in surface coatings, soaps, cosmetics, pharmaceuticals, lubricants, surfactants and polymer processing. Their broad receipt in these fields of application is characteristic to their being renewable resources, sustainability, biodegradability and environmental friendliness which are becoming more significant considerations, in recent times due to the imperative ecological confront of weather change and global warming. This expansion has given rise to a number of studies on the superiority and applications of enormous quantity of African seed oils. It has also prompted the insist for more oils desirable to expand the present provisions in the oleo-chemical industry (Moshkin, 1986). The oils used by chemical production as raw materials for manufacture can be gained from plants, animals and from marine life. Although most oils are obtained from plants (60%), a considerable amount (36%) arrived as of animal resource and the rest (4%) from marine life. Examples of animal fats and oils are unsown, fat, grease and cod liver oil (Asiagwu, 2008). These animals and marine fats and oils are used broadly in production. Therefore, development of chemical industries has encouraged a simultaneous growth of the use of fats and oils as raw materials and also as intermediate for supply of new chemicals. Alkyd resin is one of such products from oils used widely in industry. Alkyd resins are any large group of thermoplastic resins that are fundamentally polyester products produced from the polymeric condensation of polyhydric alcohol, polybasic acid and monobasic fatty acids.

They are one of the major raw materials used in the formulation of exterior varnishes. Even though additional plane varnish materials like latex resins and powder coatings were more freshly revealed; alkyd resins still remain a foundation for a number of applications due to their poise of economy and performance. It has been reported that alkyd resins donate about 70% to the conventional binder used in varnish manufacturing today. They donate to varnish elasticity, adhesion, constancy and luster. The reputation of alkyd resins as automobile for coating is mainly owing to their exclusive property such as layer stiffness, stability luster and polish retention, confrontation to scratch, etc. impacted on them through alteration with drying oil (Aigbodion and Okieimen, 2001). The oils that are frequently engaged for alkyd resin synthesis are linseed, soybean, castor and tall oils (Ogunniyi, 2000; Kildiran *et al.*, 1996 and Majumder, 1999).

These oils are largely bring in to Nigeria for the formulation of coating for metal cans used in packing of beverages, drugs, food, etc. It consequently remains very significant for a look for of an appropriate local alternative to distant resins, which will completely reduce the cost of import ones. Castor plant is a species of blossoming plant in the spurge family; which contains a huge number of plants frequently inhabitant to the tropics (Moshkin, 1987). Castor oil is derivative of the seed of castor plants. They are typically composed of triglyceride molecules (technically called polyesters) which contain a 3-carbon alcohol (glycerol) and three 18-carbons (or 16-carbons) fatty acids. Castor oil is unique among vegetable oils since it is the only marketable cause of a hydroxylated fatty acid (ricinoleic acid). The oil includes around 90% of the fatty acid (Ogunniyi, 2006). Castor oil has been honored as semi-drying

oil and has lubricating and hydraulic properties. Variation of castor oil by mounting the unsaturation resulted in oil with terrific drying property for use in the making of alkyd resin (Spyros, 2004). Its highly conjugated, linoleic properties, which aid rapid cross-linking at prominent temperature make it ideal for use as a close substitute for linseed oil. The use of castor oil as raw materials for exterior varnish function is its aptitude to polymerize or dry subsequent to they have been applied to an exterior to outline rough, adherent, impermeable and scratch confrontation films. The reward established in exterior varnish application encompasses excellent aroma, good drying properties, more uniform polymer structure, and lack of after-yellowing. The desaturated castor oil is non-yellowing oil and so can meet requirements of coating industries (Waters, 1955; Formo, 1966; Kirk, 1974; Mark *et al.*, 1964). Dehydrated castor oil (DCO) has been found to be a sustainable material for alkyd resin synthesis in terms of its accessibility, biodegradability and renewability.

Dehydrated castor oil modified alkyd resin has been manufactured using two criteria; the resin *met all* the technical and industrial standards of durability, small drying time, confrontation to chemical, etc., and *met all* the ecologically relevant standards (Mark *et al.*, 1954; Onukwuli, 2008; Hlaing *et al.*, 2008). The insist for alkyd resins has augmented in excess of the years still have technical information on local production is insufficient. Decisive appraisal of literature point out that the influence catalyst type is basically lacking. Ibanga *et al.* (2013) and Aydin *et al.*, (2004) reported the effect of anhydride type and concentration on the viscosity and film properties of cotton seed oil and sunflower oil respectively. They accomplished that maleic anhydride can substitute phthalic anhydride in alkyd synthesis devoid of compromising those properties that will lead to excellent product. Therefore, a lot of technical and financial profit may be accomplished from the appraisal of the effect of catalyst in the alkyd resin preparation. In this research work, rosinated medium alkyd resin with 52% solid was achieved by using NaOH as a catalyst.

