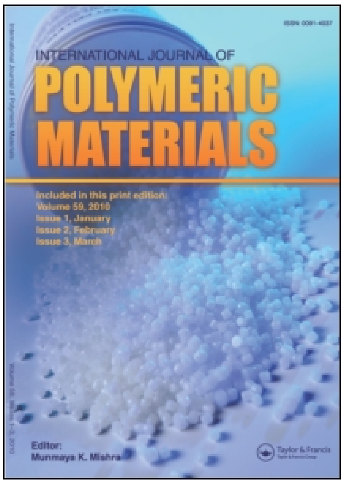

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polyesteramide-amino Resin Systems for Industrial Maintenance Coatings

T. K. Roy[a]; V. M. Mannari[ab]; D. A. Raval[ac]
[a] Department of Industrial Chemistry, VP and RPTP Science College, Gujarat, India [b] Development Manager, I.C.I. (India) Ltd., Hyderabad [c] Principal, Natubhai V. Patel College of Pure and Applied Sciences,

To cite this Article Roy, T. K. , Mannari, V. M. and Raval, D. A.(1998) 'Polyesteramide-amino Resin Systems for Industrial Maintenance Coatings', International Journal of Polymeric Materials, 42: 3, 285 — 295
To link to this Article: DOI: 10.1080/00914039808033876
URL: http://dx.doi.org/10.1080/00914039808033876

Intern. J. Polymeric Mater., 1998, Vol. 42, pp. 285–295
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in India.

Polyesteramide-amino Resin Systems for Industrial Maintenance Coatings

T. K. ROY, V. M. MANNARI* and D. A. RAVAL**

Department of Industrial Chemistry, VP and RPTP Science College, Vallabh Vidyanagar 388 120, Gujarat, India

(Received 17 January 1998)

Oil-modified polyesteramide resins, suitable for surface coating applications, have been synthesised, using a non-traditional semidrying niger seed oil (Guizota Olifera). *N,N*-bis-(2-hydroxyethyl) niger amide (HENA) has been prepared by aminolysis of the oil with diethanolamine using zinc oxide as a catalyst. HENA was reacted separately with both phthalic anhydride (PA) and isophthalic acid (IPA) in varying molar ratios to obtain two series of hydroxy-terminated polyesteramides (HTPEAs), having varying hydroxyl values. Coating compositions from these resins have been formulated by incorporation of butylated melamine formaldehyde (BMF) resin in two different ratios and their various baked film properties have been evaluated. The results reveal that the oil can successfully be used as a component of polyesteramide resins for applications in industrial stoving finishes. Further, IPA based HTPEAs show good mechanical and chemical properties compared to their PA counterparts.

Keywords: Polyesteramide; niger seed oil; HENA; embrittlement; cross-link density

INTRODUCTION

Baking finishes based on alkyd/amino resin systems are very widely used in industrial applications, especially for original equipment manufacture (OEM) finishes [1]. Such finishes have excellent balance of property requirement and cost. The type of alkyd resins used in such systems includes nonoxidising short oil alkyds generally based on

---

* Presently, Development Manager, I.C.I. (India) Ltd., Hyderabad.

** Corresponding author. Presently, Principal, Natubhai V. Patel College of Pure and Applied Sciences, Vallabh Vidyanagar – 388 120.

castor oil or coconut oil or semidrying oils such as soybean oil depending upon finished product requirements. Butylated urea formaldehyde (BUF) or melamine formaldehyde (BMF) resins are used in conjuction with such alkyds as cross-linking resins.

One of the inherent limitations of alkyd based systems is their relatively poor resistance to hydrolysis, particularly by alkalies [2]. This is believed to be due to the presence of ester linkages in their polymeric backbone, which are prone to hydrolysis [3]. Polyesteramide resins containing a significant number of amide linkages are known to improve water and chemical resistance properties of their films [4–7] and therefore are thought to successfully replace alkyd resins in certain demanding applications.

