Polyesteramides from Linseed Oil for Protective Coatings Low Acid-Value Polymers[1]

L. E. GAST, WILMA J. SCHNEIDER and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

Abstract

Linseed and soybean diethanolamides, from the sodium alkoxide-catalyzed reaction of the corresponding oil with diethanolamine, were used as diols to prepare a series of polyesteramides. The diols and dibasic acids or anhydrides were heated in refluxing xylene until the theoretical amount of water was collected in a trap. Low acid-value linseed polymers were prepared with 10, 20, and 30 mole percent excess diol over the dibasic acid, and the effect of the excess diol on molecular weight, viscosity, and film properties of the polymers was examined. Polyesteramides which contained 10 mole percent excess fatty diethanolamide were made with 11 dibasic acids or anhydrides. The polymers were brown-orange oils with Gardner viscosities of Z7 to >>Z10.

Number-average molecular weights ranged from 2,200 to 5,200. Data on drying characteristics, hardness, and chemical resistance of films were obtained. The better polymers air-dried rapidly to give hard, glossy films (Sward rocker 20–60). Films baked at 190C for 10 min were softer than the corresponding air-dried films. Xylene resistance of soybean and linseed polymer films was generally excellent, and alkali resistance was moderate. Soybean films showed the better alkali resistance.

Introduction

PREVIOUSLY WE DESCRIBED the preparation from linseed oil (1) of some new polyesteramide protective-coating vehicles. Essentially, pure N,N-bis(2-hydroxyethyl) linseed amide (HELA) was prepared by the base-catalyzed aminolysis of linseed oil with diethanolamine. A variety of polyesteramides were synthesized from equimolar quantities of HELA and either dibasic acids or anhydrides. The better equimolar polymers gave films with good drying properties, hardness, and xylene resistance. Generally films air-dried for 10 days were as hard as corresponding films baked at 190C for 10 min. Alkali resistance of the films was no better than commercial alkyds. Lowering of the acid value of a polymer usually improves alkali resistance of its films. Use of excess diol yielded polyesteramides with the expected lower acid values and these films showed resistance to alkali.

We now describe the preparation and film properties of polyesteramides containing excess HELA or HESA [N,N-bis(2-hydroxyethyl) soybean amide].

Experimental Procedures

Polyesteramides of HELA/HESA and Dibasic Acids

The general procedure used for the preparation of polyesteramides was as follows. HELA/HESA (0.11 mole), dibasic acid or anhydride (0.10 mole), and 100 ml of xylene were placed in a round-bottomed flask, fitted with a nitrogen inlet tube and a Dean-Stark trap. The reaction mixture was heated at reflux temperature (140–150C) until approximately the theoretical amount of water (based on the acid or anhydride) was collected in the trap. The trap was removed, and xylene was distilled for an additional 3 hr to azeotrope off the last traces of water. Dry xylene was slowly added to the flask to replace that which was distilled. The xylene was removed from the polymer in a rotary film evaporator under a pressure of 2 mm. Polyesteramides with larger molar excesses of HELA were prepared by the same procedure.

Number-average molecular weights were determined on a Mechrolab vapor pressure osmometer, Model 301, with benzene as the solvent. Before the molecular-weight determinations, all polymers were diluted with benzene and the solvent was removed in a rotary film vacuum evaporator. This treatment was repeated several times to ensure complete removal of solvents other than benzene.

Film Casting and Testing

Chemical resistance, hardness, and drying tests were run on films cast from solutions containing 25% solids in toluene. "Drawdowns" were made with a doctor blade set at 4 mils to give a dried-film thickness of approximately 1 mil. Dried-film thickness was measured with a Permascope coating thickness gauge. Films were air-dried or baked at the specified cycle with a drier system, when used, consisting of 0.5% lead and 0.01% cobalt as naphthenates. Hardness tests were made by the Sward rocker technique. Chemical and solvent resistance was measured by placing a 1.5-in. diameter watch glass, convex side down, on the surface of the film and introducing the reagent or solvent between the watch glass and film surface. Periodic examination was conducted until the film showed evidence of softening or other deterioration. Dry-to-touch (DTT) and tack-free (TF) times, as defined by Gardner (2), were determined on air-dried films by manually placing a small amount of sand on the film periodically.

