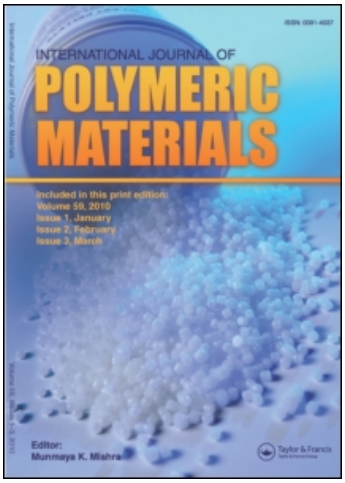

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HIGH PERFORMANCE ALKYD RESIN COMPOSITIONS FOR COATING

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New modified alkyd varnishes were prepared by partial replacement of phthalic anhydride with methylene disalicylic acid. Incorporation of this phenolic derivative led to significant improvement in hardness, gloss, and alkali resistance performance.

Keywords: alkyd, methylene disalicyclic acid, synthesis, properties

INTRODUCTION

Alkyd resin was one of the first synthetic polymers applicable in surface coating. It is a polyester-based material modified with oil or oil-derived fatty acids. This product may be further modified with a variety of other materials to bring about specific designed improvements [1–5]. The present study is mainly concerned with modification of alkyd resin by partial replacement of phthalic acid conventionally employed in the resin formulation by methylene disalicylic acid without affecting the resin constants. This new modification is excepted to improve the dry film performance.

METHODS OF PREPARATIONS

Preparation of Methylene Disalicylic Acid (MDSA) [I]

A mixture of salicyclic acid (0.2 mole, 27.6 gm), formaldehyde, 40% solution (1.4 mole; 13.62 gm) and sulfuric acid, 40% solution, (180 gm) was placed in

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a 250 ml single neck round bottomed flask fitted with water-cooled condenser. The reaction mixture was allowed to reflux for 8 h and then was cooled and filtered under vacuum. The formed white solid was collected, washed several times with hot water and finally with ethanol to remove traces of sulfuric acid and unreacted salicylic acid. It was dried at 110°C under low vacuum, and recrystallized from acetic acid (m.p. 236–238°C).

Preparation of Modified Alkyd Resins

Various MDSA-modified alkyd resins were prepared by fatty acid method via solvent process in one step reaction, where a mixture of anhydrous glycerol (G), fatty acids (FA), phthalic anhydride (PA), and/or methylene disalicylic acid (MDSA) [I] was placed in a 250 ml round bottomed flask fitted with Dean and Stark apparatus. The reaction mixture was refluxed in xylene solvent until the theoretical amount of water was collected.

Each set of resins prepared shows the characteristic resin constants given in Table 1. The various acid equivalent (e_A) for each run are listed in Table 2.

METHODS OF TESTING AND EVALUATION

Methods of testing and evaluation used in this work were performed according to standard specifications and well-recognized techniques including:

- Nonvolatile content [6].
- Color measurement by Gardner standard [7].
- Viscosity measurement [8].
- Preparation of test panels [9].
- Drying time [10].
- Dry film thickness [11].
- Determination of hardness by pendulum tester [12].
- Gloss measurement [13].
- Adhesion by cross-cut adhesion tester [14].
- Flexibility by conical Mandrel [15].
- Scratch hardness by pencil test [16].
- Chemical resistance [17].

RESULTS, DISCUSSION, AND CONCLUSIONS

The conventional alkyds can be modified by inclusion of various structural units in their backbone skeleton during resin preparation.

TABLE 1 Characteristic Resin Constant of Various Alkyds

							Average	
Excess OH%	e_O	e_A	e_B	M_O	R	K	W	Y%
0	0.520	0.260	0.260	0.271	1.00	1.04	52.22	93.6
10	0.573	0.273	0.300	0.287	1.10	1.05	52.13	93.5
20	0.656	0.298	0.358	0.309	1.20	1.03	51.46	93.3
30	0.778	0.339	0.439	0.343	1.30	1.01	51.23	93.2

e_O: Total equivalents at the start of the reaction; e_A: Number of acid equivalents; e_B: Number of hydroxyl equivalents; m_O: Total moles present at the start of the reaction; R: Ratio of total −OH group to total −COOH group (e_B/e_A); K: Alkyd constant (m_O/e_A); W: Weight of product, g; Y%: % yield.

