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Research Article

## Preparation of mineral soybean oil middle alkyd resins for the precursors for enamel paint

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**Abstract:** Alcoholysis-polyesterification method was used in the investigation of utilization of soybean oil in the formulation of alkyd resins. The extracted oil with the iodine number 126-130 was applied in the preparation of middle alkyd resins and the physicochemical characterization indicated it is semi-drying in nature with iodine value of 126.9 g I<sub>2</sub> 100 g<sup>-1</sup>. The fatty acid analysis of the oil carried out earlier revealed linoleic and linolenic as dominant fatty acids, having values of 72.1 and 10.3% respectively. 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 soybean oil.

**Keywords:** alkyd resins, alcoholysis-polyesterification, soybean oil, Phthalic anhydride, Viscosity.

### 1. INTRODUCTION

Polymerization is one of the most important industrial process. Resins and emulsion are two main divisions of polymer. Alkyd resins are by far the most significant class of coating resins. It is estimated that alkyd resins donate about 70% to the conventional binders used in exterior varnish at present. The

fame of alkyd resins as medium for coatings is mainly owing to their distinctive properties such as film hardness, durability, gloss and gloss retention, confrontation to abrasion, etc. based on them through modification with drying oil<sup>1</sup>.

The industrial finishes include primers and top coats for refrigerators, furniture and electrical equipment. In view of the development of these articles and segments, the positive growth is expected for paint industry<sup>2</sup>. Further the paint industry foresees a prospect development in view of progress in Automobile Industry, utility in Nuclear Power Station, development in Corrosion Resistant Coatings, expansion in housing activity and other industry uses. The insistence of alkyd resin being a component in Paint, Varnish and Printing ink industry would be linked with the Paint industry. There are many noteworthy attempts that have been prepared to boost alkyd resin production. Many researchers have attempted to search the different sources for alkyd resin preparation. Airegumen I Aigbodon *et al.*<sup>3</sup> studied enhancing the quality of alkyd resins using methyl esters of rubber seed oil in 2004.

A lot of alkyd resins were brought into Myanmar Paint industries every year. In order to save foreign currency outflow, it is needed to produce alkyd resin in Myanmar. The oils that are majorely employed for alkyd resin synthesis are linseed oil, soybean oil, dehydrated castor oil, fish oil and tall oil. Myanmar being rich in aquatic and terrestrial resources, every state and division is pursuing the target of putting 500,000 acres under physic nut (castor oil) in three years. Rural development tasks are included in the national development endeavors that are being carried out by the Nation target. Castor oil is useful directly in protective coatings as a plasticizer in alkyd systems, and blown castor oil is an important nitrocellulose plasticizer. In commercial manufacture of dehydrated castor oil, the aim is to produce the most valuable material used as a drying oil. By far the most important coatings use of castor oil is in the form of dehydrated castor. Dehydrated castor oil is now recognized as an individual drying oil with its own characteristic properties and advantages. The drying oils owe their value as raw materials for decorative and protective coatings to their ability to polymerize or “dry” after they have been applied to a surface to form tough, adherent, impervious, and abrasion resistance films. The advantages claimed in surface coating applications include excellent odor and heat bleachability, good drying properties, more uniform polymer structure, and lack of after-yellowing. The dehydrated castor oil is non-yellowing oil and so this can give requirements of coating industries<sup>2,4-7</sup>. Product of polyhydric alcohol and poly – functional acids modified by fatty acid or their triglyceride. Igwe and Ogbobe<sup>8,9</sup> describe it as polyesters modified with unsaturated fatty acids. Aigbodon and Pillai<sup>10</sup> define it as products of condensation between polyol, usually having an average functionality equal to or greater than 3 and a polybasic acid, usually dibasic acid or its anhydride modified with monofunctional acids, most commonly C18 fatty acid or triglyceride. Alkyd resins as products of polycondensation reaction between polybasic acids and polyhydric alcohol modified with fatty acid or drying oil is the definition given by Ikhuoria<sup>11</sup>.

Acids with more than one replaceable hydrogen atoms are called polybasic acids. Polyfunctional acids used in alkyd resins preparation include phthalic anhydride (PA), glutaric anhydride (GA), Maleic anhydride (MA), and succinic anhydride (SAN)<sup>12,13</sup>.

