International Journal of Science and Engineering Applications
Volume 8–Issue 02,64-67, 2019, ISSN:-2319–7560

Synthesis of Coating Resin from Mahua Oil by Using Alcholysis Method

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Abstract: Non-drying oil-modified coating resin having acid value (10.8) was prepared from mahua oil (a non-drying oil), phthalic anhydride and glycerol. Crude mahua oil was obtained by crushing whole or decorticated seed in expeller. The experiment was started with investigating the optimum conditions for neutrilization of the crude oils. Non-drying oil modified coating resin was prepared by using alcoholysis method in excess of glycerol and phthalic anhydride in the presence of 0.1% (wt %) lead II oxide catalyst. Then, the properties (colour, acid number, hardness) of the prepared coating resin were characterized. The chemical resistances of coating resin were also determined.

Keywords: non-drying oil, coating resin, alcoholysis, mahua, neutrilization

1. INTRODUCTION

One of the coating resin or alkyd is today normally used to cover those resins used in the paint and allied industries which are based on phthalic anhydride or some similar acid condensed with a polyalcohol and modified with a drying or non-drying oil, resin acid, etc. The fundamental and most important constituents of surface coating materials, such as oil paints and oleoresinous varnishes that "dry" by the action of oxygen in the air, are the drying oils. These oils are mostly obtained from the vegetable kingdom (renewable resources), where they occur in many fruits (in the seeds), and also from some animal life living in water. The chemical constitutions of all the different oils have very strong similarities, for example they are essentially glycerol triesters of fatty acids containing 18, or about 18, carbon atoms, hence their common name of "triglycerides". It is clear that the difference between various drying oils depend largely on the constituent fatty acids. The industrial value of vegetable oil generally depends of its constituent fatty acids and the ease with which it can be modified or combined with other chemicals. Several physical and chemical modifications of the oil enhance their initial quality have been evolved over the years. Chemical transformation of vegetable oil to fatty acid alkyl esters called transesterification or alcoholysis is one of the methods of modifying the quality of vegetable oils. Raw vegetable oils are composed of glycerol, esters of fatty acids and various amounts of solubilized impurities such as pigments, vitamins, sterols, phospholipids, etc, which may compromise the quality of the finished alkyd or coating resins.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of Raw Material

2.1.1 Collection of Raw Materials

The large amounts of mahua seeds were obtained from the village in Kyaukse Township, Mandalay Division. Laboratory grade phthalic anhydride (PA), glycerol (G) and the required catalysts are also obtained from the local chemical groups.

2.1.2 Preparation of Crude Mahua Oil

The mahua oil was extracted from the kernel of the fruit. The kernels were taken out from the smooth chestnut colored pericarp by being bruised, rubbed and subjected to moderate pressure. They were then ground and the oil obtained by expression or the kernels were pounded and boiled and then wrapped up in two or three-folds of cloth and the oils were there-after expressed.

2.1.3 Neutralization of Crude Mahua Oil

The obtained crude mahua oil contains the variable amount of nonglyceride impurities, principally of free fatty acid. Highly content of free fatty acid (FFA) and impurities preclude some of the undesirable effects. In order to remove free fatty acid and small amount of other impurities, alkali refining or neutralization method was used. These method effects an almost complete removal of free fatty acids, which are converted into oil-insoluble soap.

In the method of removing the fatty acids, the required amount of crude mahua oil with the calculated amount of strong (1N) caustic soda solution were agitated to carefully regulate the temperature of the oil. After completion of neutralization, the temperature of 90 ℃ NaCl solution was added to the mixture to ensure adequate salting or graining out of soap stock. When the mixture was put into the separating funnel at least three hours, the soda solution combined with the free fatty acids to form a soap, which falls to the bottom of the vessel and two different layers were appeared. Then, the lower soap layer was drained out and the neutralized oil was run off from above and washed with hot water. After finishing washing step, the oil was dried at 100 ℃ in oven to evaporate the moisture. Drying and cooling carried out until the weight of dried mahua oil remained unchanged. The refined mahua oil was weighed to know oil loss and their free fatty acid content were determined.

2.2 Preparation of Coating Resin from Mahua Oil

Non-drying oil-modified coating resin was prepared from mahua oil, glycerol (G) and phthalic anhydride (PA) by using PbO catalyst. The preparation was carried out in a four necked bottom flask fitted with a motorized stirrer, a nitrogen inlet and a thermometer pocket and a tap for sampling.

