

INVESTIGATION OF HEAT RESISTANT POLYESTER LAMINATES

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MARCH 1956

**MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2515
PROJECT No. 7340**

**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

Carpenter Litho & Prtg. Co., Springfield, O.
300 - June 1956

FOREWORD

This report was prepared by Cornell Aeronautical Laboratory under USAF Contract No. AF 33(616)-2515. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73400, "Structural Plastics", formerly RDO No. 614-11, "Structural Plastics" and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. Robert C. Tomashot acting as project engineer.

This report covers period of work from June 1954 to July 1955.

WADC TR 55-342

ABSTRACT

Various methods of eliminating the cracking of triallylcyanurate copolymer resins reinforced with 181-301 glass cloth were investigated.

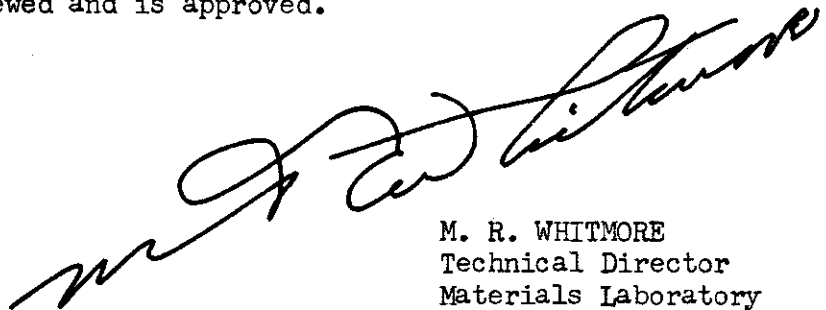
The use of .010" asbestos surface overlay on glass cloth laminates used with commercially available triallylcyanurate resins was found to be the most practical approach to prevent cracking in production applications.

Several new triallylcyanurate copolymers that exhibit reduced water absorption and heat loss were developed. Data on two resins which eliminated the cracking are described.

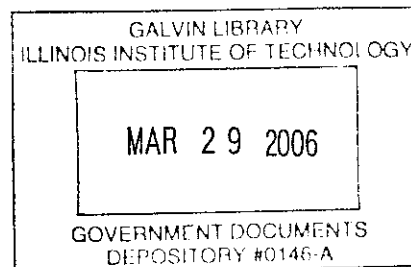
PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
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A STUDY OF HEAT RESISTANT POLYESTER LAMINATES

OBJECTIVE

The primary aim of this investigation was the development of improved, heat resistant, polyester-triallylcyanurate copolymer, glass reinforced laminates with low water absorption, and good retention of mechanical strength properties, that would not crack or craze upon post-curing or exposure to temperatures of 500°F for extended periods.

I. INTRODUCTION

Reports from various aircraft manufacturers and fabricators of plastic parts for aircraft have indicated that triallylcyanurate resin laminates are generally satisfactory and "void free" when cured at temperatures of 175° to 200°F, but when postcured in a temperature range of 400°F to 500°F the laminates usually become an opaque brown in color and acquire a dull rough surface. This postcure is required to obtain maximum strength and heat resistance of the laminate. Examination of the surface of these laminates with a low power microscope reveals the fact that the roughed surface is due to an extremely high degree of cracking of the resin.

Investigation of this phenomena has shown that these postcured triallylcyanurate copolymer resin, glass-reinforced laminates, when exposed to high humidity, adsorb over three percent by weight of water with resulting deleterious effect on certain electrical properties. (Reference 10).

For electrical applications the non-magnetic characteristics of glass reinforced laminates make their use mandatory in aircraft.

For the preparation of glass reinforced laminated structures, there are three types of thermosetting, heat resistant resins presently available. These resins which are used with woven glass fabric for reinforcement, are the triallylcyanurate alkyd copolymers, such as Laminac 4232, Selectron 5000-468-53, and Vibrin 135; phenolics, such as BVQ-11946 and CTL-91LD; and silicones, such as DC-2106 and GE-81369. In structural components for use at 500°F, the silicones do not degrade but tend to lose practically all their strength by becoming thermolabile.

The phenolics maintain the greatest proportion of their strength at 500°F but for certain types of electrical applications are unsatisfactory. The use of triallylcyanurate copolymers is desirable if this phenomenon of cracking can be eliminated, since both the electrical and strength properties at elevated temperatures are acceptable.

II. GENERAL OUTLINE OF INVESTIGATION

The various phases of work covered in this study are briefly outlined below:

- A. Evaluation of commercially available triallylcyanurate polyesters by preparing laminated 1/8" x 18" x 19" panels using 181-style cloth with 301 finish and determining the heat resistance, resistance to thermal degradation and cracking properties of these triallylcyanurate copolymers as measured by loss of flexural strength, loss in weight and increase in water absorption after exposure to temperatures in the range of 400° and 500°F for periods up to 200 hours.
- B. Evaluation of the influence of pigment type inert fillers on strength and reduction of cracking of postcured laminates.
- C. Formulation and evaluation of new alkyd-triallylcyanurate copolymers to reduce cracking when exposed to elevated temperatures.
- D. Investigation of combinations of polyester-triallylcyanurate resins with other polyester resins in varying amounts.
- E. Study of the effect of catalysts on reduction of cracking of alkyd-triallylcyanurate copolymer laminates when exposed to high temperatures.
- F. Study of the effectiveness of anti-oxidants, as well as postcuring in an oxygen-free atmosphere, on the reduction of cracking.

III. DISCUSSION AND RESULTS

A. Evaluation of Commercially Available Triallylcyanurate Polyester Resins

Triallylcyanurate has three alkene groups symmetrically substituted on a triazine ring. Its high functionality apparently helps to encourage crosslinking with alkyds which result in resins with greater thermal stability and good strength retention at elevated temperatures. Upon polymerization of this copolymer, the shrinkage and extreme brittleness of the triallylcyanurate alkyd polymer tends to cause cracking of the resin.

A variety of modified alkyds have been studied to overcome this inherent brittleness and cracking tendency of triallylcyanurate copolymers but these flexible alkyd resins tend to lower the strength at elevated temperatures and increase the thermal degradation.

There were three triallylcyanurate copolymers that were commercially available at the time this study was conducted;

1. Vibrin 135 - Naugatuck Chemical Company
2. Laminac 4232 - American Cyanamid Company
3. Selectron 5000-468-53 - Pittsburgh Plate Glass Company

Figure No. 1 shows a 25X photomicrograph of a glass reinforced laminate made with a typical commercial triallylcyanurate resin. This micrograph shows that even when the cross-linking or copolymerization has not been completed, i.e. after 2 hours press cure at 170° to 220°F and no postcure, there are fine hair-like cracks developing. In post-curing or heat aging of the laminates at 500°F, the cracks appear as isolated, usually parallel, hair-like fissures in the surface of the resin, in approximately one hour. As the postcuring time, or exposure to elevated temperatures in the range of 400° to 500°F is increased, the cracks become progressively larger and subsequently form a criss-cross pattern of hundreds of cracks extending throughout the laminate. This cracking is thought to result from mechanical stress due to the different coefficients of thermal expansion of the glass reinforcement and the resin, as well as chemical action or polymerization of the resin which causes molecular reorientation with consequent shrinkage.

Glass reinforced laminates 1/8" x 18" x 19" were prepared from these three commercially available resins and brought as closely as possible to their maximum strength by an initial cure in the press at 170° for periods ranging from 30 minutes to two hours, and put in an air circulating oven at 250°F. The oven temperature was raised in 50° increments to 400° or 500°F. If the postcure was carried out at 400°F, the laminate was held at this temperature for 24 hours. This was denoted as Condition A. If the postcure was conducted at 500°F, the laminate was held at this temperature for 3 hours. This was defined as Condition B. The panels were then subjected to various heat aging cycles as outlined under Section V on Preparation of Laminates.

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The commercial triallylcyanurate resins were evaluated for use in elevated temperature applications by visual observation of the laminates and by measuring several physical properties of the carefully prepared laminates.

Observation of the laminates made with these resins after the initial cure of 2 hours at 170°F in the press and 2 hours at 250°F and 24 hours at 400°F (Condition A) in the oven, indicated no cracks to the unaided eye and the laminate appeared smooth and a light tan in color. Examination under a 10X microscope showed a few random, extremely fine, hairline cracks in the surface of the laminates with unfilled resins. Upon further heat aging for 24 and 48 hours at 400°F, the laminates remained smooth in appearance but had turned a little darker in color. No cracks could be observed with the unaided eye. Microscopic examination showed that with these clear unfilled resins, the cracks had become larger and covered the entire laminate surface. After aging at 500°F for 24 and 48 hours, the surface of the laminates appeared slightly rough in appearance and had turned a dark brown in color. Examination under a 10X microscope revealed that the roughness of the unfilled resin laminates was due to relatively large cracks and degradation of the resin covering the glass fibers on the surface of the laminate.

In general, the cracking characteristics of all the laminates made with commercially available resins were similar when exposed to the same conditions of heating.

When heat aged at temperatures of 400°F and 500°F for periods of 24 and 48 hours, the specimens lost weight. This loss in weight was used as an indication of the degradation of the resinous portion of the laminate and was used as an aid in screening these resins. After exposure to temperatures of 400°F and 500°F for periods of 24 and 48 hours, the water absorption after 24 hours immersion was also determined.

The flexural strength and modulus of elasticity after initial curing, i.e. (Condition A or B) and further exposure to 400°F and 500°F was used for screening.

The flexural strength and modulus of elasticity were determined on all specimens according to Federal Specification L-P-406b, Amendment 1, Method 1031.1. Specimens were 1/8" x 1" x 4". Thickness dimensions were measured to 0.001"; a span length of 2 inches was used.

Early tests on these commercially available resins indicated that there was no significant change in the loss in weight, water absorption or flexural strength of the laminate after initial cure (Condition A or B) and further exposure to temperatures of 400°F or 500°F for 0.5 hours. Based upon this finding, no further screening tests were conducted after 0.5 hours at 400°F and 500°F.

It was also found that the flexural strength of these triallylcyanurate resin laminates after initial cure (Condition A or B) was not significantly changed after 200 hours additional exposure to 400°F. The tests at 400°F were therefore eliminated in the screening of these resins.

The flexural strengths and modulus of elasticity obtained with these commercial resins are outlined in Table 1. The water absorption and heat loss values are given in Tables 2 and 3.

Some variation in tendency to blister as well as loss in weight, water absorption and flexural strength has been observed in testing various batches of these commercial triallylcyanurate copolymer resins in glass reinforced laminates. Unless stated otherwise, one to two percent of benzoyl peroxide was used as catalyst as recommended by the manufacturer.

One of the causes of this variation was considered to be due to uncontrollable polymerization rates. To check this theory, the postcuring cycle of Vibrin 135, Laminac 4232, and Selectron 5000-468-53 was changed from 24 hours at 400°F (Condition A) to 3 hours at 500°F (Condition B).

As shown in Tables 4, 5 and 6, the physical properties such as water absorption, heat loss and flexural strength, were improved for Laminac 4232 and Selectron 5000-468-53. The Vibrin 135 laminates blistered badly when postcured at 500°F for 3 hours.

Although previous experience with laminates in general has indicated that the practice of storing the glass cloth and resin in a room held at a constant temperature of 70°F and 40% relative humidity gave satisfactory results, it was believed that this trouble might be due to moisture on the glass cloth. In an attempt to remedy this condition, the plys of 18" x 19" glass cloth to be used for laminating were heated to the postcuring temperature of 500°F over a period of two hours to drive off any volatile matter. Laminates were made using the preheated glass cloth with Laminac 4232, Vibrin 135, and Selectron 5000-468-53. They were cured in the press for 3 hours at 220°F and for 3 hours at 500°F in an air circulating oven. The Vibrin 135 laminate was again blistered and partially delaminated. Laminac 4232 and Selectron 5000-468-53 were again satisfactory.

This phenomenon had not been experienced previously since after post-curing at 400°F for 24 hours, the 1/8" x 18" x 19" panels were cut up into 1/8" x 1" x 4" test specimens, and supported perpendicularly to the shelf in an air circulating oven for 200 hours at 500°F. Under these conditions, no blistering of the laminate test specimens from Laminac 4232, Selectron 5000-468-53 or Vibrin 135 was observed.

It was subsequently discovered that by using 0.5% di-tertiary butyl peroxide and 0.5% benzoyl peroxide as catalyst, instead of 1.0% benzoyl peroxide, blistering of the V-135 laminates was eliminated after a three hour cure at 500°F. (Condition B)

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This variation in data on the physical properties obtained in the same laboratory by the same technicians indicates possible reasons for discordant results that have been obtained in interlaboratory comparisons on laminates made from these heat resistant resins.

During this work, it was found that the flexural strengths and flexural moduli of elasticity of these laminates were significantly higher, and the cracking and heat loss less, when the test specimens were laid flat on Transite sheet during the 200 hour heat aging cycle in an air circulating oven than when specimens were placed upright in the oven so that the circulating air could carry away any gaseous products of decomposition.

In all tests reported in this study, the specimens were placed upright in an oven during cure and heat aging.

