

Fire-Retardant Polyesters Based upon 2,3-Dicarboxy-5,8-endomethylene-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene Anhydride

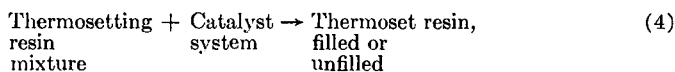
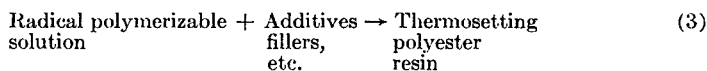
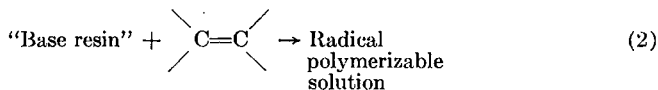
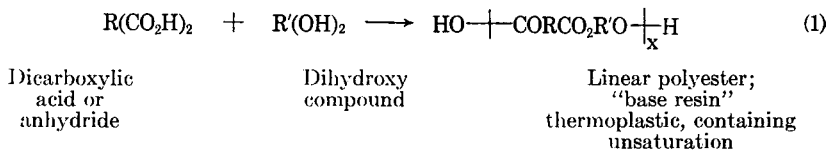
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Synopsis

The Diels-Alder adduct of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (II) with hexachlorocyclopentadiene, 2,3-dicarboxy-5,8-endomethylene-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene anhydride (compound III), has been incorporated as the fire-retardant component in polyester compositions. The structure of compound III possesses inherent properties which are exhibited as improved thermal and light stability in the derived polyesters; these improvements are based upon comparisons with polyesters prepared from the chlorendic anhydride, the fire-retardant moiety in some commercial self-extinguishing polyesters.

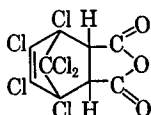
INTRODUCTION

The increased use of polyesters in applications requiring fire-retardant or self-extinguishing properties has focused attention on the methods which have been or may be used to decrease the flammability of thermoset polyester compositions.¹ For the sake of completeness the general reactions used to prepare a polyester are noted here; the introduction of self-extinguishing moieties may take place in any one of three steps.



A series of commercial self-extinguishing and fire-retardant polyesters is based on the use of a highly chlorinated anhydride introduced in eq. (1); this compound, I, is known as chlorendic or HET anhydride (chemically, it is 2,3-dicarboxy-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hept-5-ene anhydride), and it may be prepared from hexachlorocyclopentadiene and maleic anhydride² or maleic acid with subsequent dehydration.³ Typical of the utilization of this acid or anhydride in the formation of self-extinguishing polyesters are preparations described in reports from The Hooker Chemical Company.^{2,4} Many of the Hetron self-extinguishing resins are based on the incorporation of this halogenated molecule in polyester resins. A typical formulation⁵ would be one based on chlorendic anhydride, a mixture of ethylene and diethylene or triethylene glycol, adipic acid, and fumaric (or maleic) acid; this base resin, cooked to an acid number near 45, would then be dissolved in sufficient vinylaromatic monomer (styrene for example) to give a cured resin containing a high enough percentage of chlorine (25–30%) to insure fire-retardancy or actual self-extinguishing properties.

On the basis of published reports^{6,7} there appears to be some disadvantages inherent in these chlorine-containing resins; light stability, weatherability, liberation of hydrochloric acid, and thermal stability are some of the weak points. Certain of these, and, to some extent, all of these weaknesses can be and have been overcome by stabilizers and other additives. A consideration of the chemical structure of the halogen-carrying moiety (chlorendic anhydride, I) of the resin, immediately suggests the possible reason for some of the above mentioned instability



I

I

While it is well known that at elevated temperatures the Diels-Alder reaction may reverse to give, with this adduct, hexachlorocyclopentadiene, the more obvious point seemed to be the presence of two carbonyl-activated α -hydrogens, both in the anhydride and in the polyester. It was postulated that if these activated hydrogens were attacked, hydrogen chloride would be formed and the *endo*-dichloromethylene bridge would be split out. In the presence of oxygen, this *endo*-dichloromethylene bridge would give rise to phosgene and also, eventually, to hydrogen chloride. Evidence for the hydrogen chloride is certainly substantiated. It was further postulated that were the α -hydrogens to be removed or substituted by some non-reactive species, greater thermal and oxidative stability should result. A perusal of the literature indicated that the following anhydrides had been treated with hexachlorocyclopentadiene to produce Diels-Alder adducts potentially suitable for polyester formation (Table I). Other considerations being equal, it appeared that none of the tabulated dienophiles filled

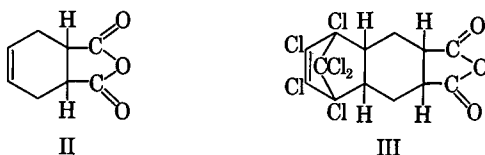
TABLE I
Diels-Alder Adducts of Hexachlorocyclopentadiene With Other Unsaturated Anhydrides or Acids^a

Dienophile	Product	
	Yield, %	M.p., °C.
Chloromaleic anhydride	40	240-247
Acetylenedicarboxylic acid	45	162-163
Citraconic anhydride	20	243.5
Itaconic anhydride	—	131-134.6
2,3-Dicarbethoxybicyclo[2.2.1]-2,5-heptadiene	93	119
1,2-Dicarboxybicyclo[2.2.1]-4-heptene anhydride	8	279-280 ^b

^a Data of Ungnade and McBee.⁸

^b Data of Reimschneider and Kerstein.⁹

the requirements envisioned. It appeared to us that a dienophile containing an anhydride and resulting in an adduct wherein the α -hydrogens would not be both activated by carbonyl groups and be adjacent to bridge-head chlorines would be the reaction product of butadiene and maleic anhydride, *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (II).



