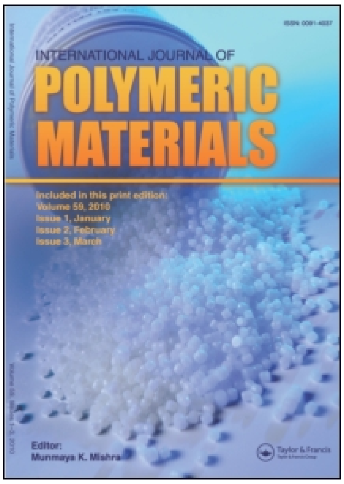

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Pulin N. Patel[a]; D. A. Raval[a]; V. M. Mannari[a]
[a] Department of Industrial Chemistry, V.P. and R.P. T.P. Science College, Vallabh Vidyanagar, Gujarat

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Two-Package Polyurethane Coatings Based on Acid-Functional Acrylic Copolymer Modified Alkyds for Industrial Maintenance Coatings

PULIN N. PATEL, D. A. RAVAL* and V. M. MANNARI

*Department of Industrial Chemistry, V.P. and R.P.T.P.
Science College, Vallabh Vidyanagar-388 120, Gujarat*

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Three series of hydroxy functional acrylated alkyds based on refined Rubberseed Oil (RSO) have been synthesized using three acid-functional acrylic copolymers (AAR), differing in their copolymer compositions. Several urethane coating compositions have been formulated using above resins as hydroxyl components in conjunction with isocyanate prepolymer in varying proportions. Various film properties of the compositions have been studied and compared to establish the influence of type and degree of acrylic modification of alkyds.

Keywords: Rubberseed oil; acid-functional acrylic copolymer resin; aromatic isocyanate prepolymer; benzoyl peroxide; monoglyceride

INTRODUCTION

Two-package urethane coating systems have been widely used for variety of surface coating applications, particularly in industrial maintenance field [1]. Two package systems have been much popular as they alleviate many technical difficulties associated with the formulation based on isocyanates [2].

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*For correspondence. Presently, Principal, N. V. Patel College of Pure & Applied Sciences, V. V. Nagar.

The two systems used in practice comprise,

(i) Catalysed isocyanate prepolymer system (ASTM type IV)
(ii) Isocyanate prepolymer/polymeric polyol system (ASTM type V).

The polymeric polyols used in ASTM type V system, mainly include, polyesters, polyethers, alkyds, acrylics, castor oil etc. Several polyurethane polymers based on many such polyols have been reported in literature [3–6].

Acrylation of alkyd resin is a classical method of improving physical, chemical and performance properties of their films [7–9]. In the present study, various acrylated alkyds have been synthesized using a nontraditional oil (RSO). Acrylation has been carried out by condensation of alkyd with three different acid-functional acrylic copolymers (AAR) in varying proportions. These resins have been formulated in such a way that the resultant products have sufficient free hydroxyl groups for further modification. Three series of acrylated alkyds so obtained have been utilized as hydroxy components in formulations of two-package urethane coating compositions.

The isocyanate component used was aromatic isocyanate prepolymer [IP (Aro)].

Since alkyd resins are reported to be used in such two package urethane systems giving satisfactory performance [10], these acrylic modified vehicles were thought to influence the performance of the compositions, which has been the principal objective of the present study.

MATERIALS AND METHODS

Raw Rubberseed Oil (RSO) was procured from Kottayam, Kerala state (India); RSO was refined according to reported method [11]. The other chemicals used viz. glycerol, calcium octoate, litharge, phthalic anhydride (PA), maleic anhydride (MA), benzoyl peroxide (BPO), o-phosphoric acid, methanol, xylene were of laboratory reagent grade. n-Butylmethacrylate was procured from M/s Gujarat State Fertilizers Company (Polymers unit) Petrofils, Baroda (India) and was used without further modification. The aromatic isocyanate prepolymer [IP (Aro)] used was a commercial sample procured from M/s Neospectra Polymers & Chemicals Ltd., Bombay.

The acid value, color, viscosity and drying time were determined as per ISI methods [12, 13]. Resistance towards water, acid, alkali and xylene were determined as per standard methods described in literature [14].

The flexibility was measured at 1/4″ and 1/8″ by conical mandrel. The films were applied on mild steel panels and tinned steel panels as per Indian Standard Specifications [14].

Molecular weights of the copolymers were determined using GPC.

The characteristics of Isocyanate prepolymer [IP (Aro)] are presented in Table I.