Discussion and Results

Low acid values are desirable for alkyd resins to lower their reaction with basic pigments and to improve their alkali and water resistance (3). Such alkyds are prepared by using an excess of the alcohol over acid groups. This procedure can be used with polyesteramides to lower their acid value and improve alkali resistance; however these polymers will have lower molecular weights, and the drying characteristics and hardness of their films may be adversely affected. We prepared a series of isophthalic polyesteramides containing excess HELA in an attempt to study the effect of the excess HELA on molecular weight and other properties (Table I) and to find a favorable balance between desirable and undesirable film characteristics.

Increasing the amount of HELA beyond the equimolar composition lowers the molecular weight of the polymer formed. To calculate the degree of

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[1] Presented at Division of Organic Coatings and Plastics Chemistry, 153rd ACS meeting, Miami Beach, Fla., April 1967.

[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I

Properties of Isophthalic Polyesteramides Containing Excess N,N-bis(2-hydroxyethyl) Linseed Amide (HELA)

Percentage molar excess HELA	Viscosity[a] (25C) poise	Color (Gardner)	Molecular weight	Iodine value	Acid number
0	7100	15	4200	113	4.3
10	7100	15	2900	114	0.9
20	3600	17	2600	118	1.6
30	850	14	2300	122	0.7

[a] Determined with a Haake Rotovisco viscometer at shear rates from 14 to 84 sec.$^{-1}$.

polymerization ($\overline{\text{X}}\text{n}$) for a polyester when there is nonequivalence of reactants, we use the expression

$$\overline{\text{X}}\text{n} = \frac{1+\text{r}}{2\text{r}(1\text{-p}) + 1\text{-r}}$$

where r = number of acid groups initially present, divided by the number of alcohol groups initially present, and p = fraction of acid groups which have reacted at a given stage (4). This expression gave an $\overline{\text{X}}\text{n}$ for the respective polymers, containing 10, 20, and 30 mole percent excess HELA, of 19.3, 10.0, and 7.5. If an average unit weight of 497 is taken for the isophthalic polyesteramides, the calculated number-average molecular weights for the 10, 20, and 30 mole excess HELA polymers are 9,600, 4,970, and 3,720. The measured molecular weights shown in Table I are much lower than the calculated values; therefore other factors are affecting the molecular weight of the polymers. The most probable cause is the 5% impurity in HELA (95% pure, based on hydroxyl analysis).

An examination of HELA by thin-layer chromatography and infrared analysis showed that the major impurity is the morpholide of linseed fatty acids. If we allow for this material in molecular-weight calculations, corrected calculated number-average molecular weights are 4,100, 3,000, and 2,510 for the respective polymers containing 10, 20, and 30 mole percent excess HELA. These values are in better agreement with experimental values.

Excess diol can also have a marked effect on drying properties of polyesteramides. The DTT and TF times of the polymers containing 0, 10, 20, and 30% excess HELA are shown in Table II. The DTT and TF times increased and hardness decreased with the amount of excess HELA. The equimolar and 10% excess polymer films showed a significant increase in hardness between 3 and 25 days.

On the basis of data in Tables I and II the compositions containing 10% molar-excess diol were chosen for additional studies with 11 dibasic acids. Table III lists the properties of these polymers prepared from HELA and HESA. All products, except the linseed dichloromaleic polymer, were orange-brown viscous oils, of which the most viscous were those derived from the three phthalic acids and maleic anhydride. All polymers had Gardner viscosities and color similar to the equimolar products (1), but acid numbers were generally lower. The acid numbers of the linseed terephthalic and fumaric polymers were relatively high because the acids were insoluble in the reaction mixture and gave a product with a small amount of unreacted finely dispersed acid. Since molecular weights of the soybean polymers were higher than the corresponding linseed products, possibly the purity of the HESA used was higher than HELA although the hydroxyl content of these dihydroxyamides was identical.

TABLE II

Air-Dried Film[a] Properties of Isophthalic Polyesteramides Containing Excess HELA[b]

Percentage molar excess HELA	Rocker hardness, days				Dry-to-touch, hr	Tack-free, hr
	3	10	17	25		
0	44	54	58	60	0.8	1.0
10	36	40	44	46	1.2	1.25
20	34	35	36	36	1.8	2.0
30	20	24	24	25	2.0	2.1

[a] Contains 0.5% Pb + 0.01% Co drier as naphthenate.

[b] Pure N,N-bis(2-hydroxyethyl)linseed amide.

