

Newer Intermediates for Plastics and Coatings. III. Polyesters Based on Methylene-di- β -Oxynaphthoic Acid

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Synopsis

A tetrafunctional dibasic acid, methylene-di- β -oxynaphthoic acid (MDNA), has been used for preparation of unsaturated polyester resins. The films obtained from these products have excellent chemical and physical properties comparable to epoxy resins and to a large extent balance some of their shortcomings such as darker color, higher viscosities, and higher cooking temperatures. The possible applications of these resins are coatings where acid, corrosion, and thermal resistance are of primary importance.

EXPERIMENTAL

Raw Materials

MDNA. Methylene-di- β -oxynaphthoic acid was prepared by condensing formaldehyde with commercially available B.O.N. acid by the method previously described¹ (Figs. 1 and 2).

Fumaric Acid. Imported fumaric acid obtained from a local user in the form of white crystalline powder, mp 284°C, was used. Purity of the acid was 98%.

Polyols. Ethylene, diethylene, triethylene, and propylene glycol of analytical grade, obtained from B.D.H., were used.

Xylene. Commercially available xylene was distilled and the fraction distilling between 135° and 138°C was collected. It was then dried over sodium wire.

Benzene. Commercially available benzene was distilled and the fraction distilling between 78° and 80°C collected. It was then dried over sodium wire.

Other Chemicals. Acetic anhydride, pyridine, acetone, phenolphthalein indicator, alcoholic KOH, styrene monomer, methyl methacrylate mono-

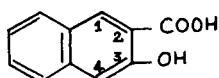


Fig. 1. 3-Hydroxy-2-naphthoic acid (B.O.N. acid).

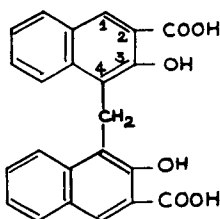


Fig. 2. Methylene-di- β -oxynaphthoic acid.

mer, benzoyl peroxide, cobalt naphthenate, and butylated melamine formaldehyde were used from a reputable distributor.

Testing Methods and Analyses

Acid value, hydroxyl value, iodine value, saponification value, and resistance to alkali, water, and solvents were determined as per ASTM standards.

Casting of Films on Glass or Metal Panels

The polyester resin was applied to the test panels prepared by standard methods by an automatic spraying machine after adjusting the viscosity of the resin between 1.25 to 1.85 poise for good flow. The films were dried at elevated temperatures to get hard and tough films.

Film properties such as color, mar resistance, gloss, flexibility, adhesion, scartch hardness, and alkali, water, and solvent resistance were checked as per standard testing methods.

Unsaturated Polyesters Based on MDNA

Standard esterification method and equipment were used for preparation of the reference polyesters and those based on MDNA.²

The reference polyester was prepared by reacting 0.6 mole phthalic anhydride and 0.4 mole fumaric acid with 1.1 moles of ethylene glycol at 180–200°C for 3 1/2 hr.

As MDNA has a comparatively high melting point, the reaction temperature had to be raised to about 240–280°C after the initial reaction of monomer formation and removal of xylene, used as entrainer together with water of reaction. A systematic work was undertaken to study the effect of polyols as well as vinyl monomers, effect of crosslinking agents, and other various additives.

Before switching over to straight MDNA-based polyesters, preliminary work was done to study the polyester resins where the saturated acids were mixtures of phthalic anhydride and MDNA in different proportions. It was, however, noticed from the evaluation of these polyesters that they lack the high-temperature resistance expected from MDNA polyesters, and therefore further work was concentrated on the preparation of polyesters based on MDNA only.

TABLE I

Preparation of Polyester Resins Based on MDNA, Fumaric Acid, and Ethylene Glycol^a

Batch no.	Composition		Unsaturation due to fumaric acid (theoretical), %	Reaction time, hr	Acid value
	MDNA, moles	Fumaric acid, moles			
6	0.25	0.75	41.42	3.0	15.2
7	0.30	0.70	36.25	4.0	17.0
8	0.35	0.65	31.81	4.0	19.0
9	0.40	0.60	27.72	4.5	15.4
10	0.45	0.55	24.16	4.5	17.2

^a Reaction temperature, 240°–280°C; ethylene glycol, 1.1 mole.