TABLE NO. 1

Ultimate Flexural Strength and Modulus of Elasticity
Glass Reinforced Laminates with Commercial Triallylcyamurate Resins

Resins: as noted Cloth: 181-301
Parallel Laminate Tested Flatwise

Resins	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure for 24Hrs-400°F	After Aging* 200Hrs-500°F	After Postcure for 24Hrs-400°F	After Aging* 200Hrs-500°F
<u>Vibrin 135</u>				
Average Flexural Strength Modulus of Elasticity	52,300 2.8	25,400 2.2	18,500 2.1	17,400 1.2
<u>Laminac 4232</u>				
Average Flexural Strength Modulus of Elasticity	44,300 2.0	21,800 2.0	18,700 1.6	19,000 1.3
<u>Selectron 5000-468-53</u>				
Average Flexural Strength Modulus of Elasticity	47,900 2.9	28,400 2.1	11,200 1.5	17,100 0.7

* Condition D-A3, see Section V under Preparation of Laminates

TABLE NO. 2

Effect of Heat Aging on Water Absorption and Weight Loss

Water Absorption After 24 Hours Immersion

Resin	Average Percent Water Absorption After 48 Hrs Aging at 400°F	Average Percent Water Absorption After 48 Hrs Aging at 500°F
Vibrin 135	0.7	3.4
Laminac 4232	3.0	5.1
Selectron 5000-468-53	2.6	3.8

TABLE NO. 3

Heat Deterioration - Average Weight Loss in Percent

Resin	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F	
	24 Hrs	48Hrs	24 Hrs	48Hrs
Vibrin 135	0.7	1.0	5.1	6.0
Laminac 4232	1.8	2.5	5.8	7.6
Selectron 5000-468-53	2.7	2.9	4.8	6.6

* All specimens in Condition A before additional heat aging for 24 and 48 hours at 400°F and 500°F

TABLE NO. 4

Effect of Postcure on Ultimate Flexural Strength and Modulus of Elasticity

Resins: Laminac 4232 - Cloth 181-301
Selectron 5000-468-53 - 181-301
Parallel Laminate Tested Flatwise

Resins	Room Temperature Strength Tested at 75°F	High Temperature Strength Tested at 500°F
Laminac 4232	After Postcure(2) After Aging(3) For 3Hrs-500°F 200Hrs-500°F	After Postcure(2) After Aging(3) For 3Hrs-500°F 200Hrs-500°F
Average Flexural Strength Mod. of Elasticity	59,500 3.4	27,700 2.8
	24,900 2.2	19,700 2.4
Laminac 4232	After Postcure(1) After Aging(4) for 24Hrs-400°F 200Hrs-500°F	After Postcure(1) After Aging(4) for 24Hrs-400°F 200Hrs-500°F
Average Flexural Strength Mod. of Elasticity	44,300 2.0	18,700 1.6
	21,800 2.0	19,000 1.3
Selectron 5000-468-53	After Postcure(2) After Aging(3) For 3Hrs-500°F 200Hrs-500°F	After Postcure(2) After Aging(3) For 3Hrs-500°F 200Hrs-500°F
Average Flexural Strength Mod. of Elasticity	48,800 2.5	24,700 2.0
	31,000 2.3	24,500 1.8
Selectron 5000-468-53	After Postcure(1) After Aging(4) for 24Hrs-400°F 200Hrs-500°F	After Postcure(1) After Aging(4) for 24Hrs-400°F 200Hrs-500°F
Average Flexural Strength Mod. of Elasticity	47,900 2.9	11,200 1.5
	28,400 2.1	17,100 0.7

Note: 1 - Condition A - see Section V under Preparation of Laminates
2 - Condition B
3 - Condition D-R3
4 - Condition D-A3

TABLE NO. 5

Effect of Postcure on Water Absorption and Weight Loss

Water Absorption After 24 Hours Immersion

Resin	Average Percent Water Absorption After 48 Hrs Aging at 400°F	Average Percent Water Absorption After 48 Hrs Aging at 500°F
Laminac 4232(1)	3.0	5.1
Laminac 4232(2)	2.6	4.1
Selectron 5000-468-53(1)	2.6	3.3
Selectron 5000-468-53(2)	3.3	4.3

TABLE NO. 6

Heat Deterioration - Average Weight Loss in Percent

Resin	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F	
	24 Hrs	48 Hrs	24 Hrs	48 Hrs
Laminac 4232(1)	1.8	2.5	8.6	10.1
Laminac 4232(2)	0.4	0.8	1.9	3.4
Selectron 5000-468-53(1)	2.7	2.9	4.8	6.6
Selectron 5000-468-53(2)	1.2	1.8	1.4	2.1

Note: 1 - Condition A
2 - Condition B

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Viscosity measurements were made with a Brookfield viscosimeter. The viscosities of the resin pigment mixtures are outlined in Table 7. below.

TABLE NO. 7

Influence of Pigments on Viscosity on Vibrin 135 Resin

Percent Filler	Viscosity (Cps) 80°F
0	1750
10 Surfex MM	2100
20 "	2300
30 "	2350
40 "	2500
0	1750
10 Kalite	2700
20 "	4000
30 "	5150
40 "	6500

Laminac 4232 Resin

0	4500
10 Surfex MM	4500
20 "	5350
30 "	7250
40 "	10,750
0	4500
10 Kalite	5300
20 "	10,000
30 "	11,200
40 "	14,250

Selectron 5000-468-53 Resin

0	7500
10 Surfex MM	7600
20 "	8000
30 "	8200
40 "	8500
0	7500
10 Kalite	9250
20 "	12,800
30 "	18,000
40 "	33,750

B. Evaluation of Inert Fillers

Preliminary work at Douglas (Reference 10) has indicated that the use of inert fillers resulted in triallylcyanurate, glass-reinforced laminates with little cracking. Therefore it seemed desirable to investigate the effect of pigment fillers on the cracking and crazing of heat resistant laminates.

The addition of an inert pigment type filler to the resin results in a decreased resin content in the finished laminate which should result in less shrinkage of the laminate system. The first variables investigated were the amount of fillers necessary to prevent cracking of the resin and the effect of various percentages of filler on the viscosity of the resin. The effect of replacing a part of the resin with pigment on the heat resistance and strength of the laminate was then studied.

It is well known that the size and shape of the pigment particles in resin mixtures have considerable effect on the thermal expansion and viscosity of the pigment resin system. It has been found in the paint industry that the viscosity of the resin pigment mixture is influenced by the so-called "oil absorption" which depends on the distribution of the pigment particles in the vehicle, pigment size, surface area and wettability of the pigment by the resin.

For electrical applications, pigments containing more than traces of metallic oxides of iron or titanium cannot usually be used. Based upon these conditions and the results obtained in previous studies of polyesters filled with various types of pigments, it was believed that the use of the carbonates would result in the highest percentage of filler and the lowest viscosities, with satisfactory electrical and physical properties of the finished laminate.

While it was realized that the selection of carbonate fillers was not the optimum for all conditions, it was believed they fulfilled the greatest number of the requirements for the specific conditions of this problem. Several other pigment type fillers were suggested such as talc, barium sulfate, china clay, silica, Wollastonite, asbestos and mica. The use of some of these fillers would result in slightly lower water absorption and perhaps slightly better electrical properties; however, the viscosity would be greatly increased even with lower percentages of filler. Douglas, in their report (Reference 10), found that over 10% of talc of the type they used, affected the laminating properties of the resin due to the increase in viscosity.

In the preliminary work, carbonate pigments (Surfex MM and Kalite) were ground into uncatalyzed Vibrin 135, Laminac 4232 and Selectron 5000-468-53 resins, using a Morehouse paint mill, in increments of ten percent from zero to forty percent by weight.

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Other types of fillers, namely Wollastonite, asbestos and mica were also investigated. It was believed that the use of these fillers would result in lower values for water absorption. However, the viscosity was found to be greatly increased with lower percentages of these fillers.

The Wollastonite used, a calcium meta silicate, was obtained from the Cabot Carbon Company, Willsboro, N.Y.

The mica used was the finest water ground. It was obtained from Whittaker, Clark & Daniels Inc., of New York. The asbestos was PM-25 grade, the finest mesh available, with no iron content. This was obtained from the Powhatan Mining Company, Baltimore, Maryland.

Vibrin 135 resin with 40 percent of mica produced a stiff paste; 30 percent of mica resulted in a high consistency but it might be used for laminating. Vibrin 135 with over 10 percent of asbestos resulted in a stiff paste which could not be used for laminating. Laminac 4232 resulted in similar viscosities. Selectron 5000 468-63 with over ten percent of asbestos or twenty percent of mica resulted in stiff pastes which were too high in viscosity for satisfactory laminating.

The viscosities obtained are shown in Table 8 below.

TABLE NO. 8

Influence of Mica and Asbestos on Viscosity of Vibrin 135, Laminac 4232
(Centipoises) 80°F

Percent Filler Based on Resins Weight	Mica	Asbestos
<u>Vibrin 135</u>		
0	2500	2500
10	4200	6500
20	9100	62,000
30	20,000	-
40	115,000	-
<u>Laminac 4232</u>		
0	6400	6500
10	8000	14,000
20	16,000	57,500
30	48,000	-

Viscosities of Vibrin 135 and Laminac 4232 containing 40% Wollastonite were within the range desirable for laminating purposes. Selectron 5000-468-53 with thirty percent of Wollastonite was quite high in viscosity for laminating and with forty percent represented the maximum in viscosity that could be used.

The viscosities obtained with Wollastonite are noted in the following Table 9.

TABLE NO. 9

Influence of Wollastonite on Viscosity of Vibrin 135, Laminac 4232, Selectron 5000-468-53 - (Centipoises) 80°F

% Filler Based on Resins Wgt.	V-135	Laminac 4232	Selectron 5000-468-53
0	2500	5000	7500
10	3250	5150	8700
20	4000	6600	10,500
30	5000	8500	14,200
40	6250	10,750	16,000

The two pigments that were found to increase the viscosity of these triallylcyanurate resins the least amount, due to their low "oil absorption", were Surfex MM and Kalite. These two pigments are specially treated calcium carbonate fillers manufactured by Diamond Alkali Company. Figures 2, 3 and 4 in the appendix are graphs of viscosity versus percentage of fillers. From these graphs, it can be observed that Surfex MM up to forty percent by weight has only a minor effect on the increase in viscosity.

Castings of the pigmented resins were made. The pigmented resins were cast in test tubes 7/8 in. diameter x 6 in. long, cured in a water bath for 4 hours at 150°F, removed from the test tube and then cured for 3 additional hours at 200°F in a circulating air oven. The cast resins all required forty percent of pigment to prevent cracking except for asbestos. In the case of asbestos, only twenty percent could be used due to the high viscosity which did not prevent cracking.

Based upon the data obtained on viscosity of Vibrin 135, Laminac 4232 and Selectron 5000 468-53 filled with the pigment noted, laminates were made to determine the effect of the various percentages of pigment filler on the reduction of cracking and on the flexural strength of the laminates.

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TABLE NO. 10

Viscosities of Various Resin-Filler Mixtures Used In Preparing Test Laminates

Resin	Filler	% Filler	Viscosity (Centipoises)
V-135	None	0	2500
V-135	Surfex MM	40	2500
V-135	Kalite	40	6500
V-135	Mica	20	9100
V-135	Asbestos	10	6500
V-135	Wollastonite	40	6250
Laminac 4232	None	0	5000
Laminac 4232	Surfex MM	40	10,750
Laminac 4232	Kalite	40	14,250
Laminac 4232	Mica	20	16,000
Laminac 4232	Asbestos	10	14,000
Laminac 4232	Wollastonite	40	10,750
Selectron 5000 468-53	None	0	7,500
Selectron 5000 468-53	Surfex MM	40	8,500
Selectron 5000 468-53	Kalite	40	33,700
Selectron 5000 468-53	Mica	20	20,000
Selectron 5000 468-53	Asbestos	10	17,000
Selectron 5000 468-53	Wollastonite	40	16,000

The clear and pigmented laminates were prepared as previously outlined. The cure cycle used was two hours at 175°F in the press, 2 hours at 250°F, and 24 hours at 400°F in an air circulating oven. The effect of further heat aging at 500°F for 200 hours in air on the ultimate flexural strength was determined on these laminates. The panels were cut up for flexural tests into specimens 1 inch x 4 inches. Flexural tests were conducted on six

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specimens of each material. A 2 inch span was used. Results of the flexural tests are summarized in Tables 11, 12 and 13. Graphical data showing average load deflection curves at room temperature for clear and pigmented resins are shown in Figures 5 through 13 of the appendix.

The loss in weight and water absorption after 24 and 48 hours additional aging at 400° and 500°F (Conditions CA-1, CA-2, D-A1 and D-A2) were determined and are outlined in Tables 14 and 15.

In these tests, it was found that the use of 40% Surfex MM and Kalite with the heat resistant resins described above, greatly reduced but did not entirely eliminate the cracking in the laminates.

The flexural strength and modulus of elasticity of the laminates were not significantly reduced by the use of Surfex MM or Kalite fillers when tested at room temperature. The flexural strength of Vibrin 135 and Selectron 5000 468-53 with 40% Surfex MM after heat aging for 200 hours and tested at 500°F was enhanced.

The use of 40% Surfex, Kalite and Wollastonite gave laminates with smoother surfaces, lower heat loss and water absorption and generally improved appearance when postcured for 24 hours at 400°F.

The effect of 20 percent mica and 10 percent of asbestos was less pronounced in the reduction of cracking. The mica filled laminates were generally more satisfactory. The effect of these two fillers on the physical properties of the three resins varied from resin to resin as shown in Tables 11 through 15.

In general, it can be stated that 40% of Surfex MM gave the best overall results with the commercially available triallylcyanurate resins.

