Reaction of Aldehyde Oils With a Resinous Polyol, Styrene-Allyl Alcohol Copolymer[1]

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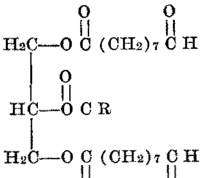
Abstract

A series of film formers based on aldehyde oils, derived by reductive ozonolysis of soybean and linseed oils was prepared by a two-step reaction with a resinous polyol, styrene-allyl alcohol copolymer. The methyl acetals of the di- and monoaldehyde oils were interchanged with the hydroxyl functionality of the resinous polyol with potassium acid sulfate as the catalyst as follows: (a) The heterogeneous mixture was heated only to clarity in the first step. This consumed about 20–25% of the hydroxyl groups of the resinous polyol. (b) Films of the partially reacted products of (a) were cast and cured at various temperatures between 100 and 175 C for variable periods of time. The films showed good hardness, scratch and chemical resistance. Some yellowing was observed. The film former in the (a) stage was compatible with melamine and urea-formaldehyde resins and, upon baking, these compositions also produced clear, hard chemical-resistant films.

Introduction

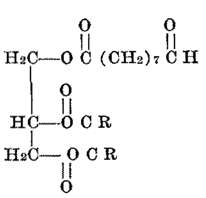
Unsaturated aldehyde oils have been recently prepared by investigators in the USDA (1–3) by reductive ozonolysis. A number of isomeric compounds are possible. Two typical structures are shown:

I



Dialdehyde Oil, DAO

II



Monoaldehyde Oil, MAO

where R represents the mixed fatty acid structures of the C_{17} moieties found in the starting unsaturated oils, which may be either soybean or linseed oils.

These aldehyde oils possess ethylene as well as aldehyde groups. The former DAO has on an average two aldehyde groups per molecule, whereas in the latter, MAO, the average is about one. Thus, the functionality of the unsaturated oil has been changed by the introduction of an aldehyde group for one (or more) ethylene group(s). Possibilities for the reactions with aldehydes now exist. Some have been explored as, e.g., reactions with alcohols (4), amines (5) and polyols (4–6).

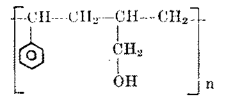
The oils typical of Structures I and II, or isomers of these, when derived from soybean or linseed oils would not be expected to be useful as film formers per se, because of insufficient ethylene functionality and low molecular weight.

Coatings compositions based entirely on drying oils without resins or resin-forming components usually yield poor quality films. The presence of resinous bodies improves gloss, hardness, chemical resistance, speed of dry, general film appearance and durability. Therefore, it was believed that a resinous polyol reacted with the aldehyde oils via the aldehyde group would be a means of combining resinous and oil structures to form large copolymers with improved film-forming properties. Since these are oil-based, film formation and molecular weight increase would be by oxidation-polymerization of the residual unsaturation in the R portions in Structures I and II.

The aldehyde oils are very reactive and form homopolymers via the aldehyde group. Hence, the aldehyde oils are converted to the more stable methyl acetals. Since the methyl groups are easily interchanged, our work was based on the di- and tetramethyl acetal derivatives.

This paper describes the reaction of the di- and tetramethyl acetals of MAO and DAO, respectively, with a resinous polyol of styrene and allyl alcohol in the molecular weight range of 1600. The styrene-allyl alcohol copolymer used in the present investigation is marketed by the Monsanto Company under the trade name of RJ-100. It has the following structural unit:

III



Variables in these reactions were the hydroxyl (OH) content of the polyols and the aldehyde (CHO) content of the oils. In the discussion which follows, the ratio CHO/OH is used to define the mole ratio of these functional groups in mixtures of the two reactants.

Experimental Procedure

Coatings Preparation of Aldehyde Oil RJ-100 Copolymers

The methyl acetals of DAO and MAO used in this work were equivalent to 1.88 and 1.18 (average) aldehyde groups per mole, as per Structures I and II. Preparation and analysis of these acetals have been described (7, 8).

The physical properties of the RJ-100 are as follows (9): softening temperature, 95–105 C; hydroxyl content, 6%; molecular weight, 1600; solubility, aromatic hydrocarbon, alcohols, esters, ethers, and ketones.

