

Polyester Amides from Linseed Oil for Protective Coatings¹

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Abstract

The sodium alkoxide-catalyzed reaction of linseed oil or linseed methyl esters with diethanolamine produces almost exclusively linseed diethanolamides. Reaction conditions, e.g., temperature, amount of excess diethanolamine and mode of adding reactants, are reported. The best conditions for producing diethanolamide directly from linseed oil (1 mole) required adding oil to the sodium alkoxide in diethanolamine (6 moles) and heating at 110–115°C for 35 min. The linseed diethanolamide isolated in 93–95% yield was an amber oil. Progress of the reaction, followed by thin-layer chromatography, showed only trace amounts of byproducts.

Polyester amides were prepared by heating linseed diethanolamide in refluxing xylene with dibasic acids or anhydrides, e.g., azelaic, maleic, fumaric, phthalic, terephthalic, itaconic, brassylic and dimer acids. Molecular weight, viscosity and film properties (air-dried and baked) of the polyester amides were determined.

Introduction

LINSEED OIL OR ALKYDS containing vegetable oil fatty acids have long been important as vehicles in protective coatings for exterior use on wood. While these products are generally satisfactory, improvement in some of their properties, e.g., durability and mildew resistance, by chemical modification of the basic vehicle has been, and continues to be, an important objective of coatings research. Many studies have been made of alkyds containing a variety of polyols and dibasic acids in combination with vegetable oil fatty acids to produce coatings having a wide range of film properties. However, synthetic resins from vegetable oils containing amide or imide linkages derived from amino alcohols have previously not been studied extensively. Wright and DuPuis (12) reported that imide-modified alkyds made from glycerylamine, phthalic anhydride and glycerol had improved film characteristics over conventional alkyds with respect to drying, hardness and water vapor resistance. The use of other amino alcohols in the preparation of synthetic resins for coatings has also been reported (6–8). This paper describes the preparation of some new polyester amides containing linseed fatty acids and some preliminary evaluation studies on their film properties.

Experimental

N,N-Bis(2-Hydroxyethyl) Linseed Amide

Method A. Distilled diethanolamine (21 g, 0.2 mole) bp 170°C/25 mm, N_D^{25} 1.4740, was placed in a round-bottomed flask fitted with a stirrer, thermometer, nitrogen inlet tube and dropping funnel. Sodium methoxide catalyst (0.13 g, 0.0024 mole) was added, and the flask was heated to 110–115°C. Linseed methyl ester (29.5 g, 0.1 mole) was added dropwise over a period of 15 min. After the addition of ester, the dropping funnel was replaced by a vac-

uum take off, and the reaction was continued for 1 hr under reduced pressure of 20 mm to facilitate removal of methanol formed during the reaction. After cooling, the reaction mixture was dissolved in ether, washed with 15% aqueous sodium chloride and dried over sodium sulfate. The ether solution was filtered and the ether removed to yield 34 g of yellow-orange oil (93% yield). Thin-layer chromatography (TLC) (9) of the product on silicic acid plates with a solvent system of 70 ml hexane, 30 ml ether, 1.0 ml HOAc showed it to be essentially pure *N,N*-bis(2-hydroxyethyl) linseed amide (HELA), except for trace amounts of linseed fatty acid.

Method B. Diethanolamine (31.5 g, 0.3 mole) was placed in a round-bottomed flask fitted with a stirrer, nitrogen inlet tube and dropping funnel. Sodium methoxide (0.19 g, 0.0035 mole) was added and the contents were heated to 115°C. Linseed oil (LSO) (44 g, 0.05 mole) was added dropwise over a period of 15–20 min. Samples for TLC analysis were withdrawn periodically to study the progress of the reaction. The reaction was usually complete in about 35 min. The product was treated as described under Method A to yield 51.9 g yellow-orange oil (94.1% yield). Analyses on a representative product are shown in Table I.

Polyester Amides of HELA and Dibasic Acids

HELA (0.05 mole), dibasic acid (0.05 mole) and 50 ml xylene were placed in a round-bottomed flask fitted with nitrogen inlet tube and Dean-Stark trap to collect the water formed. The reaction mixture was heated at reflux temperature (140–145°C) until approximately the theoretical amount of water was collected. The xylene was removed from the polymer in rotary film evaporator under pressure of 2 mm. Properties of the polyester amides prepared by this method are shown in Table II.

