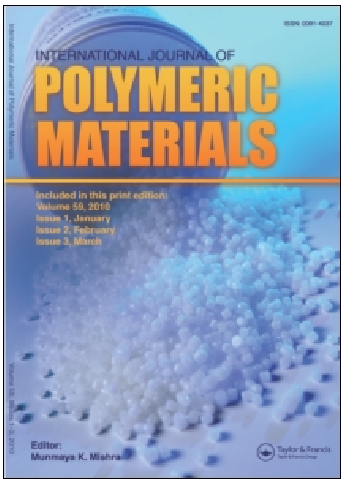

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Water-Dispersible Polyesteramide Resins for Surface Coating Applications

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To cite this Article Roy, T. K. , Raval, D. A. and Mannari, V. M.(1998) 'Water-Dispersible Polyesteramide Resins for Surface Coating Applications', International Journal of Polymeric Materials, 42: 1, 39 — 52

To link to this Article: DOI: 10.1080/00914039808041058

URL: http://dx.doi.org/10.1080/00914039808041058

Intern. J. Polymeric Mater., 1998, Vol. 42, pp. 39–52
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the Gordon and Breach Science
Publishers imprint.
Printed in India.

Water-Dispersible Polyesteramide Resins for Surface Coating Applications

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(Received 17 October 1997)

High acid value Polyesteramide resins based on Dehydrated Castor Oil (DCO) and Niger Seed Oil have been synthesised. These high acid value polyesteramides are neutralised with varying percentage of triethylamine (TEA) and dispersed in water. These water-dispersible resins are cured with Hexamethoxymethylmelamine (HMMM) in varying proportions at elevated temperature. Various film properties of the compositions have been studied and compared.

Keywords: Dehydrated castor oil; niger seed oil; hexamethoxymethylmelamine; triethylamine; co-condensation; self condensation; water-dispersible; polyesteramide

INTRODUCTION

Important advantages such as reduced air pollution, improved plant safety, reduced toxicity and energy savings have accelerated development of water-borne coating systems that can compete with and replace conventional air-drying and low bake solvent based systems [1]. Sometimes they can even successfully replace thermosetting coatings without sacrificing quality and application properties.

Water-borne systems based on alkyd systems are extensively studied and reported in the literature [2, 3]. One of the inherent limitations of

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alkyd based systems is their relatively poor resistance to hydrolysis, particularly by alkalis [4]. This is believed to be due to the presence of ester linkages in its polymeric backbone, which are prone to hydrolysis. Polyesteramide resins contain a significant number of amide linkages in their polymeric backbone. The films of coatings containing polyesteramides are known to have improved water and chemical resistance [5] and good overall mechanical properties.

Keeping these factors in mind we have attempted to prepare water-dispersible polyesteramides based on dehydrated castor oil (DCO) and niger seed oil. Isophthalic acid is used as acid component, since isophthalic esters have better resistance to hydrolysis than their phthalic anhydride counterparts [4, 5]. The scheme for preparation of polyesteramide is shown in Figure 1.