EXPERIMENTAL

Preparation of Acid Functional Acrylic Copolymer Resin (AAR)

AAR using n-butylmethacrylate (BMA) and maleic anhydride (MA) has been prepared using the reported method [15]. AAR was prepared in three varying ratios of BMA and MA viz. 80:20, 65:35, 50:50. The composition and characteristics of different copolymers are shown in Table II and Table III respectively.

Methacrylated Alkyds

Alkyd resins were prepared directly from refined RSO according to the reported method by monoglyceride process [16].

Purified RSO (200 gms) was heated with glycerol (68 gms) at 240°C with efficient stirring using calcium octoate (0.4% by weight of total charge) and litharge (0.04% by weight of total charge) as catalyst. The

TABLE I Characteristics of Isocyanate Prepolymer [IP (Aro)]

Properties	
Viscosity (74% Solution in ethyl acetate)	1.8 Poise
Colour	Pale Yellow
Specific Gravity	1.15
NCO Content (% by wt. basis on nonvolatiles)	13%
Isocyanate equivalent wt.	323

TABLE II Composition of Acrylic Copolymer

Sr. No.	*Copolymer Code**	*n-BMA (gms)*	*MA (gms)*	*BPO (gms)*	*% MA (by wt.)*	*Xylene (Ml)*
1	Copoly-20	160.0	40.0	4.0	20	100
2	Copoly-35	130.0	70.0	4.0	35	100
3	Copoly-50	100.0	100.0	4.0	50	100

* The last two digits in the copolymer code indicate percentage of maleic anhydride in the copolymer.

TABLE III Characteristics of AAR

Sr. No.	*Copolymer Code**	*BMA % Wt.*	*MA % Wt.*	*Acid Value*	*Molecular Wt.$\bar{M}_n$*	*Polydispersity*
1	Copolymer 20	80	20	163.64	2740	14.70855
2	Copolymer 35	65	35	264.04	2082	10.58165
3	Copolymer 50	50	50	322.97	1997	11.22607

* The last two digits in the copolymer code indicate percentage of maleic anhydride in the copolymer.

reaction was carried out until it gives methanol solubility test (3:1 v/v) at room temperature indicating the formation of monoglyceride (MG).

The mixture was cooled to 100°C, phthalic anhydride added and temperature raised to 160°C which was maintained for 1hr. Water of reaction was removed by azeotropic distillation using xylene. The temperature was then raised to 220–230°C and maintained until the desired acid value was obtained.

It was cooled to 100°C, AAR was added and the temperature raised to 160°C. Water of reaction was removed using xylene and the temperature was again raised to 220°C. After getting desired acid value (below 10) the reaction was stopped and the resultant resin was thinned to 40% solid with xylene after cooling it to below 100°C. The charge weights of different acrylated alkyds are shown in Table IV and their characteristics are shown in Table V.

The reaction scheme is presented in Figure 1.

The IR spectrum of the acrylic copolymer was recorded to confirm the structure of copolymer (Fig. 2). The presence of carboxylic acid group is confirmed by a strong absorption band at 2960 cm^{-1}. This further confirms the inclusion of maleic anhydride in the copolymer. A

TABLE IV Charge Weight for Various Acrylated Alkyds*

Sr. No. @	*Resin Code***	*Wt. of MG*	*Wt. of Copolymer*	*Wt.of PA*	*Molar Excess*	*% Copolymer*
1	Acr. Alk 20.05	75	5.7	32.59	0.20	5.03
2	Acr. Alk 20.15	75	18.52	29.83	0.20	15.01
3	Acr. Alk 20.25	75	33.9	26.52	0.20	25.03
4	Acr. Alk 35.05	75	5.6	31.53	0.20	5.01
5	Acr. Alk 35.15	75	18	27.45	0.20	14.94
6	Acr. Alk 35.25	75	32.75	22.50	0.20	25.14
7	Acr. Alk 50.05	75	5.55	31.47	0.20	4.95
8	Acr. Alk 50.15	75	17.85	26.1	0.20	15.06
9	Acr. Alk 50.25	75	31.87	20.25	0.20	25.07
10	Alk 0.00	75	–	33.85	0.20	–

* All the weight of compounds are in gms. (grams).

** The first two digits in the resin code indicate percentage of maleic anhydride in the copolymer and last two digits indicate weight of copolymer in Alkyd.

@ Sr. No. 9 resin get gelled after addition of copolymer.

