Urethane Coatings Based on Aldehyde Oils[1]

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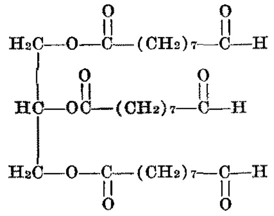
Abstract

A series of polyol acetals of aldehyde oils was prepared by an acetal interchange reaction between dimethyl and tetramethyl acetals of aldehyde oils derived by the reductive ozonolysis of linseed and soybean oils. The acetals interchanged with pentaerythritol, trimethylol propane and glycerol contained the equivalent of .93 and 1.88 aldehyde groups per oil molecule. The polyol acetals were reacted with toluene diisocyanate in an NCO/OH of 2. These products were tested as film formers. Curing was by two reactions, namely oxidation polymerization of the residual unsaturation in the oil and moisture curing of the unreacted isocyanate group. Good quality films were formed.

Introduction

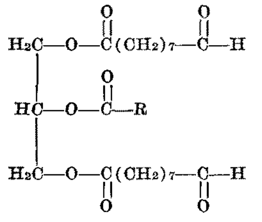
The preparation of a new class of glycerol esters has been reported by Pryde et al. (1–3). These are a family of both saturated and unsaturated aldehyde oils which are obtained by partial reductive ozonolysis of unsaturated vegetable oils, e.g., linseed and soybean oils. Some typical structures of the aldehyde oils are shown below:

I



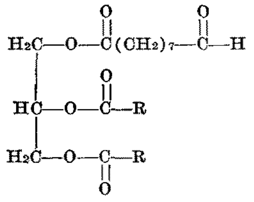
Trialdehyde oil
TAO

II



Dialdehyde oil
DAO

III



Monoaldehyde oil
MAO

where R represents the mixed structures of the C_{17} fatty acid moieties found in the starting unsaturated oils such as linseed and soybean.

The aldehyde oils used in this work were prepared by the USDA according to their previously published procedures (1–3).

Structures I, II and III for the aldehyde oils assume that cleavage has occurred at the ninth carbon atom. Cleavage is also known to have occurred at the 12th or the 15th carbon atoms in which case the aldehyde groups may be either on the 12th or 15th carbon atoms, with ethylene groups at the 12–13 or 9–10 positions. In the case of the MAO and DAO used in this work, the analysis conforms essentially to the structures as shown.

The saturated aldehyde oil TAO, the full glycerol ester of azelaldehydic acid, is obtained by the complete reductive ozonolysis of unsaturated oils with cleavage at the ninth carbon atom. This oil is characterized by the lack of olefinic unsaturation and by the presence of three aldehyde groups.

The unsaturated aldehyde oils, the MAO and DAO possess between three and four ethylene groups and between one and two aldehyde groups per mole. Ozonolysis under laboratory conditions yielded about 0.93 and 1.88 aldehyde groups per mole. Since the ozonolysis is random, the MAO has on the average one aldehyde group per molecule while the DAO averages about two.

Thus, functionality of the unsaturated oils has been changed by the introduction of an aldehyde group for one or more ethylene groups, thus creating the possibilities for aldehyde reaction. Reactions with alcohols (4), amines (5) and polyols (5–6) have been reported.

Aldehyde oils, per se, are very reactive and form polymers via the aldehyde group. Therefore, the aldehyde oils which were used in this work were in the form of their more stable methyl acetals.

This paper describes a method for increasing functionality by reacting aldehydes with polyols to form hydroxyacetals which are cross-linked by reactions with isocyanates. The complex acetalurethane is capable of film formation by oxidative polymerization of the oil portion and if there are isocyanate groups present, additional curing is possible, namely the moisture curing of the isocyanate.

Experimental Procedures

The MAO and DAO used in the present study contained on the average .93 and 1.88 aldehyde groups per mole, respectively. These were supplied in the form of their methyl acetals by the Northern Regional Research Laboratory, ARS, USDA. The acetals react readily with high molecular weight polyols by interchange to form the corresponding acetals. The oils had Gardner colors of 6 and 8 respectively.