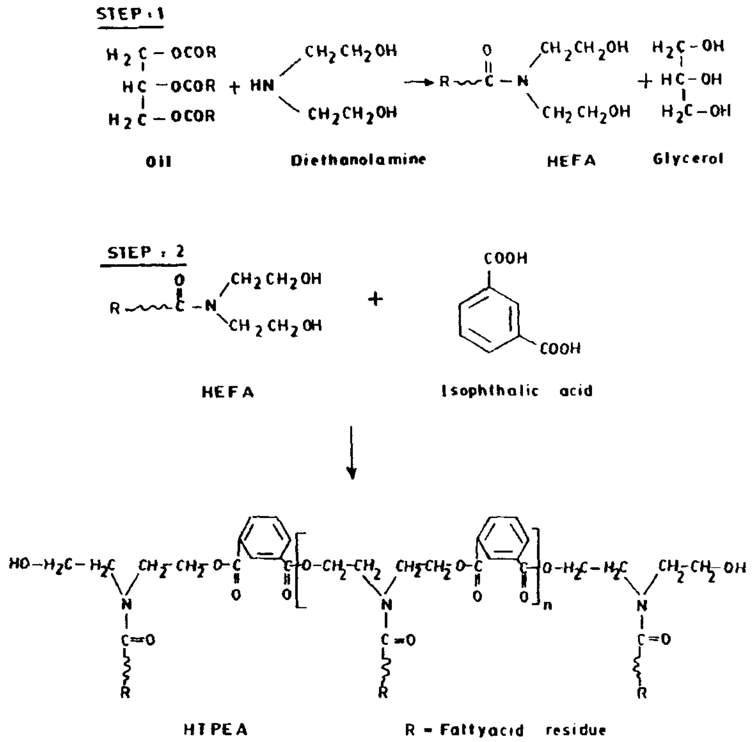

FIGURE 1 Scheme for preparation of polyesteramide.

Polyesteramides having high hydroxyl values are prepared for the present study with a view to provide sufficient number of carboxyl groups needed for water-dispersion. Cellosolve is used as co-solvent since it provides better dispersibility in water. Triethylamine (TEA) is used as the neutralising agent and hexamethoxymethylmelamine (HMMM) is used as the cross-linking agent.

MATERIALS AND METHODS

Refined DCO was procured from M/s. Jayant Oil Mills, Baroda (India) and refined niger seed oil was procured from M/s. Viscus Oil Mills, Indore (India) and were used without any modification. HMMM was prepared according to a reported method [6]. The other chemicals used *viz.* diethanolamine, zinc oxide, isophthalic acid, TEA, xylene, cellosolve, methanol, melamine, formaldehyde, sodium carbonate and hydrochloric acid were of laboratory reagent grade.

The acid value, colour and viscosity were determined as per ISI methods [7, 8]. Resistance towards acid, alkali and xylene were determined as per standard methods described in the literature [9].

The flexibility was measured at 1/4″ and 1/8″ conical mandrel. The films were applied on mild steel panels (6″ × 4″) and tinned steel panels (6″ × 2″) and mechanical properties were studied as per Indian standard specifications [7].

EXPERIMENTAL

Preparation of *N*, *N*-bis (2-hydroxyethyl) Fatty amides (HEFAs)

The HEFAs were prepared directly from DCO and niger seed oil according to a reported method [5]. The characteristics and fatty acid compositions of DCO and niger seed oil are reported in Table 1.

Purified oil (1.0 mole) was heated under nitrogen with diethanolamine (3.0 mole) at 200°C with efficient stirring for 15 minutes, using zinc oxide (0.02 mole) as a catalyst.

TABLE 1 Characteristics and Fatty acid compositions of DCO and Niger seed oil

a. Characteristics

Sr. no.	*Properties*	*DCO*	*Niger seed oil*
1	Acid Value (mg KOH/gm)	9.00	7.25
2	Saponification Value (mg KOH/gm)	187.0	191.20
3	Iodine Value (gm/100 gm)	149.0	134.50
4	Hydroxyl Value (mg KOH/g)	16.0	17.30
5	Specific Gravity	0.94	0.925
6	Refractive Index (@ 30°C)	1.438	1.4671
7	Colour (Y + 5R)(Lovibond)	11.00	7.00

b. Fatty acid composition

Sr. no.	*Fatty acid*	*DCO*	*Niger seed oil*
1	Myristic	–	1.7
2	Palmitic	–	5.0
3	Stearic	–	2.0
4	Oleic	9.0	38.9
5	Linoleic	83.0	51.6
6	Linolenic	5.0	–
7	Ricinoleic	3.0	–

The progress of the reaction was monitored by thin-layer chromatography (TLC) until disappearance of the spot of oil was observed [5]. The fatty diethanolamide was purified from glycerol, excess diethanolamine and other water-soluble impurities by washing its solution in diethyl ether with 15 percent aqueous sodium chloride followed by distilled water. The characteristics of HEFAs are reported in Table 2.