A series of resins were prepared by changing the mole ratios of dibasic acids. The products satisfactory for further evaluation on the basis of unsaturation are summarized in Table I.

Effect of Catalysts on Polyesterification Reaction

The direct polyesterification reaction is self catalyzed, but catalysts are often employed to maintain the rate of reaction. Such catalysts include sulfonic acids, e.g., paratoluenesulfonic acid and camphorsulfonic acid, in amounts 1–2% based on the weight of the reactants.

In view of this, an attempt was made to see the effect of catalysts on MDNA polyesters. It was observed that the product obtained was hazy, even though increasing amounts of *p*-toluenesulfonic acid were used. In other experiments, sulfuric acid was used as a catalyst for the esterification reaction, but it did not affect the time of reaction or help the reaction markedly, and the color obtained was darker than the PTSA catalyst. Hence, it can be concluded that these catalysts could not be used successfully for the polyesterification reactions of MDNA.

Effect of Addition of Monobasic Acid on Preparation of Polyesters

Addition of 0.1 mole benzoic acid had no marked effect with respect to color and viscosity. Therefore, 0.2 mole benzoic acid was employed, and has shown satisfactory results. The results are summarized in Table II.

Effect of Polyols on Polyesters

Further work was undertaken to prepare polyesters based on MDNA and different polyols such as diethylene glycol, triethylene glycol, and propylene glycol with or without added benzoic acid. The results are shown in Table III. Variation in selection of batches is, firstly, due to variation of unsaturation³ due to change in molecular weight of the polyol; and, secondly, though a large number of batches were actually prepared, only representative ones giving satisfactory performance are shown in the table.

TABLE II
Effect of Addition of Monobasic Acid

Batch no.	MDNA, moles	Fumaric acid, moles	Benzoic acid, moles	Unsaturation due to	Reaction time, hr	Acid value	Remarks
				fumaric acid (theoretical) %			
28	0.25	0.75	0.2	39.03	3.0	16.9	} light color and low viscosity product
29	0.30	0.70	0.2	34.49	3.0	17.1	
30	0.35	0.65	0.2	30.02	4.0	15.2	
31	0.40	0.60	0.2	25.71	4.5	19.1	
32	0.45	0.55	0.2	22.00	4.5	17.3	
33	0.50	0.50	0.2	20.00	4.5	14.3	

TABLE III
Effect of Polyols on Polyesters^a

Batch no.	Composition		Polyol	Unsaturation due to	Reaction time, hr	Acid value
	MDNA, moles	Fumaric acid, moles		fumaric acid (theoretical), %		
71	0.25	0.75	diethylene	33.02	3.5	13.93
72	0.30	0.70	glycol, 1.1 mole	29.35	3.5	15.24
73	0.35	0.65		25.01	3.5	11.38
74	0.40	0.60		22.92	4.0	16.3
75	0.45	0.55		19.00	4.0	15.83
115	0.25	0.75	triethylene	28.93	3.0	10.7
116	0.30	0.70	glycol, 1.1 mole	25.12	3.0	13.2
117	0.35	0.65		22.18	3.0	14.2
118	0.40	0.60		22.00	3.0	14.4
119	0.45	0.55		16.15	3.5	16.3
158	0.25	0.75	propylene	36.78	3.0	15.1
159	0.30	0.70	glycol, 1.1 mole	33.02	3.0	17.8
160	0.35	0.65		28.72	3.5	13.2
161	0.40	0.60		25.00	3.5	18.2
162	0.45	0.55		20.34	4.0	15.0

^a Reaction temperature 240°–280°C; benzoic acid used, 0.2 mole.

Evaluation of Polyester Resins

The various polyester resins which were found to be satisfactory on the basis of unsaturation and had possible utility for formulation of coatings in conjunction with vinyl monomers and other additives were tested for their chemical constants such as acid value, saponification value, and hydroxyl value, which are summarized in Table IV.