In the present work, polyesteramide resins (HTPEAs) using niger seed oil have been synthesized and employed as a component of a baking system in conjuction with BMF resins. Niger seed oil has been employed in such systems to explore its potential for utility in such applications.

Two series of HTPEA resins have been synthesized using phthalic anhydride (PA) and isophthalic acid (IPA) *viz.* HTPEA (P) and HTPEA(I) to investigate the influence of type of dicarboxylic acid on various film properties.

Curing in polyesteramide/amino system comprises two main reactions *viz.* (i) self-condensation of amino resins and (ii) condensation reaction involving the functional groups of polyesteramide [3, 8]. The hydroxyl groups of polyols react by either transetherification with the activated alkoxymethyl groups or by etherification of methyl groups of BMF resin to form new ether cross-links (Fig. 1). Addition of acid catalyst such as para-toluenesulphonic acid (0.5–1.5% by wt. of BMF resin) enhances curing rate. Higher acid value of polyesteramide resin also favours the etherification reaction [3, 8].

MATERIALS AND METHOD

Refined niger seed oil was procured from Viscus Oils (P) Ltd., Indore. The other chemicals used *viz.* zinc oxide, PA, IPA, xylene, methanol and butanol were of laboratory reagent grade. The BMF resin (SYNPOL MF®–310) was procured from M/s. Synthetics and

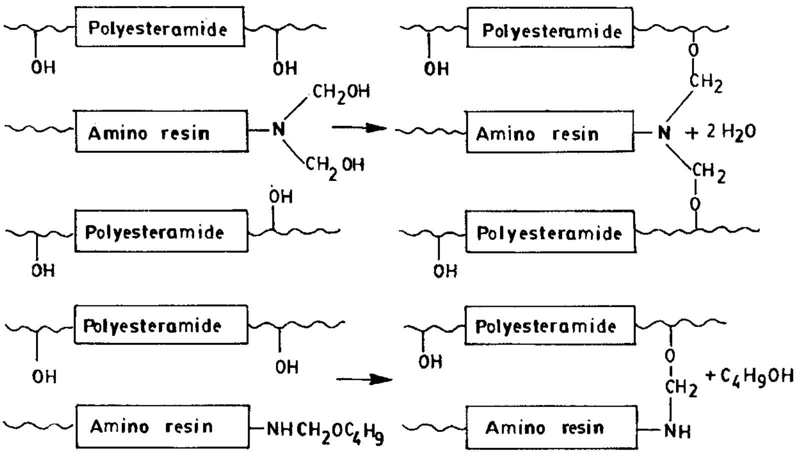

FIGURE 1 Schematic representation of curing of polyesteramide/amino system.

Polymers Ltd. and was used without any modification. Characteristics of BMF resin are shown in Table I.

The acid value, colour, viscosity, nonvolatile content, drying time, scratch resistance, flexibility and adhesion were determined as per Indian Standard Specifications [9, 10]. Resistance towards acid, alkali, water and xylene were determined as per standard methods described in the literature [11].

The infrared spectrum (Fig. 2) of a representative polyesteramide was recorded using Shimaru spectrophotometer. The flexibility was measured using 1/4″ and 1/8″ conical mandrels. The films were applied on mild steel panels (6″ × 4″) and (6″ × 2″) and mechanical properties were studied as per Indian Standard Specifications [9]. Impact

TABLE I Characteristic of BMF resin (SYNPOL BMF®-310)

Sr. No.	*Characteristic properties*	
1	Percentage non-volatile	60
2	Viscosity (Poise) (at 25°C)	16
3	Acid value (mg KOH/g)	02
4	Mineral Spirit Tolerance (ml/10 gm)	52
5	Density (at 25°C) (g/cm^2)	1.02