The reaction of RJ-100 with unsaturated aldehyde oil acetals was carried out in a 250 ml Erlenmeyer

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TABLE I

Chemical Compositions and Film Properties[a] of Aldehyde Oil RJ-100 Partial Acetals

Aldehyde oil		Ratio CHO/OH	Hydroxyl values		Film hardness[b]
Type	Per cent oil		Initial	At clarity	
MAO	49	0.5	49.0	37.5	40
MAO	57	0.6	41.0	34.2	12
MAO	67	1.0	32.4	28.0	6
MAO	79	2.0	20.0	16.0	4
DAO	44	0.5	43.8	35.1	42
DAO	51	0.6	48.0	38.0	14
DAO	62	1.0	38.5	33.2	6
DAO	76	2.0	23.9	20.0	4

[a] Tests carried out on glass plates. Baked 150 C/30 min. Film thickness 4 mil wet at 50% NV in xylene. 0.5% Pb, 0.05% Co added as driers.
[b] Sward Rocker.

flask equipped with a condenser. Stirring and heating were accomplished with a magnetic hot plate equipped with a 1 in. magnetic stirrer. The unsaturated aldehyde oil acetals, together with 1% $KHSO_4$ on the total solids, were added to 50% solution of RJ-100 in xylene. The mixture was stirred and heated to 120–125 C and held for 5–10 min, or until a drop of the solution remained clear on cooling. At this point the hydroxyl value dropped by 15% to 25%.

A number of compositions were prepared by varying the ratio of CHO/OH in both DAO and MAO, as shown in Table I.

Film Preparation

Films were applied to glass and tin as 50% xylene solutions, with 0.5% Pb and 0.05% Co (on oil weight) as driers. Dry films were essentially 0.002 in. thick.

The temperature and times of cure varied from 100 to 175 C and 15 to 60 min, respectively, as shown in Table II. The effects on film properties were recorded.

Presence of Hydroxyl Groups

Infrared spectroscopy was advantageously used to measure the degree of cure by following the disappearance of the hydroxyl groups. A drop of resin was placed on the spectrophotometer cell plate. Both films and cell plates were heated for different times and temperatures and the changes in hydroxyl group concentration determined at time intervals after cooling to room temperature. A Perkin Elmer 421 Spectrophotometer was used.

Since the hydroxyl group was the functional group involved in the curing process, it was estimated by drawing a baseline between two arbitrarily chosen frequencies 3600 cm^{-1} and 3100 cm^{-1}, according to a method previously described (10). The C-H stretching due to CH_2 and CH_3 was used as the internal standard; the frequencies for maximum absorption were between 3000 cm^{-1} and 2800^{-1}. The areas included between the baseline and the peak for each group were measured with a compensating polar planimeter. The ratio of the areas of OH/CH peaks was plotted against cure time as shown in Figure 1.

TABLE II

Film[a] Properties of Monoaldehyde Oil RJ-100 Acetal Copolymers at CHO/OH of 0.5 Cured Under Various Conditions

Cure temp °C	Cure time min	Sward hardness	Adhesion g	Scratch g
100	15	3	300	200
	30	6	350	250
	45	10	400	400
	60	14	400	500
125	15	6	200	200
	30	10	350	300
	45	25	400	400
	60	37	400	500
150	15	26	400	700
	30	40	400	>1000
	45	58	700	>1000
	60	68	700	>1000
175	15	38	400	>1000
	30	56	450	>1000
	45	56	650	>1000
	60	58	650	>1000

[a] Films cured with 0.5% Pb, 0.05% Co as driers. 4 mil wet at 50% NV in xylene on glass.

TABLE III

Film Properties of Urea Formaldehyde Resin-Aldehyde Oil RJ-100 Acetal Systems[a]

Oil	Ratio CHO/OH	Sward hardness	Adhesion	Flexibility
MAO	0.50	56	550	Good
MAO	0.66	48	450	Good
MAO	1.00	40	300	Good
MAO	2.00	20	150	Good
DAO	0.50	50	550	Good
DAO	1.00	38	250	Good
DAO	0.66	48	350	Good
DAO	2.00	18	150	Good
Control[b]		62	550	Good

[a] Resin combination of urea resin-aldehyde oil RJ-100 (1:1 w/w). Cured at 175 C and 30 min. Drier combination used 0.25% Pb and 0.02% Co. Dry film thickness, 2 mil.
[b] Control, Uformite-240 and Duraplex ND-77B (1:1).

