

# New Polyacetal, Poly(ester-acetal) and Their Urethane-Modified Coatings from Hydroformylated Linseed Oil<sup>1</sup>

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## ABSTRACT

Partly hydroformylated linseed oil, with an average of 1.3 to 3.4 meq aldehyde per gram of oil, was reacted with pentaerythritol hydroxymethyl linseed oil and trimethylolpropane in the presence of an acid catalyst to form viscous, high molecular weight polyacetals. Isophthalic acid or chlorendic anhydride-modified polyacetals [poly(ester-acetals)] were prepared by reacting the trimethylolpropane esters of the acids with the hydroformylated oils. Films of the products were cured at room temperature and at 140 C. These films showed good hardness as well as chemical and impact resistance. Further modification of these polyacetals and poly(ester-acetals) by reacting the residual hydroxyl groups with an excess of toluene diisocyanate gave the corresponding isocyanate-terminated prepolymers. Films from these prepolymers had shorter drying times and showed greater hardness than the corresponding unmodified materials.

## INTRODUCTION

Formyl groups have been introduced into unsaturated vegetable oils by the addition of carbon monoxide and hydrogen to olefinic bonds (hydroformylation) in the presence of supported rhodium and triphenylphosphine as catalyst (1,2). Here, linseed oil was partly hydroformylated to give *cis*-unsaturated aldehydic products. The aldehyde

group(s) can be readily converted with polyols (3-5) or amines (5) to polymeric products in which the *cis*-unsaturation would be expected to impart rapid drying properties.

Partly hydroformylated linseed oil (HYFLO) containing 1.36 to 3.40 aldehyde groups per glyceride molecule was reacted either with polyols to form polyacetals or with polyols and isophthalic acid or chlorendic anhydride to form poly(ester-acetals). These products were then modified further by reaction with toluene diisocyanate to the corresponding urethanes. Films of these polymers were cured by oxidative polymerization of the residual unsaturation in the oil and by reaction of the excess isocyanate groups with moisture.

## EXPERIMENTAL PROCEDURES

### Starting Materials

The partly HYFLO averaged 1.36, 2.10 and 3.40 meq aldehyde per gram oil. These products will be referred to as HYFLO 1.36, HYFLO 2.10 and HYFLO 3.40. They were prepared (2) as follows: linseed oil (500 g) and toluene (250 ml) were placed in a 2 liter rocking-shaker autoclave and heated at 110 C and 2000 psi H<sub>2</sub> + CO (1:1) initial pressure. The autoclave was refilled with H<sub>2</sub> + CO and the reaction pressure maintained at 1500-2000 psi until a given uptake was reached. A mixture of supported rhodium and triphenylphosphine served as catalyst. The reaction conditions and analyses of the reaction products are shown in Table I.

Hydroxymethyl linseed oil (HMLO) was prepared by hydrogenation (1) of HYFLO 3.40 with 5% Raney nickel at 100 C and 1000 psi H<sub>2</sub> for 3 hr. The product had a hydroxyl number of 203. It contained by gas liquid

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TABLE I  
Hydroformylated Linseed<sup>a</sup> Oils (HYFLO)

Conditions <sup>b</sup> and analyses	HYFLO 1.36	HYFLO 2.10	HYFLO 3.40
Catalyst <sup>c</sup>	Rh/CaCO <sub>3</sub>	Rh/Al <sub>2</sub> O <sub>3</sub>	Rh/CaCO <sub>3</sub>
Catalyst conc., %	0.25	0.5	0.5
Ph <sub>3</sub> P, %	0.22	0.44	0.44
Time, hr	6.5	2.5	6.0
Gas uptake, psi	1	2	3.8
GLC, <sup>d</sup> %			
Fatty esters	82.1	57.6	37.1
Monoformyl esters			
Unsaturated	15.5	28.5	19.6
Saturated	2.4	5.3	14.8
Diformyl esters	0.0	8.3	28.5
Carbonyl content, meq/g			
Chemical	1.36	2.10	3.40
GLC (calc.) <sup>e</sup>	0.56	1.51	3.16

<sup>a</sup>Fatty acid composition: palmitate 6.3%, stearate 3.3%, oleate 22.0%, linoleate 15.1% and linolenate 53.3%.

<sup>b</sup>Runs were made on a 2 liter rocking-shaking autoclave in toluene solution (250 ml) at 110 C and 2000 psi H<sub>2</sub> + CO (1:1) initial pressure.

<sup>c</sup>As 5% supported rhodium.

<sup>d</sup>Normalized analyses from diethylene glycol succinate and JXR-silicone column, see (2).

<sup>e</sup>Based on monoformyl = 3.07 meq/g; diformyl = 5.65 meq/g.