### Composition of fatty acids in castor oil

Castor oil is a source of ricinoleic acid, a monounsaturated, 18-carbon fatty acid. Along with fatty acids, ricinoleic acid is remarkable in that it has a hydroxyl functional group on the 12<sup>th</sup> carbon. This functional group causes ricinoleic acid (and castor oil) to be more polar than most fats. The chemical reactivity of the alcohol group also permits to chemical derivatization that is not achievable with most other seed oils. Because of its ricinoleic acid content, castor oil is a valuable chemical in feedstock, imposing an upper cost than other seed oils.

**Table 2. Linseed oil**

Sl no	Acid name	Percentage composition
1.	Alpha-linoleic acid	47.6
2.	Linoleic acid	23.9
3.	Oleic acid	18.8
4.	Palmitic acid	6.2
5.	Stearic acid	2.4
6.	Eicosenoic acid	-
7.	Palmitoleic acid	-
8.	Arachidic acid	0.6
9.	Others	0.5

## MATERIALS AND METHODS

Dehydrated castor oil and the linseed oil are received from Shakthi Retail stores, Phthalic anhydride, maleic anhydride were received from SRL India, pentaerithritol received from Loba Chemie India, Xylene received from Mangalore Refineries, mineral turpentine oil received from BPCL India, Glycerin received from Loba chemie India, NaOH, sodium thiosulphate, phenolphthalein and starch solution were received from Merck and used as received except the DCO and linseed oil. DCO and linseed oil were used only after the calculation of the test of unsaturation by calculating the Iodine value. For DCO Iodine number is 85-90 and for linseed oil iodine number is 175-180 then both the oils were used for the preparation of resin. The viscosity test was carried out by Ford Cup Viscosity method or Zhen cup viscosity method. Acid value was determined by titrimetry, the prepared resin was characterized by its non volatile nature, drying time by cross cut adhesion method and the color analysis was done by Lovi bond scale.

### Instrumentation

The preparation of rosinated medium alkyd resin was carried out in a glass reactor. It consists of two components; lower part of the reactor is a round bottom vessel with very ample mouth. The Flask capacity is about 2 to 2.5 dm<sup>3</sup>. The superior portion of the reactor is its lid; contain four open necks with standard joints. A motor driven agitator was put in the reactor through the middle neck, whereas one more neck was used for thermometer. A condenser was fitted with the reactor through the third neck and the fourth neck was used for sinking the chemicals in to the reactor. The reactor was heated by an electric heating mantle having unique display to control the temperature of the reactor. The speed of the stirrer was controlled by a regulator. The reaction vessel and its lid were tied jointly with the help of clamps.

### Stoichiometric Calculation for individual ingredients in rosinated medium alkyds

The functional groups (-OH and -COOH) present in the reactants of the batch of 100 gms, can be calculated as follows:

#### Calculation for -OH groups

##### Glycerol

Mol. Wt. of Glycerol = 92.12

One mole Glycerol contains 3 - OH groups.

No. of - OH groups in 286.8 Gms. Of glycerol =  $\frac{3 \times 286.8}{92.12}$

= 9.3399

**Table 1. Percentage composition of fatty acids in castor oil and linseed oil Castor oil**

Sl no	Acid name	Percentage composition
1.	Ricinoleic acid	84-89
2.	Oleic acid	2-7
3.	Linoleic acid	1-4
4.	-Linolenic acid	0.5-1
5.	Stearic acid	0.5-1
6.	Palmitic acid	0.5-1
7.	Dihydroxy steric acid	0.3-0.5
8.	others	0.2-0.6

### Pentaerithritol

Molecular weight of pentaerithritol=136.15

One mole of pentaerithritol contains 4-OH groups.

$$\text{No of -OH groups in 41.85 grams of pentaerithritol} = \frac{4 \times 41.85}{136.15} = 1.22$$

### Calculation for -COOH group

#### Rosin

$$\text{Mol. Wt. of Rosin} = \frac{56100}{\text{Acid value}}$$

Acid value of Rosin is 166.5

$$\text{Mol. Wt. of Rosin} = \frac{56100}{166.5} = 336.93$$

One mole Rosin contains one - COOH group

$$\text{No. of - COOH group in 31.5 gems. of Rosin} = \frac{1 \times 31.5}{336.9} = 0.093.$$

#### In Maleic anhydride

Mol. Wt. of Maleic anhydride = 98

One mole of Maleic anhydride contains 2 - COOH groups.