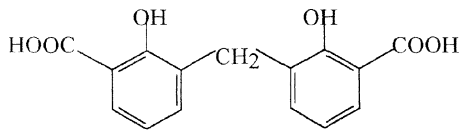
TABLE 2 Acid Equivalent (e_A) of Various Formulations

	Acid equivalent e_A	
Resin no.	PA	MDSA
a	1.00	0.00
b	0.95	0.05
c	0.90	0.10
d	0.85	0.15
e	0.80	0.20

This can be achieved experimentally by total or partial replacement of the alkyd ingredients by other materials of the same functional group.

Methlyene di-salicylic acid (MDSA) [I] is a polyfunctional acid and can be prepared readily with good yield [18] by condensing salicylic acid and formaldehyde in the presence of sulfuric acid.

The structure of MDSA (I) was suggested on the basis of the following considerations:



MDSA (I)

1. Acid value measurement (Theo. 398.7; Found 386.6 mgKOH/g).
2. Melting point (236–238°C), as in literature.
3. Micro elemental analysis of carbon (cal 62.25; found 63.20) and hydrogen (cal. 4.16, found 4.70).
4. I.R. spectrum showed ν_{OH} carboxylic (intermolecular hydrogen bonding) at 3300–2600 cm^{-1} centers at 3100, ν_{OH} phenolic (intermolecular hydrogen bonding) at 3434.9 cm^{-1}, ν_{C-H} aromatic at 3012.7 cm^{-1}, ν_{OH} aliphatic at 2916.6 cm^{-1}, ν_{C-H} stretching at 1657.7 cm^{-1} (strong), ν_{C-O} stretching at 1444 cm^{-1} (strong) and ν_{OH} deformation at 1219 cm^{-1} (strong).
5. ^{1}H-NMR spectrum, showed six aromatic protons in the form of twin doublet of doublets at δ (6.921, 6.878) and (7.383, 7.341) ppm; J = 8.6 Hz and at (7.650, 7.639) and (7.394, 7.383) ppm, J = 2.2 Hz. A singlet at $\delta = 3.85$ ppm, corresponding to the methylene bridge. The phenolic protons and carboxylic groups protons were appeared as a broad band at δ (10.8–11.8) ppm (intermolecular H-bonded protons).

This work is mainly concerned with the modification of alkyd resin by partial replacement of the phthalic anhydride, usually employed in alkyd formulations by methylene disalicylic acid without affecting the resin constant. Such replacement is expected to improve the hardness, alkali resistance, and general film performance, especially when compared with unmodified resins. This was followed by studying the optimum amount of modifier that improves the resin performance and durability without affecting other properties.

Following the successful preparation and characterization of methylene disalicylic acid (MDSA) [I], it was incorporated in alkyd formulation as ingredient source of dibasic acid. For this reason, various excess hydroxyl alkyd resins were prepared by the fatty acid method using the solvent technique through one step reaction as previously described in the experimental section. The prepared resins covered a wide range of fatty acid concentrations and excess hydroxyl percent as 0, 10, 20, and 30%. Within each type of resin, part of the phthalic anhydride was replaced by methylene disalicylic acid (MDSA) [I], the replacement corresponded to 0.05, 0.10, 0.20, and 0.30 of total acid equivalent. Even though in each set of formulations several fatty acids were used, this discussion will confine its attention exclusively to resins of linseed oil fatty acids. Table 3 shows the various characteristics of MDS-modified alkyd resins.

