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Preparation and analysis of alkyd resin from deodourizer distillate

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This study presents deodorizer (DO) distillate as a cheaper source of fatty acid to prepare alkyd resins. DO distillate-based alkyd resins provide encouraging film properties, except for color and clarity of resins. Thus, DO distillate based fatty acids are being explored as raw materials for alkyd resins in architectural coating applications.

Keywords: Alkyd resin, Deodorizer distillate, Fatty acids

Introduction

Alkyds[1] are used chiefly in coating industry. Studies[2-9] are available on preparation and application of alkyd resins using fatty acids or oils. Deodorizer (DO) distillate[6], a cheaper source of fatty acids available as a byproduct from vegetable oil refineries specially generated in deodorization process, can be used as a fatty acid source for alkyd preparation. However, it has low content of fatty acids (25-45%) and requires increase in fatty acid content before using for alkyd resin production. Also, consistency of raw material cannot be maintained as different DO distillate contains different fatty acids. Iodine value of DO distillate of different oils also varies considerably, so care is to be taken in manufacturing products, in which iodine value plays an important role. This study presents DO distillate as a substitute of fatty acids and performance characteristics of prepared alkyd resins.

Experimental

Materials

DO distillate sample was procured from Anand Regional Co-operative Oilseeds Growers Union Limited (ARCOGUL), Chikhodara, Anand, India. This sample, as a byproduct, was generated as a result of high temperature deodourization process in vegetable oil refining. All other chemicals were of A R grade and obtained from M/s S D Fine Chemicals, Boisar, India. Phthalic anhydride, glycerol and xylene were purchased from Sigma Aldrich Chemicals Pvt Ltd, Mumbai, India.

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Processing of DO Distillate

Calculated amount of DO distillate and potassium hydroxide (KOH, 25% w/v) mixture was refluxed for 2-2.5 h for saponification of material. After saponification, hot distilled water was added to dissolve soap. This solution was further subjected to acidulation process by adding methyl red indicator (2-3 drops) first and then 1:1 sulphuric acid drop wise to split soap into fatty acid until pink color was observed. Aqueous layer was separated out and fatty acid layer was washed 2-3 times to remove mineral acidity.

Acid value and iodine value of processed DO distillate were determined as per standard methods[10]. Color (dark) and viscosity (25 poise) were measured on gardner scale at 25°C. Fatty acids of processed DO distillate had following values: acid value, 182.7 ; and iodine value, 11.3. Fatty acid composition of processed DO distillate, which was determined by gas-liquid chromatography of methyl esters using a gas chromatograph (Model 86-150, Chromatography Instrument Co., Baroda, India) fitted with flame ionization detector on a 3 mm x 2 mm stainless steel column packed with 20% DEGS, was found to be (Fig. 1): caprylic, 6.6; capric, 5.2; lauric, 47.8; myristic, 20.8; palmitic, 9.0; oleic, 6.7; linoleic, 1.6; and stearic, 2.3 %, w/w.

Preparation and Analysis of Alkyd Resin with Processed DO Distillate

Required amount of DO distillate, phthalic anhydride, xylene (reflux) and glycerol were charged in three-neck flask, equipped with stirrer. One of the necks of flask was attached with dean and stark apparatus. Temperature of contents slowly raised to 180°C and first sample was

