Table XXXII. Water Vapor Transmission Hydrolyzed 0.5-Mil Mylar Film

Treatment	Grams/Square Meter 24 Hours
Film as received	15.6
	16.2
	18.5
Film exposed to 95% RH at 90 °C.	
12 days	16.4
	17.4
18 days	16.3
	17.9
25 days	15.4
	16.3

alcohols than with water. When the polymer is cold-drawn and exposed to hydrolysis, it retains tensile properties longer than undrawn polymer under the same conditions. In the form of 10-mil thick sheets, Mylar hydrolyzes less rapidly than 0.5-mil thick films. However, Dacron filaments hydrolyze much more slowly than the sheet material, even though their diameter is only 0.5 mil. It is evident that the outward form of the polymer samples influences its resistance to hydrolysis, and also that the structure of the polymer on a molecular scale is equally important in this respect.

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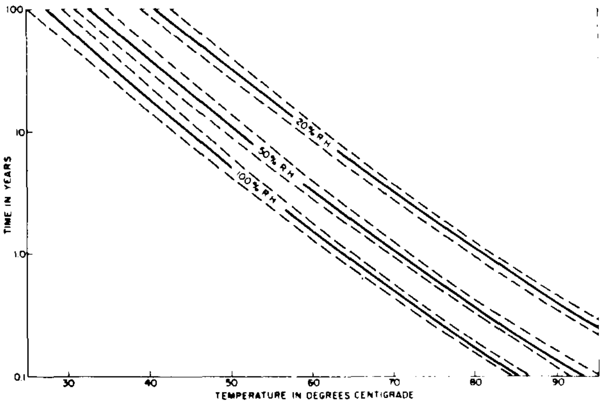

Figure 22. Degradation of 0.5-mil Mylar film

to log $\frac{A}{A\text{-}X}$ = 0.003 (confidence limit 0.95)

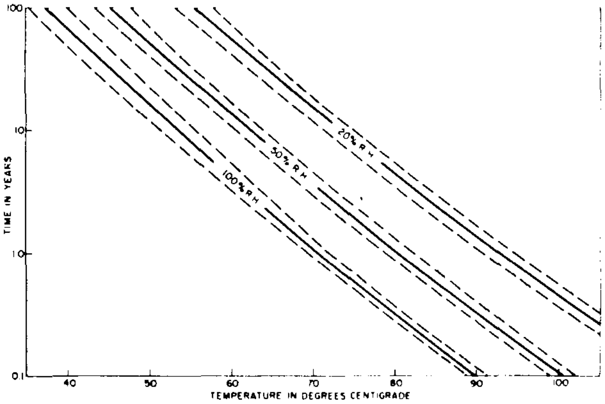

Figure 23. Degradation of 10-mil Mylar sheet

to log $\frac{A}{A\text{-}X}$ = 0.0022 (confidence limit 0.95)

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Some Anhydride Curing Agents for Epoxy Resins

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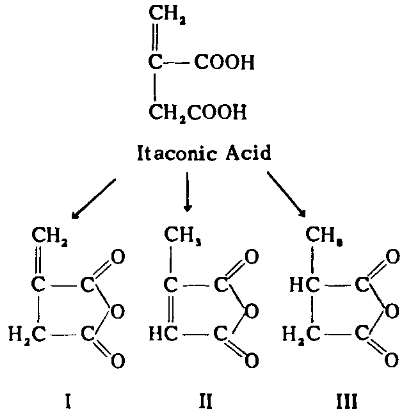
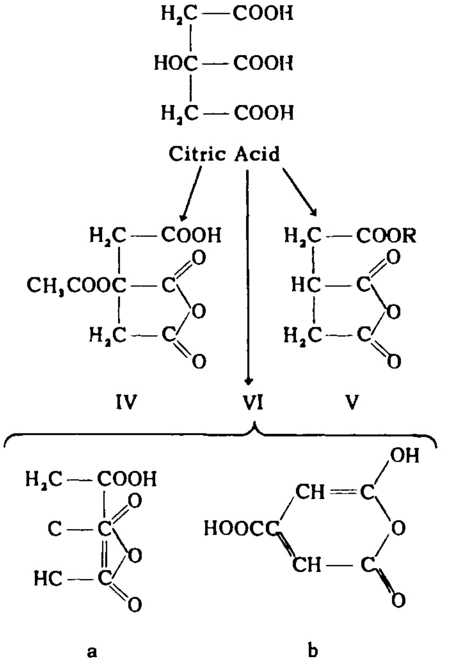
In his original patent, Castan (2) described the curing of polyolepichlorohydrin condensation products with dicarboxylic acid anhydrides, and in recent years the use of anhydrides in this application has continued to grow. Although they lack the high reactivity of polyamine curing agents and generally cannot be employed in room-temperature curing, anhydrides find use with the epoxy resins of low molecular weight because of their low exotherms, freedom from skin sensitization, and the good chemical and electrical properties which they usually impart.