TABLE 3 Various Characteristics of MDSA Modified Alkyds

Resin no.	Ingredient	Equivalent of ingredient at start of reaction			
		0% excess OH	10% excess OH	20% excess OH	30% excess OH
a	FA	0.111	0.100	0.082	0.055
	PA (1.00)	0.149	0.173	0.216	0.284
	MDSA (0.00)	0.000	0.000	0.000	0.000
	G	0.260	0.300	0.358	0.439
b	FA	0.111	0.100	0.082	0.055
	PA (0.95)	0.142	0.165	0.205	0.270
	MDSA (0.05)	0.007	0.008	0.011	0.014
	G	0.260	0.300	0.358	0.439
c	FA	0.111	0.100	0.082	0.055
	PA (0.90)	0.134	0.156	0.194	0.256
	MDSA (0.10)	0.015	0.017	0.022	0.028
	G	0.260	0.300	0.358	0.439
d	FA	0.111	0.100	0.082	0.055
	PA (0.85)	0.120	0.138	0.173	0.230
	MDSA (0.20)	0.029	0.035	0.043	0.054
	G	0.260	0.300	0.358	0.439
e	FA	0.111	0.100	0.082	0.055
	PA (0.80)	0.105	0.121	0.151	0.202
	MDSA (0.30)	0.044	0.052	0.065	0.082
	G	0.260	0.300	0.358	0.439

FA: fatty acids; PA: phthalic anhydride; MDSA: Methylene disalicylic acid; G: Glycerol.

The following observations were noticed during the resins preparation:

1. Modification with (MDSA) was successful up to 25% in all alkyds containing excess hydroxyl.
2. The presence of modifier has no significant effect on the color of the product and time of the reaction in most cases.
3. The viscosity of resins prepared was increased by increasing the modifier percent or by increasing the hydroxyl content of resin formed.
4. Gel formation occurred in all composition containing more than 30% equivalent of (MDSA) based on total acid equivalent.

The prepared alkyds were thinned with xylene to 40% solid, filtered, and followed by the addition of the driers combination (Co, Zr, and Mn octoates, 0.05, 0.10, and 0.02%, based on metal per solid resin,

respectively). The prepared varnishes were applied on glass and tin plates, then dried for 24 h or baked for 1 h at 110°C. These varnish films were subjected to preliminary evaluation in order to indicate the most suitable composition. Then they were subjected to an extensive evaluation study. The results are listed in Tables 4 and 5.

The following generalizations were deduced from the date in Tables 4 and 5.

1. The air drying time and stove-baking schedules are highly improved after modification with (MDSA). The drying time decreases with increasing the amount of modifier or increasing the hydroxyl content of varnishes.
2. In most cases, color and viscosity of modified alkyds are slightly increased as compared with unmodified alkyds. The viscosity increases with increasing the hydroxyl content.

TABLE 4 Various Characteristics Data of Various MDSA-Modified Alkyds

Resin no.	Excess-OH%	Air drying HD time (h)	Stove drying at 110°C for (½ h)	Viscosity Color at 50% solid	
				CP	Gardner
Ia	0	16	ST	20.27	8
b		13	VST	21.30	8
c		10	HD	21.30	8
d		8	HD	23.04	9
e		6	HD	32.25	9
IIa	10	12	VST	32.34	8
b		10	VST	33.00	8
c		10	HD	33.48	8
d		7	HD	40.72	8
e		5	HD	48.25	9
IIIa	20	8	VST	56.80	7
b		5	HD	63.30	7
c		4	HD	70.23	7
d		3	HD	78.28	7
e		3	HD	83.28	8
IVa	30	6	VST	102.15	7
b		4	HD	106.25	7
c		3	HD	114.30	7
d		2	HD	150.12	8
e		2	HD	174.60	8

ST: Slight tackiness; VST: very slight tackiness; HD: hard dry.

