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Development of Suitable Methodology to Synthesize Terephthalic Acid Based Alkyd Resin

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Abstract: **Alkyd resins are oil modified polyesters produced by reacting di-carboxylic acid or it's anhydride with a polyol. Phthalic anhydried is one of the most common di-carboxylic acid used in alkyd resin industry. It is an anhydride of phthalic acid (PA). Phthalic acid is an isomer of terephthalic (TPA) and isophthalic acids (IPA) . Among these three isomers terephthalic acid is water insoluble solid and it gives good water and whether resistance to alkyd based paints. But conventional alkyd making techniques cannot be apply for TPA due to its high stability and reaction temperature compare to the PA.**

Present investigation was aimed to develop new methodology to synthesis alkyd resin from TPA and it was successfully achieved by altering the order of feeding raw materials and increasing the reaction temperature (260-280 °C). At 280 °C temperature 66.5 g soya oil, 25.26 g TPA, 12.9 g glycerol and 1 g Maleic anhydride (MA) produced a long oil alkyd resin with acid value 11.4 mgKOH/g , Hydroxyl value 43.2 mgKOH/g and touch drying time 185 minutes. Total Processing time was 120 minutes.

Keywords: **Terephthalic acid, Alkyd Resin, Alcoholysis, Phthalic Anhydride.**

I. INTRODUCTION

Alkyd resins are more widely used in paint industry because of their low cost and versatility[1]. The term 'alkyd' is derived from its main ingredients alcohols and acids [1]. Theoretically any polyol or polyacid can be used to manufacture alkyd resins. However when considering cost, processabilty and required paint properties only few raw materials found commercially acceptance.

Due to the ease of production, low cost and better resin properties Phthalic anhydride is the most common polyhydric acid used in alkyd industry [2]. Phthalic anhydride is anhydried of orthophthalic acid which has another two isomers called isophthalic acid and terephthalic acid. All three isomers can be used to synthesis alkyd resins. Terephthalic acid is a white powder which is insoluble in water and hence the resins with TPA has good water and whether resistance. But it is rarely used in alkyd industry due to the difficulties faced in synthesis process. Generally phthalic anhydride based alkyd resins are synthesized by alcoholysis process [2].

Alcoholysis is two step process which is most commonly used to produce oil modified alkyd resins. Normally oils are triglycerides [3] and they are not good solvent for polybasic acid or anhydrides. Therefore first step is to convert these triglyceride oils into monoglycerides. This can be done by reacting oil with a part of polyol used in reaction. Then as the second step polyacid and remaining polyol added to the monoglyceride mixture. Both reaction steps are carried out temperature at around 235 - 245 °C [2]. But Terephthalic acid is more stable than PA and isophthalic acid hence not reacted with other alkyd making chemicals at these conditions. Other main disadvantage of alcoholysis method is long processing time. Normally monoglyceride forming step take nearly one hour period and essentially reaction mixture required to cool below 200 °C before adding PA into the reaction mixture. Then esterification (resin making) step taking 3- 5 hrs time period depending on the recipe composition.

Therefore the aim of this research was to find a suitable and less time consuming method to synthesized oil modified alkyd resin with terephthalic acid as a main polybasic acid. Soya oil, Glycerol and pentaerithritol (PE) used as other main raw materials and xylene used as azotropic solvent.

II. EXPERIMENTAL PROCEDURES

A. Recipe formulation and Initial setup:

Initial recipe was formulated with 66.50 g soya oil, 26.9 g TPA and 12.9 g Pentaerythritol. Soya oil bought from local market was tested for it's acid value [4] and saponification number [5].

TABLE 1: TESTED PROPERTIES OF SOYA OIL

Property	Value
Acid Value	3.47 mg KOH/g
Saponification number	193 mg KOH/g

All the reactions were done inside a five neck glass reactor equipped with thermo meter, nitrogen inlet, mechanical stirrer and spiral condenser with dean stark. One neck was kept free to open and close for feeding raw materials. Xylene used as azotropic solvent was fed in to the reactor via dean and stark.

B. Synthesizes of alkyd resin:

Initially, soya oil and terephthalic acid were fed in to the reactor and heated to 260 °C. Reaction mixture was continuously stirred for a one hour period while maintaining Temperature at 260° C. Then the polyol was added to the reactor via free neck. That caused to the higher rate of water emission and control of reaction become uncontrollable. Therefore for the next reactions system (oil & TPA) was first heated to 260° C and just after reaching to the desired temperature polyol was started to add in a uniform rate for a period of one hour. Due to the difficulties of feeding solid polyol continuously to the reactor PE was replaced by glycerol. Experiments were continued until reach the acid value less than 12 or until gelation occurred. Samples were taken at each 30 minutes time intervals to measure the acid values.

Process was repeated for 250 °C and 270°C temperatures. Final acid value, hydroxyl value [6], touch drying time [7], non volatile matter content [8] and bending test were done for each resin samples. Finally recipe was modified by adding 1g Maleic anhydride (MA) to improve the colour, reaction speed and drying properties of the film.

