Oxazoline Polyester Coating Resins[1]

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Abstract

Oxazoline polyester resins were prepared by reaction of oxazoline diols from linseed acids and tris(hydroxymethyl)aminomethane with each of five dibasic acids (adipic, dimer, fumaric, itaconic and maleic). Certain resins were dissolved in isopropyl alcohol to give solutions infinitely water dilutable when the free carboxyl was neutralized with an amine. Film properties of resins cast on steel plates were investigated. Drying characteristics, hardness, color stability and solvent resistance of some of these films equaled or excelled those of a commercial soy alkyd resin, although their initial color was darker. The resins prepared from itaconic and maleic acids have potential value as water-solubilizable coating vehicles.

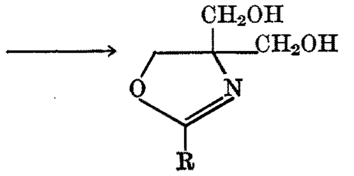
Introduction

IN A PREVIOUS PAPER (2) we described the preparation of water-solubilizable coating resins derived by reaction of tris(hydroxymethyl)aminomethane (TA), linseed acids (LA) and itaconic acid. Now we can describe the preparation and properties of such resins made with itaconic and other dibasic acids.

Discussion

The resins were prepared by reacting TA with LA to form the oxazoline as shown by Equation 1, followed by reaction with dibasic acid (DA).

$RCOOH + NH_2C(CH_2OH)_3$



$+ 2H_2O$ [1]

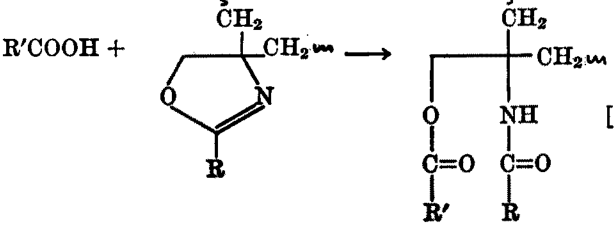
TABLE I
Analytical Data: Tris Amino-Linseed-Dibasic Acid Resins

Dibasic acid	Composition[a]	Iodine value	Acid equivalent	Oxazoline equivalent Found	Oxazoline equivalent Calculated[b]	Percent increase oxazoline equivalent[c]
Adipic	1-1-2	78	345	960	617	39
Adipic	1-2-1	137	845	870	747	17
Adipic	1-2-2	109	335	1200	893	46
Dimer	1-1-2	109	750	1800	1449	24
Dimer	1-2-1	141	1195	1240	1163	7
Dimer	1-2-2	126	635	1970	1725	14
Fumaric	1-1-2	115	660	3260	557	488
Fumaric	1-2-1	143	1940	930	717	30
Fumaric	1-2-2	143	665	2640	905	192
Itaconic	1-1-2	86	455	1800	585	225
Itaconic	1-2-1	136	1630	2150	731	194
Itaconic	1-2-2	119	590	1710	849	99
Maleic	1-1-2	82	410	2240	557	305
Maleic	1-2-1	134	1280	1090	717	52
Maleic	1-2-2	119	495	4120	905	355

[a] Tris Amino-linseed-dibasic acid respective molar quantities.
[b] Based upon no oxazoline reaction.
[c] 100 X (Found—Calculated) oxazoline equivalents ÷ calculated oxazoline equivalent.

Molar compositions of the resins prepared from each DA (adipic, dimer, fumaric, itaconic, and maleic) were: (TA-LA-DA); 1-1-2, 1-2-1 and 1-2-2.

In Table I are given the acid and oxazoline equivalents (1), together with iodine values of the resins. The resins are designated by the name of the DA used, together with three digits indicating from left to right the molar proportions of TA-LA-DA employed in the composition. Also included in Table I are the calculated oxazoline equivalents based on the assumption that no ring opening of oxazoline occurred as shown by Equations 2 and 3 and that



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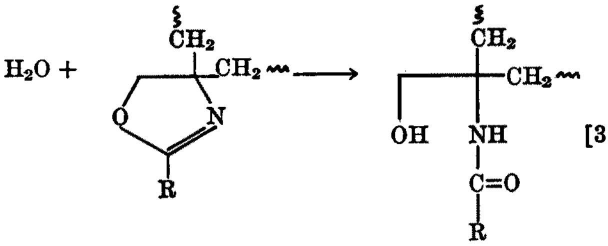

[3]

both hydroxyl groups were esterified by dibasic acid. Greatest increase in the oxazoline equivalent, corresponding to the greatest amount of oxazoline ring cleavage, occurred with the strongest acids; namely, fumaric, itaconic and maleic.