TABLE III

Properties of 10% Molar Excess Diol Polyesteramides

Acid or anhydride	Gardner		Molecular weight	Degree of polymerization	Iodine value (Wijs)	Acid number
	viscosity:color					
	Linseed polyesteramides					
Terephthalic	>>Z10	18	2900	5.8	109	8.2
Phthalic	>Z10	16	2500	5.0	114	1.1
Isophthalic	>>Z10	15	2900	5.8	114	0.9
Endic[a]	Z9	13	3020	5.9	153	1.1
Hydrogenated endic	Z10	15	2800	5.4	108	2.2
Maleic[b]	Z9–10	16	2500	7.2	122	14.9
Maleic	>Z10	14	3300	9.5	125	5.7
Fumaric	Z7	15	2200	6.4	126	20.9
Dichloromaleic	....	Black	....		133	32.0
Itaconic	Z8	16	2700	7.5	126	2.1
Brassylic	Z10	15	4000	7.0	99	1.4
Dimer[c]	Z8	13	3300	3.6	145	0.9
	Soybean polyesteramides					
Phthalic	>>Z10	....	3000	6.0	78	2.7
Isophthalic	>>Z10	.	4900	9.8	78	5.4
Endic	>Z10	15	3400	6.6	113	3.9
Hydrogenated endic	>>Z10	16	2900	5.6	74	6.8
Maleic	>>Z10	12	5200	11.6	85	8.6
Itaconic	Z8–9	15	3100	6.7	88	3.8

[a] Endic anhydride is Velsicol's designation for endo-*cis* bicyclo-(2,2,1)-5-heptene-2,3-dicarboxylic anhydride.

[b] Prepared in refluxing benzene; maximum temperature 109C.

[c] Prepared by catalytic process (1).

Previous studies with the equimolar maleic polyesteramide had shown that a reaction temperature of 140–150C gave a product in which the double bond had isomerized largely to the *trans* form. The tendency of maleic acid or esters to isomerize to fumaric during polyesterifications is well known. The effect of glycol structure on this isomerization has recently been studied by Szmercsanyi et al. (5). For example, they found that maleate polyesterifications at 140C with 1,2-propylene glycol gave a polymer in which 75% of the original maleate had isomerized to the fumarate after 300 min. A maleate polymer prepared with diethylene glycol under the same conditions was only 20% isomerized. From these data and a study of molecular models of their polyesters they showed that the molecular strain associated with the maleate molecule (tendency to isomerize) depends on the structure of the whole polyester, that is, on the glycol which was used.

We studied the extent of isomerization of maleate to fumarate in polyesteramides prepared from HELA. To obtain a predominantly *cis* maleate polyesteramide for evaluation work, a reaction was carried out in refluxing benzene where the temperature was kept below 109C. This polymer had a higher acid value and lower viscosity and molecular weight than the maleate product prepared at 140C. Comparison of infrared data from these polymers with that from the fumarate polymer revealed that the low- and high-temperature maleate polymers isomerized 37 and 57% respectively to fumarate during polyesterification. Thus maleate polyesters prepared from HELA are isomerized almost as much as those prepared from 1,2-propylene glycol.

Table IV lists the drying properties and hardness

TABLE IV

Air-Dried Film[a] Properties of 10% Molar Excess Diol Polyesteramides

Acid or anhydride	Hardness, days			Dry-to-touch, hr	Tack-free, hr	Chemical Resistance[b]	
	3	10	21			5% NaOH, min	Xylene, hr
			Linseed polyesteramides				
Terephthalic	38	38	38	2.67	4.25	P8	>240
Phthalic	30	44	46	1.25	2.25	P4	>240
Isophthalic	36	40	46	1.20	1.25	P6 D25	>240
Endic	45	58	59	0.67	0.70	P1	>240
Hydrogenated endic	44	58	60	0.70	0.75	P2	>240
Maleic[c]	20	24	28	15.1	26	D2	>240
Maleic	30	34	35	5	8.16	D2	>240
Fumaric	26	34	34	17.4	27	D2	>240
Itaconic	16	22	28	3	6	D3	P 240
Brassylic	....	....	....	30	624	P4	>240
Dimer[d]	....	....	....	24	624	P3 D4	P 0.4
			Soybean polyesteramides				
Phthalic	22	26	26	0.70	0.83	P4 D10	>220
Isophthalic	32	34	38	1.0	1.1	P8 D26	>220
Endic	22	24	24	2.4	2.6	P3 D20	1.0
Hydrogenated endic	20	22	22	4.25	4.5	P6 D140	>220
Maleic	20	20	20	0.9	1.1	D2	P 0.2
Itaconic	26	26	26	1.0	1.3	D2	>220
Soy alkyd[e]	8	14	18	2	22	D6	P 0.5