TABLE V Characteristics of Acrylated Alkyds

Sr. No	*Resin Code**	*Percentage Copolymer (by Wt.)*	*Viscosity (40% solid)*	*Colour (Gardner)*	*Acid value mgs. KOH/g*
1	Acr. Alk 20.05	5	F	12	6.78
2	Acr. Alk 20.15	15	G	12–13	7.66
3	Acr. Alk 20.25	25	I	13	9.88
4	Acr. Alk 35.05	5	M	12–13	7.98
5	Acr. Alk 35.15	15	N	13	8.66
6	Acr. Alk 35.25	25	P	13	9.79
7	Acr. Alk 50.05	5	N	14	9.11
8	Acr. Alk 50.15	15	O	15	11.07
9	Acr. Alk 50.25	25	–	–	–
10	Alk 0.00	0	D-E	11–12	5.00

* First two digits in the Resin Code indicates the percentage of maleic anhydride in the Copolymer and last two digits indicate the percentage weight of copolymer in the alkyd.

strong band at 1729 cm^{-1} can be attributed to the ester groups of acrylic monomer.

The IR spectrum of acrylated alkyd is shown in Figure 3. A very strong absorption band at 3415 cm^{-1} can be attributed to the free hydroxyl group present in the resin. Free hydroxyl groups are expected to be present since the resin is synthesized with stoichiometric excess of hydroxyl compound. Strong absorption bands from aromatic moiety at 1581 cm^{-1} and 743 cm^{-1} confirm the structure [17, 18].

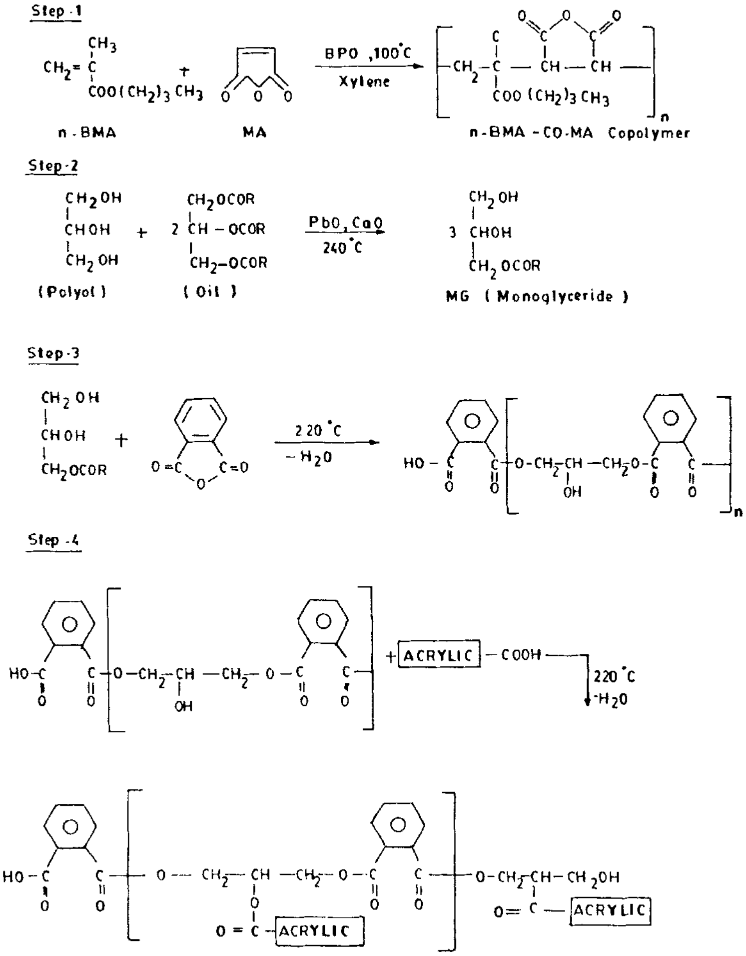

FIGURE 1 Scheme for Preparation of Acrylic Modified Alkyd (Acrylated Alkyd).

RESULT AND DISCUSSION

Table VI shows the various film properties of cured film of different acrylated alkyd isocyanate prepolymer compositions.

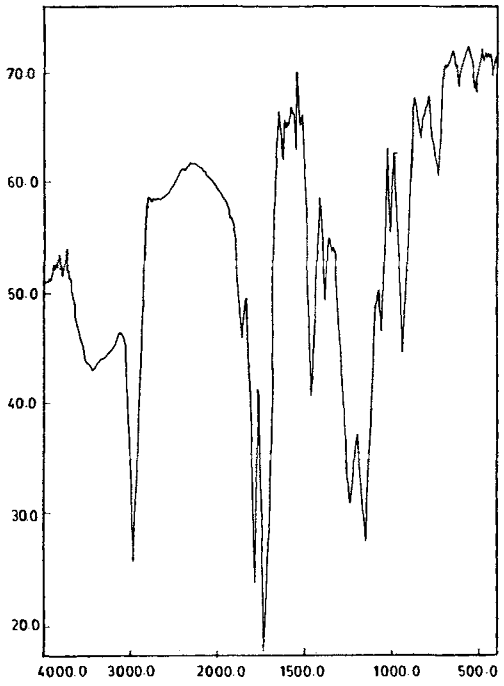

FIGURE 2 IP Spectrum of Acrylic copolymer (AAR).