In the production of coating resin, two stages were involved. To prepare the coating resin the calculated amount of raw materials were weighed firstly. The weight of raw materials for coating resin preparation was shown in (Table 1).The coating resin was prepared by using a synthesis of two stages, in which the first one stage is alcoholysis. In the alcoholysis, to be obtained glyceride, the calculated amount of oil was placed to the flask and heated with the agitation speed of (700 rpm) and inert atmosphere (N_2 sparging rate of about 0.06 ft^3/sec) at 230-240 °C. Glycerol and PbO catalyst was added and reaction was carried out at 230-240 °C for 30 minutes intervals. The reaction condition was determined by testing the mixture sample with anhydrous methanol. When the sample dissolved in the anhydrous methanol and gave clear solution, the reaction was complete. After alcoholysis reaction was completed, the reaction mixture was cooled to 140 °C.

In the esterification stage, phthalic anhydride was added to the monoglyceride mixture at 140 °C also with 500 rpm of agitation speed and 0.01 ft^3/sec of inert atmosphere and reheated to 230-240 °C. The samples were taken out every 30 minutes and determined the iodine value of the samples. The reaction was monitored by periodic determination of the acid value of the mixture. When the acid value of sample dropped to nearly 10, the reaction was stopped and the coating resin was obtained.

Table 1. Weight of Raw Materials for Mahua Oil-Modified Coating Resin

Raw Materials	Weight (g)	Weight (%)
Mahua oil	45.63	54.022
Glycerol (G)	22.7487	26.933
Phthalic anhydride (PA)	16.0868	19.045
Total	84.4655	100

The physico-chemical properties of the coating resin samples (color, refractive index, acid value, iodine value) and the chemical resistance of resin film were determined according to the India standard method.

3. RESULTS AND DISCUSSION

3.1 Characteristic of Crude Mahua Oil

The characteristics of crude mahua oils are shown in (Table 2). In this table, although the specific gravity and iodine value of the crude oils were in the range of India standard specification limits. Free fatty acid (FFA) is undesirable in resin formulation. Therefore, neutralization method was used to reduce free fatty acid from the crude oils. In the neutralization of oils, FFA content of oils was converted to oil soluble soaps. Neutralization process can remove some of materials consist of phosphatides, carbohydrates and carbohydrate derivatives, protein fragments and various resinious and mucilaginous materials and the greater part of nonglyceride portions.

Table 2. Characteristic of Crude Mahua Oil

Characteri-stics	Crude mahua oil	Mahua oil (India Standard Specifi-cation)
Free fatty acid	3.00	1.0
Refractive index, 28°C	1.4636	1.459-1.461
Specific gravity, 15°C/15°C	0.917	0.862-0.875
Viscosity, 40°C, stoke	1.48	-
Iodine value, wiji's	58.96	58-70

3.2 Characteristic of Refined Mahua Oil

The characteristics of refined mahua oils are shown in (Table 3). According to this table, the neutralization process can reduce the FFA content of the crude mahua oil from 3.00% to 1.00%. The other properties of the refined oils such as refractive index, specific gravity, viscosity and iodine value were also slightly reduced. The characteristics of refined refined mahua oil were in the range of India Standard Specification. The characteristic of refined mahua oil was suitable for preparation of coating resin.

Table 3. Characteristic of Refined Mahua Oil

Characteri-stics	Refined mahua oil	Mahua oil (India Standard Specifi-cation)
Free fatty acid	1.00	1.0
Refractive index, 28°C	1.4633	1.459-1.461
Specific gravity, 15°C/15°C	0.8885	0.862-0.875
Viscosity, 40°C, stoke	1.16	-
Iodine value, wiji's	61	58-70

3.3 Coating Resin Preparation from Refined Mahua Oil

The first stage alcoholysis reaction condition of resin preparation for mahua oil is described in (Table 4). The percentage of reaction completion for non-drying oil coating resin is presented in (Table 5).

The alcoholysis reaction was carried out with different amount of PbO catalyst of (0.01% and 0.03%) for 3 hours, the sample mixture did not completely soluble in anhydrous methanol. The reaction with the largest percentage (0.1%) of catalyst was complete at the reaction time of 2.5 hours.