Coating Compositions Based on MDNA Polyesters

The MDNA polyesters obtained in different sets of experiments using different polyols were then converted into coating compositions by addition

TABLE IV
Chemical Constants of Polyesters Selected for Evaluation

Batch no.	Unsaturation due to fumaric acid (theoretical), %	Acid value	Saponification value	Hydroxyl value	Viscosity in monomer on Gardner bubble viscometer	
					poise	Solid content, %
Reference polyester	22.32	16	390	35	1.25-1.40	80
28	39.03	16.0	316	32	1.0-1.25	100
29	34.49	17.1	297	39	1.0-1.25	95
30	30.02	15.2	325	45	1.0-1.25	90
31	25.71	19.1	340	46	1.0-1.25	80
32	22.00	17.3	346	43	1.40-1.65	80
71	33.02	13.93	311	49	1.25-1.40	100
72	29.35	15.22	322	51	1.25-1.40	100
73	25.01	11.38	291	56	1.25-1.40	95
74	22.92	16.30	364	38	1.25-1.40	95
75	19.00	15.83	352	32	1.40-1.65	95
115	28.93	10.7	270	61	1.25-1.40	95
116	25.12	13.2	318	58	1.25-1.40	90
117	22.18	15.2	342	39	1.25-1.40	90
118	20.00	14.2	324	35	1.25-1.40	95
119	16.15	14.9	328	13	1.25-1.40	85
158	36.78	15.1	364	41	1.40-1.65	85
159	33.02	17.8	378	45	1.40-1.65	85
160	28.72	13.2	308	51	1.40-1.65	85
161	25.00	18.3	379	69	1.65-2.00	85
162	20.34	15.0	358	62	1.65-2.00	75

of the appropriate amount of different types of vinyl monomers together with catalysts and accelerators, with or without added urea/melamine formaldehyde resins.

With resins where the viscosity was not very high, the coating viscosity could be obtained after dilution with the monomer. With very high viscosity products, however, it was necessary to add suitable solvents such as xylene and butanol at a ratio of 9:1 to adjust the viscosity to a desirable value. Viscosities of all the resins were adjusted between 1.25 to 1.65 poise for good flow and uniform, desirable thickness. The average solids content of the coating resin was 70-80%.

The films were applied to test panels prepared as above by using a spray technique normalized for $\frac{1}{2}$ hr and cured at predetermined temperatures. It was observed that in case of benzoyl peroxide-catalyzed films, tack-free film could not be obtained even after curing at 65-70°C for prolonged periods, indicating incomplete crosslinking. In view of this, a two-stage curing procedure was adopted in which films were first cured at 65-70°C about 1 hr and then at elevated temperature of 180-190°C for periods sufficient to make the film tack free. In all cases, cobalt naphthanate was used as accelerator. The results obtained are summarized in Table V.

TABLE V
Curing of Polyester Resins Based on MDNA Crosslinked with Styrene^a

Batch no.	Unsaturation due to fumaric acid (theoretical), %	Curing temp., °C	Curing time, hr	10% Butylated melamine formaldehyde	
				Curing time, hr	Temp., °C
28	39.03	180	2	1	120
29	34.49	180	2	1	120
30	30.02	180	2	1	120
31	25.71	190	2	1	130
32	22.00	180	3	1	130
71	33.02	180	2	1	120
72	29.35	180	2	1	130
73	25.01	180	2	1	130
74	22.92	190	2	1.5	130
75	19.00	190	3	1.5	130
115	28.93	180	2	1	130
116	25.12	180	2	1	130
117	22.18	180	2	1	130
118	20.00	190	2	1	130
119	16.15	190	3	1	130
158	36.78	160	2	1	120
159	33.02	170	2	1	120
160	28.72	180	2	1.5	120
161	25.00	180	2	1.5	120
162	20.34	180	2	1.5	130

^a Mole ratio of styrene to fumaric acid, 1.1 mole; accelerator, cobalt naphthanate, 0.5%; curing catalyst, benzoyl peroxide 2%. On a similar basis, resin was crosslinked with methacrylate. There was no marked difference in curing time and temperature; hence, they are not tabulated.

Effect of Catalyst and Accelerator on Temperature and Time of Curing

From the results of curing of polyester films, it was observed that, in general, the curing temperatures required for MDNA-based products were high where time of curing was also comparatively high. Certain experiments were carried out to study the effect of concentration of catalyst as well as accelerators on the rate of curing in order to see whether any improvement could be obtained in curing characteristic, by using different proportions. The results showed that the conventional quantities only give satisfactory results. Both these factors confirmed that the crosslinking of polyesters based on MDNA does not differ to any great extent from that based on conventional dibasic acids, except for temperature and time of curing.