TABLE NO. 11

VIBRIN 135 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Vibrin 135 - Cloth: 181-301

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F
Vibrin 135 Clear No Pigment				
Average Flexural Strength	52,300	25,400	18,500	17,400
Mod. of Elasticity	2.8	2.2	2.1	1.2
Vibrin 135 40% Surfex MM				
Average Flexural Strength	52,300	40,900	18,800	21,900
Mod. of Elasticity	2.9	2.7	1.9	1.5
Vibrin 135 40% Kalite				
Average Flexural Strength	52,500	15,800	13,400	16,100
Mod. of Elasticity	3.1	1.6	1.9	1.3
Vibrin 135 20% Mica				
Average Flexural Strength	43,800	8,400	6,000	7,800
Mod. of Elasticity	3.0	1.6	0.7	0.7
Vibrin 135 10% Asbestos				
Average Flexural Strength	61,700	10,600	10,100	12,500
Mod. of Elasticity	2.5	1.8	1.3	1.0
Vibrin 135 40% Wollastonite				
Average Flexural Strength	49,000	28,200	15,700	20,300
Mod. of Elasticity	2.2	1.8	3.5	1.4

TABLE NO. 12

LAMINAC 4232 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Laminac 4232 - Cloth 181-301

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F
Laminac 4232 No Pigment Average Flexural Strength Mod. of Elasticity	44,300 2.0	21,800 2.0	18,700 1.6	19,000 1.3
Laminac 4232 40% Surfex MM Average Flexural Strength Mod. of Elasticity	45,300 2.7	29,500 2.3	20,200 1.9	14,700 1.4
Laminac 4232 40% Kalite Average Flexural Strength Mod. of Elasticity	42,100 2.7	19,800 2.0	17,900 1.8	19,300 1.3
Laminac 4232 20% Mica Average Flexural Strength Mod. of Elasticity	45,900 2.1	15,900 1.9	11,400 1.2	12,800 1.1
Laminac 4232 10% Asbestos Average Flexural Strength Mod. of Elasticity	51,000 2.4	23,100 2.3	20,700 1.6	21,200 1.6
Laminac 4232 40% Wollastonite Average Flexural Strength Mod. of Elasticity	41,200 2.2	17,500 1.7	21,300 2.1	17,900 1.4

TABLE NO. 13

SELECTRON 5000 468-53 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Selectron 5000 468-53, Cloth 181-301

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F
Selectron 5000 468-53 Clear No Pigment				
Average Flexural Strength	47,900	28,400	11,200	7,100
Mod. of Elasticity	2.9	2.1	1.5	0.7
Selectron 5000 468-53 40% Surfex MM				
Average Flexural Strength	46,800	18,900	19,400	20,100
Mod. of Elasticity	2.7	2.5	2.2	1.4
Selectron 5000 468-53 40% Kalite				
Average Flexural Strength	55,300	25,800	18,700	17,800
Mod. of Elasticity	3.0	2.6	1.8	1.5
Selectron 5000 468-53 20% Mica				
Average Flexural Strength	46,200	21,000	9,500	9,800
Mod. of Elasticity	2.8	2.0	1.5	1.2
Selectron 5000 468-53 10% Asbestos				
Average Flexural Strength	51,600	27,200	12,500	14,300
Mod. of Elasticity	2.9	2.0	1.5	1.2
Selectron 5000 468-53 40% Wollastonite				
Average Flexural Strength	35,500	8,700	19,100	8,500
Mod. of Elasticity	2.4	1.5	1.5	1.2

TABLE NO. 114

Water Absorption After 24 Hours Immersion

Resins used in 181-301 Laminates	Average Percent Water Absorption After 48 Hrs. Aging at 400°F	Average Percent Water Absorption After 48 Hrs. Aging at 500°F in air
Laminac 4232 Clear	3.0	5.1
Laminac 4232 + 40% Surfex MM	2.7	4.5
Laminac 4232 + 40% Kalite	2.5	3.8
Laminac 4232 + 20% Mica	3.6	5.1
Laminac 4232 + 10% Asbestos	4.2	5.1
Laminac 4232 + 40% Wollastonite	4.3	5.9
Vibrin 135 Clear	0.7	3.4
Vibrin 135 + 40% Surfex MM	1.0	2.2
Vibrin 135 + 40% Kalite	2.0	3.1
Vibrin 135 + 20% Mica	1.0	3.5
Vibrin 135 + 10% Asbestos	0.4	2.0
Vibrin 135 + 40% Wollastonite	1.4	2.2
Selectron 5000-468-53 Clear	2.6	3.8
Selectron 5000-468-53 + 40% Surfex MM	2.4	3.2
Selectron 5000-468-53 + 40% Kalite	2.4	3.0
Selectron 5000-468-53 + 20% Mica	2.8	3.4
Selectron 5000-468-53 + 10% Asbestos	2.5	3.5
Selectron 5000-468-53 + 40% Wollastonite	2.9	3.7

TABLE NO. 15

Heat Deterioration
Average Weight Loss in Percent

Resins used in 161-301 Laminates	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F	
	24Hrs.	48Hrs.	24Hrs.	48Hrs.
Laminac 4232 Clear	1.8	2.5	5.8	7.6
Laminac 4232 + 40% Surfex MM	1.4	1.7	4.8	6.4
Laminac 4232 + 40% Kalite	2.5	2.6	4.1	5.9
Laminac 4232 + 20% Mica	1.4	2.6	3.4	5.5
Laminac 4232 + 10% Asbestos	2.1	3.3	4.0	5.9
Laminac 4232 + 40% Wollastonite	1.7	2.8	3.8	6.3
Vibrin 135 Clear	0.7	1.0	5.1	6.0
Vibrin 135 + 40% Surfex MM	0.7	0.9	2.1	2.7
Vibrin 135 + 40% Kalite	1.0	1.2	3.1	3.7
Vibrin 135 + 20% Mica	0.5	0.8	2.2	3.4
Vibrin 135 + 10% Asbestos	0.6	0.8	1.9	2.5
Vibrin 135 + 40% Wollastonite	0.5	0.8	1.5	2.2
Selectron 5000-468-53 Clear	2.7	2.9	4.8	6.6
Selectron 5000-468-53 + 40% Surfex MM	0.9	1.2	3.1	4.4
Selectron 5000-468-53 + 40% Kalite	1.2	1.4	3.8	4.7
Selectron 5000-468-53 + 20% Mica	1.0	1.2	3.3	4.6
Selectron 5000-468-53 + 10% Asbestos	1.0	1.4	4.0	5.8
Selectron 5000-468-53 + 40% Wollastonite	1.8	1.9	3.7	4.6

To determine if these clear and pigmented resin, glass laminates meet the electrical properties required by Specification MIL-R-25042, the following test panels were prepared and sent to Wright Air Development Center for electrical tests. The panels were made of 70 plys of 181-301 cloth impregnated with clear or pigmented resin catalyzed with 1% benzoyl peroxide as noted in Table 16 below. The panels were nominally 0.60" x 9" x 9".

TABLE NO. 16

Electrical Test Panels
70 ply - 181 cloth
Post Cured 24 Hrs. at 400°F

Resin	Filler	% Resin or % Resin + Filler by Burnoff
Vibrin 135	No filler	28.8
Vibrin 135-60%	Surfex MM-40%	29.2
Vibrin 135-60%	Kalite-40%	32.0
Laminac 4232	No filler	29.4
Laminac 4232-60%	Surfex MM-40%	28.6
Selectron 5000-468-53	No filler	29.1
CAL Resin #152	No filler	29.9

The dielectric constant and loss tangent of these clear and pigmented laminates were conducted in accordance with MIL-R-25042 Specification.

The above samples were tested at 8.5 kmc/s, using the shorted waveguide method.

After the initial testing at normal room temperature (25°C), the samples were immersed in distilled water for 24 hours, at which time the surfaces were wiped dry and the samples were retested, using the same procedure as before.

Samples submitted for testing do not meet the electrical requirements of MIL-R-25042 Specification, Type III. The dielectric constant exceeds the maximum allowable values for both dry and wet conditions. This high dielectric constant was due to low resin content of the laminate, which as noted in Table 16 is generally less than 30 percent. The dielectric constants of 4.3 dry, and 4.4 wet in Specification MIL-R-25042, are for laminates with resin contents of approximately 35 percent. The dielectric and loss tangent of CAL resin #152 was close to specification values.

TABLE NO. 17

DIELECTRIC CONSTANT AND LOSS TANGENT AT 8.5 KMC/S OF LAMINATES FROM CLEAR AND PIGMENTED RESINS

Resin	Dielectric Constant	Average	Loss Tangent	Average	Wt. in Grams	Specific Gravity	% Water Absorption	Condition
V-135 Resin, 181-301 Glass Fabric	4.624 4.672 4.672	4.66	.0115 .0119 .0116	.012	10.2556 11.5400 12.8110	1.988 1.988 1.988	- - -	As received
V-135 Resin, 181-301 Glass Fabric	4.761 4.823 4.713	4.77	.0169 .0188 .0173	.018	10.3066 11.5926 12.8567	1.997 1.997 1.996	.500 .456 .357	24Hr. Immersion
V-135 Resin, 181-301 Glass Fabric	5.014 5.095 4.992	5.03	.00985 .00950 .0107	.010	10.7013 12.0358 13.2854	2.073 2.073 2.062	- - -	As received
V-135 Resin, 181-301 Glass Fabric 40% Kalite Filler	5.130 5.168 5.147	5.15	.0166 .0176 .0158	.017	10.7360 12.0707 13.3279	2.080 2.079 2.065	.324 .290 .320	24Hr. Immersion
V-135 Resin, 181-301 Glass Cloth 40% Surfex Filler	5.179 5.170 5.153	5.17	.0113 .0106 .0106	.011	10.9123 12.2253 13.5014	2.113 2.106 2.094	- - -	As received
V-135 Resin, 181-301 Glass Cloth 40% Surfex Filler	5.238 5.245 5.279	5.25	.0135 .0141 .0164	.015	10.9305 12.2507 13.5409	2.117 2.111 2.100	.167 .208 .293	24Hr. Immersion
Laminac 4232 181-301 Glass Fabric	4.761 4.824 4.837	4.81	.0219 .0215 .0241	.023	10.0964 11.3887 12.6426	1.954 1.960 1.960	- - -	As received
Laminac 4232 181-301 Glass Fabric	5.647 6.061 6.124	5.94	.150 .154 .151	.151	10.2633 11.5674 12.8389	1.986 1.991 1.991	1.65 1.57 1.55	24Hr. Immersion

TABLE NO. 17 Continued

DIELECTRIC CONSTANT AND LOSS TANGENT AT 8.5 KMC/S OF LAMINATES FROM CLEAR AND PIGMENTED RESINS

Resin	Dielectric-Constant		Loss Tangent		Average	Wt. in Grams	Specific Gravity		Absorption	Condition
	Constant	Average	Tangent	Average			Wt. in Grams	Specific Gravity		
Laminac 4232	5.082		.0176			10.6161	2.058	-		As received
181-301 Glass Fabric	5.126		.0210			11.9920	2.066	-		
40% Kalite Filler	5.103	5.10	.0182	.019		13.3869	2.074	-		
Laminac 4232	5.646		.0494			10.7371	2.081	1.139		24Hr. Immersion
181-301 Glass Fabric	5.700		.0562			12.1299	2.089	1.149		
40% Kalite Filler	5.877	5.74	.0493	.052		13.5392	2.098	1.137		
Laminac 4232	5.186		.0137			10.9510	2.120	-		As received
181-301 Glass Fabric	5.255		.0144			12.3079	2.122	-		
40% Surfex Filler	5.254	5.23	.0113	.013		13.7490	2.132	-		
Laminac 4232	5.318		.0206			11.0111	2.132	.549		24Hr. Immersion
181-301 Glass Fabric	5.534		.0275			12.3845	2.136	.622		
40% Surfex Filler	5.374	5.41	.0169	.022		13.7951	2.139	.335		
Selectron 5000-468-53	4.738		.0184			10.1642	1.969	-		As received
Resin 181-301 Fabric	4.725		.0188			11.3434	1.955	-		
	4.712	4.73	.0175	.018		12.5486	1.945	-		
Selectron 5000-468-53	5.761		.073			10.3266	2.000	1.597		24Hr. Immersion
Resin 181-301 Fabric	5.882		.158			11.5326	1.987	1.667		
	6.047	5.90	.105	.112		12.7555	1.977	1.648		
CAL Resin #152	4.356		.0109			9.5705	1.86	-		As received
	4.412		.0103			10.9496	1.89	-		
	4.401	4.39	.0105	.011		11.7241	1.89	-		
CAL Resin #152	4.409		.0134			9.5842	-	.143		24Hr. Immersion
	4.452		.0111			10.9655	-	.143		
	4.469	4.44	.0153	.013		11.7670	-	.365		

C. Formulation of Alkyd-Triallylcyanurate Copolymers

The formulation of alkyd-triallylcyanurate copolymers is known to have been actively studied by such resin manufacturers as American Cyanamid Company, Pittsburgh Plate Glass Company, and Naugatuck Chemical Company (References 2, 3, 11). The resins they have developed represent the optimum in heat resistance but due to the high shrinkage of the triallylcyanurate monomer and the oxidation of the alkyd portion, these copolymers crack and craze upon polymerization and aging at temperatures in the range of 400° to 500°F.

Based upon this work on triallylcyanurate resins, it is believed that shrinking and crazing is due to change in molecular distance between the molecules in the resin in the initial or gelled state and that in the postcured state. When a polyester triallylcyanurate resin initially sets up or polymerizes, a relatively loose three-dimensional network is built up in the resin. After postcure at higher temperature, the still labile triallylcyanurate molecules cross-link further with the polyester molecules. Initially, the monomer molecules are randomly spaced particles connecting the polyester molecules together. As further reaction or cross-linking takes place, the molecular distance between molecules becomes less and heat is evolved which raises the temperature of the resin mass. Consequently, the shrinkage forces due to final cross linking are the greatest at the time the thermal expansion of the resin is the greatest. If the polyester triallylcyanurate resin is not strong or tough enough to overcome these opposing stresses, it will crack and craze.

Based upon this theory, it was believed desirable to formulate the alkyd portion of the triallylcyanurate copolymer so that it would be tough, elastic and resistant to oxidation.

These facts channel investigation of this resin system into a study of unsaturated alkyd and heat resistant monomer variations. The work on the formulation of new alkyd-triallylcyanurate copolymers was concentrated on the alkyd portion of the resin and is described below. The data on all the experimental resin formulations are outlined in Table 77, on pages 92 through 93 of the appendix.

In general, a 1:1 molar ratio of carboxyl groups to hydroxyl groups was used in the formulation of the resins described to increase the extent of polymerization and to lower the number of free functional groups which could act as centers for oxidation.

Hexachloroendomethylenetetrahydrophthalic acid was used in the first series of resins as it was believed that its high chlorine content would aid in retarding oxidation. Cinnamic acid was also used because of its ability to polymerize through its double bond after formation of the resin. Various amounts of these two reagents were reacted with glycols to produce low viscosity resins. Triallylcyanurate was used as the copolymerizing agent. Of the nine resins prepared in the first series, the laminate made from resin 103-1 containing 12% of weight of

methylnmethacrylate exhibited physical properties comparable to control laminates.

Resins 102-1 and 105-1 contained maleic anhydride as the sole acidic constituent. Physical properties of these laminates were definitely inferior. As can be observed in Tables 79 and 80, the water absorption and loss of weight on heating of the laminate made with this resin was somewhat higher but crazing was reduced slightly. Other members of this series, resins 101-1, 104-1, 106-1, 109-1, 111-1 and 115-1, were all considered inferior in one or more of these physical properties. The laminate from resin 109-1 exhibited improved water absorption characteristics but loss of weight was quite high and the cracking extensive. Resins 114-1 and 114-2 did not cure properly and were discarded.