Alkyd resins constitute a very high proportion of conventional binders used in the coating industry. It has become an indispensable raw material used for the production of industrial and household finishes<sup>14</sup>. Alkyd resins have acquired a good reputation because of their economy, availability of raw materials and ease of application<sup>15, 16</sup>. Additionally, they are to a greater extent biologically degradable polymer because of the oil and glycerol parts, and they are eco-friendly compared to petroleum-based polymers that constitute environmental pollution and degradation. Other unique properties of alkyd resins that make it

an indispensable raw material in surface coating industry include: gloss and gloss retention, film flexibility and durability, good adhesion, and ease of application under variable environmental conditions<sup>17-19</sup>. They are also compatible with other film formers such as acrylic resins to form alkyd hybrid systems that combine the technical benefits of both resins than when used alone.

## 2. COMPOSITION

Per 100g, soybean oil has 16 g of saturated fat, 23 g of monounsaturated fat and 58 g of polyunsaturated fat. The major unsaturated fatty acids in soybean oil triglycerides are the poly unsaturated alpha-linolenic acid (C-18:3), 7-10%, and linoleic acid (C-18:2), 51%; and the monounsaturated oleic acid (C-18:1), 23%. It also contains the saturated fatty acids stearic acid (C-18:0), 4%, and palmitic acid (C-16:0), 10%.

The high-proportion of oxidation-prone linolenic acid is undesirable for some uses, such as cooking oils. Three companies, Monsanto Company, DuPont/Bunge, and Asoyia in 2004 introduced low linolenic Roundup Ready soybeans. Hydrogenation may be used to reduce the unsaturation in linolenic acid. The resulting oil is called hydrogenated soybean oil. If the hydrogenation is only partially complete, the oil may contain small amounts of trans fat.

The alkyds are of three types

(1). Short alkyds (2). Middle alkyds (3). Long alkyds

**Table -1:** Composition of the fatty acids in soybean oil

Vegetable oil	Saturated fatty acids	Mono unsaturated fatty acids	Polyunsaturated fatty acids			Oleic acid	Smoke point
			Total poly	Linolenic acid	Linoleic acid		
Soyabean oil	15.650	22.783	57.740	7	50	24	460°F

**Drying oils:** Soybean oil is one of many drying oils, which means that it will slowly harden (due to free-radical based polymerization) upon exposure to air, forming a flexible, transparent, and water proof solid. Because of this property, it is used in some printing ink and oil paint formulations. However, other oils (such as linseed oil) may be superior for some drying oil applications.

## 3. MATERIALS AND METHODS

vegetable soybean oil received from the Shakthi sugars Tamil Nadu, Phthalic anhydride and maleic anhydride were received from IG Petrochemicals, pentaerythritol received from Prsperstrap China, Xylene received from the Mangalore Refineries, mineral turpentine oil received from the BPCL India, Glycerine received from the 3F Chemicals India, NaOH, sodium thiosulphate, phenolphthalein and starch are received from Merck and used as received except the soybean oil. The soya oil was used only after the calculation of the iodine number. If the iodine number is between the 126-130 then the soya oil was used for the Preparation of resin. The acid value and viscosity values are carried out by Ford viscosity cup and

the test unsaturation was carried out by the Iodine value. The viscosity test was carried out by the traditional ford cup method and the viscosity was fixed to 120 Seconds and the reducing the acid value to 15. The obtained final resin product was characterized Non-volatile nature, color scale analysis by Lovi band and also for drying time on the surface by cross cut adhesion method.