Preparation of Hydroxy-terminated Polyesteramides (HTPEAs)

Hydroxy-terminated polyesteramides were prepared by reacting HEFAs (1.0 mole) with isophthalic acid (1.0 mole) [5].

TABLE 2 Characteristics of HEFAs

Sr. no.	*Properties*	*HEDA*	*HENA*
1	Acid value (mg KOH/g)	4.00	5.00
2	Hydroxyl Value (mg KOH/g)	288.10	291.00
3	Iodine Value (gms/100gm)	131.00	131.00
4	Viscosity (@ 25°C, Poise)	5.00	5.00
5	Specific Gravity	0.96	0.96
6	Colour (Gardner)	12.00	12.00
7	Nitrogen Content (% by wt.)	3.47	3.39

The reactants were heated slowly with efficient stirring under the blanket of nitrogen at a temperature of 195 ± 5°C for about 3.5 hours. Water of the reaction was continuously removed in Dean – Stark moisture trap by azeotropic distillation using xylene as a solvent. The acid value of the reaction products was periodically checked to study progress of the reaction. The condensation reaction was carried out until acid value was around 60. The charge by weight of polyesteramide resins are given in Table 3. The characteristics of HTPEAs are reported in Table 4.

The structure of polyesteramide was confirmed from IR spectrum (Figs. 2 and 3). The absorption bands were found to be at 3400 $\mathrm{cm^{-1}}$ (— OH group), 1740 $\mathrm{cm^{-1}}$ (ester group), 1640 $\mathrm{cm^{-1}}$ and 1725 $\mathrm{cm^{-1}}$ (— C $=$ O stretching), 820 $\mathrm{cm^{-1}}$ (— C —N stretching), 1620 $\mathrm{cm^{-1}}$, 1070 $\mathrm{cm^{-1}}$ and 740 $\mathrm{cm^{-1}}$ (aromatic moiety) [10].

Preparation of HMMM Resin

To a reaction flask equipped with a mechanical stirrer and condenser were added 37.8 gm (03 mole) of melamine and 195 gm of 37% (2.4 mole) formaldehyde solution. The pH of the mixture was adjusted with caustic to 8.3. The reaction mixture was heated on a water bath with stirring at 50°C for about 70–80 min., at which time all the melamine went into solution. On cooling the product separated as a thick white precipitate and was filtered to afford monohydrate and dried at 50°C.

To a flask were added 3.1 gm (0.01 mole) of the above product, 20.0 gm (0.065 mole) methanol and 1.0 ml concentrated hydrochloric acid. The reaction mixture was stirred for 8 min. at 25°C, neutralised and concentrated under reduced pressure to get the final product.

Preparation of Coating Compositions

Before preparing the coating compositions the HTEPAs were neutralised (70%, 80%, 90% and 100%) with varying proportions of TEA, to promote dispersion in water. The amount of TEA required for varying percentage of neutralisation was calculated using the following formula.

TABLE 3 Charge weight of HTPEAs

Resin code	*Mole excess hydroxyl %*	*Reactants*	*Weight (gms)*	*Equivalent wt. (gms)*	*Total equivalents*	*Acid equivalents*	*Hydroxyl equivalents*	*Functionality*	*Moles*
HTPEA(DCO)	0.00	HEDA	98.0	196.0	0.5	0.5	–	2	0.25
		IPA	41.5	83.0	0.5	–	0.5	2	0.25
HTPEA(NIGER)	0.00	HENA	92.0	184.0	0.5	0.5	–	2	0.25
		IPA	41.5	83.0	0.5	–	0.5	2	0.25

TABLE 4 Characteristics of HTPEAs (60% in Xylene)