It can be seen from an inspection of the formula for the Diels-Alder product of hexachlorocyclopentadiene and this dienophile that there would result a compound, 2,3-dicarboxy-5,8-endomethylene-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene anhydride (III), having the structural requirements outlined above. This compound has been prepared and described previously,¹⁰ and the purpose of this paper is to describe the utilization of compound III in polyester compositions and to describe the effect of structural change (compound I versus compound III) on the thermal and light stability of the resins produced.

EXPERIMENTAL

Preparation of 2,3-Dicarboxy-5,8-Endomethylene-5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-Octahydronaphthalene Anhydride (Compound III)

In a 3-l., three-necked, round-bottomed resin kettle equipped with a reflux condenser, air stirrer, nitrogen inlet tube and heating mantle (controlled with a Honeywell Brown Pyro-O-Vane) was placed a mixture of 456 g. (3 moles) of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride, 816 g. (3 moles) of hexachlorocyclopentadiene and 159 g. (12.5% based on reactants) of *m*-xylene. The mixture was warmed slowly to a mantle temperature of 195°C. and a reaction temperature of 176°C.; during the course of

the reaction (16 hr.) the reaction temperature fell to 156°C. The mixture was permitted to cool to 100°C. and 300 ml. of *m*-xylene was added. The vigorously stirred mixture was cooled in an ice water bath for 3 hr. The solid was collected on a suction filter. It was washed with two 100 ml. portions of *m*-xylene and with three 200 ml. portions of *n*-heptane. The air-dried crude product was dried in a vacuum oven at 100°C. for 16 hr. The weight of crude product was 1042 g. (81%), m.p. 240°C. The crude product was recrystallized with decolorization from 4200 ml. of 1,2-dibromoethane to give 775 g., m.p., 278°C., of pure III.*

ANAL: Calcd. for $C_{12}H_8Cl_6O_3$ (m.w. 424.936): C, 36.85%; H, 1.39%; Cl, 50.35%. Found: C, 36.84%; H, 1.36%; Cl, 50.10%.

Preparations of Hetron-Type Resins

1. Preparation of Hetron-Type Polyester Resin from Compound III.

To a 1-1., three-necked, round-bottomed resin kettle equipped with an air stirrer, condenser with Dean Stark trap, thermo-well, and nitrogen inlet tube was placed a mixture of 52.8 parts (5.28 g.) of ethylene glycol, 90 parts (9.0 g.) of diethylene glycol, 424.9 parts (42.4 g.) of III and 20 ml. of xylene. The mixture was heated to 170°C. and 70.8 parts (7.08 g.) of maleic anhydride added. The temperature was allowed to rise to 190°C. and samples taken periodically to determine the acid number. When the acid number had fallen to 55, 3.6 parts (0.36 g.) of tetrahydrofurfuryl alcohol was added. When the acid number had reached 45, the cooled resin was poured into a Teflon dish and further cooled under an atmosphere of nitrogen.

TABLE II

Comparisons of Physical and Chemical Properties of a Hetron-Type Resin from Chlorendic Anhydride and Compound III Resin; Cured Cast Samples; Nonlaminated

	Hetron resin	Compound III resin
Heat distortion, °C.	86	70 ^a
Surface hardness, Shore D	85	85
Refractive index, 25°C.	1.5590	1.5600
Increase in yellowness, 100 hr. in Fadeometer	31.8	12.1
Solvent swell and/or attack: (7 days soak)		
10% NaOH	0.6952% loss	0.2853% loss
H ₂ O	0.5448% gain	1.1580% gain
37% HCl	0.2369% gain	0.5903% gain
130° Skelly	0.00	0.00
30% H ₂ SO ₄	0.3731% gain	0.3625% gain

^a Initial preparations, inadequate cure.

A mixture of 30 g. of the resin was prepared with 9 g. of styrene. When solution was effected, 1% of benzoyl peroxide (based on styrene added) was mixed into the solution. The mixture was poured into a Teflon mold

* All melting points are uncorrected.

($1\frac{1}{2} \times 2\frac{1}{4} \times \frac{1}{8}$ in.) and cured under a slight pressure for 16 hr. at 80°C. Physical properties were determined and are noted in Table II.

2. Preparation of Hetron-Type Resin from Chlorendic Anhydride.

A reaction mixture prepared essentially as above and in a comparable resin pot utilized in appropriate order the following reactants: ethylene glycol 52.8 parts (5.28 g.), diethylene glycol 90 parts (9.0 g.), chlorendic anhydride 70.8 parts (7.08 g.). This mixture was brought to an acid number of 55 and was treated with 3.6 parts (0.36 g.) of tetrahydrofurfuryl alcohol, heated until the acid number reached 45, and cooled. The resin, 30 g., was dissolved in 9 g. of styrene, 1% benzoyl peroxide added and a cured sample prepared as above. The physical data of this resin are in Table II.

3. Preparation of Glass Cloth Laminates. A mixture of 120 g. of the above base resin and 36 g. of styrene was shaken until homogeneous. To the solution was added 1% benzoyl peroxide based on the styrene. This solution was alternately padded on a total of 13 plys of OCF-181-136 glass cloth in a $6\frac{1}{2} \times 6\frac{1}{2} \times \frac{1}{8}$ in. mold. The laminate was cured in a press at about 200 psi for 20 hr. at 85°C. The cured laminate was cut to prepare standard samples: for flexural strength, $6 \times 1 \times \frac{1}{8}$ in. bars; for impact, $2\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in. notched bars; and for tensile, $6 \times \frac{1}{4} \times \frac{1}{8}$ in. dumbbell-shaped bars. The results of the testing are in Table III.