**Table-2:** Ingredients for the preparation of soya alkyd resins:

Sl no	symbol	Raw materials	Quantity (weight in grams)	Weight (%)
1.	A1	Refined soya oil	39.95	39.95
2.	A2	Glycerine	9.76	9.76
3.	A3	pentaerithritol	3.6	3.6
4.	A4	NaOH	2.5	2.5
5.	A5	H <sub>2</sub> O	2.5	2.5
6.	A6	Glycerine	0.49	0.49
7.	A7	glycerine	33.25	33.25
8.	A8	Phthalic anhydride	0.276	0.276
9.	A9	Maleic anhydride	7.8	7.8
10.	A10	Rosin		
11.	S11	xylene		
12.	S12	Mineral turpentine oil		

**3.1.Experimental :**9.76 g of Glycerin and 39.95g of soya oil charging are heated to 100<sup>0</sup>C then added the 3.6 g of pentaerithritol heated to 200<sup>0</sup>c then 2.5g added sodium hydroxide as a catalyst mixing it with water, up to saturation then added 0.49g of glycerin at temperature of 200<sup>0</sup>C then heated up to 260<sup>0</sup>c.

The progress of the reaction was monitored by monoglyceride test by taking the reaction mass and methanol in a ratio of 1:3 if it is appearing transparent (without any precipitation) keep it for cooling up to 150<sup>0</sup>C. Later phthalic anhydride,maleic anhydride and rosin were added as mentioned above in the chart heated up to 180<sup>0</sup>c. When the temperature reaches at 170<sup>0</sup>c the refluxing get started and the reactant molecules undergoes condensation and a water molecule was eliminated and it was carried with the xylene, due to relatively more gravity, water molecule was stored in decanter and the xylene was recycled for the further process, then the reaction was processed or carried out by increasing the temperature consecutively for every 10<sup>0</sup>C per hour till it reaches the 220<sup>0</sup>C. Sampling was started only after carried out the acid value and viscosity test.If the acid value drop to 15 and the viscosity elevated to 120. If the viscosity cannot build up then raised to 220<sup>0</sup>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<sup>0</sup>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 55% solvent and 45 % reaction mass was mixing for two hours. Final report: 45% solid,with 40% control.

**3.2. Driers:**Lead,Calcium,Manganese and Calcium are used as driers.

**3.3. Colour scale:** Lovi band for checking the colours.

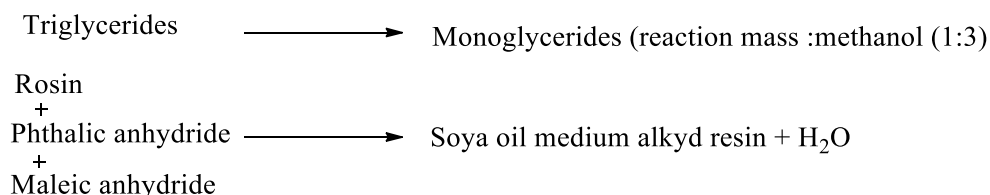
**3.4. Clarity:** looking transparent.

**Pick up:** checking thinner (turpentine oil)

Maturation was carried out after one night. Next day viscosity was checked if it is same, pickups are carried out.

**3.5. Dryingtime:** After the completion of the process the drying time was very significant. After keeping the reaction mass for one day cross cut adhesion test panel applied 4 vertical and 4 horizontal lines cutter with 1mm gap ) Then removed it with cellophane tape. If we remove the tape then it won't come, then the resin was treated as it was completely dried.

### 5.6. First stage:



**Applications of alkyd resins:** Short oil alkyd: acts as a binder for paint powder and coloring agent. Medium and long alkyds: used as enamel, primer distemper and majorly used in staying resins.

### 3.7. Experimental calculations:

Mineral turpentine oil=45% solid  
= 55% liquid

$$\text{Total percent for the preparation of middle alkyd resin are} = \frac{1000 \times 55}{45} = 12.22 \%$$

Viscosity of the resin was calculated at 45% and control at 40%

### 3.9. Ford cup method: Viscosity test:

**Ford viscosity cup:** The Ford viscosity cup is a simple gravity device that permits the timed flow of a known volume of liquid passing through an orifice located at the bottom. Under ideal conditions, this rate of flow would be proportional to the kinematic viscosity (expressed in stokes and centistokes) 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 using a Ford Cup and when retesting liquids that the temperature of the cup and the liquid is maintained, as ambient temperature makes a significant difference to viscosity and thus flow rate.

The overall reaction to complete the process is 26-30 hours to get the mineral soya oil alkyd.

