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High Temperature Laminating Resins

Polyester laminating resins with improved high temperature aging properties have been prepared

LOW PRESSURE laminating resins for use at high temperatures are of four main types: epoxy (*5, 9, 15, 18, 19, 22, 23*), phenolic (*1*), polyester (*4, 10, 11, 16, 20*), and silicone (*13, 17*). The work reported here is concerned with heat aging properties of laminating resins based on mixtures of two unsaturated polyester resins and several monomers of the benzene or cyanurate series (Table II).

Literature Background

Subject	Ref. No.
Triallyl cyanurate as a cross-linking agent gives laminating resins with improved resistance to high temperature aging	(*4, 10, 11, 24*)
Relationship between heat resistance and structure of unsaturated polyester and cross-linking agent considered	(*2, 8*)
Synergistic effect of two monomers on oxidative or heat stability of laminating resins	(*2*)

Experimental

Glass laminates were made and aged at 200° and 260° C. Some monomers and the polyesters designated as A, B, and C were purchased: styrene (Monsanto Chemical Corp.), diallyl orthophosphate (Shell Chemical Corp.), and triallyl cyanurate (American Cyanamid Co.). Other monomers were prepared in the laboratory. Polyester A contains styrene as the monomer and B contains triallyl cyanurate. Polyester C is a chlorine-containing resin formulated for flame resistance.

Diallyl Isophthalate. In a typical preparation, 540 grams of allyl alcohol was placed in a 1-liter, three-necked, round-bottomed flask equipped with a stirrer and thermometer well. The flask was attached to a 20-inch distilling column, $^3/_4$ inch in diameter, fitted with a vacuum jacket and filled with glass helices. The alcohol was distilled until the boiling point was 96–97° C., to remove traces of water. About 25 to 50 grams of distillate were removed. Bronze powder (0.2 gram) was added as a polymerization inhibitor. Sodium methoxide (2.5 grams) and commercial dimethyl isophthalate (Hercules Powder Co.) (260 grams) were added to the allyl alcohol. In some experiments, nitrogen was bubbled through the solution to maintain an inert atmosphere.

The solution was heated and stirred until methanol ceased coming off and the boiling point of the distillate was again 96–97° C. A small amount of flocculent white solid which sometimes formed was filtered off, additional bronze powder added, and the remaining allyl alcohol was distilled off under reduced pressure. The diallyl isophthalate was then distilled at 153° to 156° C. at 2.5 mm. of mercury or 148° C. at 2 mm. Yield was 215 grams (65%), but in subsequent experiments higher yields were obtained. The white solid may be a salt of isophthalic acid.

Since the dimethyl isophthalate used contained up to 15% dimethyl terephthalate, the diallyl isophthalate probably contained some diallyl terephthalate. Another type of diallyl isophthalate was therefore prepared to test the effect of diallyl terephthalate in the laminating mixture. Eastman Kodak White Label isophthalic acid was esterified with methanol in sulfuric acid. The resulting methyl ester was then allowed to react with allyl alcohol as previously described.

Diallyl Terephthalate was prepared from Eastman Kodak White Label dimethyl terephthalate by the same method as described for diallyl isophthalate.

Triallyl Trimesate was prepared from trimethyl trimesate (*21*) by a method similar to that for diallyl isophthalate. However, because triallyl trimesate tends to polymerize at elevated temperatures, the reaction mixture was not distilled to isolate the product after removal of the excess allyl alcohol.

The mixture was first heated to 40° C. at 4 mm. of mercury to remove the last traces of allyl alcohol. Triallyl trimesate was isolated by first dissolving the residue in ether which was then washed with water, dried over sodium sulfate, treated with Norite and evaporated in dried air. The resulting white solid melted at 25–26° C. Yield was 60 grams or 48% (78% in subsequent experiments). The solid product contained 66.2% carbon (65.5% calculated) and 5.7% hydrogen (5.5% calculated).

Trimethyl trimesate was prepared from methanol and trimesic acid which was either purchased from commercial sources or prepared by alkaline-catalyzed potassium permanganate oxidation of mesitylene.

Dimethyl Allyl Cyanurate was prepared by adding 29 grams of sodium hydroxide to a stirred solution containing 17 ml. of water and 350 ml. of allyl alcohol (5.2 moles). After the alkali had dissolved, 126 grams 2-chloro-4,6-dimethoxy-*s*-triazine (*6*) was added in portions at a temperature of 25° to 30° C. External cooling was necessary to maintain the reaction temperature. After standing at room temperature for 2 days, the allyl alcohol was distilled off at 30° to 40° C. under reduced pressure. The remaining liquid was diluted with ether which was washed with water and dried over sodium sulfate. The ether was removed and the liquid distilled. Eighty grams of material was obtained, boiling at 125° to 142° C. at 2 mm. of mercury. In Table I, a similar product obtained from a different preparation is also listed (boiling point, 138° to 145° C. at 1 mm. of mercury).