Film Casting and Testing

Chemical resistance, hardness and drying characteristic tests were run on films cast from solutions containing 25% solids in toluene. "Drawdowns" were made with a doctor blade set to give a dried film thickness of approximately 1 mil. Films were air-dried or baked at the specified cycle with a drier system, when used, consisting of 0.5% lead and 0.01%

TABLE I
Typical Analytical Data on *N,N*-Bis(2-hydroxyethyl)
Linseed Amide (HELA)

Property	Found	Calculated
Hydroxyl	9.00%	9.25%
Carbon	71.55	71.90
Hydrogen	11.23	11.24
Nitrogen	3.71	3.81
IV	149	148
Acid	<0.2%	0
Ester (IR, 1725 cm ⁻¹)	0	0
Amine	<0.2%	0
Viscosity (poise)	3.7
n_D^{20}	1.4903
Conj. diene	1.3%
Conj. triene	0.1

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TABLE II
Properties of Polyester Amides of HELA and Dibasic Acids

Acid	Gardner		IV	Acid No.
	Viscosity	Color		
Terephthalic	»Z10	17	117	13.3
Phthalic	>Z10	15	114	0.6
Fumaric	Z5-6	12	135	1.0
Maleic	»Z10	13	122	21.3
Itaconic	Z7-8	15	125	1.4
Dimer T ^a	V-W ^b	10	116	8.0
Dimer C ^a	Z7	14	148	19.0
Azelaic	Z6	15	107	17.0
Brassylic	Z8-9	15	95	12.1

^a T = prepared by thermal process; C = prepared by catalytic process.
^b 50% Solids in toluene.

cobalt as naphthenates. Hardness tests were made by the Sward Rucker 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 and tack-free times of air-dried films were determined by either a modified Sanderson drier operating at room temperature (5) or by placing a small amount of sand on the film periodically.

Discussion and Results

Preparation and Properties of HELA

TLC was used to follow the course of the reaction and to determine when it was complete or should be terminated. Figure 1 illustrates the technique used to study the preparation of HELA from diethanolamine and LSO and shows a chromatogram of the progress of this reaction at the indicated times. Comparison of the top spot (LSO) and the bottom (HELA) on the chromatogram shows that the reaction is essentially complete in 35 min. Intermediates formed are indicated by the fainter spots. Figure 2 is a chromatogram of the 10-min sample of the reaction mixture at *b* compared with chromatograms of related compounds. At *a* are product spots resulting from an alcoholysis-amidolysis reaction of linseed diester amide (LDA) and diethanolamine in the presence of Na catalyst. At *c* is shown a mixture of linseed mono- (MG), di- (DG) and triglycerides (LSO). The top and bottom spots at *b* are LSO and HELA, respectively. The spot above HELA is a material related to the diethanolamine derivatives and is probably the linseed monoester

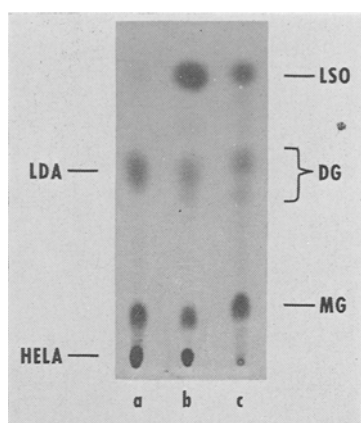


FIG. 1. Thin-layer chromatogram of a typical *N,N*-bis(2-hydroxyethyl) linseed amide (HELA) preparation from linseed oil (LSO). Solvent system: 70 parts ether, 30 hexane and 1 acetic acid.

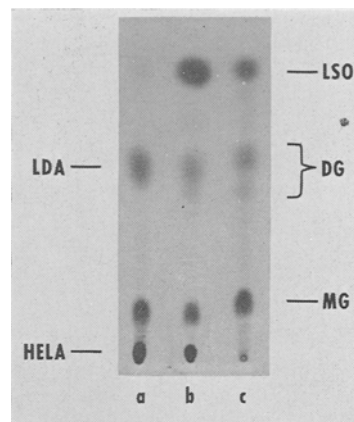


FIG. 2. Thin-layer chromatogram showing a comparison of (a) product spots from an alcoholysis-amidolysis reaction of linseed diester amide (LDA); (b) 10-min sample from Figure 1; and (c) mixture of linseed monoglycerides (MG), diglycerides (DG) and linseed oil (LSO). Solvent system is the same as for Figure 1.

amide. Formation of amine esters appears unlikely in this isomerization mixture since Trowbridge et al. (11) has demonstrated the rapid uncatalyzed conversion of amine esters to hydroxyamides at 56°C. MG is not formed in detectable amounts during this reaction. The more intense spot below LSO in *b* appears to be identical with LDA and the much weaker spot with an isomeric DG. Thus the intermediates derived from LSO apparently react almost as soon as they are formed, whereas products related to LDA are formed in detectable amounts but are converted to HELA at the end of the reaction.