Results and Discussion

The aldehyde oil acetals and RJ-100 are initially incompatible. After heating for a few minutes with a small quantity of potassium hydrogen sulfate, the reactants become compatible. The hydroxyl group on the high molecular weight polyol replaces the methyl groups of the acetal. During the initial phase of this investigation, attempts were made to obtain products in which all of the hydroxyl groups in the RJ-100 had reacted; these efforts were monitored by methanol

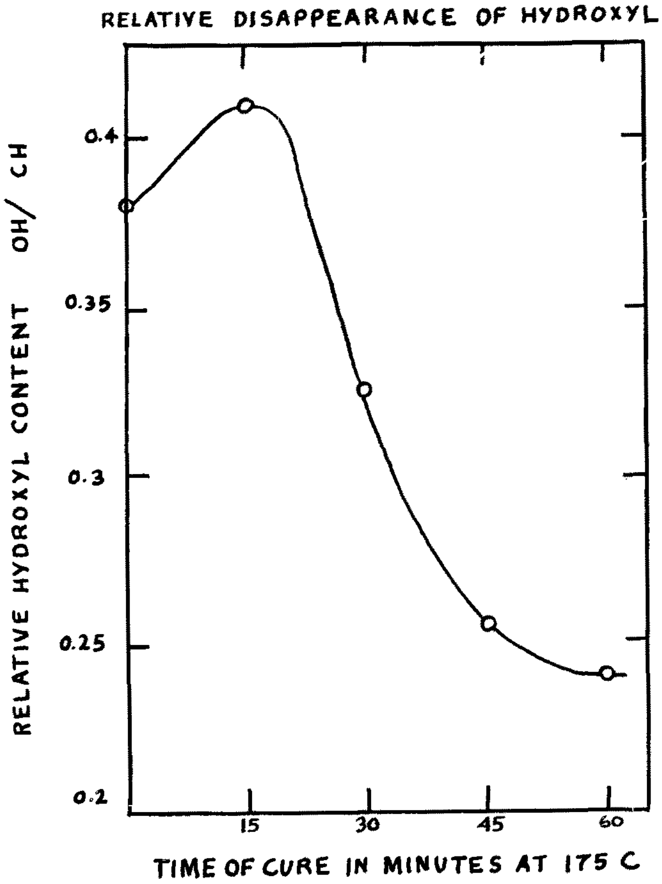


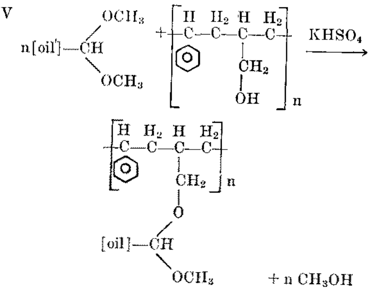
FIG. 1.

evolution and resulted in gels. Apparently the trans-acetalation reaction as shown below is very rapid and essentially complete in less than 30 min at 90 C, at which time a gel due to cross-linking is the result.

Therefore, it was believed that to obtain a useful product it would be necessary to run the trans-acetalation reaction in two steps. This was accomplished by reacting the aldehyde oil methyl acetals and polyol with the catalyst in two steps: (a) heating in bulk between 120–125 C until a clear pill was obtained; and, (b) coating a substrate, e.g., tin plate, glass, etc., with the initial product and heating further as desired, to complete the reaction.

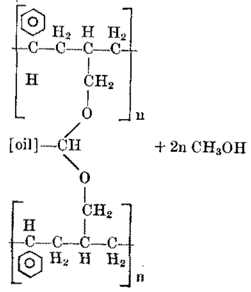
In the first reaction between 12% and 25% of the hydroxyl groups disappear. In the second stage, in film form, the hydroxyl disappearance approaches a constant value measured by infrared. It appears that an essentially linear polymer as shown by IV may be the result.

IV



This product may react further via cross-linking, to yield a gel or a cured film V, with probably the following structure:

V



The potassium hydrogen sulfate interchange catalyst settles out and the clear liquid may be decanted.