Methyl Diallyl Cyanurate. 2,4-Dichloro-6-methoxy-*s*-triazine (*6*) (72 grams, 0.4 mole) was added to a solution of 400 ml. allyl alcohol (5.9 moles), 32 grams sodium hydroxide (0.8 mole), and 20 ml. water at 25° to 30° C. After standing overnight at room temperature, the reaction mixture was diluted with water. A two-phase solution formed, and the nonaqueous phase was separated out, washed, and dried over sodium sulfate. On vacuum distillation, two cuts were obtained—9 grams which boiled at 156° to 159° C. at 6 mm. of mercury, and 15 grams which boiled at 163° to 167° C., at 8 mm. The low yield is probably caused by solubility of reaction products in the allyl alcohol–water phase.

Table I. Analysis of Allyl-Methyl Cyanurates

Compound	C, %	H, %
Trimethyl cyanurate[a]	42.1	5.3
Dimethylallyl cyanurate[a]	48.7	5.6
Methyldiallyl cyanurate[a]	53.8	5.9
Triallyl cyanurate[a]	57.8	6.1
Dimethylallyl cyanurate	51.9	5.3
Dimethylallyl cyanurate	52.1	5.5
Methyldiallyl cyanurate	55.1	6.0

[a] Calculated.

The products were a mixture of isomers—i.e. the composition of dimethylallyl cyanurate corresponds to a mixture of dimethylallyl cyanurate with methyldiallyl cyanurate, and of methyldiallyl cyanurate corresponds to a mixture of methyldiallyl cyanurate with triallyl cyanurate. Of course, all three isomers could be present in the mixtures. Since the mixtures represent cyanurate materials with a functionality less than three (as in triallyl cyanurate), dimethylallyl cyanurate was used to prepare laminating resins.

β-Hydroxyethyl Diallyl Cyanurate (*14*). Ethylene glycol acts as a monohydric alcohol on reaction with triallyl cyanurate, giving 1 mole of evolved allyl alcohol per mole of ethylene glycol (*7*).

Higher glycols such as di-, tri-, tetra- and hexaethylene glycol act as difunctional alcohols on reaction with triallyl cyanurate (*7*). Two moles of allyl alcohol were evolved per mole of glycol, and the reaction products were insoluble oils or gels. The latter phenomenon is caused by the trifunctionality of triallyl cyanurate, which caused the average functionality of the alcoholysis to be greater than two.

In these experiments, 1 mole of ethylene glycol, 1 mole of triallyl cyanurate, and 0.65% by weight of sodium methoxide were heated at approximately 100° to 140° C. until the distillate had nearly ceased coming off. A nitrogen bubbler maintained an inert atmosphere (*7*). The percentage weight of sodium methoxide was based on the total weight of reactants. The reaction apparatus consisted of a three-necked flask, equipped with a stirrer and connected to a water-cooled condenser.

The end point of the reaction was not absolute—i.e. the production of distillate did not cease completely. After the main body of distillate had come over, the temperature of the reaction mass had increased from 100° to 140–142° C. Formation rate of distillate was then slow, and it was at this point that the reaction was terminated.

In most of these experiments about 90 to 110% of distillate (calculated as allyl alcohol with methanol from the catalyst) was evolved at 100° to 140° C. Most of the yields were over 100%. As has been mentioned previously, at 140–142° C., the distillate had nearly ceased coming off. When the reaction was run at reduced pressures, the same phenomenon occurred, although yields of distillate were usually higher (110 to 130% of theory). When an excessively long time of heating or temperatures above 140° C. were employed, the yields of distillate were higher than normal.

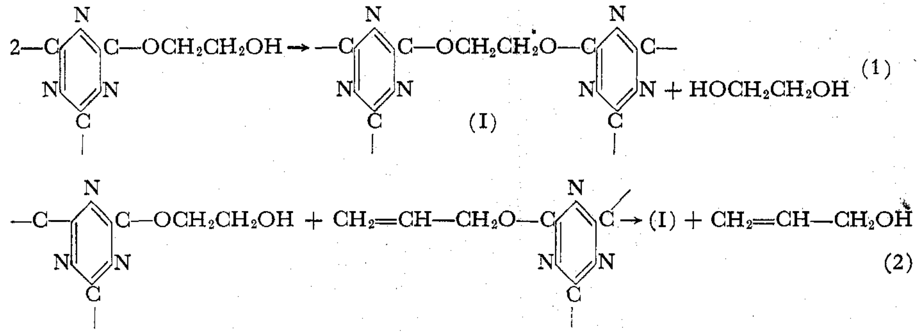
The excessive yields of distillate are probably caused by some or all of the following side reactions.