No. of - COOH group in 132 Gms of Maleic anhydride

$$= \frac{2 \times 132}{98} = 2.69$$

#### In phthalic anhydride

Mol. Wt. of Phthalic anhydride = 148

One mole of Phthalic anhydride contains 2 - COOH groups.

$$\text{No. of - COOH group in 52.5 Gms of phthalic anhydride} = \frac{2 \times 52.5}{148} = 0.7094$$

### Reaction programming

**Table 3. Reagents table for the preparation of rosinated middle alkyd resin**

Sl no	Symbol	Raw materials	Quantity in grams	Weight (%)
1.	A1	Castor oil (DCO)	195	39.01
2.	A2	Linseed oil	35	7.0
3.	A3	glycerin	9.35	1.87
4.	A4	pentaerithritol	41.85	8.37
5.	A5	NaOH	0.25	0.05
6.	A6	Water	0.25	0.05
7.	A7	glycerin	1.5	0.3
8.	A8	Rosin	31.5	6.3
9.	A9	Phthalic anhydride	52.5	10.3
10.	A10	Maleic anhydride	132.0	26.35
11.	A11	Mineral turpentine oil	---	---
12.	A12	Xylene	---	---

**Experimental:** To the 4 necked reaction vessel charge the linseed and castor oil at room temperature, refluxed both the oils frequently till it reaches 100°C, at this stage pentaerithritol was added, then heated the reaction mixture to 200°C, NaOH

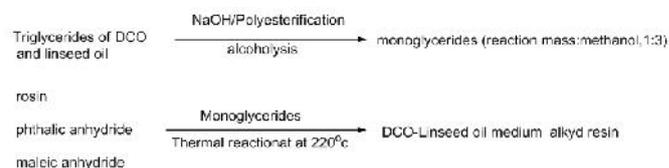
solution as a catalyst properly mixed with the glycerin solution was added to the reaction mixture to get the clear solution. Then the temperature was raised to 260°C. At this stage monoglyceride test was carried out by taking the 1: 3 ratio of reaction mass and methanol in a test tube mix it well appearance of clear solution indicates that the completion of monoglyceride formation, if clear solution not appears, then 0.1% of NaOH solution was added till the clear solution appears) then the clear solution was mixed with the glycerin, hold it for cooling to 150°C. Then rosin, Phthalic anhydride, Glycerin and Maleic anhydride were added together, with all these ingredients; 4% xylene solution was added and the reaction mass was again heated to 180°C water off reaction was carried out to recycle the xylene, water comes as a byproduct from the polyesterification to carry the xylene. Sampling was started only after carried out the acid value and viscosity test. If the acid value drop to 10.5 and the viscosity was elevated to 120. If the viscosity cannot build up then temperature was increased to 220°C. After the reaction mass reaches the viscosity value as 120 then it was thinned with mineral turpentine oil, to avoid the bubbling, the reaction mass was cooled to 190°C then thinning was get started and the turpentine oil was properly mixed for one hour. Then the reaction mass was transferred to blender containing the mineral turpentine oil thinned to 40% solvent and 52 % reaction mass was mixing for two hours. Final composition of the resin was: 52% solid, with 40% control. The overall reaction time to complete the process is 26-30 hours to achieve the DCO-linseed rosinated medium alkyd resin.

### Preliminary test for the prepared resin

**Driers:** Lead-out, manganese, cobalt octoate, calcium out are used as driers.

**Lovi bond for checking the colors;** the prepared resin was showing color at 10 in Lovi bond scale.

**Drying time:** After the completion of the reaction the drying time is very important. After keeping the reaction mass for one day cross cut adhesion method was carried out. The adhesion panel was applied 4 vertical and 4 horizontal lines sliced with 1mm gap. Then removed it with cellophane tape. If we take away the tape then it won't come, then the resin was treated as completely dried.



### Experimental calculations

Mineral turpentine oil=40%

Resin composition=52%

Total percentage for the preparation of medium alkyd resin=100X52 =10.85%

48

Viscosity of the resin was calculated at 52% and control at 40%

**Ford cup viscosity method:** The Ford viscosity cup is a simple gravity device that permits the known volume of the

liquid passing through an orifice located at the base. Under ideal conditions this rate of flow would be proportional to the kinematic viscosity (expressed in stokes and anti stokes) that is dependent upon the specific gravity of the draining liquid. However the conditions in a simple flow cup are seldom ideal for making true measurements of viscosity. It is important when we are using a Ford Viscosity and when re examination of the liquids that the temperature of the cup and the liquid is maintained, as the ambient temperature makes a makeable change in the viscosity and flow rate of the liquid.