Effect of Crosslinking Agents on Temperature and Time of Curing

After deciding the optimum conditions of temperature, the study was extended to investigate the effect of molar ratio of the crosslinking monomer

TABLE VI
Film Properties of Typical Polyester Resin Based on MDNA*

Film properties	Reference polyester	Batch no.							
		28	29	72	73	115	116	158	159
Color (Gardner standard)	9	18	18	19	18	17	17	17	18
Rocker hardness, %	64	76	75	78	72	71	75	75	69
Scratch hardness, g	1600	above 2000	above 2000	1800	1800	1900	1900	above 2000	2000
Flexibility	G	G	G	G	G	G	G	P	P
Gloss, %	75	75	78	71	70	72	68	75	72
Adhesion	E	E	E	E	E	E	E	E	E
Mar resistance	G	G	G	G	G	G	G	G	G
Abrasion resistance	G	G	G	G	G	G	G	G	G
Temperature resistance, °C	230	370	360	350	340	340	350	370	370
Water resistance	G	G	G	G	G	G	G	G	G
Acid resistance	E	E	E	G	G	G	G	E	E
Alkali resistance	P	P	P	P	P	P	P	P	P
Solvent resistance	G	G	G	G	G	G	G	G	G

* Monomer, styrene; F = fair; G = good; E = excellent; P = poor.

to the unsaturated acid, but the results showed that conventional quantities only give satisfactory results. Also, the effect of addition of crosslinking resins during curing of these resins from the point of view of improving the film properties and time and temperature of curing was studied. The results are shown in Table V.

Evaluation of Film Properties

The cured films of various MDNA-based polyesters obtained from the different resins which were expected to give promising results only were evaluated by test methods already described above, and the properties were compared with the films cast from conventional epoxy resins. The results are given in Tables VI and VII.

Structural Study of MDNA-Based Polyesters

Infrared spectroscopy of the unsaturated polyesters based on MDNA was undertaken, mainly to see whether the effect of different glycols could be delineated and the presence of functional groups could be located, which help to some extent in assigning the probable structure of these polyesters. The structures assigned are, however, purely arbitrary, and much detailed work is necessary with the use of NMR, ESR, and x-ray diffraction studies to establish the actual structures of these compounds.

The infrared curves obtained as well as the interpretation of the various peaks obtained are presented below.

TABLE VII
Comparison of Film Properties of Polyester Resin Based on
MDNA with Commercial Epoxy Resin^a

Film properties	Reference polyester	Polyesters based on MDNA		
		Batch no. 29	Batch no. 158	Epoxy resin
Color (Gardner standards)	9	18	17	4
Rocker hardness, %	64	75	75	80
Scratch hardness, g	1600	above 2000	above 2000	above 2000
Flexibility	G	G	P	E
Gloss, %	75	78	75	75
Adhesion	E	E	E	E
Mar resistance	G	G	G	E
Abrasion resistance	G	G	G	G
Temperature resistance, °C	230	360	370	270
Water resistance	G	G	G	E
Acid resistance	E	E	E	E
Alkali resistance	P	P	P	E
Solvent resistance	G	G	G	G

^a F = fair; G = good; E = excellent; P = poor.

Study of Infrared Spectra^A of Polyester Resin Based on MDNA, Fumaric Acid, and Ethylene Glycol

The spectra of this compound (Fig. 3) taken in this film form (Nujol) were studied for different groups:

1. The absorption bands in the region $730\text{--}880\text{ cm}^{-1}$ are assigned to the out-of-plane deformation vibration of the hydrogen atoms remaining on the naphthol ring. It also indicates the polynuclear aromatic compounds.

2. The absorption bands at 1030 cm^{-1} and 1090 cm^{-1} are assigned to in-plane C—H deformation vibration and those in the range of $1580\text{--}1600\text{ cm}^{-1}$ to the C=C stretching vibration in the ring.

3. The strong absorption bands at 1220 cm^{-1} and 1280 cm^{-1} are derived from the C—O stretching vibration in aromatic esters.