TABLE III
Comparison of Physical Properties of a Hetron-Type Resin from Chlorendic Anhydride and a Compound III Resin; Thirteen Ply Woven Glass Laminate. Resin 40.6%

	Hetron resin	Compound III resin
Flexural strength, psi	58,000	64,040
Flexural modulus, psi	—	26,400
Tensile strength, psi	39,000	51,930
Elongation, %	2-3	5.3
Impact, ft.-lb/in.	—	19.22
Surface hardness, Shore D	85	85
Water absorption after 72 hr., %	0.09 (24 hr.)	0.081
Flammability (ASTM D-757-49)	S.E.	S.E.

4. Preparation of Polyesters Using Other Crosslinking Agents. Using the above described resin pot and reaction conditions, a quantity of base resin was prepared from 52.8 parts of ethylene glycol, 90 parts of diethylene glycol, 424.9 parts of III, 70.8 parts of maleic anhydride and 3.6 parts of tetrahydrofurfuryl alcohol. Each run was brought to a final acid number of 45 ± 2 . From portions of the above base resin, cured polyesters were prepared using varying quantities of styrene, vinyltoluene, styrene, and methyl methacrylate, and styrene with 1% added divinylbenzene. These cured resins were prepared in only nonreinforced samples suitable for the determination of refractive index, hardness, and heat distortion (Table IV).

TABLE IV
Preparation of Polyesters from III Based on a Standard Hetron Recipe; Ethylene and Diethylene Glycols and Maleic Anhydride. Prepared at 200°C. to a 45 Acid Number

Reactants		Curing conditions		Hardness, Shore D	Heat distortion, °C.
III, g.	Monomer, g.	Time, hr.	Temp., °C.		
18	6.2 Vinyltoluene	8	85	85	56
20	20 Styrene	8	85	82	76
20	47 Styrene	8	85	88	85
20	3 Styrene 3 Methyl methacrylate	8	85	83	60
25	7.5 Styrene 0.1 Divinylbenzene	8	85	88	—

Preparation of Base Resins from Propylene Glycol, III, and Maleic Anhydride

A series of base resins was prepared from propylene glycol, III, and maleic anhydride, at varying ratios of maleic to III. Each of the several preparations was nearly identical and only one typical set of details is described here. A summary of the data is given in Table V.

In a modified resin pot equipped with stirrer, reflux condenser, Dean Stark trap and gas inlet tube (nitrogen) was placed a mixture of propylene glycol (2.16 mole-%), III (0.65 mole-%), and maleic anhydride (1.35 mole-%) with 20 ml. of xylene. The reaction mixture was warmed slowly (Pyro-Vane controlled) until the reaction temperature reached 160°C. Azeotropic distillation was continued until samples of the reaction mixture displayed an acid number of 29 ± 2 . In this example, the total reaction time was 12 hr.; the hot base resin was poured into a Teflon dish and cooled under an atmosphere of nitrogen. Each sample listed in Table V was converted to a styrene-based polyester by the typical procedure. A mixture of 30 g. of the base resin and 9 g. of styrene was stirred under nitrogen until solution was effected; 1% of benzoyl peroxide (based on the styrene) was added, and the liquid resin poured into a Teflon mold and cured at 85°C. for 20 hr.

DISCUSSION

Part of our thesis concerning the instability of the self-extinguishing resins based on chlorendic anhydride could be proven by conversion of chlorendic anhydride and compound III to Hetron-type polyesters. Non-reinforced polyesters were prepared according to a typical recipe⁵ using chlorendic anhydride (our preparation) and III; a comparison of the physical properties of these samples (Table II) shows that the III containing polyester is superior in light stability and resistance to sodium hydroxide.

TABLE V
Preparation of III-Propylene Glycol Resins With Increasing Percentages of Maleic Anhydride

PG	Mole ratio of reactants ^a		Reaction conditions				Physical properties of derived polyesters with 30% styrene			
	III	MA	Base Resin % Cl	Temp., °C. Pot	Time, hr.	Acid No. ±2	Hardness, Shore D	Heat Distortion °C.		Clarity
2.16	1.00	1.00	31.13	175	14	30	88	92	92	Opaque
2.16	0.75	1.25	26.49	160	20	35	87	>150	>150	Opaque
2.16	0.70	1.30	25.27	160	18	30	88	>150	>150	Cloudy
2.16	0.70	1.30	25.27	160	30	24	90	>150	>150	Clear
2.16	0.65	1.35	24.27	160	12	29	87	>150	>150	Clear
2.16	0.50	1.50	20.42	160	14	30	86	>150	>150	Clear
2.16	0.40	1.60	17.42	160	16	29	88	>150	>150	Clear
2.16	0.30	1.70	13.99	160	14	30	89	>109	>109	Clear

^a PG = propylene glycol; MA = maleic anhydride; III = compound III.

A sample of III-containing polyester was prepared and laminated with the standard thirteen plies of woven glass cloth; the results of testing this cured laminate and a comparison with commercial Hetron laminates are in Table III. The resin containing III had a higher flexural strength, elongation, and a better water resistance than the cured Hetron. Samples of III-containing resins were prepared using a Hetron recipe⁶ but with higher percentages of styrene and other vinylaromatic crosslinkers. The results of the tests on these nonlaminated samples are in Table IV.

A series of III, propylene glycol, and maleic anhydride-based resins was prepared with increasing concentrations of maleic anhydride and decreasing concentrations of III; these base resins were converted to styrene-based polyesters (Table V).