The flow rate of the resin is 180 seconds at final stage.

**Procedure:** About 135 g of the DCO-linseed resin was taken in the ford cup, the total resin contains a 120 g of resin and 15 g of Mineral turpentine oil with 52% solid and 48% control. 135 g of the resin mixture was filled into the Ford cup and the temperature set for 30<sup>o</sup>c and stop clock was started. If the resin flow takes up to 180 seconds, then the viscosity of the resin was normal (desirable) if the resin flow down within the 180 seconds then the viscosity of the resin was not achieved.

**Acid value:** 1.4 g of the 52% resin was taken in a conical flask and properly mixed with the 50 ml of xylene till the clear solution appears. 0.1N of the alcoholic solution of KOH solution was prepared and titrated against the uniform solution of the xylene and the resin. To the conical flask 5 drops phenolphthalein indicator was added. The alcoholic solution of KOH in the burette was titrated against the Xylene containing resin solution; the titration was carried out till the pale pink color appears. Burette reading was taken and calculated the acid value for the corresponding DCO resin.

Volume consumed during the titration = 1.4 cm<sup>3</sup>  
 Molecular weight of KOH = 56.10  
 Total percent of the resin = 52%  
 Normality of KOH = 0.1

$$\text{Acid value} = \frac{1.4 \times 56.1 \times 0.1}{1.5} = \frac{5.6 \times 100}{52}$$

Acid value = 10.06 mg of KOH per gram of resin

Acid value of the DCO-Linseed oil is 10.06 mg of KOH per gram of resin.

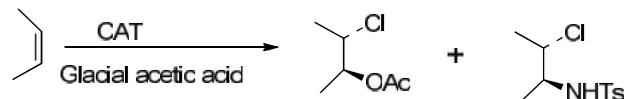
**Iodine value:** The DCO and Linseed oil received for the preparation of the resin containing both the mono unsaturated and poly unsaturated triglycerides, to check the extent of unsaturation in the oil, it is ought to find out the iodine value for the degree of unsaturation. The experimental part is given below.

#### Determination of iodine number of oil using chloramine-T

A simple titrimetric method for the determination of iodine number of oil is described. The method involves the addition of chloramine-T to alkene double bonds in the presence of ethanoic acid, followed by the unreacted chloramine-T by iodimetry.

**Introduction:** determination of iodine number of oils of industrial importance. Although various methods are reported in literature for the determination of the iodine number, two methods are commonly used. During our investigation of the synthetic utility of chloramine-T. It was observed that

chloramines-T serves as an excellent reagent for determination of the degree of unsaturation in an organic compound. This prompted us to devise an operationally simple titrimetric method for the determination of iodine number of oils and is focused in this paper.



The method reported here makes use of the fact that, in the presence of acetic acid, chloramine-T adds on to the alkene to give mainly acetoxy chloro alkane or tosyl amino chloro alkanes involving one mole of chloramine-T per alkene bond. In a typical experiment, a known excess of standard solution of chloramine-T is added to a known amount of oil in a medium of ethanoic acid. After the addition of the reaction is complete, unreacted chloramine-T is determined by titrimetry, by carrying out the blank experiment simultaneously, the amount of chloramine-T consumed is determined. As the overall addition reaction requires one mole of chloramine-T per C=C unit, which is equivalent to one mole of iodine, the iodine number is determined by using the following equations.

One ml of 0.1 mol l<sup>-1</sup> sodium thiosulphate = 12.69 mg of iodine.

$$\text{Iodine number} = \frac{(V_1 - V_2) \times 12.69 \times 100 \times M}{M \times 0.1}$$

Where V<sub>1</sub> = Volume of thiosulphate solution required for the blank.

V<sub>2</sub> = volume of thiosulphate required for the original experiment.

M = Molarity of thiosulphate solution.

m = volume of oil (mg).

#### Experimental

**Reagents:** All reagents used were in analytical reagent grade. Distilled water was used throughout, dehydrated castor oil and linseed oil was used. Chloramine-T reagent in glacial acetic acid was used.