"Dry-to-touch" and "tack-free" times on better performing films cast from toluene solution are given in Table II. These films showed better drying characteristics than the other experimental films. A commercial soy and safflower alkyd are included for comparison. Among the experimental resins, the fumaric, itaconic and maleic acid resins furnished faster setting films, except for the fumaric 1-2-2 resin. The resins from dimer acids were slow to dry. The adipic

TABLE II
Dry-To-Touch and Tack-Free Time for Films of
Tris *Amino*-Linseed-Dibasic Acid Resins
(1 mil air-dried films[a] containing 0.1% *Co* and Pb)

Dibasic acid	Composition	Dry-to-touch, hr	Tack-free, hr
Fumaric	1-1-2	1½	21
	1-2-1	5	12
	1-2-2	24	24
Itaconic	1-1-2	3	18
	1-2-1	⅕	2½
	1-2-2	2¼	19
Maleic	1-1-2	¼	½
	1-2-1	3½	18
	1-2-2	3	5
Comparison resins			
Soy alkyd[b]		1	18
Safflower alkyd[c]		2	18

[a] Cast from toluene solutions.
[b] 65% soy oil, 24% phthalic anhydride.
[c] 65% safflower oil, ca. 25% phthalic anhydride.

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[1] Presented at the 151st ACS Meeting, Pittsburgh, March 1966.
[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE III

Sward Hardness Data of Films from Tris Amino-Linseed-Dibasic Acid Resins

Dibasic acid	Composition	Sward rocker values after aging, day				
		1	2	7	14	28
Fumaric	1-1-2	7	10	12	15	16
	1-2-1	9	9	18	18	14
	1-2-2	0	8	5	9	9
Itaconic	1-1-2	10	14	20	27	36
	1-2-1	11	15	24	24	30
	1-2-2	12	22	25	28	30
Maleic	1-1-2	32	36	53	48	42
	1-2-1	15	16	28	26	28
	1-2-2	19	12	20	28	29
Comparison resins						
Soy alkyd		5	6	9	12	14
Safflower alkyd		4	5	7	9	12

1-2-1 resin film had drying characteristics equal to the commercial alkyd resin films.

Sward hardness data for the resin films versus time are compiled in Table III along with data for two commercial resins for comparison. Itaconic and maleic resins dry to an acceptable hardness in 1 day and reach hardness values of 28–42 after 28 days. Commercial alkyds and our fumaric resins were comparable to one another and significantly softer than the itaconic and maleic resins. The dimer and adipic resins were softer after 28 days than the commercial resin films, whereas the fumarates were similar and the maleic and itaconic harder.

Resistances of the experimental films to water, toluene and 5% sodium hydroxide solution were also studied. The data are summarized as follows: Almost all the films resisted toluene longer than the commercial alkyd films. Films of adipic, itaconic and maleic resins had the best toluene resistance. All films were superior to, or as good as, those from the commercial alkyds in water resistance. Films with the best drying characteristics (itaconic 1-2-1 and maleic 1-1-2) also had the best water and toluene resistance. All films were attacked by 5% sodium hydroxide within 5 min.

Solubility of the experimental resins in aqueous systems was studied (Table IV). Since none of these resins were water-soluble, isopropyl alcohol was used as a cosolvent. Four of the compositions shown in Table IV proved to be infinitely dilutable with water. Others showed phase separations but became homogeneous upon addition of further amounts of water. Still others behaved similarly but separated a second time before the end of the water addition. The composition of selected resin solutions at the first evidence of phase separation is given in Table IV. These selected resins had the best film properties based on the solvent resistance data and that in Tables II and III. Aqueous-alcohol solutions containing 49% or more water can be prepared from itaconic 1-2-1 (80%), itaconic 1-2-2 (60%), maleic 1-1-2 (20, 40 and 80%) and 1-2-2 maleic (20–80%) polymers. These resins show the best overall properties for possible water-base coatings. In Table V the resins are listed according to decreasing tolerance to water and compared to an arrangement based on decreasing acid content. The low acid value 1-2-1 resins had the lowest water tolerance. Data on the 1-1-2 and 1-2-2 resins, however, show that factors other than acid value contribute to the solubility of products in aqueous-alcohol solutions. Molecular size of the polymer and distribution of the carboxyl groups in the polymer may also affect solubility.