III. RESULTS AND DISCUSSION

Table 2 shows the initial TPA based alkyd recipe formulated for experiment and its breakdown.

TABLE 2: ALKYD RECIPE 1& ITS BREAKDOWN

	Charge			Break Down			
	W (g)	E	e_0	e_a	e_b	F	m_0
Soya Oil	**66.5**	293	0.227	0.227		1	0.227
TPA	**26.9**	83.1	0.324	0.324		2	0.162
PE	**12.9**	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	103.4			0.551	0.607		0.560

One of the most important factor in the alkyd making processes is percentage completion of the reaction at the gel point ($P_{gel\ point}$). If $P_{gel\ point}$ is less than 100%. Gelation occurs before the completion of reaction.

$P_{gel\ point} = m_0/e_a = 0.560/0.552 = 1.015 = 101.4\%$

Acording to the above calculations, theoretical P_{gel} point for recipe 1 $_{is}$ 101.4 %. Which means this recipe can be synthesized in to a alkyd resin safely (theoretically).

Reaction temperatures used in alcoholysis processes are in between 235 °C - 245 °C. But according to the literature TPA is more stable than PA and hence required higher reaction temperature than its other isomers [3]. Therefore for the proposed method initial temperature was selected as 260 °C.

In the first experiment, TPA and soya oil heated together to 260 °C and maintained at that temperature for a one hour period while stirring. Addition of PE was done after the one hour and it cases to evaporation of large amount of water at once. So reaction became uncontrollable and gel partials started to appear inside the reactor. Due to the higher temperature excess loses of PE also occurred.

To avoid above difficulties it was decided to add polyol at continuous rate for a period of time. But addition of PE (which is in the solid form) in the such a manner was became very difficult at this temperature. Therefore glycerol was selected as polyol to make TPA based alkyd resin and new recipe with its breakdown is shown in table 3. Here breakdown part of the table shows two glycerol rows one comes from soya oil.

TABLE 3: ALKYD RECIPE 2 & ITS BREAKDOWN

	Charge			Break Down			
	W (g)	E	e_0	e_a	e_b	F	m_0
Soya Oil	**66.5**	293	0.227	0.227		1	0.227
TPA	**26.9**	83.1	0.324	0.324		2	0.162
Glycerol	**12.9**	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	103.4			0.551	0.607		0.560

Following graph shows the variation of acid value with time for the recipe2.

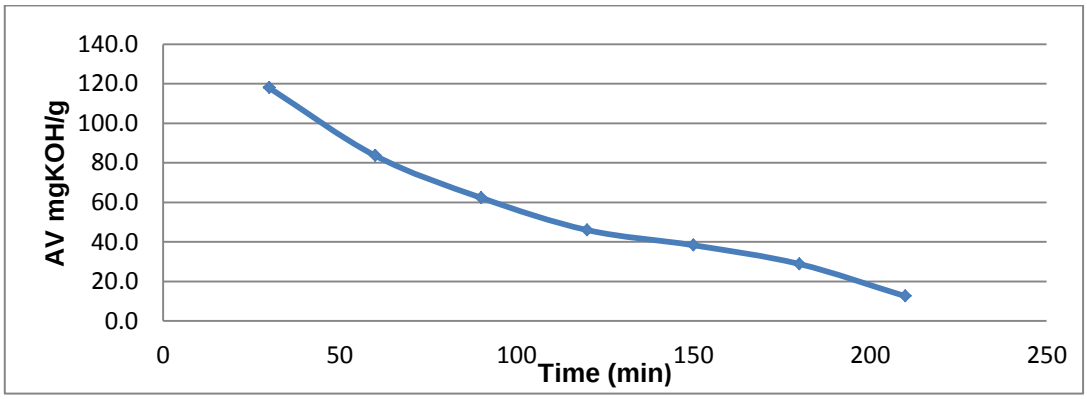

FIGURE 1: TIME VS VARIATION OF ACID VALUE FOR R2 AT 260 °C

Acid value of the reaction mixture reduced to 12.5 within nearly 210 minutes and reaction stops at that point. Colour of the final resin was light yellow and there was no evidence of gel formation. Process was repeated for 250 °C and 270 °C temperatures. Figure 2 shows the comparison of acid value variation at three different temperatures.