Resins were prepared from cinnamic acid, phthalic anhydride and maleic anhydride. Laminates prepared from resins 106-1, 107-1 and 108-1 were all badly crazed and exhibited a high loss in weight after heating as compared to the laminates made from commercially available resins, hereafter called control laminates. Water absorption of these specimens was also considered unsatisfactory.

Resins 110-1, 113-1, 113-2 and 115-1 were prepared from cinnamic acid, maleic anhydride and various chloro derivatives of phthalic anhydride. Of this series, the laminate prepared from resin 113-2 containing chlorophthalic anhydride proved superior to the control laminate in loss of weight and water absorption. Surface crazing was not decreased to any great extent however. The remaining members of the series were inferior to the control laminate in all respects.

The laminate prepared from resin 112-1, maleic and dichlorophthalic anhydrides, exhibited physical properties comparable to the control laminate. Crazing appeared to be reduced; the water absorption was also improved.

Based upon the formulation and evaluation of the resins briefly described above, it was believed that modification of resins 112-1 and 113-2 merited further study. The remaining formulations were not evaluated further.

Two resins, 116-1 and 127-1, were prepared using phenylene diacetate as one of the major constituents. Laminates prepared from these mixed phenolic-polyester type resins did not cure after several hours at 300°F. A further disadvantage was the very low viscosity of the resin and great amount of squeezeout in molding, with a resultant low percentage of resin in the laminate.

Tartaric acid was incorporated into the formulation of resins 117-1 and 118-1. Resin 117-1 also contained ethylene glycol, maleic anhydride and dichlorophthalic anhydride. Viscosity of this material was somewhat high for laminating purposes. In resin 118-1, the molar concentration of tartaric acid was increased and the chlorinated phthalic anhydride was reduced. In this resin, the dichlorophthalic anhydride was replaced by the monochlorophthalic anhydride. In an effort to reduce viscosity, the amount of

triallylcyanurate was doubled. A comparison of the two laminates indicated that resin 117-1 possessed superior heat resistance at 400°F and a lower water absorption at both 400° and 500°F. Laminates made from resin 118-1 proved superior in heat resistance at 500°F and exhibited considerably less cracking and crazing at all temperatures. Loss in weight on heating and water absorption values for both laminates were considered unsatisfactory.

The following series of resins were made to determine what effect increasing the chlorine content of a resin would have on cracking. To this end, chlorinated derivatives of maleic and phthalic anhydride were used. The resin's average chlorine content was as follows:

Resin 119-1	2.5 atoms per mol
120-1, -2	4.25 "
121-1, -2	5.0 "

Viscosity of resin 120-1 was so high that laminating proved difficult. A panel was prepared, however, but the laminate delaminated and was dry in spots. To offset this high viscosity, the amount of triallylcyanurate in resin 120-2 was doubled. Resin 121-1 gelled prematurely, prior to preparation of the laminate. A similar resin, 121-2, was prepared, the reaction being stopped at a higher acid number. The amount of triallylcyanurate was also doubled.

Of the resins in this series, resin 119-1 possessed the greatest heat stability at 400°F, losses being less than either 120-2 or 121-2. At 500°F, degradation proceeded rapidly and the resins of this series exhibited the greatest loss of weight. Resin 120-2 proved superior to 121-2 at 500°F even though it contained less chlorine. This improvement was attributed to the slightly higher percentage of triallylcyanurate rather than the influence of the halogen.

Laminates made from resin 121-2 absorbed the least water at 500°F, exactly half of that absorbed by resin 120-2. Increasing the chlorine content appeared to decrease the cracking to some extent. Laminates from resin 119-1 were badly cracked and charred while 120-2 and 121-2 showed only numerous small cracks. Resin 120-2 appeared to be the least crazed of the three but this was again attributed to the extra triallylcyanurate added to reduce viscosity. In general, the laminates were not considered satisfactory, even through the cracking was slightly reduced.

The next series of resins were designed to determine what effect the type of glycol has on the physical properties of the completed laminate. Diethylene glycol replaced ethylene glycol and maleic anhydride was used instead of chloromaleic in resin 123-1. Due to the poor results obtained with resin 122-1, methylmethacrylate was omitted from the formulation of

resin 123-1. Resin 124-1 was similar to 123-1, butanediol replacing diethylene glycol. Laminates made from resins containing diethylene glycol in these tests proved superior in both heat resistance and water absorption at 400°F and 500°F. Cracking was not as severe with resin 123-1 as with the other two of the series but still did not compare too favorably with the control laminates. A high percentage of resin in all laminates was probably a major factor contributing to the high degree of degradation and water absorption observed. A further study of the effect of glycols is included in a later portion of this section.

It has been reported that resins consisting of 50% alkyd, 37.5% triallylcyanurate and 12.5% acrylonitrile exhibited good heat stability at elevated temperatures. (Reference 2). Resins 125-1 and 126-1 were modeled along these lines. Alkyd portions of both resins were the same, chlorophthalic anhydride, maleic anhydride and propylene glycol. Resin 125-1 contained 12.5% acrylonitrile and 126-1 contained 12.5% methylmethacrylate as one of the monomeric constituents. The remainder of the monomers in both resins was triallylcyanurate, 37.5% by weight. The use of acrylonitrile proved superior in all cases in regard to the loss in weight at elevated temperatures. A slight improvement was shown over the control laminate of Laminac 4232. The methylmethacrylate monomeric system proved slightly superior at 400°F in the matter of water absorption but was inferior at 500°F. Examination of the laminates under the microscope indicated there was a slight reduction in the degree of cracking when acrylonitrile or methylmethacrylate was used.

The resins in the series 128-131 were made along the same general lines as the previous series. The acidic constituents of all resins remained constant, chlorophthalic and maleic anhydrides with some cinnamic acid, only the glycol was changed. Resins 128-1 and 129-1 contained propylene glycol while resins 130-1 and 131-1 contained butanediol. These resins are modifications of resin 113-2 discussed previously. Resin 128-1 used acrylonitrile as one of the monomers. Resin 129-1 contained methylmethacrylate. In this particular instance, resin 129-1 proved superior in weight loss due to heat degradation although resin 128-1 was slightly superior in lower water absorption characteristics.

Resin 130-1 used acrylonitrile as a monomer in addition to triallylcyanurate. Methylmethacrylate was again used in resin 131-1.

A comparison of the resins made with butanediol and propylene glycol tends to indicate that the use of propylene glycol results in a more stable, heat resistant polymer. Loss of weight and water absorption were considerably less at 500°F and cracking was not quite as severe.

Studies of alkyds with triallylcyanurate and other high temperature monomers have been previously carried out by Botwick, Cummings and Elliott (Reference 2). In this investigation, some work was conducted

on increasing the heat resistance of the alkyd portion of the resin, but the greatest amount of work was on heat resistant monomers. Review of the thermal stability of alkyds, with styrene as a monomer, was conducted by Ebers, Brucksch and Elliott (Reference 4). In this excellent piece of work, a comparison of the influence of various acids and glycols on the heat stability of polyester styrene laminates was carried out. While these studies were concerned with the heat stability of the laminates made from the various resins, no investigation of the comparative resistance to cracking and crazing was made. For comparison, resins 132 through 137, based on maleic anhydride, were prepared to determine the influence of the various glycols on the reduction of heat deterioration and cracking of the triallylcyanurate copolymers.

With the exception of the glycerol ester, the completed resins were clear, slightly viscous materials. In the case of glycerol, the resin gelled in the flask before the triallylcyanurate could be added. Two resins 137-1 and 138-1 were prepared by esterifying chloromaleic anhydride with ethylene glycol and diethylene glycol, and included in this series. Microscopic observation of the cracking of the resins in the laminates after aging for 48 hours at 500°F indicated that resin 136-1 cracked the least of the resins in the series 132-1 through 138-1. As noted in Table 80 the loss in weight due to heat deterioration is also the lowest for the group. Further work was carried out on triallylcyanurate copolymers based on this resin. The water absorption and loss in weight after aging is noted in Tables 79 and 80. The flexural strengths obtained are shown in Table 78.

A repeat formulation, resin 137-2, was prepared to determine if the physical properties could be improved by a postcure of 3 hours at 500°F. In this resin the amount of triallylcyanurate was reduced from 50% to 37.5%. An improvement was noted in the percentage of weight lost resulting from aging at an elevated temperature of 500°F. The water absorption values were almost identical. Flexural strengths were, in general, lower than those obtained from resin 137-1. However, a considerable improvement in flexural strength was noted in samples which were heat aged for 200 hours at 500°F and tested at 500°F. see Table 78. The very low flexural strengths obtained from the specimens tested at 500°F after post curing for 3 hours at 500°F are indicative of incomplete polymerization. For some unknown reason cracking appeared to be more pronounced in this laminate than in the panel prepared from 137-1. Two batches of resin 137 were prepared for the purpose of verifying previous results. Resin 137-3 contained 12.5% acrylonitrile and 37.5 triallylcyanurate, while only triallylcyanurate was added to 137.4.

In the repeat formulations of resin 137, the batch containing acrylonitrile possessed a low heat loss but was definitely higher in water absorption. Flexural strengths of the two laminates were approximately equal. A comparison of the properties of laminates prepared with resin 137-4 with those previously prepared did not show any great variation in values of the various properties except for the flexural strength after 200 hours

aging at 500°F, when tested at 500°F. In this instance, the laminate prepared from resin 137-2, possessed a strength of 37,000 psi while the other laminates ranged from 25,000 to 29,000.

A comparison of resin 138-1 with others of the series, 132-1 through 138-1, indicates that this resin had the greatest heat deterioration at 500°F. Water absorption values after aging 48 hours at 500°F were lowered in most cases. Microscopic examination of the laminate showed many large cracks throughout the surface. Flexural strengths determined at 500°F after aging for 200 hours were higher than any other members of this series with the exception of 137-1. Based upon these data, it appears that diethylene glycol in the alkyd causes the greatest loss in heat stability.

Previous work on a tartaric acid, hexanetriol, maleic anhydride alkyd in the production of heat resistant resins for foaming indicated this combination possessed a higher than average thermal stability. The high functionality of tartaric acid restricts its use to a low percentage in the resin, from the standpoint of rapidly increasing viscosities. Resin 139-1 was prepared containing ethylene glycol in addition to the tartaric acid, maleic and hexanetriol. Addition of this glycol was made to help reduce viscosity during condensation as well as decrease the possibility of gelation. Triallylcyamurate was found to be incompatible with the resultant alkyd, separation occurring within several hours after the addition. The use of diallyl maleate reduced the incompatibility, although some separation of the triallylcyamurate was observed after 24 hours. The laminate prepared from this resin was partially blistered and delaminated after postcure. The cracking was not greatly reduced and the loss of weight on heating and water absorption were lower than normal but were not of the right magnitude to be of interest. Due to the fact that the resin was generally incompatible with triallylcyamurate, and since the laminate was unsatisfactory, flexural strength and modulus of elasticity values were not determined.

Resin 140-1 was similar to 139-1 having equal amounts of tartaric acid, but due to the disadvantages noted with the previous resin, modifications were made. Maleic anhydride was replaced by chloromaleic anhydride and cinnamic acid, the hexanetriol being eliminated entirely. Preparation of the resin was carried out in two steps. First, the tartaric acid was reacted with cinnamic acid to esterify the internal secondary hydroxyl groups. The reaction was completed by adding the remaining constituents and condensing to an acid number of approximately 50. In this manner, a linear polyester was formed in which the chance for gelation was reduced. The viscosity of this resin system was found to be greatly reduced. No separation of triallylcyamurate was observed after several days. The laminate prepared from resin 140-1 was delaminated to such an extent after postcuring at 500°F for 3 hours that no tests were conducted.

Resins 141 and 142 were patterned after resins 128-1 and 129-1. In resin 141-1, cinnamic acid was replaced by benzoyl acrylic acid, with the remaining constituents remaining the same. A clear, low viscosity resin was obtained, which was easily adaptable to laminating procedures. The alkyd portion of resin 142-1 was the same as 129-1, the modification occurring in the monomeric system. Methylmethacrylate was replaced by dibenzoyl ethylene. However, several disadvantages of this last formulation were observed. First, the new monomer is crystalline in nature which tended to increase viscosity. Secondly, standing for several days, the dibenzoyl ethylene began to crystallize from the resin as it was evidently incompatible with the alkyd. Prior to use in laminates, the resin was heated for several hours at 150°F, after which time the dibenzoyl ethylene had redissolved.

Slight delamination occurred with resin 141-1 but not to a great extent. No flexural strength or modulus of elasticity tests were carried out although heat degradation and water absorption values were determined. The results obtained on these constants did not compare favorably with the data obtained from resins 128 and 129 on whose formulation resin 141-1 was based, possibly as a result of the slight delamination of the specimen. The cracking after 48 hours at 500°F was reduced considerably as shown in Figure 14.

A second formulation of resin 141-1 was prepared to further evaluate the reduction of cracking caused by the use of benzoyl acrylic acid. Heat deterioration values were quite low, less than 3 percent after 48 hours at 500°F, indicating this formulation to be quite resistant to heat aging. Flexural strengths determined at 75°F after 24 hours postcure at 400°F were quite high, over 65,000 psi. When evaluated at 500°F, after this postcure, the flexural strengths were very low, 4600 psi, indicating incomplete curing. After 200 hours at 500°F, the room temperature strength was again quite high, 38,000. This strength again dropped to 17,200 psi when tested at 500°F but was not considered unsatisfactory. After aging 48 hours at 500°F, no cracks could be observed in the laminate.

Water absorption values were very low, less than 0.5% after 48 hours aging at 500°F. This low value would tend to confirm the theory of the correlation between cracking and water absorption. This resin was considered to be one that would meet the objectives of the study.

No tests could be conducted on the laminate prepared from resin 142-1. The laminate did not cure in the press after several hours at 300°F. Decomposition of the resin was observed, and it was believed that the dibenzoyl ethylene was the cause. At the end of the cure, the laminate was still soft and flexible.