Preparation of and Comparison of Base Resins Derived from Chlorendic Anhydride and Compound III

Of the various compositions which had been used in the early portion of our work, the propylene glycol, maleic and either chlorendic anhydride or III recipe was the one chosen for use in the studies aimed at comparison of inherent stabilities (Table VI, footnote a). The base resins were dissolved in sufficient styrene so as to prepare polymerizable polyesters at 25% chlorine content. The viscosities and Gardner colors of these two resins along with the same data for the commercial Hetron 92 are in Table VI. As would be expected, those compositions having higher styrene concentra-

TABLE VI
Brookfield Viscosities and Gardner Colors of the Polyester Resins Prior to Cure

Resin sample S.E. component	Styrene, %	Brookfield viscosity, cpoise	Gardner color
III anhydride ^a	33.30	390	1
Chlorendic anhydride ^a	39.71	132	1
Hetron 92 ^b	30.00	3,275	4

^a The compositions for these formulations are: 1.5 moles of III or chlorendic anhydride, 0.5 mole of maleic anhydride, and 2.16 moles of propylene glycol; the mixture cooked to an acid number of 20 ± 2 , diluted with styrene to a 25% chlorine concentration.

^b The commercial formulation.

TABLE VII
S.P.I. Cure Data for the Several Self-Extinguishing Polyester Compositions

Resin sample S.E. component	Styrene, %	Gel time, sec.	Cure time, sec.	Peak exotherm. °F.
III Anhydride ^a	33.30	221	500	377.2
Chlorendic anhydride ^a	39.71	228	512	357.8
Hetron 92	30.00	412	512	465.0

^a These polyester compositions are comparable, see Table VI, footnote a.

TABLE VIII
Physical Properties of Cast, Unfilled Self-Extinguishing Polyester Samples

Resin sample S.E. component	Flexural		Tensile		Elongation, %	Impact, ft.-lb./in.	Heat distortion, °C.
	Strength, psi	Modulus $\times 10^{-5}$	Strength, psi	Modulus $\times 10^{-5}$			
III anhydride ^a	9,806	5.04	4,910	8.68	5.6	0.61	90
Chlorendic anhydride ^a	12,345	4.87	6,760	8.37	8.9	0.68	86
Hetron 92 ^b	14,252	5.09	9,237	11.90	9.8	1.59	163
Hetron 93LS ^b	16,892	4.78	8,420	9.56	13.4	1.70	105

^a These are comparable formulations, see Table VI, footnote a.

^b Commercial formulations; LS is the light-stabilized polyester designation.

tions have a lower Brookfield viscosity. It is also interesting to note that the chlorendic anhydride-based experimental resin had an improved color when compared to the commercial Hetron 92 resin.

The two experimental resins were compared with each other and with Hetron 92 in SPI cure studies (Table VII); while it is often misleading to compare these types of thermoset resins when different amounts of residual maleic unsaturation and different concentrations of styrene are involved, it is interesting that the III-based resin had a considerably lower gel time and a lower peak exotherm than did the commercial Hetron 92 resin. When the III- and chlorendic anhydride-based resins are compared, it is seen that the resin having the higher styrene content gave the higher cure time and the higher peak exotherm.

Samples of cast unfilled resins were prepared in aluminum sleeves; polymerization was catalyzed by 1% benzoyl peroxide (based on total resin) and complete cure was insured by running the polymerizations for 24 hr. at 80°C. Remembering that the first two samples in Table VIII are experimental resins formulated merely for internal comparisons, it is interesting that the two commercial resins are close together in many of their properties.

Initial rather severe thermal treatments were given to the polyester compositions utilized in the testing program. The results of heating the castings in their aluminum sleeves for seven days at 200°C. are compared in Table IX. Both experimental resins based on chlorendic anhydride or III showed comparable losses of weight and decreases in flexural strength and modulus. The weight loss of Hetron 92 was the lowest in the series tested.

1. Electrical Properties of Cast, Unfilled Polyester Samples. Cast samples were prepared from the resins described in Table X by molding sheets $\frac{1}{8}$ in. thick and 6 × 6 in. square. From these sheets were cut circular disks 2 in. in diameter. These samples were submitted for electrical testing, and the electrical properties are listed in Table X. The experimental samples from chlorendic anhydride and III appear superior to the other resin composition. Within the experimental compositions there

TABLE IX
Effect of Thermal Treatment (200°C. for 7 Days) on Weight Loss and Flexural Strengths of the Self-Extinguishing Polyester Unfilled Cured Samples

Resin sample S.E. component	Weight			Flexural strength, psi	
	Initial, g.	Final, g.	Loss, %	Initial	Final
III anhydride ^a	5.4667	5.2562	3.81	9,800	2,050
Chlorendic anhydride ^a	5.8495	5.2113	3.98	12,345	2,480
Hetron 92 ^b	5.8495	5.7350	1.96	14,252	11,800
Hetron 93LS ^b	5.6925	5.3875	5.36	16,892	7,860

^a Polyester base resin compositions are comparable, see Table VI, footnote a.

^b These are the commercial resins.