**Procedure:** 1.3g of an oil sample was placed in a clean dry iodine flask. A solution of 10 ml of 0.1 mol l<sup>-1</sup> Chloramine-T in glacial acetic acid was added to it and kept it at room temperature for 2 hours. A blank was prepared by transferring an equal volume of chloramine-T solution into an iodine flask which was allowed to stand for 2 hours under same conditions. After this duration 10% of potassium iodide (10 ml) and water (50ml) and 1 mol l<sup>-1</sup> sulfuric acid (10 ml) was added to each of the flasks, and the liberated iodine was titrated with sodium thiosulphate using starch as an indicator. From the difference in volumes of sodium thiosulphate solution consumed, the iodine number was calculated. The same procedure was followed for the linseed oil.

S.No.	1 (blank in cm <sup>3</sup> )	2 (For oil solution in cm <sup>3</sup> )
Initial burette reading	0.00	50
Final burette reading	50	41
Volume of the sodium thiosulphate consumed	50	9

The difference between the blank and the resin solution is 9 cm<sup>3</sup>

The iodine value is calculated as follows =  $\frac{9 \times 12.69 \times 0.1}{1.3 \times 10}$

Iodine value of the DCO oil=88

Same procedure was applied to determine the iodine value of Linseed oil, Iodine value for the linseed oil is 176.

**Non volatile material method:** Non volatile material method is studied for the volatile nature of the prepared resin.

The circular stainless steel plate or the glass plate with 20 cm diameter was taken and dried it thoroughly and weighed the plate along with the safety pin. Taken about 1.2 g of the resin and was spread over the glass plate homogeneously by safety pin. After completion of the spreading, the glass plate was kept in an oven for one hour by keeping the temperature at 120<sup>o</sup>c. After the taking away, the glass plate was kept for cooling to room temperature and then weighed the glass plate. The difference between the empty glass plate and the glass plate with the dried resin was taken for calculating the non volatile material test.

1. Weight of the empty glass plate with the pin = 26.5g
2. Weight of the glass plate with resin after kept it for oven = 27.13g
3. The weight of the resin = 0.055g

$$\text{Non volatile material} = \frac{0.63 \times 100}{1.2}$$

Non volatile material for 52% resin = 52.5%

### Preparation of enamel paint

Enamel paint was prepared using medium oil alkyd resin and evaluated for their physico-chemical and film properties.

**Composition:** The composition of the enamel paint, to be prepared, was selected in such a way that the paint would contain 27.80% of TiO<sub>2</sub> pigment, 2.78% of ZnO pigment, 0.36 % phthalocyanine blue pigment and 25.20 % of alkyd resin. The paint would have the viscosity of About 180 seconds.

**Procedure:** The preparations of the enamel paint of the above said compositions were carried in three steps.

**First step:** Preparation of alkyd resin solution of viscosity 60 seconds. A known amount of solid alkyd resin was taken in a beaker and was diluted with required quantity of solvent (a mixture of xylene and butanol in a ratio of 9:1) to get the viscosity of 60 seconds. Total weight of alkyd resin solution, obtained, was noted.

**Second Step:** Preparation of paste.

50 Gms of Titanium dioxide pigment, 5 gms of Zinc oxide pigment, 0.72gms Of phthalocyanine blue were taken in a beaker. About 90 Gms of alkyd resin solution of viscosity 60 seconds (prepared during initial step) was mixed with the pigments. They were then passed through triple roll mill to get desired fineness of grind. A thick light blue paste was obtained.

**Third step:** Dilution of paste.

The viscous paste, thus obtained, was tested for its viscosity. It was diluted with solvent to reduce the viscosity to 60 seconds.

The total quantity of paint, thus prepared, was weighed. The enamel paint thus prepared will have viscosity of 60 seconds and the weight percentage of TiO<sub>2</sub>, ZnO and phthalocyanine blue will be 27 %, 2.7% and 0.36 % respectively. Its resistance to water, acid, alkali, detergent and solvent.

## RESULTS AND DISCUSSION

In general, the reported compositions of short oil alkyds have an oil percentage of 25 to 35. If we try to reduce the content oil below this level the control of reaction is lost and there is heavy tendency of gelation of alkyd formulation. If we make use of chain stoppers like Benzoic Acid or Rosin, perhaps the proper control of the reaction can be achieved. Table-3 gives the composition of medium oil alkyd using DCO-Linseed oil. Rosin is having bulky structure with molecular weight of 300. This is bulkier molecule therefore it will arrest and regulate the growth of polymer. About 5% of Benzoic acid is known to control and to regulate the fast polymerization reaction. There are several distinct advantages in this reaction. First of all, the total time of heating is very less. It is just about 4 to 5 hours. Normally a standard alkyd cook required 12 to 16 hours for cooking therefore there is definite saving of time and energy. Highest temperature required in this process is 220<sup>o</sup>c. normally while making use of D.C.O. in alkyd we have to cross the temperature of 270<sup>o</sup>c. The energy required, fuel cost, color and quality of resin demand that the highest temperature should not go above 220<sup>o</sup>c.