Table II. Average Room Temperature Flexural Strength and Weight Loss of Laminates

(After aging at 260° C.; from various mixtures or commercial formulation)

Cross-Linking Agent or Formulation	Compn. of Resins, Parts: Monomer	Polyester	Av. Room Temp. Flexural Str., P.S.I. × 10⁻³: 0 hr.	7 hr.	50 hr.	100 hr.	200 hr.	500 hr.	Av. % Resin in Laminates	Av. % Wt. Loss Based on Resin Content: 7 hr.	50 hr.	100 hr.	200 hr.	500 hr.
					From Mixtures of Ethylene Glycol Maleate									
Diallyl orthophthalate[a]	131.4	88.6	54.0	25.5	6.0	3.4	0.6	...	33.2	39.6	69.6	75.9	77.8	
Diallyl isophthalate[b]	131.4	88.6	52.1	39.2	22.0	18.1	12.2	4.7	31.5	21.0	48.1	55.5	66.8	81.4
Diallyl terephthalate[b]	131.4	88.6	39.8	27.4	16.6	14.4	9.8	3.3	31.9	27.2	55.0	61.0	72.8	83.7
Triallyl trimesate[c]	125.5	94.5	45.4	36.2	22.7	25.4	20.3	13.4	35.8	14.3	44.1	49.1	55.1	69.0
Styrene[c]	122.4	97.6	20.0	8.0	8.0	Taken off test			24.4	39.5	68.5			
Allyldimethyl cyanurate[d]	121.5	98.5	50.7	28.4	13.6	13.0	10.8	6.2	28.7	36.7	63.1	68.4	70.1	81.2
Triallyl cyanurate[a]	110.0	110.0	37.5	40.6	22.2	17.3	12.1	8.1	37.1	10.9	32.6	41.1	48.7	61.2
β-Hydroxyethyldiallyl cyanurate[a,e,f]	132.8	87.2	61.6	47.7	34.2	31.5	28.2	19.7	38.8	8.0	21.2	20.4	27.6	40.6
β-Ethoxyethyldiallyl cyanurate[g]	138	82	52.0	38.1	26.8	23.0	15.0	9.0	33.6	21.1	36.1	42.6	49.4	61.6
Polyester A[i]			71.4	33.4	5.6	Taken off test			36.4	39.9	75.6			
Polyester B[i]			45.3	42.9	28.3	24.6	17.1	6.1	32.8	9.4	25.0	28.1	40.9	60.5
Polyester C[i]			74.5			2.8			34.5			66.3		
Ethylene glycol maleate[h]			27.3	33.5	15.4	10.0	6.5	0.0	28.7	29.4	79.9	83.5	83.3	92.7
					From Mixtures[i] of Dipropylene Glycol–Tetrahydrofurfuryl Alcohol–Maleate									
Diallyl orthophthalate	131.4	125	53.3	13.3	2.5	0.0			29.2	60.8	78.0	76.6		
Diallyl isophthalate	131.4	125	50.4		11.7	9.2	5.2		30.4		53.1	59.1	69.7	
Diallyl terephthalate	131.4	125	33.3	26.3	7.2	4.1			29.8	36.6	60.6	64.6		
Triallyl trimesate	125.5	134	38.0		17.2	14.8	10.7		33.3		39.6	43.1	49.0	
Styrene	122.4	138	47.2	10.5	2.3	3.4			27.1	49.7	64.8	68.1		
Triallyl cyanurate	110	157	33.7		13.9	10.2	3.1		31.9		49.3	56.6	68.4	
β-Hydroxyethyldiallyl cyanurate	132.8	122	63.3			24.0	18.0		34.3			37.7	41.6	
β-Ethoxyethyldiallyl cyanurate	138	116	40.3		16.1	12.3	5.7		32.5		50.8	56.4	63.4	
Polyester A			71.4	33.4	5.6	Taken off test			36.4	39.9	75.6			
Polyester B			45.3	42.9	28.3	24.6	17.1		32.8	9.4	25.0	28.1	40.9	

[a] Polyester and monomer miscible; resin applied warm because of high viscosity at room temperature. [b] Polyester and monomer miscible at about 40° C.; resin applied warm. [c] Polyester and monomer not miscible; resin applied from an acetone solution. [d] Monomer and polyester calculated, assuming monomer was a mixture of allyldimethyl cyanurate and diallylmethyl cyanurate; elemental carbon analysis used to estimate allyl content. [e] Monomer calculated assuming material was pure β-hydroxyethyldiallyl cyanurate. [f] Values from different batches of monomer prepared under various conditions. [g] Monomer calculated assuming material was pure β-ethoxyethyldiallyl cyanurate. [h] Dissolved in acetone to form resin. [i] All monomers and polyesters miscible at room temperature.



The basis for the first reaction is that tris (β-hydroxyethyl) cyanurate evolves ethylene glycol when heated at temperatures over 100° C. (7). The glycol might have been carried over by the nitrogen stream used to maintain an inert atmosphere in the experiments. In Reaction 2, ethylene glycol acts as a difunctional alcohol. Both reactions should appear under forcing conditions. Other products present in the mixture could be di(β-hydroxyethyl)allyl cyanurate and tris(β-hydroxyethyl) cyanurate.

In one method for working up the alcoholysis reaction products, the product was dissolved in benzene and the solution filtered to remove small amounts of insoluble materials. These arose either from polymerization of some type, or were more probably sodium salts from the catalyst. The benzene was washed with water, dried over sodium sulfate, and evaporated in vacuo (25° to 80° C., at 25 mm. of mercury). However, in this method an emulsion, formed during washing, lowered yield considerably. This formation could be reduced somewhat by washing with solutions containing sodium chloride.