TABLE X
Electrical Properties (Dissipation Factor $\tan \alpha$ and Dielectric Constant K) of Cast, Unfilled Self-Extinguishing Polyesters at Increasing Frequencies^a

Resin sample S.E. Component	Frequency = 10 ³ cycles/sec.		Frequency = 10 ⁴ cycles/sec.		Frequency = 10 ⁵ cycles/sec.		Frequency = 10 ⁶ cycles/sec.		Frequency = 5 × 10 ⁷ cycles/sec.	
	$\tan \alpha$	K	$\tan \alpha$	K	$\tan \alpha$	K	$\tan \alpha$	K	$\tan \alpha$	K
III anhydride ^b	0.0014	2.83	0.0019	2.80	0.0040	2.78	0.0063	2.76	0.0086	2.70
Chlorendic anhydride ^b	0.0016	2.83	0.0022	2.80	0.0033	2.79	0.0052	2.77	0.0084	2.72
Hetron 92 ^c	0.0043	3.08	0.0070	3.06	0.0100	3.00	0.0133	2.97	0.0150	2.93

^a Data of Woodland.¹¹

^b Polyester composition, see Table VI, footnote a.

^c Commercial formulation.

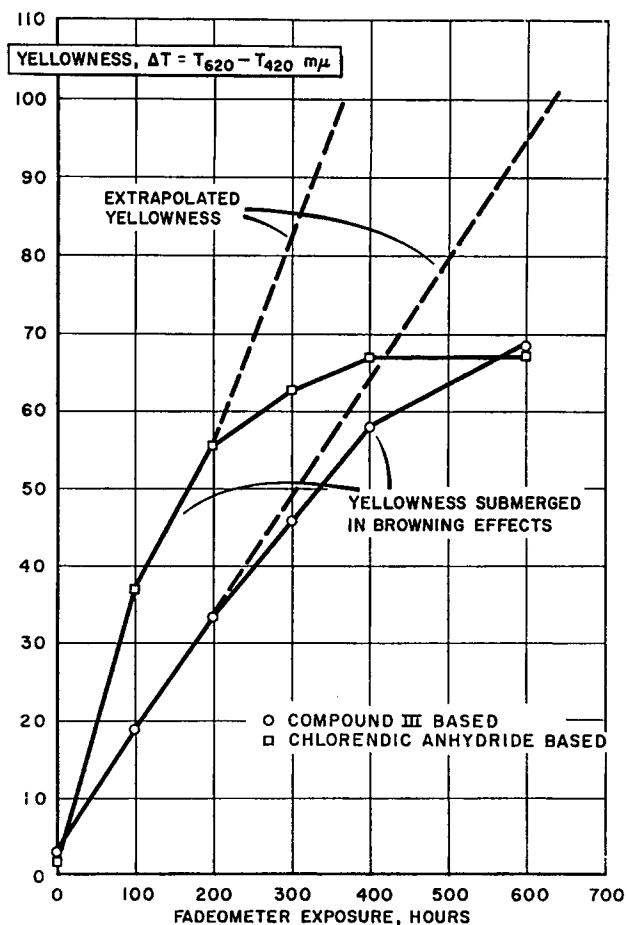


Fig. 1. Polyesters not stabilized with Tinuvin-P; blanks for Fadeometer exposures.

seems little to choose between the III- and the chlorendic anhydride-based resins; it should be added here, however, that when these resins were exposed in the Fadeometer and then subjected to electrical testing the III-based resin showed better light and electrical stability.

2. Light Stabilities of Polyester Resins With and Without Tinuvin-P Light Stabilizer. The study of the light stabilities of the experimental resins based on III and chlorendic anhydride in the standard recipe was initiated to determine whether or not the structures involved in the halogen-containing anhydrides were indeed demonstrably different. The standard base resin compositions were used throughout. A series of castings was made from each base resin and styrene with adjustments made to have 25% chlorine in each final resin. To each series was added increasing amounts of the commercial light stabilizer Tinuvin-P [2(2'-hydroxy-5'-methylphenyl)benzotriazole, Geigy Industrial Chemicals] to give castings con-

TABLE XI
Effect of Timed Fadeometer Exposures on the Transmission and Yellowness of Self-Extinguishing Polyesters Based upon III (ST) and Chlorendic Anhydride (HT) with Varying Amounts of Tinuvin-P Light Stabilizers^a

Sample series	Tinuvin-P added, %	Fadeometer exposures ^b											
		No exposure		100 hr.		200 hr.		300 hr.		400 hr.		600 hr.	
		T, %	ΔT	T, %	ΔT	T, %	ΔT	T, %	ΔT	T, %	ΔT	T, %	ΔT
ST Blank	0.0	87.0	3.0	84.8	18.7	80.8	33.5	76.0	45.8	71.3	57.7	63.8	68.8
ST 1	0.1	87.3	3.2	86.2	4.3	85.6	6.6	84.4	12.0	83.6	24.2	78.4	49.2
ST 2	0.2	96.9	3.7	85.5	4.4	85.1	5.9	84.8	8.9	84.1	13.6	82.3	31.4
ST 3	0.3	86.9	3.6	86.7	4.4	86.6	5.3	85.6	7.8	85.5	12.6	84.2	24.8
ST 4	0.4	87.5	4.4	86.9	4.5	86.5	5.4	85.8	7.2	85.7	10.8	84.4	26.8
ST 5	0.5	87.3	4.7	86.1	4.9	85.8	5.8	85.2	7.1	84.9	10.1	84.5	21.3
HT Blank	0.0	90.1	1.8	79.9	37.2	71.3	55.1	62.9	62.9	54.9	66.8	48.0	67.0
HT 1	0.1	84.7	2.7	84.0	4.5	83.5	8.0	82.2	17.3	80.1	31.5	73.5	55.5
HT 2	0.2	86.9	3.1	85.6	3.8	85.5	5.4	84.5	9.4	83.7	16.0	79.9	38.0
HT 3	0.3	88.7	2.9	87.7	3.5	87.2	5.0	86.7	7.3	86.8	11.7	84.6	27.4
HT 4	0.4	86.7	3.8	85.4	4.1	84.9	6.0	85.0	9.2	83.7	16.0	79.5	36.4
HT 5	0.5	87.5	4.4	86.7	4.6	86.3	5.6	85.8	7.2	86.2	9.4	84.4	23.1

^a Polyester composition see Table VI, footnote a.