[a] Contains 0.5% Pb + 0.01% Co drier as naphthenate.
[b] P = Puckered, D = Dissolved.
[c] Prepared in refluxing benzene.
[d] Prepared by catalytic process (1).
[e] 65% Oil-length alkyd.

of air-dried linseed and soybean polyesteramide films containing Pb-Co drier. All linseed polyesteramide films, except those from dimer and brassylic acids, had Rocker hardness values that were high at three days except for the terephthalic film and showed a significant increase at 21 days. These films air-dry more rapidly than films from the corresponding equimolar polymers (1), as shown by both hardness data and DTT and TF times. These times for the high-temperature maleate film were shorter than those for the low-temperature film, but hardness values attained after 21 days of air-drying were similar. A comparison of the drying times of both maleate films with that of the fumarate film shows that molecular weight of the polymers (Table III) rather than double-bond configuration is probably responsible for the faster drying properties of the high-temperature film. Linseed polyesteramide films from brassylic and dimer acids were soft and tacky after 26 days of air-drying. Alkali resistance of the air-dried films was no better than that of the equimolar films (1) even though the acid number was generally lower. Except for the dimer polymer, xylene resistance of air-dried linseed polyesteramide films was excellent.

Four of the six soybean polyesteramide films dried more rapidly than the corresponding linseed films. This is noteworthy in that the soybean polymers contain less unsaturation than the linseed polymers and differences in molecular weight are not great enough to account for the improvement in drying properties. Comparison of hardness data shows that, although the linseed polyesteramide films are somewhat harder than the soybean films, both have similar xylene and alkali resistance. Twelve of the 14 polyesteramide films had better drying properties and developed harder films than a 65% oil-length soy alkyd.

Properties of baked films from the soybean and linseed polyesteramides with and without drier are shown in Table V. Baked films with drier were not so hard as the corresponding air-dried films. All polymers gave moderately hard baked films except the linseed polyesteramide films from brassylic and dimer acids. In the linseed series, baked films with drier from the terephthalic, phthalic, maleic (high temperature), and itaconic polymers tended to wrinkle if the films were thicker than 1 mil. The hardest baked film was from the dichloromaleic anhydride linseed polyesteramide; however this film was almost black. The baked linseed fumarate polyesteramide film was significantly harder than the linseed maleate films. Thus, with baked films, double-bond configuration of the dibasic acid may be more important than molecular weight in obtaining hard films. Nineteen of the 32 baked polyesteramide films were harder than the film of a 65% oil-length soy alkyd. Alkali resistance of baked films was significantly better than that of the air-dried films, and it was better for the baked soybean polyesteramide films than for the corresponding linseed films. Xylene resistance of all, except one of the baked polyesteramide films, was excellent.

TABLE V

Film Properties of 10% Molar Excess Diol Polyesteramides Baked at 190C for 10 Minutes

Acid or anhydride	Hardness[a]		Alkali resistance, min		Xylene resistance, days	
	+	−	+	−	+	−
			Linseed polyesteramides			
Terephthalic	30	31	30	28	>14	>14
Phthalic	20	20	60	60	>14	>14
Isophthalic	30	29	90	90	>14	>14
Endic	16	26	55	25	>14	>14
Hydrogenated endic	20	28	450	135	>14	>14
Maleic[b]	12	4	9	9	>14	>14
Maleic	18	6	14	14	>14	>14
Fumaric	28	22	13	15	>14	>14
Dichlormaleic	33 Black	51 Black	20	20	>14	>14
Itaconic	18	16	30	30	>14	>14
Brassylic	6	8	30	132	>14	>14
Dimer[c]	4	4	90	157	1	>14
			Soybean polyesteramides			
Phthalic	18	16	>600	370	>10	>10
Isophthalic	22	34	260	90	>10	>10
Endic	12	16	100	45	>10	>10
Hydrogenated endic	20	tacky	300	65	>10	>10
Maleic	16	18	80	20	>10	>10
Itaconic	12	16	80	17	>10	>10
Soy alkyd[d]	16	16	24	150	>12	>12

[a] (+) = with 0.5% Pb + 0.01% Co drier as naphthenate. (−) = without drier.
[b] Prepared in refluxing benzene.
[c] Prepared by catalytic process (1).
[d] 65% Oil-length alkyd.

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[Received November 15, 1967]