In the second method, the resin was stirred at 60° to 70° C. with an ion exchange resin in the acid form (Amberlite IR-120) for about 1 hour. After filtering the mixture through glass wool, the cyanurate was warmed in vacuo to remove traces of allyl alcohol. The purpose of this procedure was to remove residual catalyst, although the fate of the catalyst at the completion of the reaction was not known.

In the third method, the resin was warmed to 40° to 45° C. (10 mm. of mercury) at the completion of the alcoholysis to remove traces of allyl alcohol, and then suction filtered through a Büchner funnel containing a layer of glass wool. This method was the most convenient.

All reaction conditions for this preparation yielded approximately the same amount of distillate and the final products were viscous amber liquids. Behavior of these materials in laminating resins was comparable, indicating that the method of preparation was not too critical for the purposes of this investigation.

β-Ethoxyethyldiallyl Cyanurate was prepared by an alcoholysis reaction similar to those previously described. Triallyl cyanurate (188 grams) was added to a mixture of 4.2 grams sodium methylate and 67.5 grams ethylene glycol monoethyl ether. After 4 hours at 125° to 145° C., the distillate had ceased coming off. The yield of distillate collected was 85% of theoretical. The resulting liquid was dissolved in benzene, and the solution was washed with water and dried over sodium sulfate. The benzene was removed in vacuo. The final liquid had a much lower viscosity than the β-hydroxyethyldiallyl cyanurate.

Two Polyesters were prepared—ethylene glycol maleate and dipropylene glycol maleate modified with a very small amount of tetrahydrofurfuryl alcohol. Ethylene glycol maleate was used because of its unsaturation which makes possible a high cross-linking density in the cured resin. Although it produces laminates with a high modulus of elasticity in flexure, it has disadvantages—e.g., high viscosity and incompatibility with a number of monomers. The dipropylene glycol-tetrahydrofurfuryl alcohol maleate is better in both respects.

Ethylene glycol maleate was prepared by heating ethylene glycol and maleic anhydride (1 to 1 mole ratio) under a nitrogen atmosphere at 140° to 220° C. until distillate ceased coming off. A 12-inch Vigreux column removed water of condensation. *tert*-Butyl catechol (0.2 gram per 6 moles of glycol) was used as an inhibitor. The acid number of the various batches ranged from about 85 to 112. Dipropylene glycol-tetrahydrofurfuryl alcohol-maleate was prepared via comparable techniques. The acid number was about 28. The maleate resin probably contained considerable fumarate (*12*).

Preparation and Testing of Laminates. The laminating resins were prepared by mixing the polyesters, monomers and *tert*-butyl perbenzoate. The amount of peroxide used was 1% of the total weight of resin. The resulting resins were mostly homogeneous, but sometimes, the resin and monomer were incompatible. Acetone was then used as a mutual solvent. The plies of cloth were coated with the acetone solution and left to dry overnight before being assembled in the mold.

When the resin and monomer were incompatible at room temperature but miscible at elevated temperatures and when the resin was too viscous at room temperature to allow easy impregnation, the laminating resin was warmed slightly and the peroxide was added immediately before use.