Ford cup method for the calculation of viscosity: Ford cup method is a traditional and conventional method for viscosity measurements during preparation of the soya mid alkyd resin. The method is as follows

The flow rate is 180 seconds

About 13.5g of the alkyd resin is taken in the Ford cup, the total resin contains the 12.0g of the alkyd resin and 1.5 g of the mineral turpentine oil with 45% solid and fixed for 45% control. Filled the 13.5 g of

the resin and the mineral turpentine oil to the Ford cup, set the temperature to 30<sup>0</sup>c and stopcock was started. If the resin flow was takes place up to 180 seconds then the viscosity of the resin was normal, if the resin flow down within the 180 seconds then the viscosity of the solution was not in a normal range for the preparation of the middle alkyd resin for the precursors for the preparation of enamels and solvent based paints.

**3.10. Acid value:** About 1 to 1.2 g of the 45% resin was taken in a conical flask and properly mixed with the 50 ml of xylene till the homogeneous solutions appears. 1N of the alcoholic solution of KOH solution was prepared and titrated against the homogeneous solution of the xylene and the resin. To the conical flask added 5 drops phenolphthalein indicator. The alcoholic solution of KOH in the burette was titrated against the Xylene containing resin solution, the titration was run till the pale pink colour appears. Taken the burette reading and calculated the acid value for the corresponding resin.

Volume consumed during the titration=1.5cm<sup>3</sup>

Molecular weight of KOH=56.10

Total percent of the resin =45%

Normality of KOH=0.1

$$\text{Acid value} = \frac{1.5 \times 56.1 \times 0.1}{1.5} = \frac{5.6 \times 100}{45}$$

Acid value =12.46 mg of KOH per gram of resin

**3.11. Iodine value:** The soybean oil received for the preparation of the resin was containing both the mono unsaturated and poly unsaturated triglycerides, to test the degree of unsaturation in the oil, it is must to determine the iodine value for the degree of unsaturation. The experimental part is as follows.

About 1.2 g of the soybean oil was taken in an 100 standard flask and make to 100 ml by adding the chloroform or carbon tetrachloride as a solvent. 10 ml of the stock solution was pipetted out and poured into the iodine flask 1 and added the 25 ml of wiz solution and closed the stopper tightly. Take another iodine flask 2 added the wiz solution and it is a blank without the aliquot. Keep both the iodine flasks in a dark room for one hour. After completion of one hour about 10ml of the 10% of KI solution was added and flushed it with about 50ml of water for both the iodine solution.

Blank solution is titrated against the 0.1N sodium thiosulphate solution and after the addition of sodium thiosulphate to the mixture it turns to brownish yellow, then added the 5 ml of the starch then the solution turns to yellow then the aliquots are titrated till the yellow turns to dark blue solution further to clear liquid it was the end point of the titration. Taken the burette reading for the blank. The same procedure was followed for the standard resin solution.

Sl no	1(blank in cm <sup>3</sup> )	2 (For resin solution in cm <sup>3</sup> )
Initial burette reading	0.00	50
Final burette reading	50	38.0
Volume of the sodium thiosulphate consumed	50	38.0

The difference between the blank and the resin solution is 12.0 cm<sup>3</sup>

The iodine value is calculated as follows = 
$$\frac{12 \times 12.69 \times 0.1}{1.2 \times 10}$$

Iodine value of the soybean oil =126.9

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

The circular steel plate or the glass plate with 10 diameter was taken and dried it very well and weighed the plate along with the safety pin. Taken about 1.2 g of the resin and was spreaded over the glass plate uniformly by safety pin. After the completion of the spreading the glass plate was kept in an oven for one hour by maintaining the temperature at 120<sup>0</sup>c. After the removal of the glass plate kept it for cool 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

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 =27.05g
3. The weight of the resin =0.055g

$$\text{Non volatile material} = \frac{0.55 \times 100}{1.2}$$

Non volatile material for 45% resin =45.83%

## CONCLUSION

The resin prepared from the soybean oil comes under the middle alkyd resin and it was further used in the application of paint technology for solvent based paints and binders. The present work includes only the preparative part for the synthesis of the middle alkyd resins, further it was applied in the enamel and paint.

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