Table I lists analytical data on a representative sample of HELA. The product contains 97.5% of the theoretical hydroxyl function as determined by the method of Fritz and Schenk (4), has no loss in unsaturation during its preparation as evidenced by the iodine value and contains only a trace amount of acid. The IR spectra of this product shows no absorption for ester carbonyl at 1725 cm^{-1} , and titration for amine with perchloric acid in acetic acid was essentially zero (2). Thus no isomeric esteramines are present in this product.

Polyester Amides

The preparation of polyester amides from compounds exemplified by HELA and dibasic acids has received little attention. The preparation of resins from diethanolamine (2 moles) and adipic acid (3 moles) has been described by Brintzinger and Weinmann (1), but insoluble products were formed when the acid number fell below 190. Figure 3 illustrates the preparation of polymers from HELA and dibasic acids. If the reaction proceeded ideally, one would expect a polyester chain (I) as shown; however, the possibility of side reactions exists. Acyl migration from nitrogen to oxygen could yield a polymer (II) containing both ester and amide linkages in the backbone. Acidolysis could also occur with displacement of the linseed acyl group by a dibasic acid to produce a trifunctional molecule capable of forming a nonlinear polymer. If a dihydroxyamide was prepared containing a volatile acid instead of linseed acids and if acidolysis occurs, some volatile acid should appear in the xylene-water distillate in the Dean-Stark trap. To furnish evidence for acidolysis, a polyesteramide was prepared from an equal molar mixture of *N,N*-bis(2-hydroxyethyl) caproamide and brassylic acid. Examination of ma-

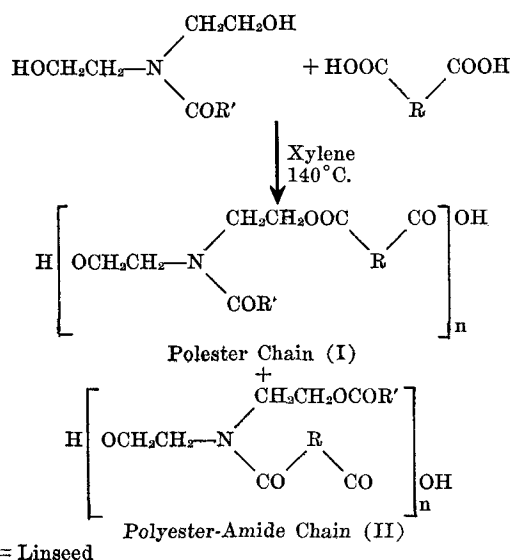


FIG. 3. Synthesis of polyester amides from N,N-bis (2-hydroxyethyl) linseed amide (HELA) and dibasic acids.

terial collected in the trap revealed the presence of caproic acid (identified by GLC) equivalent to 1.2% of that in the initial caproamide. This observation shows that acidolysis does in fact occur.

Acidolysis should also lead to gelation. A soluble polyester amide from N,N-bis(2-hydroxyethyl) stearamide and brassylic acid was prepared in xylene by collecting approximately the theoretical amount of water during 24 hr. However, removal of the xylene and continued heating of the polymer for an additional 11 hr at 140–145C/1 mm formed a partially gelled product. Heating another portion of the solvent-free polymer for 1.5 hr at 165C/1 mm produced an insoluble gel. Thus, more severe conditions than those used in our preparations are required for gelation to occur.

TLC was used to follow the course of the polyesterification as shown by the chromatogram in Figure 4. At left is the pattern for the reaction at zero time. After refluxing for 15 min at 145C, the monomeric materials were disappearing rapidly to form low-molecular-weight polymers. At 60 min the monomers had essentially disappeared and, as revealed by the long streak at the upper half of the chromatogram, had been converted to higher molecular weight species. After 6-hr reaction, the average molecular weight of the polyester had continued to increase as demon-

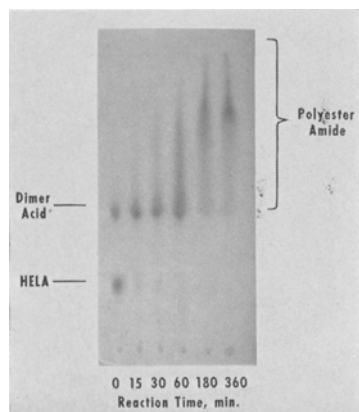


FIG. 4. Thin-layer chromatogram of a polyester amide from thermally polymerized dimer acid and N,N-bis(2-hydroxyethyl) linseed amide (HELA). Solvent system: 95 parts ethyl acetate, 5 methanol and 1 acetic acid.

strated by the shift of most of the material from the lower to the upper region of the polymeric product streak. These data are in agreement with certain features that distinguish a condensation polymerization (10); i.e., any two molecular species can react and thus the monomers disappear early; the molecular weight of the polymer increases steadily with time; and a long reaction time is necessary for high-molecular weight products.