The availability of itaconic and citric acids from fermentation sources affords an interesting opportunity to compare the effect of various modifications of a basic succinic anhydride structure on the properties of epoxy-resin curing agents. Itaconic (I), citraconic (II), and methylsuccinic (III) anhydrides may be derived from itaconic acid, while citric acid affords acetylcitric (IV), tricarballylic (V, R = H), and the aconitic (VI a and b) anhydrides.





The present article describes the effect of some of these anhydrides in cast epoxy resins. Dodecenylsuccinic anhydride was included in the study because of its structural relationships to the other anhydrides.

EXPERIMENTAL

Citraconic and methylsuccinic anhydrides are Pfizer development chemicals.

Itaconic anhydride was prepared by treating the acid with acetyl chloride, concentrating the resulting solution in vacuum, and recrystallizing from ether.

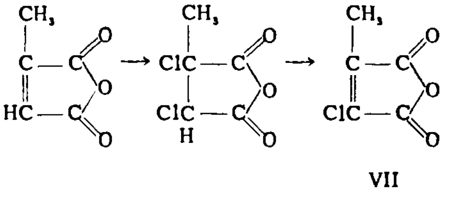
Acetylcitric anhydride was prepared from citric acid by treatment with acetic anhydride using sulfuric acid as catalyst.

Tricarballylic anhydride was prepared from the acid in a manner similar to the preparation of acetylcitric anhydride. The product was recrystallized from chloroform-acetic acid. An attempt to duplicate Emery's preparation (*4*), treatment with acetyl chloride followed by evaporation in vacuum, was unsuccessful, and the melting point reported by this author could not be duplicated.

Tricarballylic anhydride methyl ester (V, *R* = CH_3) was prepared by treating tricarballylic anhydride with anhydrous methanol to obtain the α-monomethyl ester, which on distillation splits out water to give the desired product. As an unequivocal synthesis, tricarballylic anhydride was treated with anhydrous diazomethane in ether to give the same product.

β,γ-anhydroaconitic acid (VIa) and α,γ-anhydroaconitic acid (VIb) were prepared by treatment of *trans*-aconitic acid with acetic anhydride (*6*). Upon filtration of the reaction slurry, VIa is recovered from the filtrate and VIb from the cake. The structures shown are those assigned in the reference.

Chlorocitraconic anhydride was prepared by chlorination and dehydrochlorination of citraconic anhydride according to the procedure of Michael and Tissot (*7*).



VII

Dodecenylsuccinic anhydride was used as received from National Aniline.

Epon resins 562 and 828, containing 0.65 and 0.54 epoxy equivalent and 0.25 and 0.08 hydroxyl equivalent per 100 grams, respectively, were obtained from the Shell Chemical Corp.

Benzyldimethylamine was obtained from the Fisher Scientific Co.

For physical testing $^1/_8$-inch sheets were cast in a chromeplated mold coated with Dow Corning 20 emulsion as release agent. After curing in a laboratory oven the sheets were removed from the mold and postcured for 1 hour at 100° C. to release stresses. Optimum curing schedules were not determined.

RESULTS AND DISCUSSION

Molecular weights and melting points of the anhydrides used in this study are given in Table I.

The low melting points of methylsuccinic, dodecenylsuccinic, and citraconic anhydrides permit incorporation in liquid epoxy resins at room temperature or slightly above with the result that low viscosity casting liquids of long pot life are obtained. Some pot lives are given in Table II.