Drying Time

The tack-free time of various coatings has been reported as they give an indication of drying time of the film after application. The tack-free time for all the systems are reasonably low, which is expected of a two package urethane system. Further, it is observed that the tack-free time decreases with increase in loading of AAR to alkyd and increase in percentage of MA in AAR. This might be attributed to the increase in T_g of acrylated alkyd which increases with increase in MA content of copolymer [19], which in turn decreases the drying time [20].

It is also observed that the tack free time increases with increase in ratio of alkyd to isocyanate prepolymer. This may be due to the fact that with increase in $-NCO$ content, the number of crosslinks and hence crosslink density increases. With increase in crosslink density,

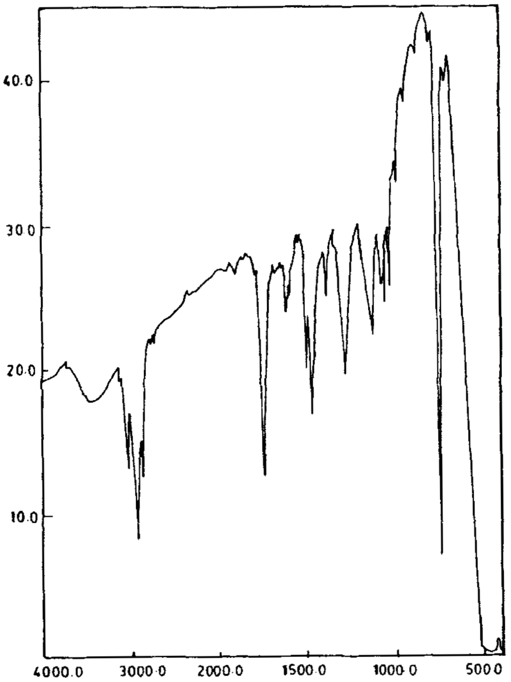

FIGURE 3 IR Spectrum of Acrylated Alkyd.

the drying time decreases. Drying time for various acrylated alkyds are shown in Table VII.

Flexibility and Adhesion

All the samples passed flexibility test on 1/4″ and 1/8″ conical mandrel and stripping test for adhesion except for Sr. No. 3, 6 and 8 (1/4″ and 1/8″ for 2:1 and 3:1 ratio). The failure of these samples might be due to excessive crosslink density resulting from inclusion of higher percentage of AAR and MA in alkyd and also due to the higher amount of isocyanate employed for curing.

Scratch Hardness and Impact Resistance

Scratch hardness increases with increase in percentage of AAR in alkyd, percentage of MA in AAR and ratio of isocyanate prepolymer

TABLE VI Cured Film Properties of Acrylated Alkyd/Isocyanate Prepolymer System[@]

Sr. No	Resin Code	Scratch hardness (gms) Passes			*Impact resistance						Flexibility						Adhesion		
					2:1		3:1		4:1		2:1		3:1		4:1		2:1	3.1	4:1
		2:1	3:1	4:1	R	D	R	D	R	D	1/4	1/8	1/4	1/8	1/4	1/8			
1	Alk 20.05	2700	2100	1900	300	300	300	300	300	300	P	P	P	P	P	P	P	P	P
2	Alk 20.15	2850	2500	2300	275	300	300	300	300	300	P	P	P	P	P	P	P	P	P
3	Alk 20.25	3250	2800	2600	250	275	275	275	300	300	F	F	F	P	P	P	F	F	P
4	Alk 35.05	2900	2700	2300	300	300	300	300	300	300	P	P	P	P	P	P	P	P	P
5	Alk 35.15	3200	2900	2650	175	250	225	250	250	250	P	P	P	P	P	P	P	P	P
6	Alk 35.25	3800	3200	2800	150	150	150	175	225	225	F	F	F	P	P	P	F	F	P
7	Alk 50.05	3200	2900	2500	275	300	300	300	300	300	P	P	P	P	P	P	P	P	P
8	Alk 50.15	3400	3050	2700	150	200	200	200	250	300	F	F	F	F	P	P	F	F	P
9	Alk 50.25	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
10	Alk 0.00	1800	1600	1450	300	300	300	300	300	300	P	P	P	P	P	P	P	P	P

* The values are arrived by multiplying wt. of indentor in lbs (6.25 lbs) with maximum height in inches from where indentor falls without any visible damage to the films.