TABLE 5 Film Characteristics of Various MDSA-Modified Alkyds

Resin no.	Gloss at 45° a*	Gloss at 45° s*	Thickness (μ) a	Thickness (μ) s	Hardness (sec) a	Hardness (sec) s	Scratch test a	Scratch test s	Flexibility a & s	Adhesion a & s	Water resistance a & s	Acid resistance a & s	Alkali resistance** a	Alkali resistance** s	Solvent resistance a & s
Ia	85	87	22	20	15	21	<1 kg	>1 kg	Pass test	Good	Ex	Ex	2	7	Ex
b	88	88	20	20	18	24	>1 kg	>1.5 kg	Pass test	Good	Ex	Ex	3	7	Ex
c	88	89	20	20	17	25	>1 kg	>1.5 kg	Pass test	Good	Ex	Ex	7	14	Ex
d	91	92	20	20	20	28	>1.5 kg	>1.5 kg	Pass test	Good	Ex	Ex	14	21	Ex
e	95	97	22	20	22	34	>1.5 kg	>2 kg	Pass test	Good	Ex	Ex	18	23	Ex
IIa	88	88	20	20	18	20	<1 kg	>1 kg	Pass test	Good	Ex	Ex	2	7	Ex
b	85	87	22	19	24	32	>1 kg	<1 kg	Pass test	Good	Ex	Ex	4	9	Ex
c	89	89	22	20	26	40	>1 kg	<1.5 kg	Pass test	Good	Ex	Ex	7	15	Ex
d	92	93	22	19	25	30	1.5 kg	>2 kg	Pass test	Good	Ex	Ex	12	21	Ex
e	94	96	21	20	29	45	>1.5 kg	>2 kg	Pass test	Good	Ex	Ex	17	24	Ex
IIIa	80	81	21	20	32	43	<1 kg	>1 kg	Pass test	Good	Ex	Ex	2	9	Ex
b	83	83	20	20	48	52	>1 kg	>1.5 kg	Pass test	Good	Ex	Ex	7	11	Ex
c	86	87	21	22	53	56	>1 kg	>2 kg	Pass test	Good	Ex	Ex	13	15	Ex
d	89	90	21	21	61	68	>1.5 kg	>2 kg	Pass test	Good	Ex	Ex	16	16	Ex
e	92	91	20	19	64	72	>1.5 kg	>2 kg	Pass test	Good	Ex	Ex	7	13	Ex
IVa	83	84	20	18	40	46	<1 kg	<1 kg	Pass test	Good	Ex	Ex	12	21	Ex
b	89	89	2–	20	45	60	>1 kg	>1.5 kg	Pass test	Good	Ex	Ex	14	25	Ex
c	91	92	20	19	58	65	>1.5 kg	2 kg	Pass test	Good	Ex	Ex	18	27	Ex
d	94	95	21	20	67	75	>1.5 kg	2.5 kg	Pass test	Good	Ex	Ex	21	>30	Ex
e	95	97	20	18	72	93	>1.5 kg	>2.5 kg	Pass test	Good	Ex	Ex	22	>30	Ex

*"a" and "s" represent air-drying and stove-baked film respectively; **Alkali resistance data are given in days; Ex: Excellent (almost no film defect).

3. Increasing the percent modifier of the prepared alkyds results in substantial increase in the gloss values of dried film.
4. Pendulum and scratch hardness of air and stove-baked dry films were improved by increasing the amount of modifier.
5. It is not possible to predict the effect of modification on film appearance, flexibility and adhesion, because all films examined exhibit uniformly satisfactory properties.
6. Extensive studies on film performance showed that water, acid, and solvent resistance are excellent for all films. The alkali resistance is improved on modification with (MDSA), compared with un-modified varnish compositions of the same resin type.
7. In general, stove-baked films showed better performance when compared with air-dried films.

CONCLUSIONS

Evaluation studies have shown that the compositions modified with methylene disalicylic acid improve the gloss, hardness, drying time, and alkali resistance and their films are free from tackiness. On the other hand, adhesion, flexibility, and films appearance of dried film showed at least the same performance as unmodified alkyds.

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