The trans-acetalation reaction continued in the film when it was heated. A decrease in hydroxyl concentration occurred to form V. This reaction was also followed by coating the infrared spectrophotometer cell with compositions in the (a) stage. The spectra at given times of cure were determined. A typical relative disappearance curve of the hydroxyl group was obtained by plotting the ratios of the peak area between 3600 cm^{-1} and 3100 cm^{-1}, 3000 cm^{-1} and 2800 cm^{-1}. Figure 1 shows a typical curve obtained for a monoaldehyde oil RJ-100 prepared at CHO/OH ratio of 0.5, and cured at 175 C for variable periods of time. An initial increase in the OH/CH ratio was observed during the primary stages of the cure. This possibly could be due to the formation of hydroperoxides. With prolonged cure time, a decrease is obvious in the total hydroxyl content. This method was used in several other systems with different curing temperatures. In all cases, curves were similar. These values are considered to be qualitative and not quantitative.

Properties of the resin-aldehyde oil films are shown in Tables I and II. All resins were applied at 50% xylene solutions.

When about 12.0% of the hydroxyl groups of the copolymer had reacted, a clear resin solution was obtained. All excepting two resin systems had a viscosity of <0.5 stoke. When about 20.0% of the hydroxyl groups had reacted in the 0.5 ratio products, a sudden increase in viscosity was noticed. The lower viscosities observed in the other higher ratio systems could be due to the dilution effect of the oil.

Four different vehicles with each type of unsaturated aldehyde oil, MAO and DAO, and resinous polyols were prepared. The CHO/OH ratios were 0.5, 0.66, 1.0 and 2.0. These varied in oil content between 49% and 79% for MAO and 44% and 76% for DAO products. Their film properties were evaluated.

The effect of time and temperature of cure as measured by Sward Rocker and Princeton adhesion and scratch tests (11) on the film properties of one film former based on MAO/RJ-100 at a ratio of 0.5 is shown in Table II. Data in this table show that films with improved properties are obtained when the cure is at the higher temperatures or longer times, or both. Thus, films cured at 150 C were harder than those cured at 125 C. Also, harder films resulted when the cure was for longer periods of time. A plot of Sward Hardness and cure temperatures is shown in Figure 2. An inspection of these curves indicates that the optimum curing conditions are between 150 C and 175 C at 30 or 45 min. The break in the 45 and 60 min curves at 150 C may indicate some dissociation of the acetal structure on prolonged heating.

A series of polyol (RJ-100) aldehyde oil condensates was prepared with CHO/OH ratios between 0.5 and 2.0. The films were cured at 150 C for 30 min

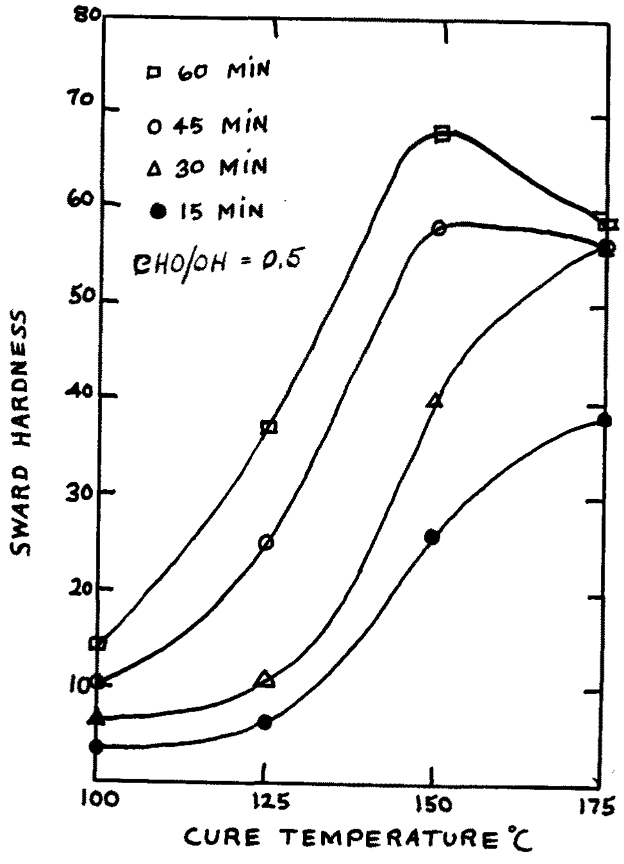


FIG. 2. Influence of cure-temperature on hardness aldehyde oil RJ-100 acetals.

and the Sward Hardness determined. These data are plotted in Figure 3 as essentially superimposable curves. Apparently, harder films are obtained at the lower CHO/OH ratios. This would be expected because of the lower oil content.