In the next series of resins, further evaluation was made of the methylmethacrylate and acrylonitrile monomeric systems. A large batch of resin was prepared and divided into three parts. To the first part only triallyl-

Contrails

cyanurate was added, the resin being designated as 143-1 NM. Triallylcyanurate (37.5%) and methylmethacrylate (12.5%) were added to the second portion designated as 143-1 MMA. The same proportions of triallylcyanurate (37.5%) and acrylonitrile (12.5%) were added to the last portion designated 143-1 ACN. After postcuring for 3 hours at 500°F, all laminates were badly blistered and delaminated.

A repeat batch of this resin was then prepared, containing equivalent amounts of the various monomers and designated 143-2. Laminates were prepared and postcured for 24 hours at 400°F. At 400°F, the laminate containing methylmethacrylate proved superior in heat deterioration. At 500°F, the acrylonitrile laminate was considerably superior. Flexural strengths of the laminates at 75°F of 143-2 MMA proved to be superior, as well as after the long high temperature aging cycle of 200 hours at 500°F. The laminate containing only triallylcyanurate possessed the highest strength when tested at 500°F after aging 24 hours at 400°F. After exposure to 500°F for 200 hours, the acrylonitrile laminate proved superior when tested at 500°F. These results agree with previous evaluations of these two monomers.

Water absorption values were quite low for laminates containing the methylmethacrylate and acrylonitrile monomer. After aging at 400°F, the methylmethacrylate laminate proved superior. The laminate with the acrylonitrile monomer absorbed less water after aging at 500°F. The straight triallylcyanurate laminate absorbed a considerably greater percentage of water after aging at 400° and 500°F temperatures; however, it was not considered unsatisfactory.

Based upon the success of the work using resin 143 described above, investigation of the use of various monomers was continued using resin 143 as the alkyd portion of the copolymer. A large batch of this resin was prepared and divided into five parts.

To the first part, 143-3 NM, 50% triallylcyanurate was added to the resin making a 50-50 mixture. In this panel, in addition to the 12 plies of cloth normally used, the outer surfaces of this laminate were covered with one ply of thin overlay glass fiber mat approximately 5 mils in thickness. During the polymerization process or "setting up" of the laminate, the resin has its greatest fluidity just prior to gelation and tends to flow away from the glass fibers leaving small voids. By using glass fiber overlay, the resin is not allowed to flow as freely away from the fibers, and a more uniform and smooth surface results. These small voids are readily seen in the 10X photomicrographs. It was believed that this would tend to reduce the stress concentration in the surface resin and might reduce the cracking.

Methylmethacrylate (12.5%) and triallylcyanurate (37.5%) were used as the monomer in the second resin 143-3 MMA, for comparison with results obtained previously, as well as those determined in the present series.

Excellent results have been reported by Naugatuck Chemical Division of the United States Rubber Company using a monomeric system consisting of a 50-50 mixture of triallylcyanurate and diallyl carbate. As a result of this work, diallyl carbate was prepared and used in the third portion of resin 143-3 DAC. This was used in the proportion of 25% diallyl carbate and 25% triallylcyanurate, with 50% of resin 143-3.

As an extension of the work with diallyl carbate, some diallyl tetrahydrophthalate was prepared and incorporated with triallylcyanurate, in the fourth portion of resin 143-3; this was coded 143-3 DATP. The structure of these two materials is quite similar, differing only by an endomethylene bridge. It was believed that a comparison of the relative heat stability of these two monomers will be of value for possible future modification. Resin 143-3 (50%) with diallyl tetrahydrophthalate (25%) and triallylcyanurate (25%) was resin 143-3 DATP.

Isobutylmethacrylate (12.5%) and triallylcyanurate (37.5%) were the monomer combination added to the fifth portion of resin 143-3. It was believed that the use of this monomer would increase the flexibility of the resin to a greater extent than methylmethacrylate with an accompanying decrease in cracking. The formulations are given in Table 18 below.

TABLE NO. 18

Experimental Resins with Various Monomers - Mols

Resin	PG	MA	CPA	CA	Monomer	TAC
143-3 NM	2.0	1.5	0.25	0.5	None	1.57
143-3 DAC	2.0	1.5	0.25	0.5	DAC 0.74	0.77
143-3 DATP	2.0	1.5	0.25	0.5	DATP 0.78	0.77
143-3 MMA	2.0	1.5	0.25	0.5	MMA 0.97	1.14
143-3 IBMA	2.0	1.5	0.25	0.5	IBMA 0.68	1.14

All the resins prepared in this series were of sufficiently low viscosity to make laminating procedures easily accomplished. They were all catalyzed with 1.0% benzoyl peroxide.

The rating index system was used to compare the resin in this series. As can be seen from this index, Table 19, the methylmethacrylate, diallyl carbate and diallyl tetrahydrophthalate were very similar in total rating. Although the diallyl tetrahydrophthalate laminate was not the best in any of the properties rated, it was consistently above average in all tests except the room temperature flexural strength, indicating that the postcure of 24 hours at 400°F was not satisfactory.

The laminates containing diallyl carbate degraded the least after 48 hours exposure at 500°F. Water absorption values of the methylmethacrylate laminate were the lowest after 48 hours exposure at 500°F. See Table 79.

TABLE NO. 19

Comparative Rating Index for 143 Resin with Various Monomers

Resin No.	143-3 Resin 50% with Monomer	Heat Deterioration 48Hrs-500°F	Flexural Strength		Water Absorption 48Hrs-500°F	Cracking	Comparative Index
			Tested 75°F	Tested 500°F			
143-3 NM	50 TAC	1	4	5	3	1	14
143-3 MMA	12.5 MMA 37.5 TAC	4	3	1	5	5	18
143-3 DAC	25 DAC 25 TAC	5	5	3	2	3	18
143-3 DATP	25 DATP 25 TAC	3	2	4	4	4	17
143-3 IBMA	12.5 IBMA 37.5 TAC	2	1	2	1	2	8

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- 5 Best of series
- 1 Most unsatisfactory of series

Abbreviations

DAC Diallyl carbate
 DATP Diallyl tetrahydrophthalate
 NM No second monomer - TAC only
 MMA Methylmethacrylate
 IBMA Isobutylmethacrylate

After postcuring 200 hours at 500°F, the diallyl carbate laminate possessed the greatest flexural strength when tested at 75°F. The laminates containing triallylcyanurate as the sole monomeric constituent and those containing diallyl carbate, diallyl tetrahydrophthalate and isobutylmethacrylate possessed satisfactory flexural strengths when tested at 500°F, after 200 hours at 500°F. See Table No. 78.

Cracking was again shown to be closely related to water absorption. The laminate which showed little cracking, methylmethacrylate, also showed the least water absorption. The diallyl tetrahydrophthalate laminate was rated second in cracking and water absorption.

A comparison of resin 143-3 methylmethacrylate with resin 143-2 methylmethacrylate indicates that the latest resin possessed a considerably higher flexural strength after the 200 hour cure at 500°F when tested at both 75° and 500°F. Heat deterioration and water absorption values of 143-3 methylmethacrylate were somewhat improved. The laminate made from the latest resin possessed a slightly lower resin content, 36.6% as compared to 37.3% for 143-2 methylmethacrylate made previously. Resin 143-3 NM with glass overlay gave a laminate whose surface was pit free but the cracking seemed to be accentuated.

In the work of Ebers, Brucksch, and Elliott on the heat stability of polyester styrene laminates, the superiority of fumaric acid over maleic anhydride was demonstrated, (Reference 4). For this reason, a series of resins based on fumaric acid was investigated.

In resins 144-1 and 145-1, the alcohol used was ethylene glycol. Fumaric acid was the main acidic constituent of resin 144-1, but in resin 145-1 one-half the fumaric acid was replaced by chloromaleic anhydride. Use of the chloromaleic anhydride was suggested as a result of the increased strengths obtained with previous resins of this type at elevated temperatures. The loss in weight due to heat deterioration of the straight fumaric acid resin was less than the resin containing half chloromaleic anhydride; the percent water absorption was greater however. Flexural strengths of resin 145-1 were higher in all cases except those specimens tested at 500°F after 24 hours postcure at 400°F, which indicates incomplete cure.

Propylene glycol replaced ethylene glycol in resins 146-1 and 147-1, other constituents being kept constant. Resin 146-1 contained only fumaric acid while 147-1 was half fumaric and half chloromaleic anhydride. Heat deterioration values of the fumaric resin were again considerably superior to the fumaric-chloromaleic mixture. In this instance, water absorption values of resin 147-1 were lower after aging at 400°F but inferior after aging at 500°F. Flexural strengths of resin 147-1 were higher than those of resin 146-1. In the case of the specimens which were tested at 500°F after 24 hours postcure at 400°F, low values were obtained which indicates incomplete cure.

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In the final pair of resins in this series, diethylene glycol was the sole alcoholic constituent. Fumaric acid was used in resin 148-1 and the fumaric-chloromaleic mixture made up resin 149-1. Continuing the trend shown with previous members of this series, the pure fumaric resin once again proved considerably superior to the fumaric-chloromaleic mixture in regard to heat deterioration. Water absorption values of resin 149-1 were lower after aging at 400°F but were higher after aging at 500°F. Flexural strengths followed the trend set by other members of the series. The fumaric-chloromaleic mixture gave the highest strengths after aging for 200 hours at 500°F and testing at 500°F. The low strengths obtained on the laminates tested at 500°F after postcuring 24 hours at 400°F, as well as the low values given by resins 145-1 and 147-1, were believed to be caused by incomplete postcuring of the laminate. After aging for 200 hours at 500°F, strengths were in almost all cases higher when tested at either 75°F or 500°F, than those specimens postcured 24 hours at 400°F and tested at 500°F.

Several other comparisons can be made among the members of this series. With the resins containing only fumaric acid, resin 144-1 using ethylene glycol as the alcoholic constituent proved superior in the matter of heat deterioration at both 400° and 500°F. Resin 146-1 containing propylene glycol and resin 148-1 containing diethylene glycol exhibited approximately equal losses at 400°F, although resin 146-1 was slightly superior at 500°F. Water absorption characteristics of these three laminates were approximately equal, resin 148-1 (diethylene glycol) being slightly superior after aging at 400°F and 146-1 exhibiting a slightly lower absorption after aging at 500°F.

Strengths of resin 144-1 (ethylene glycol) were higher than either 146-1 or 148-1 in all cases except specimens postcured for 24 hours at 400°F and tested at 75°F. In this case, both 146-1 and 148-1 exhibited higher strengths with 148-1 being the highest.

With resins containing the fumaric-chloromaleic mixture, resin 145-1 proved to be considerably superior in the matter of heat deterioration at both 400° and 500°F. Resin 149-1 containing diethylene glycol exhibited the lowest water absorption after aging at 400°F, but after aging at 500°F, resin 145-1 proved considerably superior. Flexural strengths of resin 145-1 were superior under all testing conditions.

A comparison of the physical properties from the viewpoint of the glycol indicates the use of ethylene glycol results in the lowest heat losses on aging at both 400° and 500°F and the highest flexural strengths after exposure to 500°F.

Use of fumaric acid results in considerable decrease in heat deterioration when compared with the fumaric-chloromaleic mixture at both 400° and 500°F. The fumaric-chloromaleic mixture exhibits a lower water

absorption at 400°F, but at 500°F the straight fumaric acid laminates possess the lowest absorption in most cases. Higher flexural strength values are obtained by use of the fumaric-chloromaleic mixtures after 200 hours at 500°F. Although all the resins exhibited cracking, resin 144-1 showed a considerable reduction in cracking tendency.

Table 20 is a comparative rating of the general properties, obtained with the fumaric acid series of resins. The index indicated that resins 144-1 and 145-1 merited further evaluation.

Based upon the results obtained with benzoyl acrylic acid in preparation of alkyds that copolymerized with triallylcyanurate without cracking, it was believed that further work along this line was desirable. Resins 150-1 through 152-1 are three resins similar to resin 141-1 in which the amount of benzoyl acrylic acid was reduced. In resin 152-1, ethylene glycol was used in place of propylene glycol.

In resin 150-1, one-half the benzoyl acrylic acid was replaced by cinnamic acid. In this respect, this resin was similar to the formulation of resin 129-1. The first laminate prepared from this alkyd was delaminated after a postcure of 24 hours at 400°F. A second resin was made and a second laminate, 150-2, was then prepared with no delamination.

Ethylene glycol replaced propylene glycol in resin 151-1 while the content of benzoyl acrylic acid remained the same as in resin 141. One-half of the cinnamic acid of resin 151-1 was replaced by benzoyl acrylic acid to formulate resin 152-1.

In resin 153-1, 12.5 percent of triallylcyanurate was replaced by methylmethacrylate. Postcuring of this laminate resulted in blistering and delamination. A second batch was prepared which also delaminated on postcuring. No tests were conducted on these laminates.

To further investigate the synergistic effect caused by a mixture of diallyl carbate and triallylcyanurate as reported by Naugatuck Chemical Company, 50% of the triallylcyanurate of resin 145 was replaced by diallyl carbate. This copolymer was designated as resin 154-1.

An increase of 0.25 mols of ethylene glycol over that of resin 153 and the addition of 0.5 mols of benzoyl acrylic acid constituted resin 155-1. Percentages of methylmethacrylate and triallylcyanurate were the same as in resin 153.

Resin 156-1 also contained additional ethylene glycol and benzoyl acrylic acid. One-half of the triallylcyanurate in this alkyd was replaced by diallyl carbate. The first laminate prepared blistered badly and was discarded. The same result occurred when a second laminate was prepared and postcured.

TABLE NO. 20

Rating of Fumaric Acid Series

Resin No.	Composition	Heat Deterioration 48Hrs-500°F	Flexural Strength		Water Absorption 48Hrs-500°F	Cracking	Index
			Tested 75°F 200Hrs-500°F	Tested 500°F 200Hrs-500°F			
144-1	EG, FA	6	3	5	3	6	23
145-1	EG, FA-CMA	3	6	6	6	5	26
146-1	PG, FA	5	1	1	5	3	15
147-1	PG, FA-CMA	1	4	3	2	4	14
148-1	DEG, FA	4	2	2	4	2	14
149-1	DEG, FA-CMA	2	5	4	1	1	13

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- 6 Best of series
1 Most unsatisfactory of series

TABLE NO. 21

Rating of Experimental Resins

Resin No.	Composition	Heat Deterioration 48Hrs-500°F	Flexural Strength		Water Absorption 48Hrs-500°F	Cracking	Index
			Tested 75°F	Tested 500°F			
150-2	PG, CA, BAA	3	1	1	2	4	11
151-1	EG, CA	4	2	5	4	1	16
152-1	EG, CA, BAA	5	4	3	5	5	22
154-1	DAC	1	3	4	1	2	11
155-1	BAA, MMA	2	5	2	3	4	16
156-2	EG, BAA, DAC	*	*	*	*	*	*

Note * Laminates made from resins 153-1, 151-2, 156-1 and 156-2 delaminated on post cure.