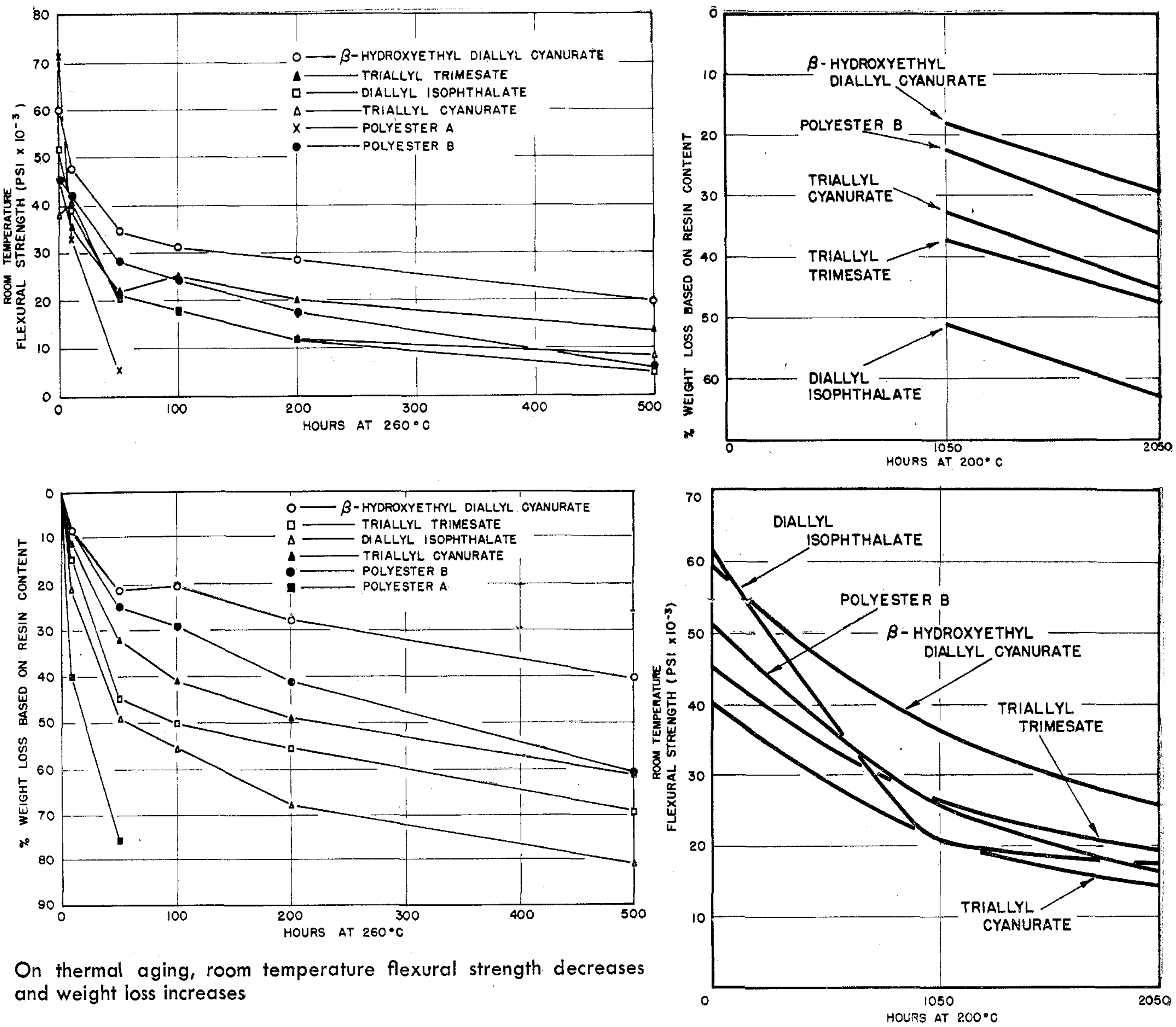
The relative amounts of ethylene glycol maleate and monomer were so adjusted that the ratio of double bonds in the polyester to the double bonds in the monomer was constant. The constant was arbitrarily based on a 50 to 50 mixture of triallyl cyanurate and ethylene glycol maleate. The relative amounts of dipropylene glycol-tetrahydrofurfuryl alcohol maleate and monomer were based

Table III. Average Room Temperature Flexural Strength and Weight Loss of Laminates

(After aging at 200° C.; either commercial preparations or mixtures prepared from ethylene glycol maleate)

	0 Hr.	1050 Hr.		2050 Hr.	
Cross-Linking Agent or Formulation	Flex. str., P.S.I. × 10^{-3}	Flex str., p.s.i. × 10^{-3}	Wt. loss[a], %	Flex str., p.s.i. × 10^{-3}	Wt. loss[a], %
Diallyl orthophthalate	60.9	9.5	67.9	5.2	78.4
Diallyl isophthalate	62.6	20.5	51.1	17.7	63.5
Diallyl terephthalate	42.4	13.6	51.7	13.7	66.4
Triallyl trimesate	45.4	26.3	37.8	19.3	47.5
Styrene	20.0	7.4	48.1	7.7	66.6
Allyldimethyl cyanurate	50.7	17.3	51.8	11.2	64.2
Triallyl cyanurate	40.2	20.1	33.0	14.2	45.6
β-Hydroxyethyldiallyl-cyanurate	59.5	36.2	18.7	26.4	29.2
β-Ethoxyethyldiallyl cyanurate	53.8	20.2	33.5	13.1	44.8
Polyester A	70.9	21.4	57.2	12.7	75.7
Polyester B	52.2	25.6	23.5	16.8	36.7
Polyester C	74.5	23.2	45.6	19.1	55.8
Ethylene glycol maleate	33.7	15.9	71.1	10.5	84.6

[a] Based on resin content.



On thermal aging, room temperature flexural strength decreases and weight loss increases

on a 50 to 40 mixture of triallyl cyanurate and ethylene glycol maleate.

Glass cloth, No. 181-136 (silane sized), was used to make all the laminates. Each laminate consisted of 13 plies of cloth, 7¹/₄ by 8¹/₂ inches. Most of the laminates were prepared by laying a fresh ply of cloth on the previously coated ply in a ¹/₈-inch positive stop mold and coating the glass with laminating resin. After the mold was closed, the laminates were cured in a Preco press for 1 hour at 160° C.

The cured laminates were cut either into ¹/₂ by 3 inch or 1 × 3 inch sections on an abrasive wheel to give smooth edges. Comparable flexural strengths were obtained from ¹/₂- or 1-inch wide specimens. The sections were aged at 200° or 260° C. After weight loss was measured, the sections were tested for room temperature flexural strength in a Tinius Olsen tester. The specimens were usually tested for flexural modulus prior to the flexural strength determination. Their resin content was determined either by burning of the resin from sections of the laminate or by determining the difference in weight between the glass and final laminate.