In the esterification stage, it was observed that the longer the reaction time, the more viscous the mixture is. In this process, adequate agitation was necessary for complete mixing of mono-glyceride mixture and phthalic anhydride. Unless adequate mixing was supplied in this stage, the un-qualify coating resin would be resulted. So, the N_2 sparging rate was increased in order to remove liberated reaction product and to increase the heat and mass transfer of chemical reaction. The non-drying oil-modified coating resin with acid number of 10.8 was obtained after the esterification reaction was carried out for 150 minutes. It should not try to proceed the reaction after the acid number of coating resin had dropped to 10.8, because the reaction was closed to gel point.

Table 4. First Stage Alcoholysis Reaction Conditions for Coating Resin

Raw oils	Alcoholy-sis catalyst	Weight % of catalyst	React-ion time (hr)	Completing of alcoholysis reaction*
Mahua oil	PbO	0.03	3	Not complete
		0.05	3	Not complete
		0.1	2.5	Complete

*It was determined by testing the solubility of sample mixture in anhydrous methanol

Table 5. Yield of Mahua Oil-Modified Coating Resin

Initial wt (g)	Final wt (g)	Yield (%)	Initial acid value	Final acid value	% of reaction completed (p)
84.47	62.95	74.53	316.15	10.8	96.58 %

AN initial charge = 561000 (0.476)/84.466 = 316.15
P = [(initial acid number – final acid number)/initial acid number] × 100

According to the (Table 4) and (Table 5), degree of completion of the reaction for the mahua oil-modified coating resin was completed at 96.58% when the final acid value of non-drying oil-modified coating resin was 10.8.

3.4 Characteristic of Crude Mahua Oil Modified Coating Resin

The characteristics of coating resins are presented in (Table 6) and the chemical resistances of coating resin are shown in (Table 7).

Table 6. Characteristics of Mahua Oil-Modified Coating Resin

Properties	Mahua oil modified coating resin	Rubber seed oil-modified coating resin
Acid value	10.8	13.8
Iodine value	51.45	71.69
Color	Brown	Brown
Refractive index	1.4664	1.5018
Gouge hardness	HB	HB
Starch hardness	B	B

In (Table 6), there is no common standard to compare coating resins. Each coating resin has its own properties. It was found that acid value of the coating resins was 10.8. The coating resin that has acid number of less than 15 is suitable for application of paint, according to the literature.

Table 7. Chemical Resistance of Mahua Oil-Modified Coating Resin

Resins	Media	Immersion time (hrs)	Appearance of Films*
Mahua Oil-modified coating resin	water	24	Not effect
	3N NaOH	7	Whitening
		15	Blistering
		24	Removal

***** It was examined after the films were air dried for 30 minutes.

The resistance of coating film was determined in two media, distilled water and NaOH solution. According to (Table 7), although the immersion of coating film in water for 18 hours was sufficient time to examine the water resistance, it was found that the mahua oil-modified coating film were no effect after immersion in distilled water for 24 hours. Then, the coating film was immersed in strong alkali solution, 3N NaOH.

The alkali resistance of this coating resin was the immersion time of whitening was 8 hours, blistering time was 16 hours and removal time was 24 hours. Therefore, the above results show that the prepared coating resin has high chemical resistance.

4. CONCLUSION

The characteristic of refined mahua oil was found to be standardized with India Standard Specifications. Therefore, this oil was suitable to carry out the next step. The alcoholysis of mahua oil by also using 0.1% of the PbO_2 catalyst, the reaction completed after 2.5 hours. The mahua oil-modified coating resin was prepared by using alcoholysis method from mahua oil, glycerol and phthalic anhydride with the help of 0.1% PbO catalyst and its acid value was 10.8. The physicochemical properties and high chemical resistance of coating resin showed that the non-drying oil modified coating resin in stoving finish.

5. RECOMMENDATIONS

Recommendations for further research works are outlined as follow.

- Coating resin should be prepared from other non-edable oil (linseed oil, tung oil, rubber seed oil).
- .The reaction of kinetic of coating resin preparation should be explored.
- The synthesized coating resins should be enhanced for better results.

6. ACKNOWLEDGEMENTS

The authors wish to express their gratitude to all teachers, especially their supervisor, for guiding the knowledge, as well as invaluable experiences and other valuable kindness supports.

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