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- 5 Best of series
- 1 Most unsatisfactory of series

Continued

A comparison of laminates in the series of resins 150 through 156 indicates the laminate prepared from resin 152-1 was the best from a standpoint of elimination of cracking. Heat deterioration and water absorption values after postcuring at 500°F for 48 hours were the lowest of any specimens tested. It was observed that substitution of part of the cinnamic acid content of the resin by benzoyl acrylic acid reduces heat losses and water absorption (resins 151-1 and 152-1). It can also be pointed out that the use of ethylene glycol has a similar effect when compared with propylene glycol (resins 150-2 and 152-1). After postcuring for 200 hours at 500°F, flexural strength of 152-1 was the highest when tested at 75°F but was considered too low when tested at 500°F.

The laminates made in this series again indicates that the use of benzoyl acrylic acid in the resins is desirable. Heat losses and water absorption values of 155-1 containing this material in conjunction with methylmethacrylate were lower after exposure to 500°F for 48 hours than the laminate containing the DAC-TAC monomeric system. Cracking of the resins was also considerably decreased.

An all over comparison of both series indicates that the laminate prepared from resin 152-1 was the most satisfactory. For a comparative summary of this series of resins see Table 21.

In further evaluation work on the use of benzoyl acrylic acid in the preparation of alkyds that would copolymerize with triallylcyanurate without cracking, ten resins were prepared in four series. In the first series, resin 157-1 was similar to resin 152-1 except the benzoyl acrylic acid content was reduced by one-half and an equivalent amount of maleic anhydride was added in an effort to increase the strength at 500°F after 200 hours cure at that temperature. In resin 158-1, one half of the benzoyl acrylic acid was replaced by chlorophthalic anhydride instead of maleic anhydride as in resin 157-1.

The laminates prepared from resins 157-1, 158-1 were very satisfactory in both heat deterioration and water absorption after exposure to 500°F for 48 hours. Cracking in the laminates made from resins 157-1 and 158-1 was greatly reduced after 48 hours at 500°F. The flexural strength of the laminates from resin 157-1 and 158-1 was less than 15,000 psi when tested at 500°F after 200 hours aging at 500°F. Based upon the data obtained with these and previous resins, it would appear however, that a small increase in the amount of chlorophthalic anhydride tends to lower the heat deterioration and water absorption characteristics. The data obtained on heat deterioration, water absorption and flexural strength are outlined in Tables 78, 79 and 80.

The second series, resins 159-1, 160-1 and 161-1, were all similar to resin 152-1. In each case the amount of benzoyl acrylic acid was reduced by one-half and an equivalent amount of cinnamic acid was added in an effort to increase flexural strengths at elevated temperatures. In resin 159-1, ethylene glycol was replaced by propylene glycol. Resin 161-1 also

contained 5 percent of Paraplex G-50 to reduce cracking.

Resin 162-1 and 163-1 made up the third series. These resins were also similar to resin 152-1, the exception being that maleic anhydride was replaced by fumaric acid. In resin 163-1, an additional one-half mole of ethylene glycol was added to compensate for an increase of both fumaric acid and chlorophthalic anhydride. Improvement in elevated temperature strengths was hoped for by these modifications.

In the fourth series of resins, variations were made on the formulation of resin 137, which to date possessed the highest strength after 200 hours heat aging at 500°F when tested at this temperature. Resin 164-1 contained one-half mole of benzoyl acrylic acid, an equivalent amount of ethylene glycol being added. Resin 165-1 also contained benzoyl acrylic acid but methylmethacrylate was added as a second monomer with the triallylcyanurate. In resin 166-1, a diallyl carbate-triallylcyanurate monomeric system was employed, the other constituents remaining constant. In the last resin of the series 167-1, the benzoyl acrylic acid content was reduced by one half which was replaced by cinnamic acid. A second change was also made in the monomer part of the resin, 25 percent of the triallylcyanurate being replaced by diallylmalate. This material would tend to eliminate any slight degree of incompatibility as well as to enter into the cross-linking reaction.

Resins 159-1, 160-1, and 161-1, when compared to resin 152-1 from which they were derived, were generally inferior. Heat deterioration and water absorption values were considerably higher and cracking was much more extensive. Flexural strengths at temperatures of 500°F after 200 hours aging at 500°F were generally unsatisfactory. Resin 161-1 was the best of this group.

The resins containing fumaric acid, resin 162-1 and 163-1, gave laminates in which the heat losses and water absorption were low, however, the flexural strengths after aging for 200 hours at 500°F were not satisfactory. Resin 152-1, containing maleic anhydride, proved to be superior in all respects to 162-1 in which fumaric acid was used.

Resins 164-1 through 167-1 were based on resin 137 but contained benzoyl acrylic acid. All laminates made from these resins were badly blistered upon postcuring at 400°F for 24 hours, however some would not polymerize into a rigid state. Consequently no tests were conducted on any of the members of this series. All data obtained on these resin formulations, ultimate flexural strength, modulus of elasticity, water absorption, and heat loss are given in Tables 78 through 80.

Based upon the results of this study, it is believed that definite advances have been made in the elimination of cracking, reduction in heat deterioration and water absorption.

Contrails

In order to objectively determine which resin or resins formulated in this study had the most desirable properties, the most satisfactory resin from each series, as determined by the rating index, was selected and rated against the best resins of the other series. Table No. 22 below shows resins 141 and 152 eliminated the cracking problem and were superior to the others in some or all of the properties tested.

TABLE NO. 22

Final Rating Index of Experimental Resins

Resin No.	Heat Deterioration 48Hrs-500°F	Flexural Strength		Water Absorption 48Hrs-500°F	Cracking	Total Rating Index
		Tested 75°F 200Hrs-500°F	Tested 500°F 200Hrs-500°F			
128	8	3	6	8	8	44
129	9	4	4	7	7	31
137	4	7	11	4	7	33
137 ACN	5	9	10	2	10	36
141	7	10	4	10	11	42
143 ACN	10	9	9	9	9	46
143 MMA	6	5	2	8	10	31
143 DAC	8	8	5	6	9	36
144	4	6	7	3	8	28
145	3	10	8	5	9	35
152	11	11	3	11	11	47

The most satisfactory resin formulated was resin 152. It possessed the lowest heat loss and water absorption values of all the resins. No cracking was evident in the laminate when examined under 10X magnification, as shown in Figure 15. Flexural strengths were acceptable at 75°F and at 500°F. The flexural strength after 200 hours heat aging at 500°F and tested at 500°F was approximately 16,000 psi which is considered comparable to laminates made from commercially available triallylcyanurate copolymer resins. Further work on modifications of resin 152 could undoubtedly improve the flexural strength at 500°F without impairment of the other physical properties.

Contrails

Resin 143-ACN had a high rating index but the cracking was not completely eliminated. Resin 137 had high flexural strength after aging for 200 hours and testing at 500°F. It was believed that resins 137, 141, 143 ACN and 152 were the best of the group formulated and merited further evaluation. New laminates were prepared from these resins and compared with commercially available resins. The results are outlined in Section H on pages 79, 80 and 81.

D. Investigation of Resin Combinations

In the formulation of new alkyd triallylcyanurate copolymers, an attempt was made to internally plasticize the copolymer since it was believed that this would result in crack-free resins with the highest heat distortion temperature. It was also decided to study the addition of external resinous plasticizers to the commercially available triallylcyanurate resins, to determine if this procedure would result in reduced cracking and satisfactory strength at elevated temperatures.

With this in mind, two plasticizers with low volatility and good resistance to elevated temperatures were arbitrarily selected for evaluation. The polymeric resinous plasticizers used were Paraplex G-50 and G-60 obtained from the Rohm and Haas Company. The resins plasticized for this evaluation were Laminac 4232, Vibrin 135, Selectron 5000 468-53 and Selectron 5900 603-4. Two laminates were prepared from each resin, one containing 5 percent Paraplex G-50 and the other 5 percent Paraplex G-60.

Five percent of G-50 plasticizer was not compatible with Laminac 4232 but was miscible with the other resins used in the series. In spite of this incompatibility the Laminac 4232 with 5 percent G-50 produced a laminate showing no cracking. In the laminate of Laminac 4232 with G-50, improvements were noted in heat deterioration and water absorption but the flexural strength after 200 hours at 500°F was unsatisfactory.

It was found that all the resins were compatible with 5 percent of G-60 plasticizer. G-60 with Laminac 4232 produced a laminate in which the cracking was practically eliminated. The heat loss, water absorption and the ultimate flexural strength at 500°F after 200 hours at 500°F were satisfactory.

The data obtained are shown in Tables 23, 24 and 25 below.

The reduction in cracking obtained with Laminac 4232, G-50 and G-60 is illustrated in Figure 16.

TABLE NO. 23

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs.	48Hrs.	24Hrs.	48Hrs.	
4232 G-50	0.6	1.0	1.5	2.4	39.8
4232 G-60	1.2	1.8	1.8	2.6	40.0

TABLE NO. 24

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
4232 G-50	2.3	3.2
4232 G-60	1.7	2.1

TABLE NO. 25

Ultimate Flexural Strength And Modulus of Elasticity
Cloth: 181-301

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F
4232 G-50				
1	27,525	12,592	23,730	9,923
2	35,326	11,988	19,162	12,870
3	32,660	14,437	23,914	13,361
4	32,541	14,479	21,812	9,254
5	29,159	16,110	17,558	13,827
Average	31,442	13,921	21,235	11,847
Modulus of Elasticity	2.1	1.9	1.3	1.4
4232 G-60				
1	49,504	24,081	19,890	19,970
2	42,515	18,580	21,696	21,821
3	40,508	19,428	22,716	18,306
4	40,772	23,387	22,759	15,732
5	40,668	21,450	21,971	15,778
Average	42,793	21,385	21,806	18,321
Modulus of Elasticity	2.3	1.6	1.9	1.5

The use of 5 percent of G-50 and G-60 plasticizers with Vibrin 135 resulted in laminates showing improved physical characteristics but only slight reduction in cracking. Especially noteworthy is the increase in flexural strengths at 500°F. Heat deterioration and water absorption values were generally lower than the unplasticized resin after exposure to 500°F for 48 hours.

The cracking of Vibrin 135 laminates was eliminated with 15 percent of G-60 but the loss due to heat deterioration was higher but satisfactory. The water absorption was satisfactory and the flexural strength at 500°F after 200 hours aging at 500°F was over 18,000 psi compared with 17,000 psi for the straight unplasticized V-135 aged under similar conditions.

Based upon this study, it was considered that 15 percent of G-60 would be the maximum amount that could be used without loss of strength after exposure to 500°F for 200 hours. The cracking is eliminated and probably would be satisfactory for most laminating applications.

TABLE NO. 26

Ultimate Flexural Strength and Modulus of Elasticity
181 Cloth - 301 Finish
Parallel Laminate Tested Flatwise

Resin	Room Temperature Strength Tested at 75 F		High Temperature Strength Tested at 500°F	
	After Postcure For 24Hrs-400°F	After Aging For 200Hrs-500°F	After Postcure For 24Hrs-400°F	After Aging For 200Hrs-500°F
<u>V-135 G-50 - 5%</u>				
1	65,312	43,135	15,114	28,000
2	66,306	46,827	15,913	28,795
3	66,716	47,763	14,276	30,189
4	64,668	47,802	14,559	27,292
5	65,200	50,914	15,844	28,617
Average	65,640	47,288	15,141	28,579
Modulus of Elasticity	2.7	2.4	1.7	2.0
<u>V-135 G-60 - 5%</u>				
1	46,279	34,333	15,127	23,389
2	60,085	36,261	15,881	25,092
3	58,011	36,085	15,881	16,779
4	56,964	35,470	15,628	31,396
5	49,755	39,026	15,222	25,455
Average	54,219	36,235	15,548	24,422
Modulus of Elasticity	2.4	2.1	1.6	1.8
<u>V-135 15% G-60</u>				
1	55,532	24,309	13,508	17,938
2	49,800	22,518	15,334	22,378
3	49,835	25,942	15,295	18,627
4	50,252	24,694	15,171	15,529
5	50,609	25,570	15,591	18,658
Average	51,206	24,607	14,979	18,626
Modulus of Elasticity	2.3	1.3	1.7	1.0
WADC TR 55-342		46		

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24 Hrs.	48Hrs.	24Hrs.	48Hrs.	
V-135 5% G-50	0.7	1.0	0.9	1.3	37.0
V-135 5% G-60	0.7	1.0	1.0	1.3	37.5
V-135 15% G-60	0.8	1.3	2.1	2.9	35.7

TABLE NO. 28

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs. Aging at 400°F		Average Percent Water Absorption After 48Hrs. Aging at 500°F	
V-135 5% G-50		0.4		0.5
V-135 5% G-60		0.7		0.6
V-135 15% G-60		1.0		1.6

Additional work was carried out on the use of these resinous plasticizers using Selectron 5000-468-53. Two laminates were prepared, one containing 5 percent G-50 and the other 5 percent G-60. The plasticizers were compatible with Selectron 5000-468-53 in this amount. After initial cure, each laminate was cut in half, one half being cured at 400°F for 24 hours, and the other half at 500°F for 3 hours.

When these laminates were compared with the straight resin laminate, a considerable improvement was noted in all the water absorption values, the greatest decrease being found in the G-50 laminate. Heat deterioration values were satisfactory after 48 hours at 500°F. Flexural strengths of the laminates plasticized with 5 percent G-60 were satisfactory after testing at 500°F, after 200 hours at 500°F.