The analysis of this medium oil alkyd is given in table 3. The viscosity of composition is quite high. Drying time is quite satisfactory. The surface dry time is only 15 minutes, which is remarkable property of this composition. Synthetic enamel paint was prepared based on this alkyd using TiO<sub>2</sub>, ZnO as a pigment. The sample has high hiding power. The viscosity is quite satisfactory for application by spray or brush. The hiding power of paint is excellent i.e.14 to 15 square meters per liter. The adhesion of paint sample is also excellent. The surface dry time is very less it is just 15 minutes while hard dry time is 6 hours. Scratch hardness of the paint sample is above 1000 grams. The resistance to water, 3% sulphuric acid for 48 hours is excellent while resistance to all detergent and 3 % sodium hydroxide is poor. Finally, the resistance of paint sample for all the solvents is excellent. In general, the resistance of paint samples to solvents, 3% detergent, 3% alkali and water is excellent. Resistance in water is good even after 7 days. The only defective part is poor resistance for 3% H<sub>2</sub>SO<sub>4</sub>.

### Conclusion

The resin prepared from the DCO-linseed oil was comes under the medium alkyd resin and it was further used in the application of paint technology for solvent based paints as a binders. The present work includes both the preparative part for the synthesis of the medium alkyd resins and further it was applied in the field of paints and coating technology and also in making polymer thin films by doping it with the graphenes and the metal nano composites.

- Normally, medium oil alkyd contains 45 to 55% oil in the final composition. Here we have made an attempt to prepare alkyd with medium oil length. The oil has been kept medium (30 to 40 %). Normally sample gel at such a medium percentage of oil. However by making using of chain plugs, we control reaction in feasible choice.

- Thus the chain stopper such as rosin is used to control reaction. Phthalic anhydride is used as major acid ingredient. The polyol used is glycerol.
- The major advantage is saving of time in cooking of batch. Usually the alkyd batch required cooking schedule of 12 to 16 hours. While here the complete schedule is of 8 to 10 hours. Thus using this composition we can increase the capacity of the plant. Thus overall efficiency of process can be improved.
- In D.C.O. rosinated alkyd for dehydration stage we have to increase temperature 275°C. Thus higher temperature in the range of 270 to 280°C is required. Here in present work, the highest temperature required is 220°C. usually we work in lower temperature of 180 to 190°C. From the view point of controlling reaction, the lower cooking temperature is attractive feature. The energy consumption is also reduced. Looking to the high prices of fuel and electricity, a lower temperature is positively prudent and beneficial.
- Useful emulsion paste based on alkyd has been prepared. In the composition emulsion paste distilled water to the extent of 33 to 56 % can be incorporated. The solvent used in paste is smaller quantity of isopropanol, pine oil and moderate quantity of xylene and butanol. Small amount ammonia has been incorporated for the residual acidity of alkyd. A small quantity of P.V.A. 1 to 3 % has been incorporated to improve the homogeneity, adhesion and other film properties of paints. A small quantity of commercial homogenizer 1 to 2 % has been used in emulsion paste. This paste has low acid value and contains 40 to 50 % non-volatile.
- The paste has stability of more than three month. A small quantity of sodium penta chloro phenol has been incorporated to improve stability. In general, excellent paint composition can be prepared by using 20 to 60 % paste.
- The paint compositions have excellent physicochemical properties. The fineness of grind, specific gravity, hiding and viscosity is comparable to commercial sample.
- Resistance of film to water even for 7 days is excellent. Many formulations have excellent resistance to detergent and solvent. Acid and alkali resistance needs improvement.
- Most important and attractive feature of this work is thinning paint with organic solvent as well as water. Thus addition of 10 % of organic and 10% of water will not adversely affect consistency of paint.
- Pilot Plant trials and commercial marketing of these products should be undertaken to prove these experimental results.