Experimental Results

Since a number of test specimens were usually prepared from the same monomer-polyester combination, the results are averages of all the experimental data (Tables II through IV).

The average initial flexural modulus of elasticity of the laminates ranged from 2 to 3 × 10⁶ p.s.i. On thermal aging, the decrease in room temperature flexural modulus paralleled the weight loss and flexural strength data. After 200 hours at 260° or 100 hours at 200° C., the flexural modulus of elasticity of the better laminates ranged from 1.9 to 2.4 × 10⁶ p.s.i. After 500 hours at 260° C., the room temperature modulus

Table IV. Laminates Prepared from Diallyl Isophthalate

(From mixtures of ethylene glycol maleate; cross-linking agent contained different amounts of diallyl terephthalate; after aging at 260° C.)

Diallyl Isophthalate	Resin in Laminate, %	Flex. Str., P.S.I. × 10⁻³ 0 hr.	50 hr.	100 hr.	200 hr.	Wt. Loss, %[a] 50 hr.	100 hr.	200 hr.
From commercial dimethyl isophthalate (15% diallyl terephthalate)	30.5	45.8	19.4	17.0	10.2	45.9	54.8	69.6
From Eastman Kodak White Label isophthalic acid	30.6	50.3	21.1	18.9	10.6	43.0	54.7	68.2

[a] Based on resin content.

of the β-hydroxyethyldiallyl cyanurate-ethylene glycol maleate laminate was 2.5×10^6 p.s.i.

A polyester molding compound was prepared from diallyl isophthalate (21.1 grams), ethylene glycol maleate (14.9 grams), ASP-100 clay (44.5 grams), and 1/2-inch chopped glass fibers (18.5 grams). The components were kneaded together to form a molding mix. The diallyl isophthalate–ethylene glycol maleate mixture was previously catalyzed with 1.5% *tert*-butyl perbenzoate. The compound was molded for 45 minutes at 135° C. in a 2 1/2-inch diameter cylindrical mold (25,000 p.s.i. on plunger). Because the polyester-peroxide system was relatively slow curing there was some run off of resin. Another molding was prepared with polyester A substituted for the mixture of ethylene glycol maleate and diallyl isophthalate. In this case the molding time was 10 minutes, because of the apparent faster rate of cure of polyester A under the conditions chosen.

The two moldings were then aged at 260° C. After 50 hours, the molding based on polyester A (38.1% resin) had lost 67% of the original resin. The diallyl isophthalate–based molding had lost only 26.5% of the resin (33.2% resin originally).

Discussion

The combination of β-hydroxyethyldiallyl cyanurate and ethylene glycol maleate was the best laminating resin tested both with regard to retention of room temperature flexural strength and weight loss.

In the benzene carboxylic acid ester series, the order of high temperature performance was triallyl trimesate > diallyl isophthalate > diallyl terephthalate > diallyl orthophthalate. Triallyl trimesate was far superior to the others. Diallyl isophthalate was better than diallyl terephthalate, but the difference was not striking enough to presuppose that with a different polyester, the two would not have comparable performance. Diallyl orthophthalate and styrene were poor materials for use at elevated temperatures. Allyl benzoate has also been found to have poor high temperature aging properties in combination with ethylene glycol maleate (*3*).

Some of these derivatives (triallyl trimesate and diallyl isophthalate) showed very good high temperature properties, comparable in retention of room temperature flexural strength to some of the cyanurates. Their weight losses on aging, however, were higher.

In the cyanurate series, the order of high temperature stability was β-hydroxyethyldiallyl cyanurate > triallyl cyanurate–β-ethoxyethyldiallyl cyanurate > allyl dimethyl cyanurate. These derivatives gave lower weight losses on aging than did their benzene or hydrocarbon analogs. As mentioned above, some of the phthalates and the trimesates were comparable in retention of room temperature flexural strength. It is felt that testing of flexural strength at more elevated temperatures would have disclosed a greater difference in favor of the cyanurates. However, these results do show that heat stable materials can be prepared from materials containing only carbon, hydrogen, and oxygen. This is certainly true of temperatures below 200° C.

In general, the relative performance of the various monomers was comparable at 200° and 260° C. However, the difference between some of the better and poorer materials decreased as the aging temperature was lowered, as would be expected.

In general, performance of the various monomers with dipropylene glycol–tetrahydrofurfuryl alcohol–maleate was poorer than the behavior of the same monomers with ethylene glycol maleate. Although no attempt was made to examine the optimum proportions of monomer to polyester, the difference in performance between the laminating resins based on the two polyesters is large enough to establish the superiority of the ethylene glycol maleate system.

Polyester C was rapidly degraded after aging at 260° C. The resin did have a good retention of room temperature flexural strength after aging at 200° C., comparable to that of polyester B, which contained triallyl cyanurate. The weight loss, however, was, higher. Of course, there is always the possibility of releasing hydrogen chloride or chlorine when such chlorine-containing resins are degraded at elevated temperatures. If true, this might tend to limit its application in some instances at elevated temperatures.