The polyesters from HELA and eight dibasic acids are described in Table II. All polymers were viscous oils ranging from Z6 to >Z10 (Gardner scale). The polyester amide from thermally prepared dimer acid (Dimer T) could not be isolated without gelation. The effect of structure of the dibasic acid on the viscosity of polyester amides was noted. Although the double bond in the polymers from maleic and fumaric acids is essentially in the *trans* form, as shown by the IR spectra at 973 cm^{-1} and by the NMR spectra (3), the isomeric relationship still leads to product differences. The fumaric product (MW 5900, based on acid value) was markedly less viscous than the maleic polymer (MW 2700). Film properties, discussed later, also show differences. Itaconic, brassylic and azelaic polyesters, which would give relatively linear polyesters, have viscosities of Z6–8 similar to fumaric polymer.

Polyester Amide Film Properties

Table III lists the drying properties and hardness of air-dried polyester amide films containing Co-Pb drier. Rocker hardness values were decidedly higher after 10 days than they were at 3 days for all but one of the six best air-drying films. The film from the fumaric acid polymer developed very satisfactory hardness in less than 3 days.

The best dry-to-touch and tack-free time was exhibited by the polymer containing terephthalic acid. The phthalic polymer required a significantly longer drying time. A difference in drying was noted between the polymer films prepared from the *trans* and *cis* acids, fumaric and maleic. Apparently, the more rapid drying characteristics of terephthalic and fumaric polyesters are associated with the more linear structure inherent in the dicarboxycyclic acid. Polyester amide films from saturated aliphatic dibasic acids air-dried slowly, probably due to insufficient functionality. The dimer acid polymer films remained soft and were not tack-free after 20 days. Film from Dimer T polymer had a shorter dry-to-touch time than film from Dimer C polymer (Table III) although iodine value showed that the latter had significantly higher functionality (Table II).

In the absence of driers, most of the polymers gave unsatisfactory films at room temperature because of

TABLE III
Air-Dried Film Properties of Polyester Amides^a

Acid	Rocker hardness			Dry-to-touch, hr	Tack-free, hr	Resists 5% NaOH, min	Resists xylene, hr
	3 days	10 days	25 days				
Terephthalic	5	20	46	1	5	51	>220
Phthalic	5	16	32	2.7	21	13	>220
Fumaric	20	28	48	3.5	8	4	>220
Maleic	8	28	34	32	48	4	32
Itaconic	8	22	38	3	21	4	32
Dimer T ^b	90	>500
Dimer C ^b	168	>500
Azelaic	>250	>250	9	>220
Brassylic	72	>500	3	>220
Soy alkyl ^c	8	14	18	2	>22	6	0.5

^a Contains 0.5% Pb + 0.01% Co drier as naphthenates.

^b T = prepared by thermal process; C = prepared by a catalytic process.

^c 65% Oil length alkyl.

slow drying characteristics. However, films from the terephthalic and fumaric polymers were tack-free after air-drying 20 days.

Table IV lists properties of baked films prepared from polyester amides with and without Co-Pb drier. These data reveal that for each polymer, except for the one from itaconic acid, there was little or no difference in Rocker hardness between films with and without drier. The terephthalic polymer formed a dry, hard, but wrinkled, film. The best films were as hard as, or significantly harder than, a soy alkyd film included for comparison. The polyester amide films with drier had as good, or significantly better,

alkali resistance as films without drier. The soy alkyd films with and without drier showed the opposite trend. Xylene resistance of all films was excellent.

These preliminary experiments show that polyester amides of linseed fatty acids have promise as coating materials. Improvement or modification of film properties by use of other dibasic acids and mixtures thereof is being investigated.

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TABLE IV

Film Properties of Polyester Amides Baked at 190C for 10 Minutes

Acid	Rocker hardness		Alkali resistance, min		Xylene resistance, hr	
	+ ^a	- ^a	+	-	+	-
Terephthalic	W ^b	W	14	13	>270	>270
Phthalic	38	38	14	10	>270	>270
Fumaric	18	18	14	6	>270	>270
Maleic	26	22	45	25	>270	>270
Itaconic	26	16	3	4	>270	>270
Dimer T ^c	4	2	43	35	>270	>270
Dimer C ^c	4	2	15	3	7	>270
Azelaic	4	4	5	4	>270	>270
Brassylic	6	6	27	27	>270	>270
Soy alkyd	16	16	24	150	>270	>270

^a + Drier (0.5% Pb + 0.01% Co).

- No drier.

^b W = wrinkled.

^c T = prepared by thermal process; C = prepared by catalytic process.