TABLE II  
Properties of the Polyacetals and  
Poly(ester-acetals) From Hydroformylated Linseed Oils (HYFLO)

Polymer	Composition of polymer <sup>a</sup>	Color <sup>b</sup>	Viscosity <sup>b</sup> poises at 25 C	Hydroxyl value <sup>c</sup>
A	HYFLO (1.36)–PE	7	4.0	42.3
B	HYFLO (2.10)–HMLO	5	27.0	94.6
C	HYFLO (2.10)–TMP	7	27.0	48.8
D	HYFLO (2.10)–PE	6	148.0	46.4
E	HYFLO (2.10)–TMP–IPA	6	63.4	46.8
F	HYFLO (2.10)–TMP–CA	14	148.0	58.1
G	HYFLO (3.40)–PE	---	Gel	---

<sup>a</sup>HYFLO, hydroformylated linseed oil; in parentheses, the indicated milliequivalent of aldehyde/gram of oil; PE, pentaerythritol; TMP, trimethylolpropane; IPA, isophthalic acid; CA, chlorogenic anhydride.

<sup>b</sup>Gardner (6).

<sup>c</sup>Acetic anhydride-pyridine (7).

chromatography (GLC) analysis (run on methyl esters): fatty esters 34.5%, monohydroxymethyl 43.6% and dihydroxymethyl 21.9%. Calculated hydroxyl number was 202.

#### HYFLO Polyacetals

HYFLO and the polyol (ratio of OH/CHO = 2) were mixed with an equal weight of Cellosolve acetate in a three-neck flask equipped with a mechanical stirrer, nitrogen inlet tube, a Dean-Stark trap and a water cooled condenser. Potassium acid sulfate (1% by weight based on reactants) was added as catalyst and the mixture heated at 140–145 C for 1-1/4 hr. After cooling, the reaction mixture was dissolved in chloroform, neutralized with sodium acetate and dried over anhydrous sodium sulfate, followed by removal of the solvent under reduced pressure to yield a light-colored product (Table II).

#### HYFLO Poly(ester-acetals)

Trimethylolpropane (TMP) and the dibasic acid or anhydride (OH/COOH = 3) were placed in a round-bottom flask equipped with an air condenser and heated in an oil bath at 225 C for 2 hr. During this time the reactants dissolved to form esters of TMP. After cooling, the condenser was rinsed down with Cellosolve acetate and the reaction flask equipped with a Dean-Stark trap. The residual hydroxyl groups in the polyester were further reacted with HYFLO (OH/CHO = 2) in the presence of 1% potassium acid sulfate at 140–145 C for 1-1/4 hr to form the poly(ester-acetal).

#### Modified-Urethane Polyacetals and Poly(ester-acetals)

The polyacetals and poly(ester-acetals) were converted to urethanes by reaction of the residual hydroxyl groups

(based on hydroxyl value) with toluene diisocyanate at an NCO/OH = 2.0. The isocyanate and moisture-free oil were dissolved in dried xylene to give a 50 wt % solution and heated under nitrogen with stirring at 110 C for 2 hr.

#### Film Studies

Lead and cobalt naphthenate driers were added to the oil solutions in concentrations of 0.5 and 0.05% w/w (as metals), respectively. The dry-to-touch times were determined on 2 mil dry films cast on glass plates. Sward Rocker hardness measurements were carried out on these films aged for 1 day and 1 week (6).

Baked films were prepared by heating the 2 mil films in an oven at 140 C for 20 min. The chemical resistance of the films to 5% sodium hydroxide, 5% hydrochloric acid and xylene was determined by placing a 1.5 in. diameter watch glass, convex side down, on the surface of the film and introducing a few drops of the reagent on the film surface beneath the watch glass. Periodic examination was conducted until the film showed evidence of softening or other deterioration. Flexibility of the films cast on steel Q panels and aged for 1 week (6) was determined both by an impact tester and a conical mandrel.

### RESULTS AND DISCUSSION

Aldehyde groups in the partly HYFLO were reacted with polyols in the presence of an acid catalyst to form polyacetals. The progress of reaction was estimated by collecting water in the Dean-Stark trap and by observing the increase in viscosity of the reaction mixture. The time of reaction is critical and care must be taken to avoid gelation caused by crosslinking between the several aldehyde groups on the linseed glyceride. As soon as the

TABLE III  
Film Properties of Air Dried and Baked Films From Polyacetals and Poly(ester-acetals)

Polyacetal or poly(ester-acetal)	Air dried		Baked at 140 C/20 min hardness		Impact resistance, in./lb		Chemical resistance, min			
	Touch dry time, min	Hardness <sup>a</sup>		1 Day	7 Days	Direct	Reverse	Xylene	5% HCl	5% NaOH
		1 Day	7 Days							
A	75	4	4	8	8	>160	>160	>1440	>1440	10
B	150	Tacky		Tacky						
C	75	4	4	8	8	>160	>160	>1440	>1440	5
D	75	10	12	12	14	>160	>160	>1440	>1440	7
E	60	10	10	16	16	>160	>160	>1440	>1440	12
F	80	12	16	16	18	>160	>160	>1440	>1440	70
LSO-alkydb	285	10	26	28	28	>160	>160	>1440	>1440	3

<sup>a</sup>Sward Rocker (6).