4. Free —OH group is indicated at 3500 cm^{-1} as —OH stretching vibration.

5. Two consecutive absorption bands at 1650 cm^{-1} and 1800 cm^{-1} show the unsaturation in the compound.

6. A strong absorption at 2900 cm^{-1} is assigned to Nujol.

DISCUSSION

The present investigation is an outcome of the search for new intermediates for plastics and coatings which is being undertaken in this laboratory at present. Methylene-disalicylic acid,⁵ which is obtained by condensation of salicylic acid with formaldehyde, was proved to be an interesting dibasic

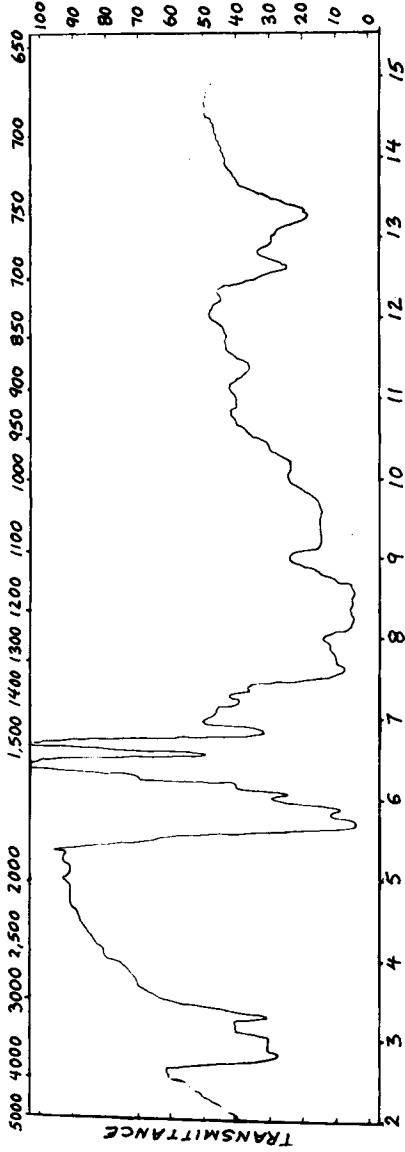


Fig. 3. Unsaturated polyester resin based on MDNA, fumaric acid, and ethylene glycol.

acid for preparation of alkyds,⁶ polyesters,⁷ polyamides,⁸ etc. It was, therefore, quite in order to speculate whether a similar product could be obtained from the higher homolog of salicylic acid i.e., 3-hydroxy-2-naphthoic acid (B.O.N. acid).

In addition, B.O.N. acid also is a commercial product and is readily available locally. It was also expected that the higher molecular weight of this product, as well as its enhanced aromaticity, in comparison to methylenedisalicylic acid, should impart specific properties to the products prepared from it, such as high heat resistance, higher chemical resistance, better mechanical properties, etc.

Unsaturated Polyesters Based on MDNA

From the general information available in case of unsaturated polyesters based on commonly used dibasic acids, the range of unsaturation which is reported to give optimum properties is known. The results given in Table I and the preliminary evaluation of these products confirmed that only the products having a 20–40% unsaturation gave useful products, as in the case of commonly known polyesters.

An additional factor for excluding the polyesters above 40% unsaturation was that they contained comparatively a very low per cent MDNA and were not of much interest from the point of view of utilization of MDNA. Products containing a larger proportion of MDNA, more than 55 parts on a molar basis, were not useful either, because the curing of the films was not sufficient or the resins themselves gelled during preparation, owing to the factors indicated earlier.

Effect of Addition of Monobasic Acid

The use of monobasic acids is common in the preparation of polyesters, particularly when the intermediates used have high functionality and are likely to give complex products leading to high viscosity and poor control over the reaction. The results given in Table II showed that, up to 0.1 mole benzoic acid, materially no effect on the properties of the various polyesters was observed, which may be due to the fact that the quantity of monobasic acid was insufficient, compared to the molecular complexity and excess functionality. Use of benzoic acid beyond 0.2 mole had the additional advantage of low color, but naturally such a high proportion of benzoic acid is not advisable both technically and commercially; 0.2 mole benzoic acid, which gave satisfactory properties, except for a slight dark color, was therefore selected for further work.