^b Data of Milner.¹²

taining 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5% stabilizer. The comparable series (ST from compound III and HT from chlorendic anhydride) were run in parallel. Each set of samples was exposed to the accelerated Fadeometer testing procedure; after 100, 200, 300, 400, and 600 hr. exposure the test specimens were removed from the apparatus and changes in transmission T and yellowness development during the indicated exposure sequence were

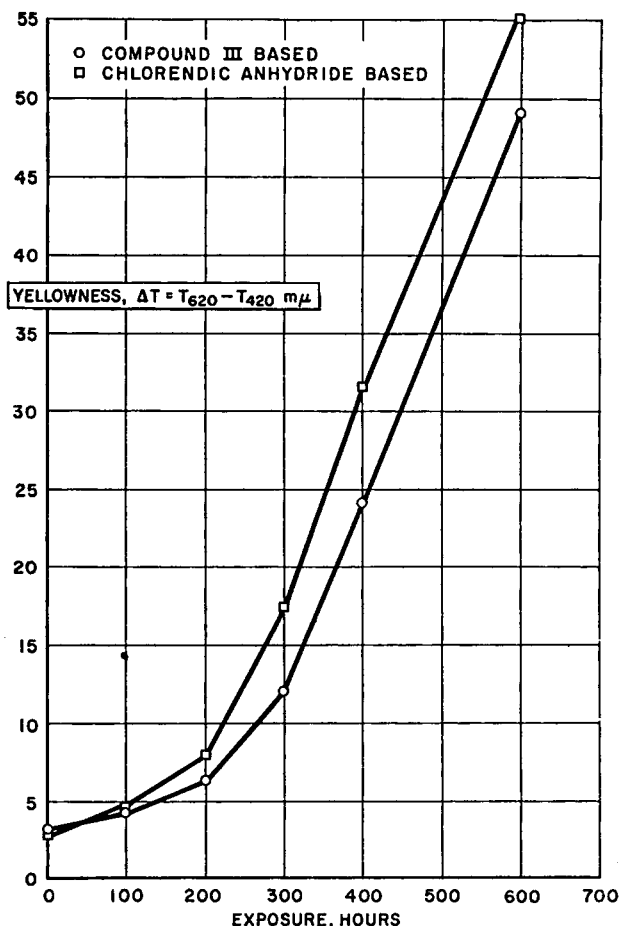


Fig. 2. Polyesters stabilized with 0.1% Tinuvin-P; Fadeometer exposures.

determined. The data are tabulated in Table XI, where ΔT is yellowness measured as $T_{620\text{m}\mu} - T_{420\text{m}\mu}$.

There are several ways in which these data may be used to represent graphically the change in transmission and development of yellowness during exposure; the four sets of curves shown in Figures 1-4 appear the most informative. It should be noted that, at higher (0.3% or higher) concentrations of Tinuvin-P, we are measuring the effectiveness of the

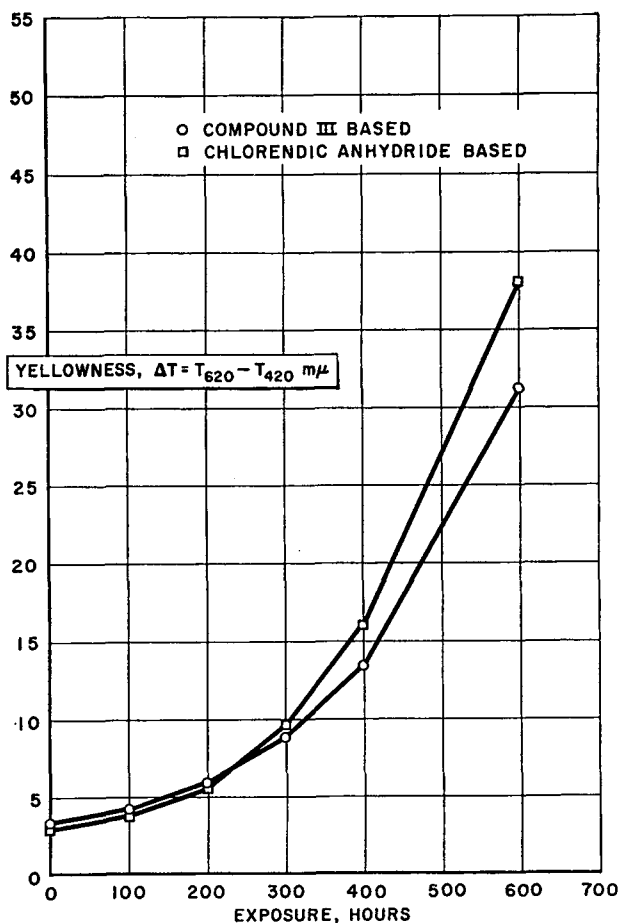


Fig. 3. Polyesters stabilized with 0.2% Tinuvin-P; Fadeometer exposures.

stabilizer rather than the inherent stabilities of the chlorine-containing portions of the polyester compositions.