<sup>b</sup>Commercially available.

TABLE IV  
Air Dried Film Properties of Isocyanate-Modified Polyacetals and Poly(ester-acetals)

Polyacetal <sup>a</sup> or poly(ester-acetal)	Touch dry time, min	Hardness <sup>b</sup>		Impact resistance, in./lb		Conical mandrel	Chemical resistance, min		
		1 Day	7 Days	Direct	Reverse		Xylene	5% HCl	5% NaOH
A	65	14	20	>160	>160	Pass	>1440	>1440	26
B	50	12	20	>160	>160	Pass	20	300	>1440
C	65	12	18	>160	>160	Pass	>1440	>1440	65
D	25	18	24	>160	>160	Pass	>1440	>1440	>1440
E	30	26	32	>160	>160	Pass	34	>1440	>1440
F	70	22	28	>160	>160	Pass	4	>1440	>1220
Soy-alkyd <sup>c</sup>	90	20	30	>160	>160	Pass	>1440	>1440	38

<sup>a</sup>NCO/OH = 2.

<sup>b</sup>Sward Rocker (6).

<sup>c</sup>Commercially available; urethane content unknown.

viscosity started to increase rapidly the reaction was considered complete, and IR spectrum showed no aldehyde bands at 1730, 2708 and 2820  $\text{cm}^{-1}$ . Evidence for acetal formation was demonstrated by bands in the IR and Raman spectra at 1000-1200  $\text{cm}^{-1}$ .

Although the aldehyde groups were reacted with stoichiometric amounts of hydroxyl, some residual hydroxyl groups were present in the products as evidenced by their IR spectra and hydroxyl numbers determined chemically (Table II). Presumably hemiacetals are also present in the reaction products along with the desired spiroacetal structure (3). HYFLO 1.36 and pentaerythritol (PE) gave a low viscosity oil. When HYFLO 2.10 was reacted with PE, TMP or HMLO, higher viscosity (and presumably higher molecular weight) polymers were formed compared to the HYFLO 1.36-PE product. With the HYFLO 2.10 polymers, the PE product was significantly more viscous than those from TMP and HMLO suggesting a higher molecular weight polymer. Possibly, PE yields a more linear polymer since biacetals with a spiroacetal ring structure would be readily formed. When HYFLO 3.40 was reacted with PE under the same conditions, crosslinking occurred and a gel resulted.

The polyacetals and poly(ester-acetals) were evaluated for their air dried and baked film properties (Table III) and compared with medium-LSO-alkyd. Polymers from HYFLO 2.10 gave films considerably harder than those from HYFLO 1.36; for example, the PE film from HYFLO 1.36 was softer than the corresponding film from HYFLO 2.10 (compare A and D, Table III). The product from HYFLO 2.10 and HMLO formed unsatisfactory air dried and baked films. The TMP film with HYFLO 2.10 (C) was equivalent in hardness to the PE film from HYFLO 1.36. Among the polyacetal films tested (A-D) those containing PE had the best film properties.

Poly(ester-acetal) polymers were made from the reaction of the dibasic acid and polyols followed by reaction with HYFLO. Although the reaction with isophthalic acid (IPA) and chlorendic anhydride (CA) with TMP gave soluble products that could be further reacted with HYFLO, the corresponding PE products could not be made to react under the conditions studied. Baked and air dried film properties of the TMP poly(ester-acetals) are significantly harder than properties of the TMP polyacetals and flexibility is retained.

Polymers listed in Table II were treated with toluene diisocyanate (NCO/OH = 1.1) to form urethane polyacetals

and poly(ester-acetals). While selected films of these materials appeared to have satisfactory hardness and flexibility, film properties were not evaluated in detail because the polymeric materials tended to gel on standing. When the ratio of NCO/OH = 2, relatively stable products with a longer shelf life were obtained. Suitable air dried films were prepared from these isocyanate products (Table IV). These films were cured in part by the reaction of isocyanate with atmospheric moisture, and they yielded ultimately a coating crosslinked by substituted urea linkages. The urethane-modified polyacetal films with driers showed considerable improvement in drying and other properties over the unmodified oils (Table IV). However, the urethane oils with the higher viscosities (and molecular weights) had the shortest pot life and gelled during storage. With these products films were prepared from samples before gelation.

The higher molecular weight urethane oils (D, E and F) had the best film properties. In general the urethane-modified products are significantly harder and have better alkali resistance than the unmodified polymers. A comparison of TMP-urethane products (C with E and F) shows that incorporation of dibasic acids improves hardness and alkali resistance without influencing flexibility. Xylene resistance of E and F was markedly reduced. With urethane-modified PE products (A and D) increasing hydroformylation from 1.36 to 2.10 aldehyde meq/g improved alkali resistance of the films. As a comparison, film properties of isocyanate-modified soy-alkyd are shown in Table IV.

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