Combinations of ethylene glycol maleate with diallyl isophthalate, prepared either from commercially available dimethyl isophthalate which may contain up to 15% dimethyl terephthalate, or from Eastman Kodak White Label isophthalic acid, gave laminates with comparable heat aging properties. Although it is not known what, if any, percentage of terephthalic acid was present in the isophthalic acid used, it is probable that the percentage of diallyl terephthalate in the two batches of diallyl isophthalate was quite different.

Comparison of high temperature performance with chemical structure was sometimes facilitated by the extent of differences involved and purity of the materials. In other instances, however, the comparison became less certain, because no attempt was made to examine all the possible monomer-polyester combinations and because the monomers could contain other isomers. An attempt was made to keep the combinations tested on a comparable basis both by keeping the ratio of unsaturation in the monomer and polyester constant within any one polyester series and by keeping comparable ratios between series of the same monomer and different polyesters. However, such factors as glass cloth weave and sizing, catalyst concentrations, cure schedules, solubility of monomer and polymer phases, relative reactivities of monomer and polymer, play an important part.

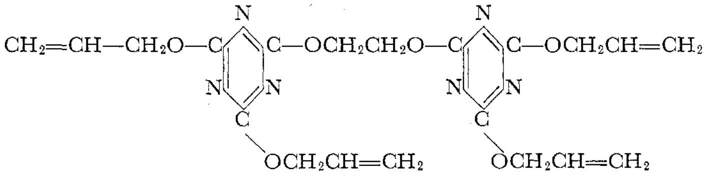
Within the benzene and triazine series, increased weight loss was accompanied by decreased room temperature flexural strength—i.e., in a given series, the materials with the greater weight loss had the lowest strengths. In such cases, both weight loss and room temperature flexural strength were considered as an index of high temperature stability. However, this correlation did not hold for comparing monomers having a benzene nucleus with those possessing a triazine nucleus. For example, the cyanurate-based systems had lower weight losses than systems based on the allyl esters of benzene carboxylic acids, but did not always have better retention of room temperature flexural strength. In comparisons of this type, the more stable materials were arbitrarily considered as those with the lower weight losses. This consideration was assumed to be the more important one because all the laminates did not have the same initial flexural strength and since the inert glass and its sizing would be more important in determination of flexural strength than of weight loss. This criterion was assumed only for the purposes of this discussion. In applications of these materials, the flexural strength might well be the prime consideration in determining high temperature stability.

In the benzene carboxylic acid ester series, several factors seem to be important in enhancing high temperature stability. One is increased functionality of the monomer, as evidenced by the relative superiority of triallyl trimesate to the diallyl phthalates and allyl benzoate. This would cause a more highly cross-linked laminate. Another possible factor is the symmetry of triallyl trimesate and the fact that it has three negative substituents attached to the ring. The relatively poor performance of diallyl orthophthalate as compared to diallyl iso- and terephthalate is most logically ascribed to the ability of the orthophthalate to form a cyclic anhydride on degradation.

In the cyanurate series, the situation is not so straightforward. Substitution of an allyl group in triallyl cyanurate by an ethoxyethyl group did not affect the high temperature properties adversely. In fact, there was even a slight improvement in retention of room temperature strength. Substitution of some of the allyl groups in triallyl cyanurate by methyl groups caused a general decrease in aging properties. Substitution of an allyl group in triallyl cyanurate by a β-hydroxyethyl group caused a striking improvement in aging properties.

However, at least one explanation for these phenomena can be given. A reduction of functionality of the cyanurate from three to two (allyl groups per molecule) apparently does not adversely affect the high temperature performance of laminating resins containing such monomers. This would account for β-ethoxyethyldiallyl cyanurate. However, a reduction below a functionality of two would be expected to have an adverse effect by reducing the density of cross-links markedly in the cured resin. This would account for the behavior of allyl dimethyl cyanurate, whose elemental analysis corresponds to a mixture of allyl dimethyl cyanurate and diallyl methyl cyanurate.

The improvement in performance of the β-hydroxyethyl derivative may actually result from an increase in functionality of the monomer over that of triallyl cyanurate. Some of the side reactions would lead to the presence of cyanurates with a functionality of four.



Other possible explanations for the high temperature behavior of the β-hydroxyethyl derivative would involve reaction of the hydroxyl groups in the cyanurate with the polyester or degradation products of the polyester to produce a stabilizing effect. Such reaction mechanisms are not too apparent at present. The hydroxyethyl groups in the cured polymer might react with one another on aging further to cross-link the polymer. This again would be the same as increasing the functionality of the cyanurate.

This hypothesis of functionality as a basis for the difference in behavior of the various cyanurate derivatives would correlate with the previously stated observations on the allyl esters of the benzene carboxylic acids. Cummings and Botwick (*2*) have reported that polyfunctionality of the unsaturated monomer is an important factor in determining heat stability of laminating resins.