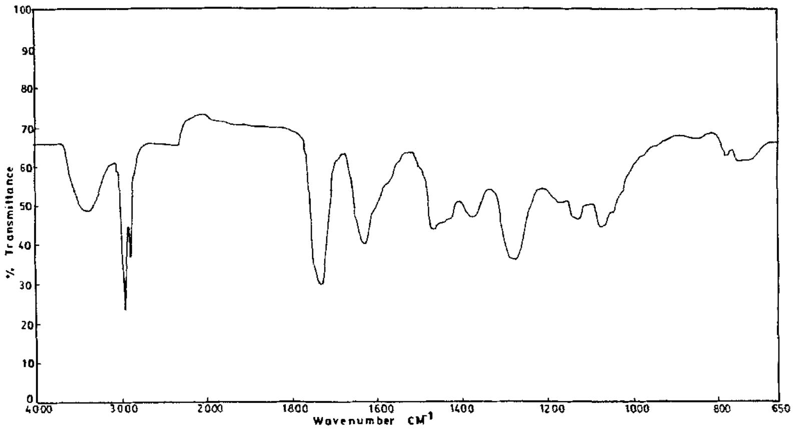

FIGURE 2 IR Spectrum of polyesteramide.

resistance of films has been determined by falling weight type impact tester [11].

EXPERIMENTAL

Preparation of HENA

Fatty acid diethanolamides were prepared directly from niger seed oil according to the reported method [6, 7, 12, 13, 14]. The percent by weight fatty acid composition of the niger seed oil is Myristic: 1.7, Palmitic: 5.0, Stearic: 2.0, Oleic: 38.9, Linoleic: 51.6, Arachidic (trace) and Behemic (trace). The characteristics of niger seed oil are shown in Table II.

Purified niger seed oil (1.0 mole) was heated under nitrogen with diethanolamine (3.0 mole) at 200°C with efficient stirring and under nitrogen for 15 minutes, using zinc oxide (0.02 mole) as a catalyst. The progress of the reaction was monitored with the help of thin layer chromatography (TLC), until the disappearance of the spot of oil was observed [6, 14, 15]. The fatty acid diethanolamides were purified from glycerol, excess diethanolamine and other water soluble impurities by washing its solution in diethyl ether with 15% aqueous sodium

TABLE II Characteristics of niger seed oil (Guizota Olifera) and its amide (HENA)

Sr. No.	*Characteristic properties*	*Niger seed oil*	*HENA*
1	Acid value (mg KOH/g)	7.25	5.00
2	Saponification value (mg KOH/g)	191.20	–
3	Iodine value	134.50	131.00
4	% UN.sap.matter	0.76	–
5	Hydroxyl value (mg KOH/g)	17.30	291.00
6	Specific gravity	0.925	0.96
7	Refractive index @ 30°C)	1.4671	–
8	Colour	7.00 (y + 5R) (Lovibond)	12.00 (Gardner)
9	Viscosity @ 25°C Poise	–	5.00

chloride solution, followed by distilled water. The characteristics of HENA are reported in Table II.

Preparation of HTPEAs

Hydroxy-terminated polyesteramides were prepared by reacting HENA (1.15–1.45 mole) with both PA and IPA (1 mole), separately [6, 12, 13].

The reactants were heated slowly with efficient stirring under nitrogen at the temperature of 190 ± 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 the progress of the reaction. The condensation reaction was carried out until low acid values were obtained. Resultant resins were thinned to 60% solid using xylene as solvent. The characteristics of HTPEAs are shown in Table III.

Preparation of Coating Compositions

Coating compositions were prepared by combination of BMF and different HTPEAs in two different ratios, *viz.* 4:1 and 3:1. The various HTPEA/BMF coating compositions prepared for the study are presented in Table IV. The compositions were thinned to the required viscosity for application and the films were applied and baked at 150°C for 15 minutes, for studying various film properties.