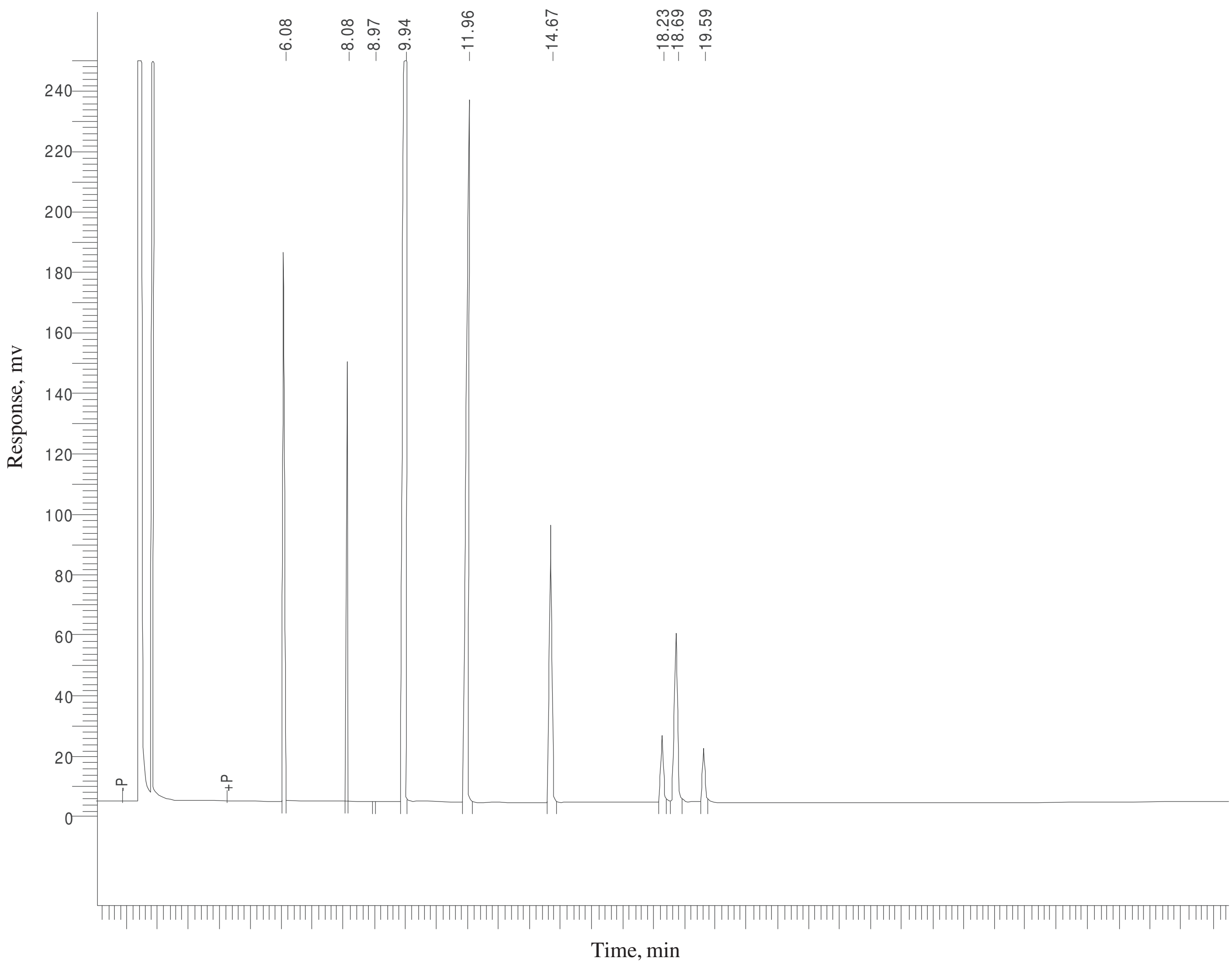
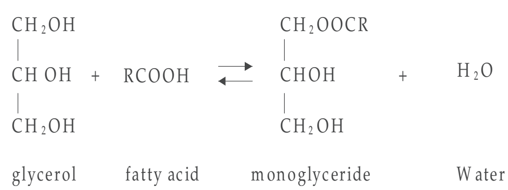
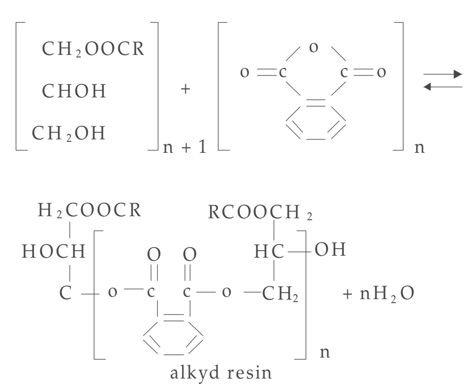


Fig. 1—Gas chromatogram of DO distillate fatty acid

withdrawn for acid value determination. Samples were then withdrawn at regular interval at constant temperature (240°C). Reactions were monitored continuously by measuring acid values and viscosities. Heating was continued till acid value dropped below 15. Then, mixture was cooled to room temperature and thinned to 50% by xylene. Alkyds were prepared to oil lengths of 64%, 49% and 37% for long, medium and short respectively (Table 1). Chemical reactions of alkyd formation are given as



(1)



(2)

Prepared alkyds were analyzed for physicochemical characteristics (color, viscosity, molecular weight, acid value etc). GPC (Perkin Elmer, USA, Series 200) with R I detector was used to determine molecular weight of alkyds. Chromatograms given for GPC are depicted for long (Fig. 2a), medium (Fig. 2b) and short oil xylene solvent and applied on test panels to study film performance properties [drying, gloss, flexibility and adhesion (cross hatch test)] by standard methods[11].