@ Cured at ambient temperature.

TABLE VII Drying time for different Acrylated Alkyd/Isocyanate Composition

Sr. No	*Resin Code*	*Tack Free Time (min)* 2:1	3:1	4:1
1	Acr. Alk 20.05	19	21	24
2	Acr. Alk 20.15	16	18	21
3	Acr. Alk 20.25	15	17	20
4	Acr. Alk 35.05	17	20	22
5	Acr. Alk 35.15	14	17	20
6	Acr. Alk 35.25	13	15	18
7	Acr. Alk 50.05	15	17	20
8	Acr. Alk 50.15	13	15	18
9	Acr. Alk 50.25	–	–	–
10	Alk 0.00	25	30	35

to alkyd. This may be due to increase in crosslink density of the film [21, 22] arising due to the higher MA percentage in alkyd and higher amount of isocyanate prepolymer.

Impact resistance is measured using falling weight type impact tester. In this method a hemispherical indenter of known weight is dropped down onto the panel which is fixed at the base of the instrument. An opening opposite the indenter in the base support on which the panel rests permits deformation of the panel. The indenter is dropped from greater and greater heights until the film cracks. (The maximum height of the instrument used is 48 inches and weight of the intender is 6.25 lbs). If the coated side is up, that is, it is directly hit by the indenter, the test is called direct impact test. If the back of the panel is up, the test is called reverse impact test.

Impact resistance decreases with increase in percentage of AAR in alkyd, percentage of MA in AAR and ratio of isocyanate prepolymer to alkyd. This may be due to excessive crosslink density [21, 22] of the film arising out of the presence of higher amount of MA in alkyd leading to embrittlement.

Acid and Alkali Resistance

The acid and alkali resistance tests results are shown in Table VIII.

The results reveal that with increase in percentage of AAR in alkyd and percentage of MA in AAR, the resistance towards alkali decreases, which may be due to inclusion of more MA in the AAR and

TABLE VIII Chemical Resistance Properties of Acrylated Alkyd/IP (Aro) System@

Sr. No.	*Resin Code*	*2 % NaOH Resistance**			*2% HCl Resistance**		
		2:1	3:1	4:1	2:1	3:1	4:1
1	Acr. Alk 20.05	a	c	c,d	a	b,d	d
2	Acr. Alk 20.15	c,d	e,g	e	b,e	d,e	c,e
3	Acr. Alk 20.25	c,e	c,f	c,f	d	d,e	c,f
4	Acr. Alk 35.05	c	d	c,d	a	d,e	c,e
5	Acr. Alk 35.15	f	e	c,e	d	f	c,f
6	Acr. Alk 35.25	c,f	c,f	c,f	d,e	b,f	c,f
7	Acr. Alk 50.05	c,e	c,d	e	b,d	c,d	f
8	Acr. Alk 50.15	c,f	c,f	c,e	b,d	c,d	c,f
9	Acr. Alk 50.25	–	–	–	–	–	–
10	Alk 0.00	c,f	c,f	g	b,d	d,e	c,f

a = Not affected; b = Loss of gloss; c = Slight loss of adhesion; d = Slight blistering; e = Slight swelling; f = Swelling and blistering; g = Partially ruptured; * The test panels were immersed for 10 days; @ The test panels were ambient temperature cured. – Passes, water and xylene resistance test for 240 hrs and 24 hrs.

finally higher percentage of AAR in alkyd. Same trend was observed for acid resistance.

The acrylated alkyds show much better resistance towards acid and alkali than unmodified alkyd. This may be due to the inclusion of higher molecular wt. acrylic copolymer into the alkyd resin moiety since acrylic polymers are known to give better alkali and acid resistance [23].

Water and Solvent Resistance

All samples show good water and solvent resistance.

Yellowing of Cured Film

No notable yellowing was observed in acrylated alkyd/IP(Aro) system as compared to unmodified alkyd/IP(Aro) system. This may be attributed to the presence of low oil content in modified alkyd compared to unmodified alkyd, which is responsible for giving yellowness to the film. The low yellowness of the modified alkyd/IP(Aro) system may also be due to the presence of acrylic moiety in the modified alkyd structure.

CONCLUSION

From the above study it is concluded that acrylated alkyds could be used as hydroxyl component of a two-package urethane coating system for industrial maintenance coatings. It has also been found that percentage of MA in AAR and percentage of AAR in alkyds control most physical, chemical and mechanical properties of the films. Also the acrylated alkyd shows better overall properties than unmodified alkyd resins.

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