Effect of Polyols on Polyesters

As the molecular-weight of polyol increased, the actual amount used in the reaction also increased; and, as pointed out earlier, the reaction was comparatively smoother. One of the major advantage which was found with the higher molecular weight polyols was reduction in reaction time,

again possibly due to the larger weight of the reactants, which made the condensation reaction comparatively easy. Though the effect of monobasic acid was comparable in case of diethylene and triethylene glycols when 0.2 mole benzoic acid was used, with propylene glycol slightly higher quantities were necessary. This is in accordance with the results obtained with unmodified polyesters based on propylene glycol, which had longer reaction periods and slightly higher viscosities, mainly due to the sluggish secondary hydroxyl and presence of pendent methyl groups.

Evaluation of Polyester Resins

The constants indicated in Table IV showed that all the polyesters selected for evaluation had unsaturation sufficient for further crosslinking, reasonably low acid value, and hydroxyl and saponification values in the range of the usual polyester products. In general, the benzoic acid-modified products had lower viscosities than their unmodified counterparts. Of the various polyols used, polyesters based on propylene glycol had comparatively higher viscosities, the reasons for which have already been explained.

Effect of Crosslinking Monomers

The two monomers used for crosslinking, viz., styrene and methyl methacrylate, showed no marked differences from the point of view of temperature as well as time of curing when compared with each other. But both temperature and time required for curing were much higher than those of the reference polyester. It was noticed that the curing temperature used in case of the reference polyester was not suitable for these polyesters. The films were comparatively soft and tacky. Hard and nontacky films were obtained only after curing them at 180°C for 2 hr, in contrast to 130°C for 1 hr sufficient for reference polyester. As the polyesters were based on new dibasic acid, an attempt was made to see whether better performance can be obtained by changing the proportions of crosslinking monomers. The lesser monomer quantities lead to tacky films, while an increased ratio gives undue brittleness.

In addition to the effect of ratio of monomer to polyester, the effect of catalyst and accelerator used for crosslinking was also investigated by using different proportions. It was seen that conventional quantities only give satisfactory results.

The curing behavior of these polyesters may possibly be explained on the basis of two factors. Firstly, the presence of large amounts of free phenolic groups might be inhibiting the copolymerization of vinyl monomers; and secondly, the excess of hydroxyl groups might be adding to the tackiness of the films. Curing at higher temperatures and for increased period could lead to partial etherification of the hydroxy groups with phenolic —OH, minimizing the inhibition of polymerization reaction and also decreasing tackiness of the films.

The use of butylated melamine formaldehyde resins during curing was investigated to overcome this problem, because it is known that the butylated melamine could react with alcoholic as well as phenolic hydroxyl groups.⁹ The results given in Table V showed that both reaction time and temperature of curing could be reduced and brought to the level of the reference polyester.

Evaluation of Film Properties

The evaluation of film properties as given in Table VI brings out various points.

Although the color of all the polyesters based on MDNA is darker than that of the reference polyester, this is understandable because of the initial color of the intermediate used as well as the higher temperatures required during the preparation of these polyesters.

The higher rocker and scratch hardness could be explained on the basis of the higher molecular weight and greater complexity of the resins as well as increased aromaticity because of the naphthalene rings present. Slightly higher values for rocker hardness in the case of propylene glycol-based resins is likely to be due to the pendent methyl group. The formation of ether linkages, which is quite likely under the conditions of curing, would also add to the hardness of the films.

Though the connecting methylene bridge should give better flexibility, this is counteracted to some extent by the effect of the bulky naphthalene rings. The improved flexibility observed in the case of diethylene and triethylene glycols may be attributed to their extended structures as compared to the polyesters based on ethylene and propylene glycols.

In view of the better hardness properties as explained above, the gloss of the films should have been normally better. But the flow properties of the resin appear to affect this to a certain extent, and the gloss is more or less the same as that of the reference polyester. A marginal increase is noted in case of ethylene and triethylene glycol where the viscosities of the corresponding resins is of a lower order, which might have given better flow properties.

The excellent adhesion which was observed in all cases, including the reference compound, is readily explained on the basis of the highly polar ester linkages and free carboxyl and hydroxyl groups which are normally present in all polyesters. The MDNA polyesters would have additional advantage of ether linkages as well as free phenolic groups.