Preparation of Aldehyde Oils Polyol Acetals

The general method for the preparation of the polyol acetals was a modification of the one described by Pryde et al. (7). The MAO and DAO and the polyol with 1% by weight of potassium acid sulfate were reacted at temperatures as shown in Table I. The reactor consisted of a 500 ml three-neck flask, equipped with a mechanical stirrer, inert gas inlet, a Dean and Stark side arm, and a water cooled condenser. A nitrogen atmosphere was maintained throughout the reaction. After the preliminary reaction at the lower temperature of 140 to 155 C for 30 min, the temperature was raised to and held at 160 to 175 C for 1 hr. Methanol recovery was essentially complete under these reaction conditions. At the end of this heating, 50 ml of toluene were added and the solution was refluxed for 30 min, after which

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TABLE I
Preparation and Properties of Polyol Acetals

Base oil		Polyol		OH/ CHO[c]	Temp. C	Methanol recovery, ml		OH value[d]	Polyol acetal properties viscosity mol.[a]		
Type[b]	Grams	Type	Grams			Found	Calc.		Stokes[e]	Weight	Appearance
MAO[f]	175	PE	27.2	4	155–175	8.0	16.0	59.2	20.0	1330	hazy
MAO	175	PE	20.4	3	155–175	8.2	16.0	37.4	20.0	1420	hazy
MAO	175	Gly	24.5	4	155–175	11.8	16.0	63.5	2.7	945	clear
MAO	175	Gly	18.4	3	155–175	11.3	16.0	62.7	4.0	970	clear
MAO	175	TMP	35.7	4	140–155	11.3	16.0	76.5	4.0	1040	clear
MAO	175	TMP	26.8	3	140–155	11.0	16.0	55.5	4.0	1150	clear
DAO[g]	148.3	PE	45.3	4	160–175	19.0	26.4	98.0	63.0	1750	hazy
DAO	148.3	Gly	40.8	4	145–160	19.0	26.4	136.2	6.0	1240	clear
DAO	148.3	TMP	59.5	4	140–160	20.0	26.4	174.5	33.7	1380	clear

[a] Mechrolab 30 A vapor pressure osmometer (11).
[b] As dimethyl acetal.
[c] Ratio of hydroxyl to aldehyde equivalents.
[d] Acetic anhydride-pyridine (10).
[e] Gardner (9).
[f] Color 6, Gardner 1933.
[g] Color 8, Gardner 1933.

the toluene was removed by a gradual increase in heat.

The viscous oil solutions were dissolved in ether. The ethereal solution was washed several times with water until the washings were free of polyol as indicated by a negative test for hydroxyl groups (8). The ethereal solution was dried over anhydrous sodium sulfate, followed by removal of the ether.

The details concerning the properties of the polyol acetal oils are also shown in Table I.

Preparation of Modified Urethane Oil

The hydroxyacetal oils were converted to urethanes by reaction with toluene diisocyanates at an NCO/OH ratio of 2.

To be certain there was no moisture in the oils prior to the reaction with isocyanates, a small quantity of ethyl acetate was added and then removed by distillation. The moisture free oil was cooled and the requisite amount of toluene diisocyanate with previously dried butyl acetate to give a 50% solution were added. A blanket of dry nitrogen was used throughout the reaction.

The charge was heated to 70 C for ½ hr, followed by an increase to 110 C which was maintained for 2½ hr. The properties of urethane oils are shown in Table II.

Film Evaluation Studies

Films were cast from the butyl acetate oil solution with naphthenate driers added as 0.5% Pb, and 0.05% Co on the oil weight. The dry to touch and tack free times were determined.

Sward hardness measurements were carried out on films 2 ml thick on glass after aging one day and one week respectively. The chemical resistance to 5% sodium hydroxide and 5% sulfuric acid were determined by placing a few drops of the reagent on the film and covering with watch glass. The conditions of the films were examined periodically, after washing off the reagents with distilled water and drying with filter paper.

Analytical Methods

Standard methods were used in all analytical determinations (8–11).

Results and Discussion

In the presence of an acid catalyst, such as $KHSO_4$, the di- and tetramethyl acetals of aldehyde oil reacted with polyfunctional alcohols to yield the corresponding higher acetals. This transacetalation reaction occurred very readily at the appropriate reaction temperature (Table I), as was evident by the steady evolution of methanol during the progress of the first stages of the reaction.