Table I. Dicarboxylic Anhydrides

Anhydride	Molecular Weight	Melting Point, °C.
Methylsuccinic	114.1	36–37
Dodecenylsuccinic	266.4	<12
Itaconic	112.1	68
Citraconic	112.1	6–7
Tricarballylic	158.1	143–144
Tricarballylic, methyl ester	172.1	69–69.5
Acetylcitric	216.1	123–125
β,γ-anhydroaconitic acid	156.1	76
α,γ-anhydroaconitic acid	156.1	135

Table II. Pot Life of Epoxy Resins at 25° C.[a]

Anhydride	Epon Resin	Days to Gelation
Methylsuccinic[b]	562	8
Methylsuccinic[c]	562	>40
Methylsuccinic[b]	828	7
Methylsuccinic[c]	828	>40
Citraconic[b]	562	7
Citraconic[c]	562	22
Citraconic[b]	828	5
Citraconic[c]	828	40

[a] One mole of anhydride per epoxy equivalent.
[b] 1% benzyldimethylamine.
[c] No added catalyst.

Side Reactions. Some of the anhydrides may possibly have application in the preparation of foamed resins because of a tendency to form gaseous by-products under certain curing conditions. While it has been reported (*5*) that citraconic anhydride decarboxylates readily at temperatures above 160 °C., this has not been found to be correct. When pure citraconic anhydride was heated for an hour at 190 °C. no carbon dioxide evolution was detected. However, in the presence of 0.4% of benzyldimethylamine approximately half a mole of carbon dioxide was evolved per mole of anhydride at 150 °C. Attempts to isolate other decomposition products yielded only a black base-soluble resin. As a consequence of this behavior, dark foamed plastics result under all but the mildest of curing conditions when citraconic anhydride is used together with a tertiary amine catalyst in curing epoxy resins. Preparation of the citraconic anhydride–Epon 562 casting described in Table VI required curing with 0.3% of benzyldimethylamine at 55 °C. for 48 hours and at 100 °C. for 24 hours to avoid bubbling. With Epon 828 it was not possible to avoid bubbles, even at 46 °C., with 0.08% of amine. Dark, foamed resins also resulted where itaconic anhydride was substituted for citraconic anhydride. The itaconic anhydride probably first rearranges to the thermodynamically more stable citraconic anhydride, which then partially decarboxylates.

Chlorocitraconic anhydride (VII) decarboxylates even more readily, while maleic anhydride, dichloromaleic anhydride, and methylsuccinic anhydride are all stable in the presence of the amine. The evidence indicates that in the presence of base, citraconic anhydride loses an allylic hydrogen and undergoes a self-condensation of unknown nature, eliminating carbon dioxide in the process.

The tricarboxylic acid anhydrides [IV, V(R = H) and VIa and b] do not require the tertiary amine catalyst to cure epoxy resins. In spite of this, acetylcitric anhydride (IV) and aconitic anhydride (VIa and b) also resulted in foamed castings. Because tricarballylic anhydride (V) gives bubble-free, light-colored products with Epon 828, it is believed that the foaming with IV results from the elimination of acetic acid, and with VI, from decarboxylation (*1*).

Physical Properties of Cured Resins. The effect of methylsuccinic anhydride on heat distortion temperature was determined with Epon 828, and results are given in Table III. As expected, best results are obtained at, or close to, a value of 1 mole of anhydride per epoxy equivalent. This is in agreement with previous reports of work with other anhydrides (*8*). Benzyldimethylamine catalyst was employed.

Tricarballylic anhydride is unusual, in that it contains a free carboxyl group. No tertiary amine catalyst is required, and optimum molar concentration is remarkably low (Table IV). While these experiments were conducted at 150 °C., homogeneous castings have also been prepared at temperatures as low as 115° by careful stirring at the start to ensure complete solution of the anhydride in the resin.