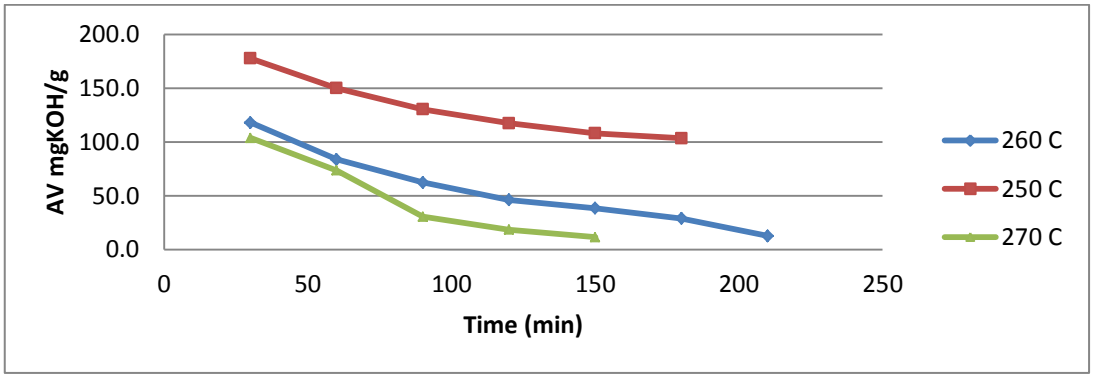

FIGURE 2: COMPARISON OF ACID VALUE VARIATIONS FOR R2 AT DIFFERENT TEMP.

At 270 °C acid value reduced to less than 12 (11.4 mgKOH/g) within 150 minutes time. Resin had good quality and no evidence about formation of gel. But 250 °C gel particles start to appear after about 270 minutes and acid value recorded at that point was 103 mgKOH/g. That results clearly indicated that TPA required higher temperature than 250 °C . Table 4 shows tested properties for produced resins at all three temperatures.

TABLE 4: TESTED PROPERTIES OF ALKYD RESINS PRODUCED FROM RECIPE 2 AT DIFFERENT TEMP.

Temp (°C)	AV (mg KOH/g)	Processing time (min)	HV (mg KOH/g)	Touch Drying time (min)	Bending	Non volatile content (%)	Viscosity (second B4 cup at 1:1 Diluted)	Resin Color	Evidence of Gel formation	Remarks
250	103	180	-	-	-	-	-	Light brown	yes	Reject
260	12.5	210	45	180	<5mm	91.1	82	Light yellow	no	Ok
270	11.4	150	43.1	185	<5mm	87.2	79	Light yellow	no	Ok

According to the results, properties of the resins synthesized at 260 °C and 270 °C are within the commercially acceptable level. That means the proposed method was successful to make TPA based alkyd resins..

Basic difference between the alcoholysis method and proposed new method is an order of feeding raw materials in to the reactor. In the alcoholysis method initial step is formation of monoglyceride by reacting tryglyceride oil with polyol. But in the proposed method oil and terephthalic acid first fed in to the reactor. The second difference is no cooling period in proposed method. Alcoholysis is two step method and has a cooling period between these two steps which increases the total processing time. But in our proposed method polyol was added to reactor just after the heating period. Therefore acid - oil reaction and esterification reaction can occur simultaneously. This reduces the total processing time drastically. New method also reduces gel formation ability by balancing acid-oil and alkyd forming reactions.

Commercial resins makers are normally added small amount of maleic anhydride (MA) for their alkyd recipes to improve the drying properties, reaction speed and also to improve the colour {XXX}. Here also recipe was slightly modified by adding 1 g of MA. Accordingly TPA content reduced to 25.26 g to kept theoretical $P_{gel\ point}$ constant. Modified recipe was synthesized for 260 °C , 270 °C and 280 °C temperatures and results are tabulated below.

Temp (°C)	AV (mg KOH/g)	Processing time (min)	HV (mg KOH/g)	Touch Drying time (min)	Bending	Non volatile content (%)	Viscosity (second B4 cup at 1:1 Diluted)	Resin Color	Evidence of Gel formation	Remarks
260	103	180	41.1	189	<5mm	88.1	71	Light yellow	no	Ok
270	12.5	150	41.0	190	<5mm	82.1	75	Light yellow	no	Ok
280	11.4	120	43.2	185	<5mm	91.1	79	Light yellow	no	Ok

All three resins were successful and there was a clear indication that when temperature goes up reaction times goes down and down. But maximum temperature was limited to 280 °C due to the inability of alkyd making equipment to withstand high temperature.

Finally lengths of the resins were calculated using the following equation.

$$Oil\ length = \frac{(mass\ of\ oil\ used\ to\ make\ alkyd\ resin) * 100}{(mass\ of\ reactants) - (mass\ of\ water\ evolved\ in\ process)}$$

Water produced during reaction was collected separately by using dean and stark. 2.80 g, 2.85 g and 2.81g of water collected at 260, 270 and 280 °C respectively. Calculated Oil length of the resin produced at 260 °C was 66.94 %, at 270 °C it was 66.98 and 280 °C it was 66.95 %. If oil length is greater than 55% those resins consider as long oil alkyds [2][3] . Therefore above all resins are belong to the long oil alkyds.

III. CONCLUSIONS

Soya oil, TPA and glycerol based alkyd resins can be easily synthesized by proposed new methodology under following conditions.

Reaction temperatures 260 °C or above.

Continuous and uniform addition of polyol to the system just after the system reaching to its maximum temperature.

Alkyd processing time reduces with increasing temperature. Minimum time achieved was 120 minutes at 280 °C.

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