It should also be emphasized that when the yellowness figures are higher than 20 to 30 they may have little meaning; this failure of higher yellowness figures to give good indications of stabilities is explainable as follows. First, as the yellowness values increase they become submerged by the development of a severe browning effect; this is evidenced by the apparent leveling off of yellowness values after prolonged exposure. Visual examination of the test bars shows more clearly than the yellowness data that the browning increases while the yellowness tends to remain constant. Second, as the browning effect becomes predominant, the interior of the sample is protected by the surface coloration. This can again be seen when the samples are examined visually. The ST series showed development of color of the surface to a much greater extent than throughout the sample;

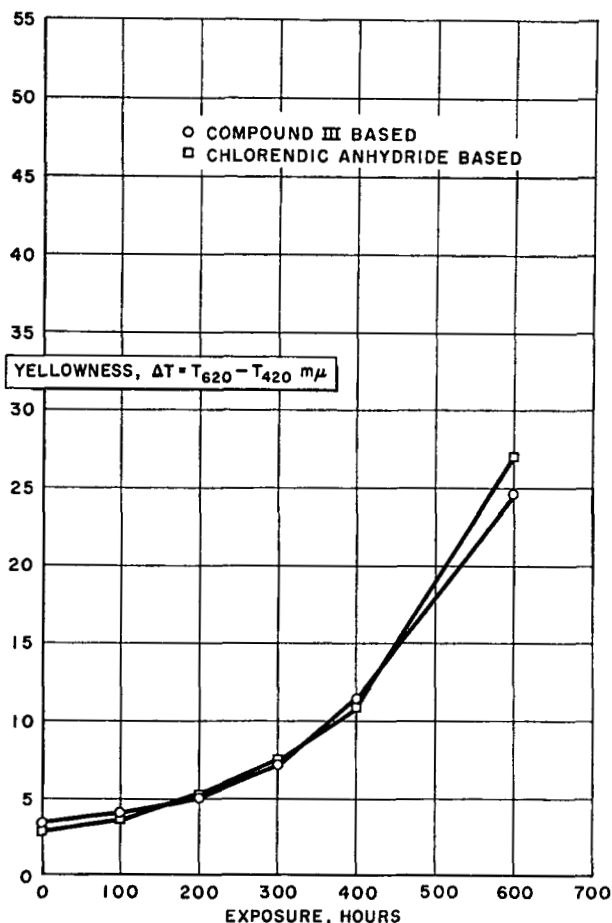


Fig. 4. Polyesters stabilized with 0.3% Tinuvin-P; Fadeometer exposures.

the HT series showed increasing browning throughout the thickness of the sample. Visually, and to a lesser extent from measured values, the ST series displayed greater light stability than the HT series.

Consideration of the data in Table XI and the derived figures leads us to conclude that, when both chlorine-containing anhydrides are initially pure, they still show a difference in light stability when incorporated into polyesters. If we consider the data from the several series, it is reasonable to conclude the following. ST blank has the development of the same degree of yellowness at 100 hr. that the HT has at 50 hr. At 200 hr. the ST series has the same degree of yellowness which has been shown in the HT series at 85 hr.; at 400 hr. the ST series has a yellowness comparable to that shown in the HT series at 220 hr. If we make a similar set of comparisons in the other two series, we see that at 0.1% Tinuvin-P stabilizer the ST series at 400 hr. exposure has the same yellowness as was shown by the HT series

at 345 hr. In the 0.2% Tinuvin-P stabilized systems we see that at the end of 400 hr. the ST series has developed the same amount of yellowness as was shown by the HT series at 360 hr. At lower exposure times a similar set of comparisons may be made.

Other Self-Extinguishing Resins Based Upon Compound III and Various Glycols

Polyester compositions which utilize compound III have ranged from the patent examples for chlorendic anhydride⁵ through a series of propylene glycol resins to the experimental composition utilized throughout for comparison of chlorendic anhydride and III under thermal and light exposure conditions. As was noted before in discussion of these studies, we did not feel that the formulation used possessed, in cast resin form, the best obtainable physical properties. With this in mind we initiated studies aimed at determining the effect of composition of base resin on the physical properties of cast unfilled resins. By use of the standard polyester preparative techniques a series of 22 different polyester base resins from III, maleic anhydride, and varying concentrations of different glycols were prepared.

TABLE XII
Formulations of Compound III (1.25 Mole-%), Maleic Anhydride (0.75 Mole-%)
and Various Dihydroxyl-Containing Compounds (2.10 Mole-%)

Formulation number	Dihydroxyl-containing dipropylene, mole-%			
	Propylene glycol	Ethylene glycol	Diethylene glycol	Dipropylene glycol
1	1.05	1.05	---	---
2	1.05	---	1.05	---
3	1.05	---	---	1.05
4	---	---	---	---
5	---	1.05	---	1.05 ^a
6	1.05	---	0.525	0.525
7	---	1.05	0.525	0.525
8	1.55	0.55	---	---
9	1.55	---	0.55	---
10	1.55	---	---	0.55
11	---	1.55	---	0.55
12	1.55	---	0.225	0.225
13	---	1.55	0.225	0.225
14	0.55	1.55	---	---
15	0.55	---	1.55	---
16	---	0.55	1.55	---
17	---	1.55	1.55	---
18	0.55	---	---	1.55
19	---	0.55	---	1.55
20	0.55	---	0.775	0.775
21	---	0.55	0.775	0.775
22	2.10	---	---	---
23	---	2.10	---	---

^a Formulation 4 a repeat of the standard formulation used previously.