TABLE III HTPEA composition and properties

	HTPEAs							
	P-I	*P-II*	*P-III*	*P-IV*	*I-I*	*I-II*	*I-III*	*I-IV*
Components								
HENA	443	481	520	558	443	481	520	558
PA	148	148	148	148	–	–	–	–
IPA	–	–	–	–	166	166	166	166
Properties								
Acid value (mg KOH/g)	14	12	10	11	12	11	9	9
Hydroxyl value (mg KOH/g)	37	60	81	97	42	64	83	102
Viscosity (@ 30°C)	4.20	4.00	3.40	3.00	4.70	4.25	3.70	3.40
Colour (Gardner)	16	16	15	14	16	15	14	14
Specific gravity	0.98	0.97	0.96	0.96	0.97	0.97	0.96	0.95

P-I–HTPEA with HENA/PA ratio 1.15; P-II–HTPEA with HENA/PA ratio 1.25; P-III–HTPEA with HENA/PA ratio 1.35; P-IV–HTPEA with HENA/PA ratio 1.45; I-I–HTPEA with HENA/IPA ratio 1.15; I-II–HTPEA with HENA/IPA ratio 1.25; I-III–HTPEA with HENA/IPA ratio 1.35; I-IV–HTPEA with HENA/IPA ratio 1.45.

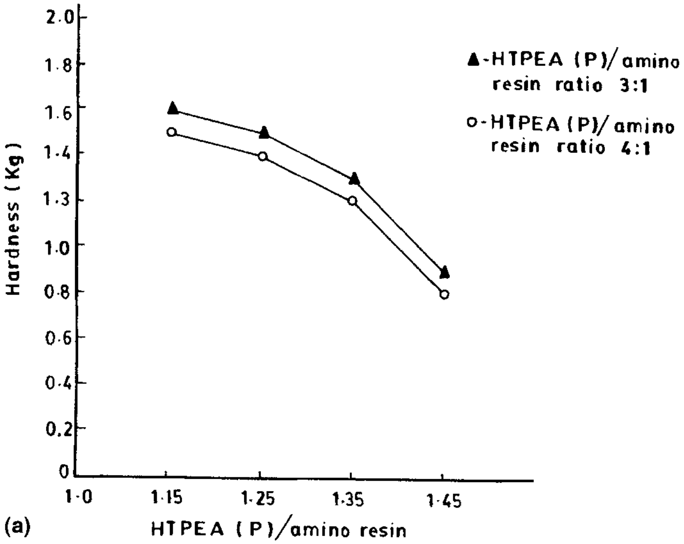

FIGURE 3 (a) Dependence of the change in film hardness of the HTPE (P) resin/amino resin ratio. (b) Dependence of the change in film hardness of the HTPEA (I) resin/amino resin ratio.

RESULTS AND DISCUSSION

An attempt has been made to evaluate structure property relations and to study various applications of the coatings prepared from the

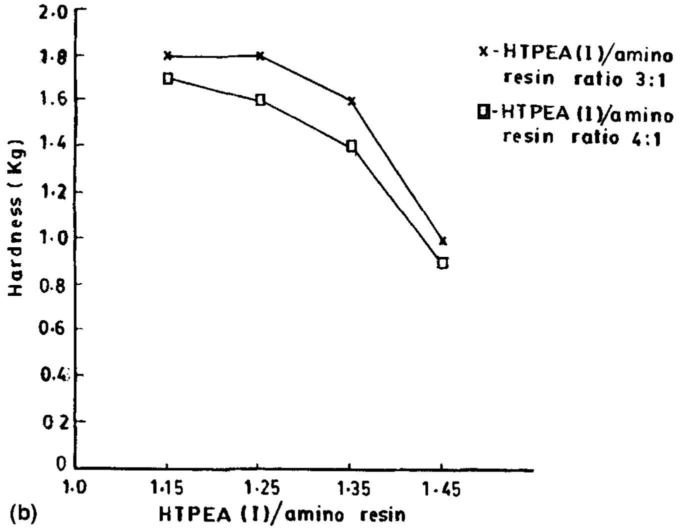

FIGURE 3 (Continued).

polyesteramides. These coatings on application using brush, baked at 150°C produced hard, adherent and flexible coatings.