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### REFERENCES

- Ahmad, S., Ashraf, S. M., Sharmin, E., Zafar, F. and Hasnat. A. 2002. Studies on ambient cured polyurethane modified epoxy coatings synthesized from sustainable resource, *Progress in Crystal Growth and Characterization of Materials*, vol. 45, no. 1-2, pp. 83–88.
- Aigbodion, A.I. and Okieimen, F.E. 2001. An Investigation on the Utilization of African Locust Bean Seed Oil in the Preparation of Alkyd Resins. *Industrial Crop and Products*, 13, 29-34.
- Aigbodion, A.I., Pillai, C. K. S., Bakare, I.O. and L.E. Yahaya. 2011. Synthesis, Characterisation and evaluation of heated rubber seed oil and rubber seed oil-modified alkyd resins as binders in surface coatings, *Indian Journal of Chemical Technology*, vol. 8, no. 5, pp. 378–384.
- Alam M. and Al-Andis, N. M. 2013. Synthesis and characterization of poly(etherfattyamide) coatings from non edible seed oil, *Pigment and Resin Technology*, vol. 42, no. 3, pp. 195–201.
- Alam, M. and N. Al-Aandis. 2012. Synthesis and characterization of poly(styrene-co-maleic anhydride) modified pyridine polyesteramide coating from sustainable resource, *Pigment & Resin Technology*, vol. 41, no. 1, pp. 20–24.
- Alam, M., Akram, D., E. Sharmin, F. Zafar, and S. Ahmad. 2014. Vegetable oil based eco-friendly coating materials: a review article, *Arabian Journal of Chemistry*, vol. 7, no. 4, pp. 469–479.
- Asiagwu, A.K., Omuku, P.E., Okoye, P.A.C., Olisa, M.A. and Ajiwe, V.C.E. 2008. Evaluation of the Suitability of Conophor Oil for the Production of Alkyd Resins and Surface Coatings. *Oriental Journal of Chemistry*, 24, 405-408.
- Aydin, S., Akcay, H., Ozkan, E., Guner, S. and Erciyes, T. 2004. The Effects of Anhydride Type and Amount on Viscosity and Film Properties of Alkyd Resin. *Progress in Organ Coating*, 51, 273-279.
- Behzadnasab, M. S. M. Mirabedini, K. Kabiri, and S. Jamali. 2011. Corrosion performance of epoxy coatings containing silane treated ZrO<sub>2</sub> nanoparticles on mild steel in 3.5% NaCl solution, *Corrosion Science*, vol. 53, no. 1, pp. 89–98.
- Can, E., S. K'usefoglul, and R. P.Wool. 2002. Rigid thermosetting liquid molding resins from renewable resources. II. Copolymers of soybean oil monoglyceride maleates with neopentyl glycol and bisphenol A maleates, *Journal of Applied Polymer Science*, vol. 83, no. 5, pp.972–980.
- Chaudhari, A., Gite, V., Rajput, S., Mahulikar, P. and Kulkarni, R. 2013. Development of eco-friendly polyurethane coatings based on neem oil polyetheramide, *Industrial Crops and Products*, vol.50, pp. 550–556.
- Dutta, S. and N. Karak. 2005. Synthesis, characterization of poly(urethane amide) resins from Nahar seed oil for surface coating applications, *Progress in Organic Coatings*, vol. 53, no. 2, pp.147–152.
- E.S. and Frilette, V.J.1954. Resins, Rubbers, Plastics Yearbook. *Interscience Publishers*, a Division of John Wiley and Sons, Inc., New York.
- Formo, M.W., et al. 1965. Bailey's Industrial Fats and Oils Products. Vol. 1. 4th Edition. *John Wiley and Sons, Inc., New York*.
- Guo, L., W. Yuan, Z. Lu, and C. M. Li. 2013. Polymer/nanosilver composite coatings for antibacterial applications, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 439, pp. 69–83.
- Hlaing, N.N. and Mya, O. 2008. Manufacture of Alkyd Resin from Castor Oil. *World Academy of Science and Engineering and Technology*, 24,115-161.