The most striking difference in behavior between monomers of the different series was the lower weight losses on extensive aging of the cyanurate-polyester combinations as compared with most of the phthalate- or trimesate-polyester series. As mentioned previously, this difference could not always be correlated with differences in degradation as measured by room temperature flexural strength.

The main difference between the monomers in the phthalate and cyanurate series is not one of functionality but resides in differences in the nuclei of the molecules. The phthalates have a benzene nucleus, while the cyanurates have a *s*-triazine nucleus. Therefore, any difference in properties would most logically be associated with this factor. The *s*-triazine ring, because of its electron withdrawing character or electronegativity, might compete with oxygen which also seeks electrons from the polymer molecules to form peroxides or hydroperoxides. This would have the ultimate effect of decreasing the rate of oxidation of the triazine nucleus and possibly of atoms or groups of atoms close to the triazine nucleus. This would result in a lowered rate of degradation and weight loss. Also, the relative reactivities of the unpolymerized allyl phthalates and the free radicals derived from them might be different from those of the allyl cyanurates, because of the electronegativity of the triazine ring, so that one might have different copolymer systems in the two cases.

The lower weight losses of the cyanurate-based laminating resins were more apparent with ethylene glycol maleate than with dipropylene glycol-tetrahydrofurfuryl alcohol-maleate. Since nearly all combinations of the latter polyester with the various monomers had poorer heat aging properties than the ethylene glycol maleate systems, this difference in relative weight loss can be attributed to a masking of the stabilizing effect of the cyanurates by the greater instability of the polyester. It is not known why triallyl trimesate afforded a lower weight loss with the dipropylene glycol polyester than did most of the cyanurates.

The poorer high temperature performance of the dipropylene glycol system as compared to that of the ethylene glycol system may be associated with the presence of more easily oxidizable linkages in the former—i.e., such as aliphatic ether groups. Also, because the maleate groups in the dipropylene glycol maleate system would be farther apart than those in ethylene glycol maleate, the latter system would have a higher density of cross links. Even if the rates of degradation of the two systems were comparable, this factor would tend to favor lower weight losses and greater degree of retention of flexural strength on aging of the ethylene glycol maleate-based laminating resins.

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References

(1) Campbell, J. B., *Materials & Methods* **38,** 87 (November 1953).
(2) Cummings, W., Botwick, M., Ind. Eng. Chem. **47,** 1317 (1955).
(3) Cypher, G. A., General Electric Co., Schenectady, N. Y., unpublished results.
(4) Day, H. M., Affleck, J. G., *SPE Journal* **9,** 22 (February 1953).
(5) Delmonte, J., *Materials & Methods* **40,** 93 (August 1954).
(6) Dudley, J. R., Thurston, J. T., Schaeffer, F. C., Holm-Hansen, D., Hull, C. J., Adams, P., *J. Am. Chem. Soc.* **73,** 2986 (1951).
(7) Dudley, J. R., Thurston, J. T., Schaeffer, F. C., Hull, C. J., Holm-Hansen, D., Adams, P., *Ibid.*, p. 2999.
(8) Ebers, E. S., Bruckach, W. F., Elliott, P. M., Holdsworth, R. S., Robinson, H. W., Ind. Eng. Chem. **42,** 114 (1950).
(9) Elam, D. W., Hopper, F. C., *Modern Plastics* **31,** 141 (October 1954).
(10) Elliott, P. M., *Ibid.*, **29,** 113 (July 1952).
(11) Elliott, P. M., "Vibrin X-1047—New Heat Resistant Polyester Resin," Naugatuck Chemical, Naugatuck, Conn.
(12) Feuer, L., Bockstahler, T. W., Brown, C. A., Rosenthal, I., Ind. Eng. Chem. **46,** 1643 (1954).
(13) Hyde, J. K., *Brit. Plastics* 174 (May 1954).
(14) Kropa, E. (to American Cyanamid Co.), U. S. Patent **2,557,667** (June 19, 1951).
(15) *Machine Design* **26,** 125 (July 1954).
(16) McLand, E., Gustafson, F., *Prod. Eng.* **25,** Pt. 2, 161 (August 1954).
(17) *Materials & Methods* **40,** 98 (July 1954).
(18) Minnesota Mining and Manufacturing Co., Tech. Data Sheet **2,** Sept. 1, 1956.
(19) O'Brien, F. R., Oglesby, S., Jr., Covington, P. C., *Modern Plastics* **33,** 158 (August 1956).
(20) Power, G. E., "Appraisal of High Temperature Behavior of Laminates with Time," Am. Inst. Elec. Engrs., Conf., New York, N. Y., 1955.
(21) Rohm & Haas Co., Brit. Patent **754,537** (Aug. 8, 1956).
(22) Shell Chemical Corp., Tech. Bull. **SC56:18,** March 1956.
(23) *Ibid.*, **DS-56:3** April 1957.
(24) Wahl, H. E., Preston, M., *Modern Plastics* **35,** 153 (October 1957).

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