The satisfactory mar resistance as well as abrasion resistance are due to the combination of hardness and flexibility, the reasons for which have already been explained.

As to the chemical resistance of the films, although from the results one could get the impression that all have similar characteristic so far as water, acid, and solvent resistance is concerned, it should be remembered that these tests were performed according to ASTM, and the ultimate failure of

the films has not been studied. The polyesters based on MDNA do not differ to any great extent in their resistance to the above agents.

It is generally known that the polyester resins have poor resistance to alkali because of the ester linkages, which are sensitive to attack by alkali. This could be, however, improved by having a complex, high molecular weight structure, whereby the accessibility to alkali is reduced, and also by decreasing the number of ester linkages per unit length of the molecule. The improved behavior of the MDNA polyester is shown by comparison to the reference polyesters, whereby the time of alkali immersion is nearly doubled.

Of greatest importance appears to be the thermal resistance of these films. As compared to the reference polyester, which can withstand up to 230°C, these polyesters can be subjected to a temperature as high as 340–370°C. The propylene glycol-based products had the highest thermal resistance, and this was followed by ethylene, diethylene, and triethylene glycols, respectively. The better performance of propylene glycol may be due to the methyl side chain, while the lower resistance of diethylene and triethylene glycols may be attributed to the ether linkages present in the glycol. This thermal resistance of MDNA polyester is attributed to the higher molecular weight and greater complexity of the resin together with the presence of naphthalene rings, which have greater stability than the benzene ring present in the conventional polyester.

Comparison of MDNA-Based Polyesters with Epoxy Resins

Epoxy resins are known for their excellent physical, mechanical, and chemical properties, the only commercial shortcoming being their high cost. In view of the comparatively good properties of MDNA-based polyesters, it was expected that, if they were compared for their properties with epoxy resins, the results should be encouraging. One could look upon these as comparatively cheaper substitutes for epoxy resins. This is more pertinent in our country, because epichlorohydrin required for epoxy resins is imported, while MDNA required for these polyesters could be obtained from local sources.

A glance at the results given in Table VIII shows that, barring alkali resistance and color, most of the other properties of these polyester resins are equivalent or slightly better than epoxy resins, while the temperature resistance is definitely superior.

The coatings based on MDNA polyesters could, therefore, be definitely useful as substitutes for epoxy coatings, particularly for acid and corrosion resistance as well as coatings required for elevated temperatures. The performance of these coatings could be further improved by appropriate pigmentation. Though the color of the coatings is dark, in case of special-purpose and high-temperature coatings, where the chemical and thermal properties of the films are of primary importance, the color of the coatings could be of secondary importance.

CONCLUSIONS

Unsaturated polyesters based on MDNA, fumaric acid, and different glycols present no difficulty in processing, though they have certain drawbacks such as dark color, high viscosity, and higher temperature of cooking. Use of monobasic acid such as benzoic acid can yield MDNA polyesters of much less color and low viscosity.

The film properties of the unpigmented coatings obtained from MDNA-based polyesters vary to a certain extent depending upon the polyols used, but are superior to the reference polyester and equivalent to the epoxy resin, in general, except for alkali resistance. The thermal resistance of these polyesters is far superior to that of the epoxy resins, and they could be recommended where acid corrosion and thermal resistance is of primary importance.

References

1. N. Kondekar and S. P. Potnis *Ind. Eng. Chem., Prod. Res. Devel.* (1973).
2. *Encyclopedia of Polymer Science and Technology*, Vol. 11, p. 88.
3. Herman Boing, Unsaturated Polyesters.
4. Bellamy, L. J., *Infrared spectra of complex molecule*, 1954.
5. M. H. Parulekar, H. A. Bhatt, and S. P. Potnis *J. Ind. Chem. Soc.*, **49**, 1201 (1972).
6. A. G. Khanolkar, Ph.D. Thesis, University of Bombay, December 1972.
7. S. N. Aklujkar, M.Sc. (Tech.) Thesis, University of Bombay, August 1972.
8. S. V. Bhagwat, M.Sc. (Tech.) Thesis, University of Bombay, August 1972.
9. *Encyclopedia of Polymer Science*, Vol. II, Page 27.

Received December 5, 1973

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