During the preparation of the various acetal oils, the possibility of transesterification of the oil with the polyol was also considered. The conventional qualitative test for the detection of monoglycerides by testing their solubility in methanol 1/3 v/v gave negative results. Thus, it appears that the transesterification of aldehyde oils with a polyol, if it occurs, is in a negligible amount, within the limitations of the qualitative test, especially if aldehyde or acetal groups are also present. A similar observation is reported by Pryde et al. (12).

The temperature required to effect the acetal interchange varied with the type of polyol used. As seen in Table I, temperature for the interchange reaction with trimethylol propane (TMP) as the polyol source was 140–155 C. Glycerol (GLY) and pentaerythritol (PE) required a higher temperature for the reaction, namely 150–160 C.

The color of the aldehyde oil-polyol products also varied with the polyol type. The TMP and GLY reacted oils were clear and light in color (Gardner 6), whereas the PE oil was darker (Color 8) and hazy. This could be very well related to the reaction temperature, since, in order to effect the reaction with PE, the temperature used was on the high side of the listed temperature range. A slight improvement in the color was observed, when the oils were subjected to a water wash, as described in the Experimental section.

The properties of the acetal polyol oils are shown in Table I. All of them showed the presence of hydroxyl groups. With one exception, the hydroxyl values in the final oils appeared to be related to the polyol and the amount of the polyol, or the OH/CHO ratio used in the reaction. With monoaldehyde oil as the aldehyde source, and at similar reactant ratio, OH/CHO = 4, the TMP product had the highest hydroxyl value, followed in order by that of GLY and PE products. This was true also when the aldehyde source was derived from dialdehyde oil. The reaction of monoaldehyde oil with PE at a reactant ratio OH/CHO = 3, had, as before, the lowest hydroxyl value of the three polyols investigated in this part of the study. However, the GLY product had a higher hydroxyl value than the TMP product. It appears that products with the higher number of hydroxyl groups are favored at the higher polyol to oil ratio. It should also be pointed out that the extent of reaction of PE with the aldehyde oils as computed from the milliliters of methanol collected was in the range of 40% to 50%. This incompleteness of the reaction may very well be one of the causes

TABLE II
Film Properties of Acetal Urethane Oils

Polyol acetal[b]			Urethane derivatives[a]						
			Dry times (min)		Hardness[c,d]		Chemical resistance[e]		
Base oil	Polyol	OH/CHO	Set	Tack free	1 Day	7 Days	5% NaOH	5% H_2SO_4	Xylene
MAO	PE	3	50	140	4	6	....	....	....
MAO	PE	4	40	120	4	6	....	....	....
MAO	Gly	3	50	140	4	4	....	....	....
MAO	Gly	4	75	140	4	4	5 min	8 hr	Immed.
MAO	TMP	3	55	200	6	8	....	....	....
MAO	TMP	4	75	180	8	8	10 min	24 hr	Immed.
MAO			240	......	..	..	....	....	....
DAO[f]	PE	4	30	60	40	48	3 hr	72 hr	40 min
DAO	Gly	4	80	200	18	20	....	....	....
DAO	TMP	4	20	60	30	36	4 hr	24 hr	60 min
	Control[g]		30	90	40	46	....	....	....

[a] Ratio of NCO/OH = 2.
[b] Colors 6 to 8, Gardner 1933.
[c] Driers as .5% Pb and .05% Co.
[d] Sward Rocker Hardness (9).
[e] Time to fail.
[f] Tests run of oil prior to gelation.
[g] Control, Urethane Alkyd, Cargill 1285.

for the observed low hydroxyl value with PE based products. Also, this may be due to transesterification of PE with glycerol under the conditions of transacetalization as mentioned earlier.

In the case of monoaldehyde oil products, the ratio of polyol to oil had some effect on the properties of the acetal oil. This was quite significant when PE and TMP was used as the polyol source. Changing the OH/CHO ratio from 4 to 3 yielded products with higher molecular weights but with lower hydroxyl values. This tendency to yield a higher molecular weight product at the expense of hydroxyl content with the reduction in the amount of polyol in the reactant ratio, could possibly be attributed to the preferential formation of bisacetals, such as in the case of PE. With TMP, it is suspected that complex hydroxyacetals are also formed, probably at the expense of the hydroxyl substituted dioxane which presumably is the favored initial reaction product. Reactant ratios apparently have virtually no effect on the properties of acetal oil when glycerol is used as the polyol source.