- Ibanga, O.I. and Edet, W.N. 2013. Influence of Polybasic Acid Type on the Physicochemical and Viscosity Properties of Cotton Seed Oil Alkyd Resins. *International Journal of Engineering and Sciences*, 2, 1-14.
- Kildiran, G., Yucek, S.O. and Turkay, S. 1996. In-Situ Alcoholysis of Soyabean Oil. *Journal of American Oil Chemical Society*, 73, 252-812.
- Kirk, R.F. and Othmer, D.F. 1947. Alkyd Resin: *Encyclopedia of Chemical Technology*. Vol. 9, John Wiley and Sons, Inc., New York.
- Knothe, G., S. C. Cermak, and R. L. Evangelista. 2012. Methyl esters from vegetable oils with hydroxy fatty acids: comparison of lesquerella and castor methyl esters, *Fuel*, vol. 96, pp. 535–540.
- Li, F. D.W.Marks, R. C. Larock, and J.U. Otaigbe. 2000. Fish oil thermosetting polymers: synthesis, structure, properties and their relationships, *Polymer*, vol. 41, no. 22, pp. 7925–7939.
- Majumder, S., Kumar, D. and Nirvan, Y.P.S. 1999. Acrylate Grafted Dehydrated Castor Oil Alkyd. A Binder for Exterior Paints. *Paint India*, 60, 57-65.
- Mark, H.F. 1964. Alkyd Resin: *Encyclopedia of Polymer Science and Technology*. Vol. 1, Interscience Publishers, a Division of John Wiley and Sons, Inc., New York.
- Meshram, P.D., R.G. Puri, A. L. Patil, and V.V.Gite. 2013. Synthesis and characterization of modified cotton seed oil based Polyesteramide for coating applications, *Progress in Organic Coatings*, vol. 76, no. 9, pp. 1144–1150.
- Moshkin, V.A. 1986. *Castor Amerind*, New Delhi,
- Nayak, P.L. 2000. Natural oil-based polymers: opportunities and challenges, *Journal of Macromolecular Science Part C: Polymer Reviews*, vol. 40, no. 1, pp. 1–21.
- Nimbalkar, R. V. and Athawale, V. D. 2010. Synthesis and characterization of canola oil alkyd resins based on novel acrylic monomer (ATBS), *Journal of the American Oil Chemists Society*, vol. 87, no. 8, pp. 947–954.
- Ogunniyi, D.S. and Njikang, G.N. 2000. Preparation and Evaluation of Alkyd Resins from Castor Oil. *Pakistan Journal of Scientific and Industrial Research*, 42, 378-380.
- Ogunniyi, D.S. 2006. Castor Oil: A Vital Industrial Raw Material. *Bioresource Technology*, 97, 1086-1091.
- Onukwuli, O.D. and Igbokwe, P.K. 2008. Production and Characterization of Castor Oil-Modified Alkyd Resins. *Journal of Engineering and Applied Science*, 2, 161-165.
- Ramamurthi, S. Manohar, V. and Mani, V. V. S. 1998. Characterization of fatty acid isomers in dehydrated castor oil by gas chromatography and gas chromatography-mass spectrometry techniques, *Journal of the American Oil Chemists' Society*, vol. 75, no. 10, pp. 1297–1303.
- Sharma, H.O., M. Alam, U. Riaz, S. Ahmad, and S. M. Ashraf. 2007. Miscibility studies of polyesteramides of linseed oil and dehydrated castor oil with poly(vinyl alcohol), *International Journal of Polymeric Materials and Polymeric Biomaterials*, vol. 56, no. 4, pp. 437–451.
- Sharmin, E., S. M. Ashraf, and S. Ahmad. 2007. Synthesis, characterization, antibacterial and corrosion protective properties of epoxies, epoxy-polyols and epoxy-polyurethane coatings from linseed and Pongamia glabra seed oils, *International Journal of Biological Macromolecules*, vol. 40, no. 5, pp. 407–422.
- Spyros, A.J. 2004. Characterization of Unsaturated Polyester and Alkyd Resins Using One- and Two-Dimensional NMR Spectroscopy, *Journal of Applied Polymer Science*, 88, 1881-1888.
- Thakur, S. and N. Karak, 2013. Castor oil-based hyperbranched polyurethanes as advanced surface coating materials, *Progress in Organic Coatings*, vol. 76, no. 1, pp. 157–164.
- Toker, R. D., N. Kayaman-Apohan, and M. V. Kahraman. 2013. UV curable nano-silver containing polyurethane based organicoorganic hybrid coatings, *Progress in Organic Coatings*, vol. 76, no. 9, pp. 1243–1250.
- Waters, R.T. 1955. Resins-Synthetic, Alkyd Resins, Section 2. Wyman and Sons, Ltd., London.
- Yabuki, A. Urushihara, W. Kinugasa, J. and Sugano. K. 2011. Self healing properties of TiO<sub>2</sub> particle-polymer composite coatings for protection of aluminum alloys against corrosion in seawater, *Materials and Corrosion*, vol. 62, no. 10, pp. 907–912.
- Zafar, F., E. Sharmin, S. M. Ashraf, and S. Ahmad. 2004. Studies on poly (styrene-co-maleic anhydride)-modified polyesteramide -based anticorrosive coatings synthesized from a sustainable resource, *Journal of Applied Polymer Science*, vol. 92, no. 4, pp. 2538–2544.

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