TABLE NO. 29

Ultimate Flexural Strength and Modulus of Elasticity
Resins: Experimental, Cloth 181-301

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure For 24Hrs-400°F	After Aging 200Hrs-500°F
Selectron 5000				
<u>468-53 5% G-50</u>				
1	59,590	31,431	21,307	18,857
2	59,605	34,304	21,146	17,734
3	54,075	33,104	16,588	15,655
4	59,025	34,109	18,735	16,116
5	56,781	34,680	20,966	17,087
Average	57,815	33,526	19,748	17,090
Mod. of Elasticity	2.4	1.9	1.7	1.2
 Selectron 5000				
<u>468-53 5% G-60</u>				
1	48,527	35,696	15,023	22,094
2	50,390	31,764	16,013	23,083
3	48,113	31,924	20,312	21,383
4	47,799	33,274	13,620	22,507
5	47,267	30,526	12,572	20,254
Average	48,419	32,637	15,508	21,864
Mod. of Elasticity	2.3	1.7	1.6	1.4
 Selectron 5000				
<u>468-53 5% G-60</u>		<u>3Hrs-500°F</u>	<u>3Hrs-500°F</u>	
1	48,213	33,348	12,164	22,036
2	46,576	41,136	15,018	24,262
3	54,160	34,605	14,933	24,382
4	48,086	-	14,769	25,034
5	-	-	-	-
Average	49,259	36,363	14,221	23,928
Mod. of Elasticity	2.4	2.3	1.7	1.5

TABLE NO. 30

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in Panel
	24Hrs.	48Hrs.	24Hrs.	48Hrs.	
Selectron 5000 468-53 G-50	1.3	2.0	2.4	3.3	35.3
Selectron 5000 468-53 G-60	1.4	2.2	3.3	4.5	35.8
<u>Postcured 3Hrs-500°F</u>					
Selectron 5000 468-53 G-50	*	*	*	*	
Selectron 5000 468-53 G-60	0.6	1.1	1.8	2.7	35.8
* Delaminated					

TABLE NO. 31

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs. at 400°F	Average Percent Water Absorption After 48Hrs. Aging at 500°F
Selectron 5000-468-53 G-50	0.9	1.0
Selectron 5000-468-53 G-60	1.4	1.9
Selectron 5000-468-53 G-50	*	*
Selectron 5000-468-53 G-60	2.1	2.5
* Delaminated		

Work was continued on the blending of triallylcyanurate copolymers with other heat resistant polyester resins. A mixture of 70 parts Selectron 5000-468-53 and 30 parts Selectron 5016 containing no monomers was received from the Pittsburgh Plate Glass Company. This material was coded Selectron 5900-603-4. A 1:1 blend was made of this resin and triallylcyanurate.

Contrails

Properties of the laminate prepared from this mixture are given below. Heat losses and water absorption values are considerably higher than desirable in all cases. The resin surface of the laminate was cracked considerably after postcure for 24 hours at 400°F. Flexural strengths were generally lower when compared with other commercial resins tested under similar conditions.

TABLE NO. 32

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Sel. 5900-603-4 Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F
Selectron 5900 603-4				
1	43,355	12,956	13,804	11,698
2	43,355	15,182	18,537	14,720
3	43,820	19,408	16,495	11,015
4	42,213	18,489	20,522	13,622
5	41,751	19,917	17,355	11,664
Average	42,899	17,190	17,418	12,544
Mod. of Elasticity	2.0	2.2	1.4	1.9

TABLE NO. 33

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs.	48Hrs.	24Hrs.	48Hrs.	
Selectron 5900 603-4	2.1	3.5	4.9	7.7	36.0

TABLE NO. 34

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs. Aging at 400°F		Average Percent Water Absorption After 48Hrs. Aging at 500°F	
Selectron 5900 603-4		4.7		6.6

Contrails

The use of 5 percent of Paraplex G-50 and G-60 in Selectron 5900-603-4 in laminates, produced little change on the heat deterioration and water absorption values over the straight resin. Flexural strengths were slightly lower but the cracking was not reduced.

TABLE NO. 35

Ultimate Flexural Strength and Modulus of Elasticity
181 Cloth - 301 Finish

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F
Selectron 5900 603-4 G-50				
1	46,509	27,393	25,242	11,061
2	48,276	17,231	23,089	15,458
3	38,145	23,373	21,521	13,663
4	48,216	22,296	19,915	12,783
5	42,796	22,636	20,497	14,649
Average	44,788	22,586	22,059	13,523
Mod. of Elasticity	2.2	2.0	2.0	1.6
Selectron 5900 603-4 G-60				
1	37,038	12,785	16,990	9,958
2	31,015	12,047	20,996	9,958
3	41,083	13,034	20,224	8,933
4	37,951	12,074	17,421	8,770
5	36,966	13,557	18,653	8,520
Average	36,811	12,699	18,857	9,228
Mod. of Elasticity	2.3	1.7	1.8	1.2

TABLE NO. 36

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Selectron 5900 603-4 G-50	1.9	3.1	3.4	5.0	38.0
Selectron 5900 603-4 G-60	3.4	5.4	4.8	7.4	36.7

TABLE NO. 37

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs. Aging at 400°F	Average Percent Water Absorption After 48Hrs. Aging at 500°F
Selectron 5900-603-4 G-50	3.6	4.9
Selectron 5900-603-4 G-60	7.0	8.2

Based upon the results of the initial work carried out at Douglas Aircraft, on the problem of cracking (Reference 10) in which they blended triallyl-cyanurate copolymers with other heat resistant polyester resins, it seemed desirable to conduct further studies along this line. The formulation developed at Douglas Aircraft that had the least cracking consisted of 100 parts of Laminac 4232 blended with 30 parts of Selectron 5016 and 10 parts of talc #400.

Work at Cornell Aeronautical Laboratory on blends of Laminac 4232 with Selectron 5016 and Laminac 4119 did not result in the development of crack-free laminates. Resin blends were made and one laminate was prepared from a mixture of 70 parts of Laminac 4232, 22 parts of PDL-7-732 and 8 parts of asbestos. The asbestos used was the PM-25 grade obtained from the Powhatan Mining Corporation, Baltimore, Md. Half of this laminate was postcured for 24 hours at 400°F, the other half for 3 hours at 500°F. No blistering occurred when cured for 3 hours at 500°F. The results of the tests on ultimate flexural strengths are shown in Table 38. Exposure to 500°F for 200 hours resulted in low strengths. Considerable cracking was noted also. The water absorption was satisfactory but the heat deterioration values as shown in Table 39 were excessive.

TABLE NO. 38

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Laminac 4232 Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F
Laminac 4232				
PDL-7-732-Asbestos				
1	56,447	4,571	8,857	6,474
2	67,584	6,364	11,754	6,120
3	62,645	4,979	10,026	8,223
4	58,353	5,838	10,760	6,844
5	60,780	6,875	10,056	6,873
Average	61,162	5,725	10,392	6,907
Mod. of Elasticity	2.8	-	0.7	-

TABLE NO. 38 (Continued)

Ultimate Flexural Strength and Modulus of Elasticity

Resin: Laminac 4232 Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure After Aging		After Postcure After Aging	
	24Hrs-400°F	200Hrs-500°F	24Hrs-400°F	200Hrs-500°F
Laminac 4232				
PDL-7-732 Asbestos				
1	69,455	14,715	8,685	10,141
2	69,722	15,414	8,284	11,043
3	71,702	16,826	11,264	10,243
4	61,709	15,898	11,762	10,853
5	62,174	15,819	11,762	10,804
Average	66,956	15,734	10,351	10,817
Mod. of Elasticity	2.9	2.1	1.3	1.9

TABLE NO. 39

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in Panel
	24 Hrs.	48Hrs.	24Hrs.	48Hrs.	
Laminac 4232					
<u>PDL 7-732 Asbestos</u>					
3Hrs-500°F	1.3	2.8	9.2	14.4	38.2
24Hrs-400°F	0.7	1.4	8.5	14.0	38.2

TABLE NO. 40

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs. Aging at 500°F
Laminac 4232		
PDL 7-732 Asbestos		
3Hrs-500°F	2.3	2.5
24Hrs-400°F	1.2	3.1

The blending of triallylcyanurate with other heat resistant polyester resins was continued. A solid polyester resin, Atlas 382, was obtained from the Atlas Powder Company, Wilmington, Delaware. Several different mixtures were prepared using this material. A 1:1 blend of Atlas 382 and triallylcyanurate was prepared. The solution of the Atlac into the triallylcyanurate was quite slow, so the mixture was heated, with stirring, to approximately 90°C until a clear straw colored liquid was obtained. Upon cooling, the viscosity of this resin was rather high but a laminate was prepared. Using the same proportions, another Atlac triallylcyanurate blend was prepared to which 5 percent acrylonitrile was added to reduce the viscosity. Laminating procedures were more easily carried out with this second resin.

Another blend consisting of 35 percent triallylcyanurate, 32.5 percent Atlas 382 and 32.5 percent V-135 was prepared. This material was also more viscous than desirable but a laminate was made.

All laminates prepared in the above manner after a final cure of 3 hours at 500°F were found to be badly cracked, blistered and showing signs of delamination. No tests were conducted on any of these specimens.

A 1:1 mixture of Laminac 4119, a styrenated alkyd, and Laminac 4232 was made and a laminate prepared. Heat deterioration and water absorption values after aging at 400°F were satisfactory. After similar exposure at 500°F, excessive degradation occurred which tended to result in high water absorption values. Cracking was also unsatisfactory; much of the surface resin was burned off leaving the glass fibers visible. Flexural strengths at elevated temperatures were also lower than desirable.

Two more laminates were made using this blend of Laminac 4119 and 4232. One was pigmented with 40% Surfex MM and the other 40% Kalite. Slight improvements were noted in cracking and degradation of surface resin as well as in the percent loss of weight after aging 48 hours at 500°F, see Table 41. Water absorption values as noted in Table 42 were similarly improved but were of too great a magnitude to be acceptable. Flexural strengths were also lower than desirable at 500°F, see Table 45.

TABLE NO. 41

Heat Deterioration
Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Laminac 4119 Clear 50%+ 4232 Clear 50%	0.9	1.3	14.6	18.0	35
Laminac 4119 50%+ 4232 50%+ 40% Surfex MM	1.2	1.7	13.1	16.5	42
Laminac 4119 50%+ 4232 50%+ 40% Kalite	1.1	1.6	11.1	14.7	43

TABLE NO. 42

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
Laminac 4119 Clear 50%+ 4232 Clear 50%	0.6	9.7
Laminac 4119 50%+4232 50%+ 40% Surfex MM	1.7	9.1
Laminac 4119 50%+4232 50%+ 40% Kalite	2.0	8.6

Selectron 5016, a styrene modified heat resistant alkyd, was also evaluated. Physical properties of the laminate prepared from the resin were satisfactory at 400°F but at 500°F, the resin deteriorated badly. Fillers were used to alleviate this degradation at 500°F but the pigmented laminates were still unsatisfactory.

Data on heat loss and water absorption are given in Tables 43 and 44. The data on ultimate flexural strength is given in Table 46.

TABLE NO. 43

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs.	48Hrs.	24Hrs.	48Hrs.	
Selectron 5016 Clear	1.1	2.0	15.3	20.6	38
Selectron 5016+ 40% Surfex MM	0.8	1.3	12.7	17.0	40
Selectron 5016+ 40% Kalite	2.2	3.6	8.4	14.8	39

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
Selectron 5016 Clear	1.0	10.3
Selectron 5016+ 40% Surfex MM	1.4	9.8
Selectron 5016+ 40% Kalite	2.4	10.2

Contrails
TABLE NO. 45

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Laminac 4232 Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure	After Aging	After Postcure	After Aging
	24Hr-400°F	200Hrs-500°F	24Hr-400°F	200Hrs-500°F
50% Laminac 4232+				
50% Laminac 4119				
No Pigment				
1	45,259	10,261	10,285	6,300
2	45,191	9,813	11,157	5,273
3	46,525	10,043	11,861	5,479
4	42,740	-	9,044	7,998
5	42,240	-	8,698	6,134
Average	44,391	10,039	10,209	6,237
Mod. of Elasticity	2.6	0.9	2.1	-
50% Laminac 4232+				
50% Laminac 4119				
40% Surfex MM				
1	51,171	19,731	8,523	10,464
2	47,692	21,934	9,348	10,593
3	44,982	26,229	9,188	11,755
4	41,187	14,801	10,217	10,748
5	41,455	18,614	9,078	11,208
Average	45,297	20,262	9,271	10,954
Mod. of Elasticity	2.5	1.9	1.3	1.0
50% Laminac 4232+				
50% Laminac 4119				
40% Kalite				
1	43,491	33,522	9,383	7,495
2	42,245	37,680	10,845	8,916
3	39,216	37,005	11,165	9,385
4	39,177	40,503	11,460	8,005
5	42,683	46,079	11,614	9,160
Average	41,362	38,957	10,893	8,592
Mod. of Elasticity	2.4	2.4	1.5	0.9

TABLE NO. 46

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Selectron 5016 Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°F
Selectron 5016				
No Pigment				
1	40,274	No load	7,574	918
2	44,246	"	8,786	356
3	44,735	"	9,055	578
4	43,279	"	9,064	3,059
5	46,813	"	8,072	-
Average	43,869	-	8,510	1,228
Mod. of Elasticity	2.4		1.5	-
 Selectron 5016				
40% Surfex MM				
1	44,984	No load	12,296	4,323
2	44,141	"	10,883	2,906
3	46,687	"	10,721	3,536
4	45,512	"	10,896	5,203
5	46,066	"	11,257	5,025
Average	45,478	-	11,211	4,199
Mod. of Elasticity	2.7		1.9	-
 Selectron 5016				
40% Kalite				
1	46,785	28,246	12,967	7,779
2	42,371	29,060	10,497	7,518
3	46,970	32,131	10,719	6,680
4	44,014	24,451	14,067	7,689
5	44,368	30,949	12,054	6,258
Average	44,902	28,967	12,061	7,185
Mod. of Elasticity	2.8	1.9	1.8	0.7

E. Evaluation of New Triallylcyanurate Copolymers and Other Heat Resistant Resins

Four triallylcyanurate copolymer resins were received from the Pittsburgh Plate Glass Company for evaluation. These resins were all prepared from the same batch of triallylcyanurate and other raw materials were likewise from the same lots whenever possible.