The participation of the carboxyl group in the curing is evidenced by the fact that when tricarballylic anhydride methyl ester (V, R = CH_3) was employed at a level at 0.5 mole per epoxy equivalent with Epon 828, the resulting casting had a heat distortion temperature of only 48 °C. In addition (Table V), considerably harder resins with higher heat distortion temperatures are obtained with tricarballylic anhydride than with methylsuccinic anhydride. Yet it may be maintained that the "abnormality" of tricarballylic anhydride is more probably associated with the fact that no amine catalyst was used rather than with the presence of a free carboxyl group. The authors are not in agreement with this point of view, because it has been shown (*3*) that the addition of free carboxylic acids to their resin system (Epon 834–phthalic anhydride) accelerated the rates of cure. In addition, acids react directly with epoxide groups to produce secondary alcohols, which in turn react with the anhydride, regenerating carboxylic acid groups. It appears, therefore, that the free carboxyl group in tricarballylic anhydride is acting both as a catalyst and as a center for further cross linking.

Table III. Effect of Anhydride Concentration on Epon 828 Cured with Methylsuccinic Anhydride[a]

Moles Anhydride per Epoxy Equivalent	Heat Distortion Temp., °C.[b]
0.5	65
0.75	80
1.0	90
1.25	75

[a] Curing conditions. 1% of benzyldimethylamine; 2 hours at 85 °C. and 24 hours at 150 °C.

[b] ASTM D648-45-T, 264 p.s.i.

Table IV. Effect of Anhydride Concentration on Epon 828 Cured with Tricarballylic Anhydride[a]

Mole Anhydride per Epoxy Equivalent	Gel Time, Min.	Heat Distortion Temp., °C.[b]
0.2	75	85
0.3	70	139
0.4	55	147
0.5	45	108
0.75	25	99
1.0	5	65

[a] Curing conditions: 5 hours at 150 °C.

[b] ASTM D648–45T, 264 p.s.i.

Table V. Physical Properties of Epon 828 Cured with Various Anhydrides

Anhydride	Methyl Succinic[a]	Dodecenyl Succinic[a]	Tricarballylic[b]
PHR[c]	62	144	34
Cure shrinkage, linear, %, in./in.	0.2	0.6	...
Polymer density, grams/cc.	1.22	1.08	1.25
Flexural strength, p.s.i.[d]	15,500	12,000	16,400
Flexural modulus, p.s.i. × 10^{-5}[d]	4.1	3.3	4.3
Rockwell hardness	L98.5	L89.0	M105.5
Heat distortion temp., °C.[e]	90	69	147
Dielectric constant[f]			
60 cps.	6.12	5.08	3.95
10^6	5.57	4.76	3.45
Power factor[g]			
60 cps.	0.00321	0.00368	0.0144
10^6	0.02040	0.00935	0.0257

[a] Anhydride per epoxy equivalent 1.0 mole. Curing conditions: 1% BDMA; 2 hours at 85° C. and 24 hours at 150° C.

[b] Anhydride per epoxy equivalent, 0.4 mole. Curing conditions: 150° for 5 hours without added catalyst.

[c] Parts by weight of anhydride per 100 parts of epoxy resin.

[d] ASTM D790–49T, flatwise.

[e] ASTM D785–51.

[f] ASTM D648–45T, 264 p.s.i.

[g] ASTM D150–47T.

When temperatures close to the anhydride melting point are employed to homogenize tricarballylic anhydride with Epon 828, curing is rather rapid, particularly at the higher anhydride concentrations (see Table IV). The castings obtained, as with methylsuccinic anhydride, are very light in color. Bubble-free castings could not be prepared with Epon 562 and tricarballylic anhydride, perhaps because the higher hydroxyl content of this resin reacts with the free carboxyl groups to produce appreciable quantities of water. This explanation is being investigated further.