TABLE IV

Water Titrations of Isopropyl Alcohol Solutions of Tris Amino-Linseed-Dibasic Acids Resins at 25C

Dibasic acid	Composition	Initial percent resin in PrOH	Composition of solution at phase separation			
			Resin	Amine	PrOH	H_2O[a]
			Percent by weight			
Fumaric	1-1-2	40		No phase separation		
		60	20.5	2.8	10.9	65.8
		80	37.8	5.1	4.3	52.8
	1-2-2	40,80		No phase separation		
		60	8.6	1.1	4.5	85.8
Itaconic	1-1-2	20,40		No phase separation		
		80	44.5	8.7	2.3	44.5
	1-2-1	80	40.8	2.2	8.0	49.0
	1-2-2	60	27.2	4.1	14.6	54.0
		80	60.6	9.2	60.0	24.2
Maleic	1-1-2	80	29.0	6.3	0.9	63.8
	1-2-1	40	35.7	2.5	51.1	10.7
		60	25.8	1.8	16.5	56.9
		80	48.7	2.4	9.9	39.0
	1-2-2	20		No phase separation		
		60	24.0	4.5	11.7	60.0
		80	40.8	7.3	2.9	49.0

[a] Water tolerance for specific composition at initial phase separation.

TABLE V

Comparison of Water Tolerance[a] of Resins with Acid Content

Dibasic acid	Composition	Rank of decreasing acid content	Rank of decreasing water tolerance
Maleic	1-1-2	1	5
Itaconic	1-1-2	2	2
Maleic	1-2-2	3	3
Itaconic	1-2-2	4	6
Fumaric	1-1-2	5	4
Fumaric	1-2-2	6	1
Maleic	1-2-1	7	7

[a] Data from Table IV.

Table VI lists data on the dry-to-touch and tack-free times for fumaric, itaconic and maleic resins films cast from aqueous isopropyl alcohol solutions. The 1-1-2 fumaric resin films had equivalent drying properties when cast from either toluene or aqueous alcohol. Drying times of the other resins were considerably extended when cast from aqueous alcohol. Possibly the long drying time of films cast from aqueous alcohol could be overcome by use of suitable additives.

Color changes of pigmented resin films were evaluated by measuring color on a Photovolt (4) colorimeter and expressed in National Bureau of Standards' color difference units, ΔE (3). The ΔE values computed for films heated for 8 hr at 100 C are compared in Table VII with the same films after 3 days of air drying in the dark. The Hunter uniform chromaticity coordinates α and β and the luminosity factor Y (3) are included for 3-day air-dried films to indicate their color. A pure white film would have an α and β of zero and a Y of 100. Comparisons may be made with similar data for a pigmented linseed oil and soy alkyd films. Except for the fumaric 1-1-2 and 1-2-2 resins, all the pigmented films fall between linseed oil and the soy alkyd films in color difference. The small ΔE for the 1-1-2 and 1-2-2 fumaric resins resulted because the films were initially dark.

TABLE VI

Drying Properties of Resin Films from Aqueous Solutions Tris Amino-Linseed-Dibasic Acid Resins (1 mil air-dried films containing 0.1% Co and Pb)

Dibasic acid	Composition	Dry-to-touch, hr	Tack-free, hr
Fumaric	1-1-2	1.5	20
	1-2-1	6.5	15
	1-2-2	24.0	30
Itaconic	1-1-2	20.0	20
	1-2-2	15.0	18
Maleic	1-1-2	2.5	20
	1-2-1	5.0	20
	1-2-2	10.0	20

TABLE VII
Color Differences Between Pigmented Resin Films Initially and After Heating at 100C, 8 hr

Dibasic acid	Composition	Initial color[a]			ΔE[b] Between air-dried (3 days) and heated (100C, 8 hr) films	ΔE[b] Between air-dried for 3 and 28 days
		$\alpha \times 10^3$	$\beta \times 10^3$	Y		
Fumaric	1-1-2	2.4	2.3	75	6.42	1.11
	1-2-1	2.8	8.9	83	17.50	4.99
	1-2-2	12.3	19.8	81	6.11	4.43
Itaconic	1-1-2	5.6	9.0	90	17.72	5.72
	1-2-1	8.1	12.9	92	20.63	5.48
	1-2-2	11.2	11.2	91	16.18	5.88
Maleic	1-1-2	13.3	3.2	91	21.65	7.17
	1-2-1	8.5	8.0	93	21.41	2.78
	1-2-2	14.2	11.9	90	18.98	6.18
Comparison resins						
Linseed oil		5.3	7.4	93	34.35	3.39
Soy alkyd		2.5	1.0	94	13.68	4.82

[a] α, β = Chromaticity coordinates; Y = luminosity factor (3). Films dried 3 days at room temperature.
[b] National Bureau of Standards units.