Both PA and IPA have been used as acid components for the preparation of polyesteramides. Isophthalic esters have better resistance to hydrolysis than their PA counter parts [2, 4–6]. IPA based polymers on comparison with PA based polymers have high molecular weights [2] which give improved mechanical and chemical properties to their films [6, 7].

From the results, it has been found that the hydroxyl values of HTPEAs derived from both the oils increase with increase in molar excess of HENA. Further, with increase in molar excess of HENA, the viscosity and colour of the resins decrease. The decrease in viscosity can be accounted for the lower molecular weight of polymers due to molar excess of hydroxyl groups over acid functions [11, 16]. The lowering of colour intensity can be due to the shorter processing time with increasing excess of HENA.

The structure of the polyesteramide was confirmed from IR spectrum (Fig. 2). The absorption bands are at 3400 cm^{-1} (—OH group), 1740 cm^{-1} (ester group), 820 cm^{-1} (—C—N stretching), 1640 cm^{-1}

TABLE IV *Baked film properties of HTPEA/BMF compositions

	P-I		*P-II*		*P-III*		*P-IV*		*I-I*		*I-II*		*I-III*		*I-IV*	
HTPEA/BMF ratio (by wt.)	3:1	4:1	3:1	4:1	3:1	4:1	3:1	4:1	3:1	4:1	3:1	4:1	3:1	4:1	3:1	4:1
Scratch hardness (kg)	1.6	1.5	1.5	1.4	1.3	1.2	0.9	0.8	1.8	1.7	1.8	1.6	1.6	1.4	1.0	0.9
Impact resistance (Ibs/inch)																
Direct	225	250	250	275	175	200	100	125	250	275	250	300	200	225	150	175
Diverse	200	250	225	250	175	175	100	100	225	275	250	275	175	200	125	125
Adhesion (Stripping)	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Flexibility (Mandrel)	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Resistance to chemicals																
2% NaOH (hrs.) (Passes)	2.45	2.30	3.30	3.15	3.50	3.35	4.15	3.50	3.10	2.50	3.50	3.4	4.20	4.00	4.40	4.25
2% HCI (200 hrs.)	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Xylene (200 hrs.)	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Water (200 hrs.)	P	P	P	P	P	P	P	P	P	P	P	P	P	P		

P = Passes;
*150°C for 15 minutes.

and $1725\,\mathrm{cm}^{-1}$ (—C=O stretching), $1620\,\mathrm{cm}^{-1}$, $1775\,\mathrm{cm}^{-1}$, $1070\,\mathrm{cm}^{-1}$ and $740\,\mathrm{cm}^{-1}$ (aromatic moiety) [17].

Film Properties

Table IV shows various properties of cured films of different polyesteramide compositions.

Flexibility and Adhesion

All samples passed flexibility test on 1/4″ an 1/8″ conical mandrel, which is expected of oil-based coatings. All samples passed stripping test for adhesion.

Scratch Hardness and Impact Resistance

The results reveal that the impact resistance properties of coatings improve with increasing hydroxyl value of HTPEAs at a given HTPEA/MF ratio. This can be attributed to the increase in cross link density of the film due to higher number of hydroxyl groups which provide cross-linking sites during curing. This in turn imparts higher scratch hardness to the films. However, the compositions containing HTPEAs having higher hydroxyl value show reduction in scratch hardness probably due to excessive high cross link densities leading to reduction in segmental mobility [18, 19]. It, therefore, follows that there is an optimum level of cross-link density beyond which, impact resistance decreases. Thus in general, scratch hardness and impact resistance are found to increase with increase in hydroxy value of HTPEA. However, there is maximum limit beyond which these properties decrease. In the present case, the maximum scratch hardness was observed for composition P-I (3:1 ratio).