Resin Code	*Specific gravity*	*Viscosity @ 30°C (Poise)*	*Colour (Gardner)*	*Acid value (mg KOH/g)*	*Iodine value (gm/100 gm)*	*Hydroxyl value (mg KOH/g)*
HTPEA(DCO)	0.97	4.7	15	59.7	78.4	18.68
HTPEA(NIGER)	0.97	4.3	16	58.01	72.6	20.42

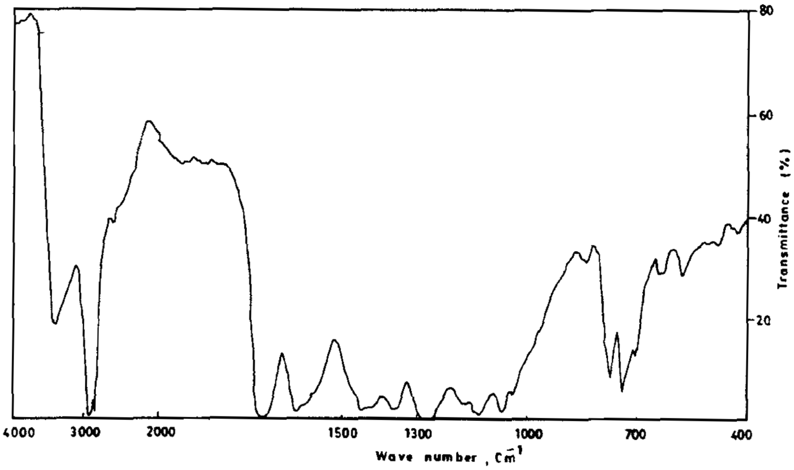

FIGURE 2 IR Spectrum of HTPEA (DCO).

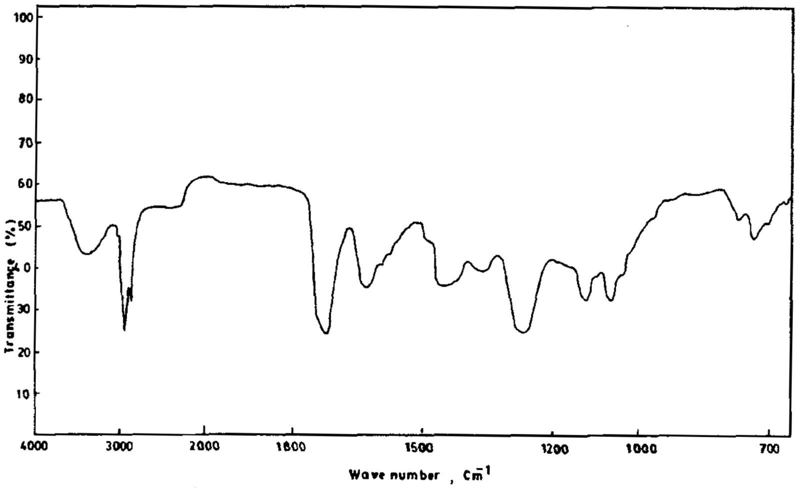

FIGURE 3 IR Spectrum of HTPEA (Niger).

$$\text{Amount of TEA required for 100 gms. of HTPEA} = \frac{A \times E \times S \times D}{56{,}100}$$

where,

A = Acid Value of HTPEA
E = Equivalent wt. of TEA

S = Solid content of HTPEA

D = Degree of neutralisation (%).

After neutralisation, coating compositions were prepared by mixing HTPEAs with HMMM cross-linker (50% solid) in three different ratio *viz.* 1:1, 2:1 and 3:1. Bentonite was incorporated in the composition to control flow and levelling during application.

The coated panels were baked at 175°C for 20 minutes. Various coating compositions are listed in Tables 5.1 and 5.2.

RESULTS AND DISCUSSION

The results reveal that water-dispersible polyesteramide resins can be formulated with the components used and by selecting their suitable ratios. Further, the choice of neutralising agent *i.e.*, triethylamine is justified as the stability of resin solution in water is very good.

Further, as the percentage of neutralisation increases, the viscosity of the resultant resin increases. This may be attributed to the bulky structure resulting from neutralisation of the polymeric carboxyl group with triethylamine.