The polyol-aldehyde oil reaction products were evaluated for their film forming capabilities. Their films had very poor film characteristics evident by their tacky surface after days of exposure to ambient cure conditions. This was true even upon the addition of conventional metallic driers.

Conversion of the residual hydroxyl groups in the acetal oils, to the urethanes by further reaction with technical 2,6 and 2,4-toluene diisocyanate mixtures (Nacconate 80 or Hylene TM or equivalent) gave products with improved drying characteristics. Table II summarizes the film properties of the modified urethane oils, designated as acetal urethane oils. An excess isocyanate was employed in the preparation of the urethane oils. The NCO/OH ratio used was 2.

The excess isocyanate which was left after the formation of the monourethane permits moisture curing of the film. As a control, a standard commercially available uralkyd was used.

In the presence of metallic driers, 0.5% Pb and 0.05% Co, the modified urethane oils derived from monoaldehyde oil gave films which attained a tack-free state between 2–3 hr. The considerable improvement in the drying characteristics of the toluenediisocyanate reacted acetal oils is self evident. No definite correlation could be found between the properties of the acetal oils from which the urethanes were prepared and the dry time. The Sward hardness of the various oil films showed some difference but the best overall performance was exhibited by the trimethylol propane product.

With the dialdehyde oil polyol acetal urethanes, the glycerol products showed a slower drying rate to a tack-free state. The trimethylol propane and the pentaerythritol products showed a marked improvement in their drying rates. The samples of pentaerythritol dialdehyde urethane oils, on which film tests were conducted, and are reported, were taken prior to the gelation in the early stages of the reaction. These systems gelled prior to the termination of the reaction.

The dialdehyde oil-derived urethane systems gave films considerably harder than their monoaldehyde oil counterparts. The hardest film was obtained when pentaerythritol was used as the polyol source. Apparently this improvement in film quality is due to the higher molecular weight and increased functionality. One week old films of all the oil samples showed good flexibility characteristics. All had a reverse impact of better than 80 in. lb. Their flexibility, as determined by the conical mandrel test, was also good.

Chemical resistance tests were run on a few selected films. Their performance toward 5% aqueous sodium hydroxide, 5% sulfuric acid and xylene is shown in Table II. Moderate resistance towards alkali was exhibited by all films. Resistance towards acid solution was good. The dialdehyde oil-based urethane oil films exhibited superior performance towards chemical reagents than the urethane oil prepared from monoaldehyde oil.

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REFERENCES

1. Pryde, E. H., D. E. Anders and J. C. Cowan, J. Org. Chem. *25*, 618 (1960).
2. Pryde, E. H., D. E. Anders and J. C. Cowan, JAOCS *38*, 375 (1961).
3. Pryde, E. H., D. E. Anders and J. C. Cowan, Ibid. *40*, 497 (1963).
4. Pryde, E. H., D. J. Moore, H. M. Teeter and J. C. Cowan, J. Chem. Eng. Data *10*, 61 (1965).
5. Sharpe, R. E., D. A. Berry, E. H. Pryde and J. C. Cowan, JAOCS *42*, 835 (1965).
6. Sharpe, R. E., D. A. Berry, E. H. Pryde and J. C. Cowan, Ibid. *44*, 167 (1967).
7. Pryde, E. H., R. A. Awl, H. M. Teeter and J. C. Cowan, J. Polymer Sci. *59*, 1 (1962).
8. Cheronis, N. D., and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, New York 1961, p. 237–238.
9. Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Gardner Laboratory, Inc., Bethesda, Md., 1962, p. 138.
10. Siggia, S., "Qualitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York 1949, p. 4–5.
11. Mecrolab, Inc., Instruction Manual, CIM-2.
12. Pryde, E. H., D. J. Moore, H. M. Teeter and J. C. Cowan, J. Org. Chem. *29*, 2083 (1964).

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