Also in Table VII are shown the color differences obtained with pigmented resin compositions between 3 and 28 days of dark, air-dry exposure. Linseed oil films were among those exhibiting the smallest color differences. With few exceptions, all values are fairly close together.

Experimental

Resin Components

Linseed acids (Woburn Chemical) (4) were distilled before use. The distilled acids had bp 185–190C/0.5 mm, iodine value 185 and equivalent weight 276. Adipic acid (Fisher Scientific), dimer acid (Emery Industries Empol 1014), fumaric acid (Eastman White Label), maleic acid (Matheson, Coleman, and Bell) and tris(hydroxymethyl)aminomethane (Commercial Solvents) were used as received.

Resin Preparation and Properties

The resins were prepared as previously described (2) except xylene served as the solvent. With fumaric resins of the 1-1-2 and 1-2-2 compositions, dimethylsulfoxide was mixed with xylene for the solvent. After removing the solvent in a rotary vacuum evaporator, iodine value, acid equivalent and oxazoline equivalent (1) were determined on resin samples. The resins were viscous dark-amber liquids or dark solids (fumaric and maleic 1-1-2 compositions). Occasionally a solid material separated from the resins on standing, but these resins readily formed homogeneous solutions upon adding an aromatic solvent.

All resins were soluble in toluene or isopropyl alcohol but insoluble in water. Water tolerance of isopropyl alcohol solutions was determined by the following procedure: Solutions containing 10, 20, 40, 60 and 80% of each resin neutralized with dimethylaminoethanol were prepared with isopropyl alcohol. Samples containing 1 g of resin were then titrated with water to phase separation and the amounts of water required noted. Titrations were continued until 250 ml of water had been added (Table IV).

Film Evaluation

Dry-to-touch and tack-free times were determined on 1 mil films containing 0.1% cobalt and lead driers as naphthenates and cast from toluene solution on steel plates (2). Sward hardness was determined after 1, 2, 4, 7, 14, 21 and 28 days of drying time. The films were maintained at 23C and 50% relative humidity for the rocker measurements. The films were tested for resistance to water, toluene and 5% sodium hydroxide as follows: A small (1.5 in. diameter) watch glass was placed convex side down in several drops of reagent placed on the film. An additional quantity of reagent was placed in the watch glass. The watch glass was then covered by a 2.5-in. inverted Petri dish. Condition of the film was observed after blotting off the reagent with tissue frequently during 24 hr exposure.

Aqueous solutions (50% by weight) were prepared from 14 of the 15 resins (all except itaconic 1-2-1). After appropriate amounts of 2-dimethylaminoethanol (equivalent to acid present), isopropyl alcohol and water plus cobalt and lead driers were added, films were cast at 2 mil wet thickness. With some polymer films wetting of the steel substrate was not uniform. The dry-to-touch and tack-free measurements were carried out as with toluene solution cast films.

Pigmented films were prepared from each experimental resin, linseed oil (Spencer-Kellogg OKO-M-25) and commercial soybean alkyd (Beckosol P470-70), according to the following formula:

Ingredients	Percent
Resin, oil or alkyd	13.4
Toluene	53.4
TiO_2 (Ti Pure R510-1)	33.0
Lead and cobalt driers	0.2

The ingredients were blended under nitrogen in a Lourdes mixer for 15 min. Films were prepared in duplicate from each experimental resin, linseed oil and alkyd paint on 3 × 5-in. steel panels with a doctor blade set to give a 2.3 mil dry thickness. After the films had dried in the dark for 3 days, initial readings of the color were taken with a Photovolt Model 610 colorimeter equipped with tristimulus color filters. Color of one set of films was determined after heating in an oven at 100C for 8 hr. The other set of films was kept in the dark and readings were taken after 3 and 28 days.

ACKNOWLEDGMENT

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