FILM PROPERTIES

The results of various chemical and mechanical properties of the films of baked water-dispersible HTPEA/HMMM coating compositions are reported in Tables 6.1 and 6.2.

Scratch Hardness and Impact Resistance

The scratch hardness decreases with increase in the amount of cross-linking agent. This can be attributed to the fact that at high levels of cross-linking agent (HMMM) the cross-link density of the films reaches a brittle point and consequently hardness decreases. Scratch hardness is found to increase with increase in percent of neutralisation upto a certain limit (upto 90%), beyond which it decreases. This may be due to the fact that at high percentages neutralisation, the free

TABLE 5.1 Coating compositions of HTPEA (DCO)/HMMM resins (percentage)

Type of HPTEA resin	*Percentage neutralisation*	*Viscosity of neutralised HTPEA (Poise)*	*HPTEA/HMMM ratio*	*HTPEA (60%)*	*HMMM (50%)*	*Cellosolve*	*Water*	*Additives*
HTPEA(DCO)	70	2.25	1:1	28.0	33.6	6.0	28.4	5.0
			2:1	35.0	28.0	6.0	26.0	5.0
			3:1	40.0	16.0	7.0	24.0	5.0
HTPEA(DCO)	80	3.0	1:1	28.2	33.6	6.0	28.2	5.0
			2:1	35.2	28.0	6.0	25.8	5.0
			3:1	40.2	16.0	7.0	23.8	5.0
HTPEA(DCO)	90	5.0	1:1	28.4	33.6	6.0	28.0	5.0
			2:1	35.4	28.0	6.0	25.6	5.0
			3:1	40.4	16.0	7.0	23.6	5.0
HTPEA(DCO)	100	10.7	1:1	28.6	33.6	6.0	27.8	5.0
			2:1	35.6	28.0	6.0	25.4	5.0
			3:1	40.6	16.0	7.0	23.4	5.0

TABLE 5.2 Coating compositions of HTPEA (NIGER)/HMMM resins (percentage)

Type of HPTEA resin	*Percentage neutralisation*	*Viscosity of neutralised HTPEA (Poise)*	*HPTEA/HMMM ratio*	*HTPEA (60%)*	*HMMM (50%)*	*Cellosolve*	*Water*	*Additives*
HTPEA(NGR)	70	2.0	1:1	28.0	33.4	6.2	28.4	5.0
			2:1	35.0	27.8	6.2	26.0	5.0
			3:1	40.0	15.7	7.3	24.0	5.0
HTPEA(NGR)	80	2.7	1:1	28.0	33.2	6.4	28.2	5.0
			2:1	35.0	27.6	6.4	25.8	5.0
			3:1	40.0	15.4	7.6	23.8	5.0
HTPEA(NGR)	90	4.3	1:1	28.0	33.0	6.6	28.0	5.0
			2:1	35.0	27.6	6.6	25.6	5.0
			3:1	40.0	15.1	8.0	23.6	5.0
HTPEA(NGR)	100	8.8	1:1	28.0	29.8	6.8	27.8	5.0
			2:1	35.0	27.4	6.8	25.4	5.0
			3:1	40.0	14.8	8.3	23.4	5.0

TABLE 6.1 Baked* film properties of water-dispersible HTPEA(DCO)/HMMM systems

Type of HPTEA resin	*Percentage Neutralisation*	*HPTEA/ HMMM ratio*	*Impact resistance*	*Scratch hardness*	*Flexibility and adhesion*	*Chemical resistance***			
						2% *NaOH* (24 *hrs*)	2% *HCl* (24 *hrs*)	*Water* (24 *hrs*)	*Xylene* (24 *hrs*)
HTPEA(DCO)	70	1:1	150	1.6	F	3	4	P	P
		2:1	200	2.1	P	2	4	P	P
		3:1	275	2.6	P	3	6	P	P
HTPEA(DCO)	80	1:1	200	1.3	F	5	3	P	P
		2:1	250	2.5	P	3	4	P	P
		3:1	300	3.0	P	6	4	P	P
HTPEA(DCO)	90	1:1	225	1.5	P	5	4	P	P
		2:1	300	2.7	P	3	5	P	P
		3:1	300	3.2	P	6	4,5	P	P
HTPEA(DCO)	100	1:1	250	1.0	P	2	3	P	P
		2:1	300	1.2	P	2	4	P	P
		3:1	300	0.8	P	5	4	P	P

* At 175°C for 20 min.