The compositions used are listed in Table XII. Each of these base resins was dissolved in the appropriate quantity of styrene so as to give nearly 25% chlorine in the final cast resin; polymerization at 80°C. for 24 hr. in the presence of 1% benzoyl peroxide, based upon total resin weight, appeared to give satisfactorily cured samples. For screening purposes the cast resins were subjected to a preliminary evaluation. The physical properties of the several polyester compositions are given in Table XIII. From

TABLE XIII
Physical Properties of Cast, Unfilled Polyester Samples Prepared from Experimental Formulations in Table XII

Formulation number	Flexural		Heat distortion, °C.	Impact, ft.-lb./in.	Hardness, Shore D
	Strength, psi	Modulus $\times 10^{-5}$			
1	10,810	2.93	100.0	0.90	90
2	12,010	2.66	88.5	0.90	88
3	7,880	2.71	91.0	0.50	89
4	—	—	—	—	—
5	7,520	2.69	89.5	0.50	88
6	10,570	5.38	89.0	0.50	88
7	10,270	5.32	91.5	0.80	87
8	9,460	5.80	112.5	0.60	90
9	9,280	5.32	108.0	0.80	90
10	9,540	3.45	105.0	0.90	90
11	7,940	3.05	95.5	0.50	88
12	9,580	3.56	105.5	0.40	89
13	10,570	3.53	103.0	0.80	90
14	12,880	6.57	98.0	0.80	88
15	10,400	4.90	81.0	1.00	—
16	11,880	4.93	81.0	0.80	85
17	7,340	5.31	95.0	0.70	89
18	2,980	0.51	80.0	0.40	89
19	5,740	5.41	72.0	0.20	87
20	8,010	5.98	80.0	0.40	88
21	10,750	5.49	78.5	0.80	89
22	9,400	5.87	104.0	0.70	89
23	10,150	6.05	98.0	0.60	89

the data presented in Table XIII it would appear that the best formulations discovered to date are based upon mixtures of propylene and ethylene glycol (sample 14), propylene and mixed diethylene and dipropylene glycols (sample 6), and mixtures of ethylene and mixed diethylene and dipropylene glycols (sample 12).

Cast samples of glass filled polyester samples (181 Glass Cloth) were prepared from III, chlorendic anhydride, and Hetron 92; these were prepared and tested according to Military Specification 7575B. The results are in Table XIV. Conclusions from these data are that the III and chlorendic anhydride based resins of this formulation are comparable to each other, but are both poorer than the commercial Hetron 92 resin.

TABLE XIV
Physical Properties of Cast, Filled Self-Extinguishing Polyesters; Reinforced with 13 Plys of 181 Glass Cloth

Resin sample S.E. component	Tensile		Flexural		Elongation, %	Impact, ft.-lb./in.
	Strength, psi	Modulus $\times 10^{-6}$	Strength, psi	Modulus $\times 10^{-6}$		
Compound III ^a	47,230	9.83	53,000	1.388	5.4	18.78
Chlorendic anhydride ^a	49,800	9.88	58,000	1.355	5.8	18.82
Hetron 92 ^b	48,200	8.17	57,120	1.310	5.9	18.10

^a These polyester base resin compositions are comparable, see Table VI, footnote a.

^b The commercial formulation.

Relative Thermogravimetric Analysis of Compound III

As part of the work to prove the hypothesis that the instability of chlorendic anhydride was structurally explainable we compared the thermal stability of compound III with chlorendic anhydride. The results of these experiments are in Table XV. At an arbitrary temperature of 220°C.,

TABLE XV
Thermal Stability of Compound III and Chlorendic Anhydride^a in the Presence of Air (6.4°C./min.)²

Chlorendic anhydride, m.p. 238°C.		Compound III m.p. 278°C.	
Temp., °C.	Decomposition, %	Temp., °C.	Decomposition, %
105	0.05	210	0.10
125	0.20	220	0.50
140	0.40	230	1.10
160	1.15	240	1.90
180	2.80	250	3.10
200	5.70	260	4.80
210	8.50	270	6.70
220	11.70 ^b	280	9.00
230	15.60 ^b	290	12.00

^a Data of Donald.¹³

^b Extrapolated values.

chlorendic anhydride is 11.7% decomposed, and III is 0.50% decomposed. Preliminary thermogravimetric studies and determinations of the pyrolysis products from chlorendic anhydride- and compound III-based polyesters are underway and will be reported separately. The stability shown in the parent anhydrides appears to carry over into the polyesters.

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Résumé

On a incorporé comme agent de retard à la cuisson dans les compositions de polyester les produits d'addition Diels-Alder de l'anhydride *cis*-4-cyclohexène-1,2-dicarboxylique

(II) avec l'hexachlorocyclopentadiène l'anhydride-2,3-dicarboxy-5,8-endométhylène-5,6,7,8,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalène (composé III). La structure du composé III possède des propriétés inhérentes qui entraînent une stabilité à la température et à la lumière améliorées dans les polyesters qui le contiennent. On base ces améliorations par comparaison avec les polyesters préparés avec l'anhydride chlорendique l'agent de retard à la cuisson dans quelques polyesters commerciaux auto-extincteurs.

Zusammenfassung

Das Diels-Alder-Addukt von *cis*-4-Cyclohexen-1,2-dicarbon säureanhydrid (II) und Hexachloreyclopentadien, 2,3-Dicarboxy-5,8-endomethylen-5,6,7,8,9-hexachlor-1,2,3,4,4a,5,8,8a-octahydronaphthalin anhydrid (Verbindung III) wurde als nicht entflammbare Komponente bei Polyester mischungen verwendet. Die Struktur der Verbindung III besitzt spezifische Eigenschaften, die sich in einer verbesserten Wärme- und Lichtbeständigkeit der davon abgeleiteten Polyester bemerkbar macht. Die Verbesserungen beziehen sich auf einen Vergleich mit Polyestern aus "chlорendic anhydride," dem feuerbeständigen Bestandteil einiger käuflicher flammensicherer Polyester.

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