Results and Discussion

Viscosity of Alkyd Resins

As oil length increases, viscosity (Table 1) decreases. Long oil alkyds, being low functionality material, show low viscosity and also lower molecular weight (Table 2) as against their short and medium oil counterparts (Fig. 2).

Acid Value

Reaction was continued till acid value dropped below 15, which indicates progress of reaction. Lower acid value in long (8 mg KOH/g) and medium oil (12 mg KOH/g) alkyds indicates more complete reaction and higher degree of polymerization as compared to short oil (15 mg KOH/g) alkyd.

Color and Clarity

As oil length increases, color value increases; color of resin becomes dark. Color of short oil alkyd was better than that of long oil alkyd, due to high proportion of oil present in composition of long oil alkyd as compared to short and medium oil alkyd. Clarity of long oil alkyd was slightly poorer than that of short oil alkyd due to longer processing time, which generates gel polymerized moieties from fatty oil oxidation products as well as certain phthalate reaction products[1,12].

Air Drying

Higher oil content in long 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.

Flexibility

As oil length increases, flexibility increases; flexibility of long oil alkyd was excellent. Also, amount of oil was even sufficient in short oil alkyd so as to pass flexibility test of bending mandrel at 1/8 inch. Thus, oil moiety plays important role in imparting flexibility to resulting dry film.

Hardness

As percentage of oil decreases, hardness of alkyd resin increases. Long aliphatic chains present in oil structure impart more mobility and thus lower hardness. Also, when oil content decreases, resulting glyceride phthalate resin moiety has high functionality and so higher cross-linking density, which in turn, provides higher hardness to the film.