**0 – Film completely removed, 1 – Film cracked and partially removed, 2 – Film partially removed, 3 – Severe blistering, 4 – Slight blistering, 5 – Film darkened, 6 – Unaffected.

TABLE 6.2 Baked* film properties of water-dispersible HTPEA(NIGER)/HMMM systems

Type of HPTEA resin	*Percentage neutralisation*	*HPTEA/ HMMM ratio*	*Impact resistance*	*Scratch hardness*	*Flexibility and adhesion*	*Chemical resistance***			
						2% *NaOH* (24 *hrs*)	2% *HCl* (24 *hrs*)	*Water* (24 *hrs*)	*Xylene* (24 *hrs*)
HTPEA(NGR)	70	1:1	125	1.4	F	3	4	P	P
		2:1	200	1.9	P	1	4	P	P
		3:1	250	2.4	P	3	5	P	P
HTPEA(NGR)	80	1:1	175	1.1	F	4	3	P	P
		2:1	225	2.3	P	3	4	P	P
		3:1	275	2.8	P	6	4	P	P
HTPEA(NGR)	90	1:1	200	1.3	P	5	3	P	P
		2:1	275	2.5	P	4	5	P	P
		3:1	275	3.0	P	5	5	P	P
HTPEA(NGR)	100	1:1	225	1.0	P	3	3	P	P
		2:1	275	1.1	P	3	3	P	P
		3:1	300	0.7	P	5	4	P	P

* At 175°C for 20 min.

** 0 – Film completely removed, 1 – Film cracked and partially removed, 2 – Film partially removed, 3 – Severe blistering, 4 – Slight blistering, 5 – Film darkened, 6 – Unaffected.

functional groups available for cross-linking reaction will be less. This can lead to high degree of co-condensation and self condensation of remaining HMMM resins [11], which in turn make the film brittle. Hence the hardness decreases.

Imapct resistance is measured using falling weight type impact tester [9]. Impact resistance was found to increase with increase in percent neutralisation and with increase in amount of HMMM. This can be attributed to the high cross-link density resulting from the use of high amount of HMMM.

Type of oil was not found to have much effect on the scratch hardness and impact resistance properties.

Flexibility and Adhesion

Flexibility and adhesion of all the samples passed the test except those with 70 and 80 percent neutralisation having HTPEA/HMMM ratio 1:1. The failure of these samples might be due to brittleness arising out of excessive cross-link density of their films.

Acid and Alkali Resistance

The films become increasingly less resistant to alkali and acid as the amount of curing agent is increased. This can be due to the presence of unreacted HMMM which is leached out during immersion test. Type of oil was not found to have influence on the chemical resistance properties.

Water and Solvent Resistance

Water and solvent resistance were found to decrease with increase in the amount of cross-linking agent. This can be accounted for the same reason as in case of acid and alkali resistance.

CONCLUSION

It can be concluded from the work that, water-dispersible polyesteramide can be prepared by the method employed. There is a significant effect of amount of cross-linking agent and percentage of neutralisation on the film properties of the coatings. A properly formulated polyesteramide and its composition can be used and can replace conventional solvent based systems. Such a product would not only be cost effective, but also environmentally safer.

Acknowledgement

The authors wish to thank Principal and Head of Industrial Chemistry Department, V.P. and R.P.T.P. Science College, Vallabh Vidyanagar for providing necessary facilities for carrying out the research work.

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