Acid, Alkali, Water and Solvent Resistance

Acid and alkali resistance increases with increase in hydroxyl content of HTPEA. Chemical resistance mainly depends upon the chemical composition of polymer back-bone and the degree of cross-linking in the films [8, 11]. The data obtained indicate that the systems comprising HTPEAs with more BMF content exhibit a superior chemical resistance. The higher amount of BMF resin provides the films with a higher potential for cross-linking, thus creating a dense molecular network, which is responsible for its superior chemical resistance [8]. These systems are more resistant to water and solvents than the systems containing less amount of BMF resin. Further, HTPEAs based on IPA show good alkali resistance compared to their PA counterparts.

CONCLUSION

The polyesteramide resins derived from niger seed oil can successfully be employed as components of industrial stoving finishes. It has been observed that the mechanical property, such as impact resistance, is a function of hydroxyl value of the resins and hence optimum level of excess hydroxy components should be used in synthesis of resins to achieve good balance between performance properties. Further, IPA based HTPEAs show good mechanical and chemical properties compared to their PA counterparts.

Acknowledgement

The authors wish to thank Principal, V.P. & R.P.T.P. Science College, Vallabh Vidyanagar for providing necessary facilities for carrying out the research work.

References

[1] Wicks, Z. W. Jr., Jones, F. N. and Pappas, S. P. (1994). "Organic Coatings: Science and Technology", Vol. 2, John Wiley and Sons, New York, p. 178.

[2] Swaraj, P. (1985). "Surface Coatings, Science and Technology", John Wiley and Sons, New York, p. 133.

[3] Mannari, V. M., (1995). Ph.D. Thesis, Sardar Patel University, Vallabh Vidyanagar, p. 37.

[4] Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G. (1985). "Encyclopedia of Polymer Science and Engineering", John Wiley and Sons, New York, **1**, 2nd edn., p. 652.

[5] "Surface Coatings", Vol. 1, Editors, Oil and Colour Chemists' Association, Australia, Chapman and Hall, London, 1987, p. 95.

[6] Raval, D. A., Roy, T. K. and Mannari, V. M. (1996). *J. Sci. Ind. Res.*, **55**, 263.

[7] Roy, T. K., Mannari, V. M. and Raval, D. A. (1996). *J. Sci. Ind. Res.*, **55**, 971.

[8] Kalendra, P. and Kalendova, A. (1995). *JOCCA*, **78**(12), 508–11.

[9] "Methods of Sampling and Testing for Varnishes and Lacquers", IS-197-1967, (First Revision, 1981), Bureau of Indian Standards, New Delhi.

[10] "Indian Standard Methods of Sampling and Test for Resins and Paints", IS-354-1967, Bureau of Indian Standards, New Delhi.

[11] Lambourne, R. (1987). "Paint and Surface Coatings, Theory and Practice", Ellis Horwood, Chichester, p. 605.

[12] Varghese, T. M. and Krishnan, V. (1990). *J. Colour Society*, **29**, 1.

[13] Gast, L. E., Schneider, W. J. and Cowan, J. C. (1966). *JAOCS*, **43**, 418–421.

[14] Raval, D. A. and Mannari, V. M., *Res. and Ind.*, **38**(3), 129–132, September (1993).

[15] Varghese, T. M. and Krishnan, V., *J. Colour Society*, **29**, 1, July–September (1990).

[16] Solomon, D. H. (1977). "The Chemistry of Organic Film Formers", Robert, E. Krieger Publishing Co., Huntington, New York, p. 110.

[17] Urbanski, J., Czeriwinskim, W., Janicka, K., Majevska, F. and Zowall, H. (1977). "Hand Book of Analysis of Synthetic Polymers and Plastics", Ellis Horwood Ltd. Chichester, p. 234.

[18] Kaning, G. (1967). *Journal of Polymer Science*, **16**, 1957.

[19] Shibayama, K. (1975). *Prog. in Org. Coat.*, **3**, 245.