All resin systems showed a tendency to yellow during curing. More yellowing was noticed when a higher temperature or a longer baking schedule was employed; yellowing was judged visually. Yellowing may be explained by the structure of R in Formulas I and II. If the MAO and DAO are derived from linseed oil, $R\overset{\displaystyle O}{\overset{/\!/}{C}}-O'$ may be the linolenic acid radical. Products which contain this acid will produce films which are yellow.

Resistance to 5% sodium hydroxide and 5% sulfuric acid was very good. Films cured at 150 C and at least 30 min were unaffected by the acid for one week. The resistance towards alkali was excellent.

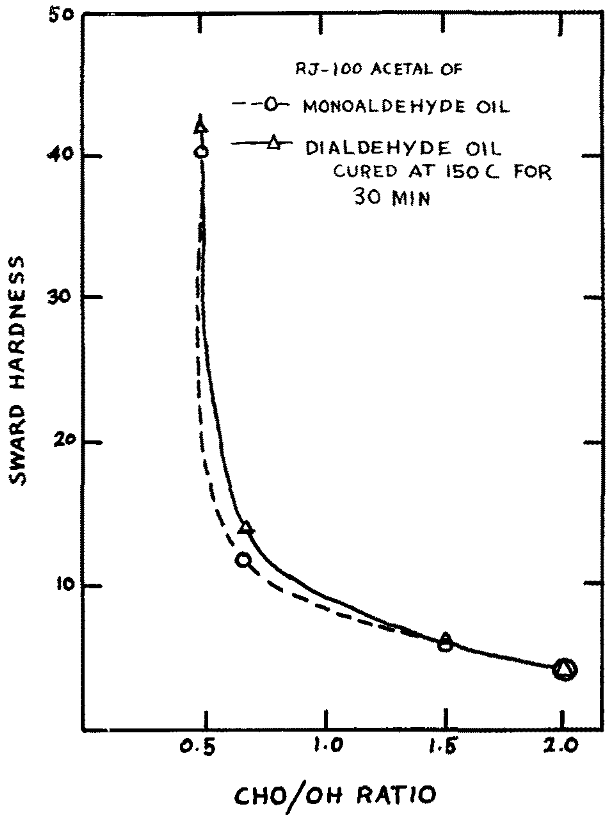


FIG. 3. Effect of CHO/OH ratio on Sward hardness.

The only type of failure observed after a day's test was loss of adhesion to the glass substrate. These films showed very good flexibility as determined by conical mandel test and reverse impact tests. The resistance towards alcohol and toluene was also excellent for those films cured above 150 C and longer than 30 min.

All of the soluble aldehyde oil RJ-100 reaction products at (a) stage, after reaction to clarity, had good compatibility with urea formaldehyde, melamine formaldehyde, acrylic and alkyd resins. Clear solutions and clear baked cured films were obtained. The baking temperature was 175 C at 30 min.

A limited study was carried out on the film properties of 1:1 blends of aldehyde oil RJ-100 systems with a urea formaldehyde resin (Uformite 240, Rohm and Haas). Table III shows results of this study. The blends were in a 1:1 ratio of weight of the experimental resin and Uformite-240. As a control, a blend of nondrying alkyd Duraplex ND-77B Rohm and Haas and Uformite-240 was included. Both the DAO and MAO aldehyde oil RJ-100 acetal systems prepared at CHO/OH of 0.5 were equivalent to the control. The blend improved the hardness of films prepared at lower ratios of CHO/OH.

It is possible that in the urea resin systems both the urea resin and partially reacted aldehyde oils RJ-100 acetals cross-linked via the residual functional groups to yield hard films. The effect of the larger amount of oil in the acetal oil at the higher CHO/OH ratios is reflected in the decreasing Rocker hardness readings.

These acetals are the basis of a new family of film formers with desirable characteristics. The film-forming compositions are sufficiently interesting to carry this study further to include other hydroxyl-bearing resins.

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