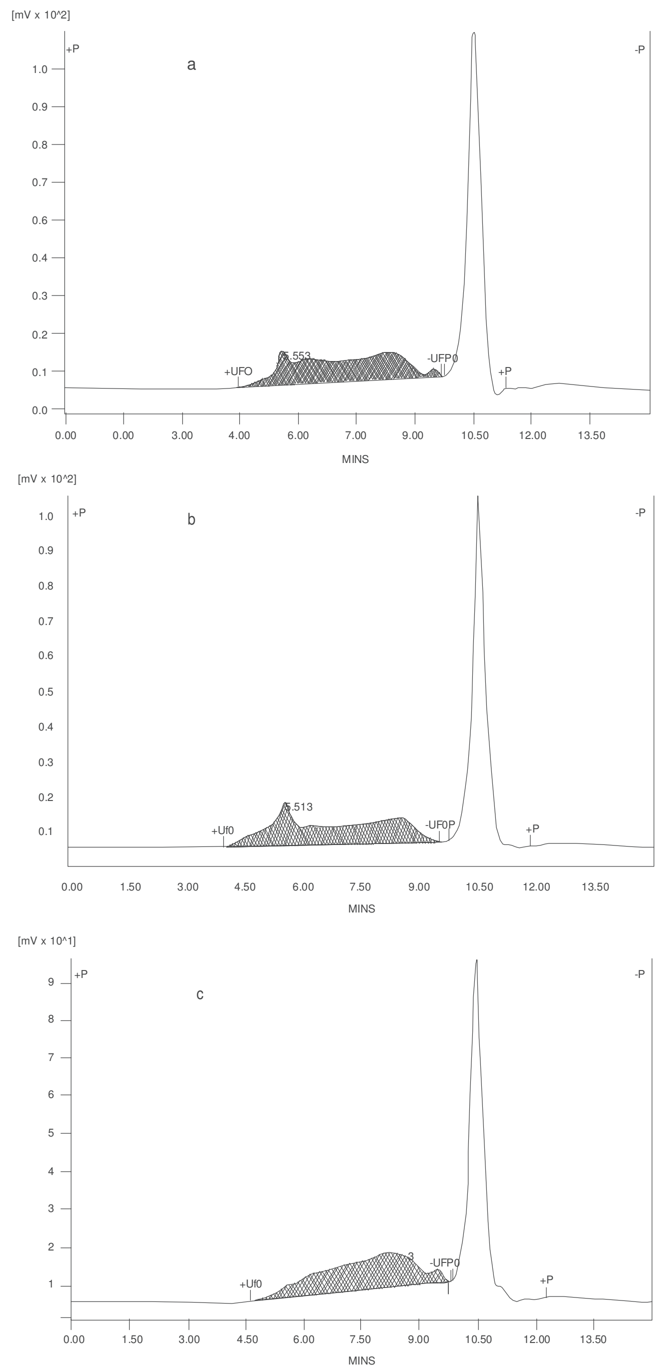


Fig. 2—Gel permeable chromatograms of alkyds: a) long oil; b) medium oil; and c) short oil

Gloss

As oil length increases, initial gloss of film increases, due to better orientation of oil and fatty acid chains on

Table 1—Composition of alkyd resins

S No	Ingredients	Weight, g	Mol wt	Eq wt	e_A	e_B	Fu^n	M_O
Long oil (K= 1.057, Excess OH= 10.6 %, oil length=60%)								
1	DO distillate	37.84(56.86)*	280	280	0.2030	-	1	0.2030
2	Glycerol	12.259(18.42)	92.09	31	-	0.5941	3	0.1980
3	Phthalic anhydride	16.45(24.72)	148.11	74	0.3340	-	2	0.167
	Total	66.54(100.00)	-	-	0.5370	0.5941	-	0.568
Medium oil (K= 1.008, Excess OH= 15.43%, oil length=49%)								
1	DO distillate	22.33(43.09)	280	280	0.1538	-	1	0.1538
2	Glycerol	11.53(22.25)	92.09	31	-	0.7180	3	0.2393
3	Phthalic anhydride	17.96(34.65)	148.11	74	0.4682	-	2	0.2341
	Total	51.82(100.00)	-	-	0.6220	0.7180	-	0.6272
Short oil (K= 1.0075, excess OH = 24.4 %, oil length=37%)								
1	DO distillate	17.68(34.51)	280	280	0.1232	-	1	0.1232
2	Glycerol	13.10(25.63)	92.09	31	-	0.8245	3	0.2748
3	Phthalic anhydride	20.46(39.93)	148.11	74	0.5395	-	2	0.2697
	Total	51.48(100.00)	-	-	0.6627	0.8245	-	0.6677

*Figures in parentheses are wt%; e_A= Acid equivalent; e_B= Base equivalent; Fu^n =Functionality; M_O =Moles

Table 2—Physico-chemical and film performance properties of prepared resins[a]

S No	Test	Alkyd resins Long (60% oil length)	Medium (49% oil length)	Short (37% oil length)
1	Acid value (mg KOH/g)	8.1	10.3	14.9
2	Color (50% xylene) gardner	16	14	10
3	Clarity	Clear	Clear	Clear
4	Viscosity at 25°C			
	gardner	(60%) N	(50%) M	(40%) S
	cSt	340	320	500
5	Hardness (pendulum) sec	16	32	50
6	Gloss (60°)	90	88	82
7	Flexibility (bending mandrel 1/8 “)	Passes	Passes	Passes
8	Adhesion (cross hatch)	Passes	Passes	Passes
9	Drying properties			
	Surface dry	3.0 h	2.0 h	1.5 h
	Tack free dry	Over night	Over night	6.0 h
	Hard dry	Over night	Over night	Over night

[a]After 7 days of curing, using dryers 0.05% cobalt, 0.5 % calcium, 0.2 % zirconium drier on solid resin basis

test panel and subsequently better flow and leveling of dry film. Thus, same trend is observed in long, medium and short oil alkyd films. Short oil alkyds showed lower initial gloss due to poor flow and leveling of resin solution on test panel. Also, film with lower oil dry faster and thus very limited time is available for polymer molecules for orientation on panel. But when it comes to retention of gloss in dried film, reverse trend has been observed practically.

Conclusions

DO distillate based fatty acids were successfully prepared and composition of resulting fatty acids was quite similar to commercial fatty acid used in preparation of alkyd resins. Alkyd resins of various oil lengths (long, medium and short) were successfully prepared in laboratory. Long oil alkyds have been preferred resin choice for interior paint system and short oil alkyds have been used for exterior and high performance applications.

These alkyds have potential for the use in architectural paints as binders.

Acknowledgement

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