Physical test results obtained with a number of the anhydride-epoxy resin systems are given in Tables V and VI. Comparison of the data for dodecenylsuccinic anhydride and methylsuccinic anhydride demonstrates the plasticizing effect of the large hydrocarbon substituent: Flexural

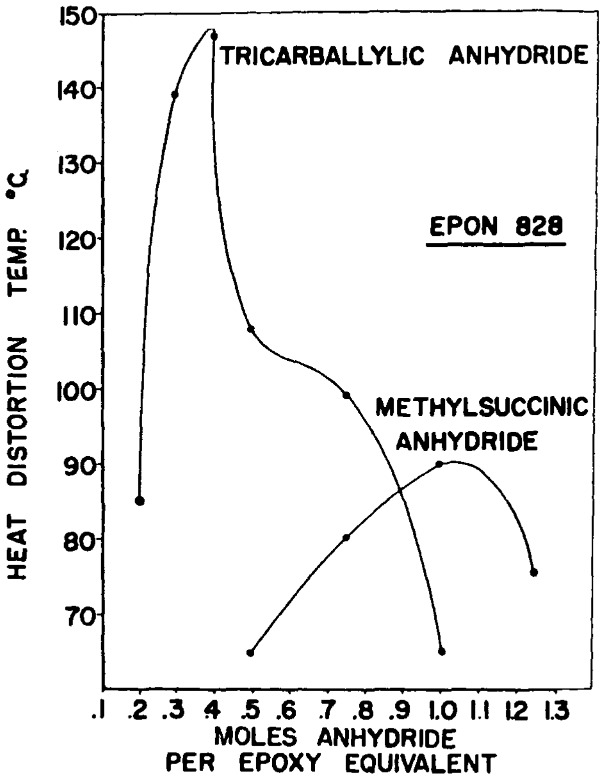


Figure 1. Plot of heat distortion temperature as a function of anhydride concentration for Epon 828 cured with tricarballylic and methylsuccinic anhydrides

strength, modulus, hardness, and heat distortion temperature are all reduced. The rigidity of the citraconic anhydride molecule is clear from a comparison of the values obtained with citraconic and methylsuccinic anhydrides (Table VI).

Solvent resistance properties are reported in Table VII. It is not surprising that increasing hydrocarbon substitution in the anhydride reduces resistance to organic solvents and improves resistance to aqueous media, although the difference of behavior between methylsuccinic- and dodecenylsuccinic-cured resins in benzene is indeed remarkable.

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Table VI. Physical Properties of Epon 562 Cured with Various Anhydrides[a]

Anhydride	Methyl Succinic[b]	Dodecenyl Succinic[b,c]	Citraconic[d]
PHR[e]	74	186	73
Cure shrinkage, linear, %, in./in.	1.0	1.6	0.2
Polymer density, grams/cc.	1.30	1.11	1.33
Flexural strength, p.s.i.	9100	7800	18,200
Flexural modulus, p.s.i. × 10^{-5}	3.1	2.6	5.1
Rockwell hardness	L79.0	...	L105.5
Heat distortion temp., °C.	41	38	55.5
Dielectric constant			
60 cps.	7.29	...	4.58
10^6	6.51	...	4.12
Power factor			
60 cps.	0.00592	...	0.00762
10^6	0.02950	...	0.03200

[a] Anhydride per epoxy equivalent, 1.0 mole.
[b] Curing conditions. 1% BDMA; 4 hours at 100°C.
[c] Shell Bulletin SC. 56-7.
[d] Curing conditions. 0.3% BDMA; 48 hours. at 55°C. and 24 hours at 100°C.
[e] Parts by weight of anhydride per 100 parts of epoxy resin.

Table VII. Solvent Resistance of Anhydride-Cured Epoxy Resins[a]

			% Weight Increase in		
Anhydride	Epon Resin	Water	50% H_2SO_4	10% NaOH	Benzene
Citraconic[b]	562	1.3	-0.24	-11	0.04
Methylsuccinic[b]	828	0.68	0.12	0.50	0.34
Dodecenylsuccinic[b]	562	1.3	1.8	0.65	c
Dodecenylsuccinic	828	0.28	0.07	0.22	c
Tricarballylic[d]	828	1.5	0.23	3.2	0.22

[a] Samples, 1½ × 1 × ⅛ inch, immersed in 60 ml. for 30 days. Values calculated by measuring weight increases both immediately after removing specimens from the solvent and after reaching equilibrium upon drying.
[b] Anhydride per epoxy equivalent, 1.0 mole.
[c] Disintegrated.
[d] Anhydride per epoxy equivalent, 0.4 mole.

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