Selectron 5000-468-53, which is commercially available, has been previously evaluated and the data outlined. This possessed a high crosslinking density and was included in the group to act as a control of the other three products.

Selectron 5000-603-26 possessed a somewhat lower crosslinking density than the control resin as a result of less unsaturated acid being used in the formulation. Selectron 5000-603-27 was of a still lower crosslinking density. Selectron 5000-603-28 was an alkyd in triallylcyanurate which has shown a considerable decreased tendency to crack or craze in the cast form.

After the recommended cure of 30 minutes at 170°F, 30 minutes at 300°F and 3 hours at 500°F, the laminate prepared from Selectron 5000-603-27 was delaminated to such an extent that no tests were conducted on it. All other laminates of this series showed no signs of blistering or delaminating after this curing cycle.

Another laminate from Selectron 5000-603-27 was prepared and cured as follows: 30 minutes at 170°F in the press, 30 minutes at 300°F and 24 hours at 400°F in an air circulating oven.

The laminates were examined for cracking, heat loss on exposure to 400° and 500°F, and water absorption. The modulus of elasticity and ultimate flexural strength at room temperature and at 500°F after 200 hours at 500°F were also determined.

The cracking was practically eliminated in the laminate made from Selectron 5000-603-27 and was considerably reduced in the laminate made from Selectron 5000-603-28. Figure 17 on page 115 shows a 10X microphotograph of the typical cracking obtained on laminates made from these four resins.

The data on heat deterioration and water absorption are given in Tables 47 & 48. The water absorption and heat loss for these four resins were considered satisfactory.

TABLE NO. 47

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Selectron 5000-468-53**	1.4	2.1	1.2	1.8	39.2
Selectron 5000-603-26**	1.2	1.7	0.9	1.4	40.4
Selectron 5000-603-27*	0.4	2.4	2.4	3.3	37.3
Selectron 5000-603-28**	1.4	2.0	1.2	1.9	39.3

TABLE NO. 48

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F		Average Percent Water Absorption After 48Hrs Aging at 500°F	
Selectron 5000-468-53**	4.3		4.3	
Selectron 5000-603-26**	3.8		3.7	
Selectron 5000-603-27*	0.8		0.8	
Selectron 5000-603-28**	4.0		4.0	

* Postcured 24 hours at 400°F

** Postcured 3 hours at 500°F

The modulus of elasticity and ultimate flexural strength are given in Table 49.

The flexural strength at 500°F after exposure to 500°F for 200 hours for laminates made from Selectron 5000-468-53, 5000-603-28 and Selectron 5000-603-27 is considered to be very good. Selectron resin 5000-603-27 particularly merits further evaluation due to its small amount of cracking and high flexural strength after 200 hours exposure to 500°F.

TABLE NO. 49

Ultimate Flexural Strength and Modulus of Elasticity
181 Cloth 301 Finish
Parallel Laminate Tested Flatwise

Resin	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 3Hrs-500°F	After Aging 200Hrs-500°F	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F
<u>Selectron 5000-468-53</u>				
1	45,558	31,803	26,357	24,832
2	49,294	32,148	23,678	23,698
3	47,689	32,043	-	26,385
4	48,241	25,751	23,874	20,985
5	48,524	33,299	24,715	26,622
Average	47,861	31,009	24,656	24,504
Mod. of Elasticity	2.5	2.3	2.0	1.8
<u>Selectron 5000-603-26</u>				
1	46,550	-	21,992	17,418
2	45,302	32,430	22,538	21,246
3	40,808	32,816	22,310	20,971
4	45,232	26,492	16,273	17,279
5	49,055	33,348	19,887	20,089
Average	45,389	31,017	21,200	19,401
Mod. of Elasticity	2.2	2.1	1.6	1.5
<u>Selectron 5000-603-27</u>				
1	51,693 *	42,254	19,523 *	31,618
2	54,075	45,076	18,969	32,154
3	55,485	43,682	19,208	27,960
4	54,217	44,404	19,032	30,743
5	51,471	50,514	19,332	29,547
Average	53,388	45,186	19,213	30,404
Mod. of Elasticity	2.4	2.3	1.7	1.6
<u>Selectron 5000-603-28</u>				
1	48,682	30,396	24,236	23,822
2	49,857	30,533	27,136	24,279
3	46,448	32,067	29,904	23,642
4	50,713	28,498	30,970	24,498
5	48,602	28,771	26,234	25,105
Average	48,860	30,053	27,696	24,269
Mod. of Elasticity	2.7	2.4	2.1	1.8

* Postcured 24 hours at 400°F

Continued

Laminac 4233 which contains 25 percent instead of 50 percent of triallyl-cyanurate was compared with Laminac 4232 containing 50 percent triallyl-cyanurate. Cured for 3 hours at 500°F, Laminac 4232 is somewhat superior to Laminac 4233 in respect to weight loss on heat aging. The water absorption values after 48 hours at 500°F are about equal, however. Resistance to cracking of Laminac 4233 is rather poor. Cracking was quite noticeable after the initial press cure and became worse after the post curing cycle. Flexural strengths of Laminac 4233 laminates were about equal to laminates prepared from Laminac 4232. The data obtained on water absorption, heat loss and flexural strength on laminates from this resin are outlined in Tables 50, 51, 52. below. Due to the extreme amount of cracking, no further evaluation tests were conducted on Laminac 4233. See Figure 14.

TABLE NO. 50

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Laminac 4233	2.7	4.1	3.4	5.0	39.3

TABLE NO. 51

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
Laminac 4233	4.3	4.6

TABLE NO. 52

Ultimate Flexural Strength and Modulus of Elasticity
181 Cloth - 301 Finish

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure For 3Hrs-500°F	After Aging 200Hrs-500°F	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F
Laminac 4233				
Average	49,020	20,338	24,268	21,343
Mod.Elasticity	2.4	2.7	2.0	1.4

Vibrin X-1068, a new heat resistant resin developed by Naugatuck Chemical Co. (Reference 3) was also briefly examined for cracking, heat loss, water absorption and flexural strength.

The cracking of the X-1068 laminates was found to be slightly less than standard triallylcyanurate laminates. The heat loss, water absorption and flexural strengths are given in Tables 53, 54 and 55.

TABLE NO. 53

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Vibrin X-1068	0.8	1.4	5.0	6.9	31

TABLE NO. 54

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
Vibrin X-1068	2.7	3.1

TABLE NO. 55

Ultimate Flexural Strength and Modulus of Elasticity
181 Cloth - 301 Finish

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F
Vibrin X-1068 Average	73,873	32,448	13,799	24,316
Mod. Elasticity	3.0	2.4	2.0	1.8

Contrails

Laminac 4119, Selectron 5016, Hetron IX-VIII and X-63 resins were included in this evaluation since previous work had indicated that these resins were above average in heat resistance or did not degrade rapidly upon exposure to elevated temperatures.

Specimens 1/8" x 1" x 3" were cut from these test laminates. One set of three specimens from each laminate was postcured in a circulating oven for 48 hours at 400°F and one set of three specimens at 500°F for 48 hours. After cooling to room temperature in a dessicator, the loss in weight of each sample was recorded. Specimens were then placed in distilled water for 24 hours at 75°F. At the completion of the immersion, samples were wiped dry of excess water and weighed again as outlined in Specification L-P-406B. The average percentage gain in weight for three specimens was calculated and is tabulated in the table below.

All the specimens except Hetron X-63 and IX-VIII had turned a light brown after exposure to 400°F for 48 hours. The Hetron resins had turned a dark brown. Observation of the specimens with the naked eye showed no cracking and no loss in gloss of the laminate surface. Upon examination with the 10X microscope, all the laminates showed small cracks running through the laminate surface.

All the specimens after heating for 48 hours at 500°F had turned to a very dark brown or black color. The surface of the laminates showed bare glass fabric where the resin had degraded or charred off. The laminates with Hetron X-63 and IX-VIII, Selectron 5016 and Laminac 4119 + 4232 all showed signs of delamination when viewed from the edge. Examination under a 10X microscope indicated that the resins had cracked and degraded so there was no resin covering the woven glass fabric on the surface.

The laminates with clear and pigmented Selectron 5016, under microscopic examination, showed only fine cracks in the resin surface when exposed to 400°F; however, the same specimens when exposed to 500°F were very soft and flexible and had deteriorated so that they could be considered to have failed. Laminac 4119 + 4232 was similar in appearance to the Selectron 5016 specimen.

This removal of resin from the laminate surface probably accounts for the high heat loss and high percentage of water absorption of 5 to 10 percent for the laminates listed in Tables 56 and 57.

Based upon this preliminary evaluation of these styrene-copolymer resins, it can be stated that they were unsatisfactory at temperatures above 400°F due to their rapid degradation. However, the Laminac 4119 and Selectron 5016 resins were combined with triallylcyanurate resins to determine if this would reduce cracking. These data are outlined in the section on resin combinations.

Contrails
TABLE NO. 56

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs-	48Hrs	
Hetron X-63	0.8	1.2	16.8	19.8	36.2
Hetron IX-VIII	0.9	2.0	13.4	14.3	37.3
Selectron 5016	1.1	2.0	15.3	20.6	38.0
Lam. 4119 + 4232	0.9	1.3	14.6	18.0	35.0

TABLE NO. 57

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48 Hrs Aging at 400°F		Average Percent Water Absorption After 48 Hrs Aging at 500°F	
Hetron X-63	0.1		7.2	
Hetron IX-VIII	1.7		1.0	
Selectron 5016	1.0		10.3	
Lam. 4119 + 4232	0.6		9.7	

F. Investigation of Catalysts

Previous work on triallylcyanurate copolymers at Cornell Aeronautical Laboratory indicated that catalyst systems had considerable influence on ultimate high temperature strength. One catalyst, di-t-butyl peroxide was found to give the highest strength.

To investigate the effect this catalyst had on cracking, as well as other properties, laminates were prepared from Vibrin 135, Laminac 4232, and Selectron 5000-468-53, catalyzed with 1 percent di-t-butyl peroxide. In general, a longer initial curing period was required as a result of the use of this high temperature catalyst. Approximately three hours in the press at 220°F was required for initial cure. No significant reduction in the cracking of the laminates made from these three resins was noted. Considerable improvement was noted in flexural strengths of the laminate after 200 hours at 500°F. The tendency of the V-135 laminate to blister also appeared to be eliminated by the use of di-t-butyl peroxide. The comparative data on heat deterioration and water absorption are given in Tables 58 and 59. The results obtained on flexural strengths are outlined in Table 60.

TABLE NO. 58

Heat Deterioration - Average Weight Loss in Percent
Commercially Available Resins with 1 Percent Di-t-Butyl Peroxide

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
Laminac 4232	1.4	2.0	1.8	2.8	41.1
V-135	0.4	0.7	1.6	2.1	34.8
Selectron 5000-468-53	1.1	1.6	1.2	2.0	38.6

TABLE NO. 59

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48 Hrs Aging at 400°F	Average Percent Water Absorption After 48 Hrs Aging at 500°F
Laminac 4232	5.2	5.8
V-135	3.7	4.3
Selectron 5000-468-53	3.4	4.7

Ultimate Flexural Strength and Modulus of Elasticity
Resins: Laminac 4232, Vibrin 135, Selectron 5000 468-53
Cloth: 181-301

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F	After Postcure 3Hrs-500°F	After Aging 200Hrs-500°F
Laminac 4232				
1% DTBP				
1	58,098	35,186	27,003	20,087
2	56,043	25,316	25,940	18,961
3	52,208	27,098	29,049	20,087
4	58,476	25,079	25,124	20,572
5	56,938	26,849	25,882	20,533
Average	56,353	25,906	26,600	20,048
Mod. of Elasticity	2.8	2.1	1.0	2.5
Vibrin 135				
1% DTBP				
1	72,909	36,792	25,540	34,379
2	72,036	36,007	28,763	35,480
3	74,308	42,756	27,915	33,834
4	67,753	35,496	25,346	30,351
5	74,974	40,283	26,344	35,843
Average	72,396	38,267	26,782	33,977
Mod. of Elasticity	3.4	3.0	1.1	2.7
Selectron 5000 468-53				
1% DTBP				
1	51,060	34,622	29,820	27,242
2	50,609	32,120	28,640	28,468
3	50,721	31,600	27,780	28,750
4	49,840	31,900	25,982	26,200
5	51,200	32,250	26,400	29,052
Average	50,684	32,498	27,724	27,942
Mod. of Elasticity	2.6	2.3	2.1	1.7

Continued

The results of these tests and others previously conducted, indicates that there is probably greater cross linking of the triallylcyanurate and the alkyd which accounts for the generally higher flexural strengths after exposure to 500°F for 200 hours, especially with Vibrin 135. The use of this and other catalyst systems merits further investigation to determine their influence on resistance of the triallylcyanurate copolymer resins to thermal degradation.

Preliminary tests had been conducted on the use of overlay sheets of glass fibers or asbestos and it was found that the use of asbestos tended to reduce the cracking of the resin on the surface but the flexural strength after 200 hours exposure at 500°F was not satisfactory. However, due to the results of the tests of Vibrin 135 with di-tertiary butyl-peroxide, another laminate was prepared using these two ideas.

This particular laminate used V-135 catalyzed with di-tertiary butyl-peroxide. In addition to the usual 12 plies of 301 cloth, it contained overlay sheets of asbestos 9526 obtained from the Raybestos Manhattan Company, Asbestos Textile Division, Manheim, Pa. This asbestos sheet, used on each surface, was nominally .010" in thickness.

This laminate exhibited no signs of cracking even when examined under a 10X microscope. Also there were no signs of resin degradation on the surface of the laminate after 200 hours exposure to 500°F as is normally seen with woven glass surfaced laminates.

The room temperature and 500°F flexural strength after exposure to 500°F for 200 hours, on a comparative basis, was excellent. See Table 61.

The water absorption after 24 hours immersion and the heat deterioration were low and very satisfactory. The data obtained on the properties are outlined in Tables 62 and 63.

If there are no unforeseen conditions militating against the use of asbestos overlays, this method appears to be a satisfactory solution to the problem of cracking and water absorption. It also improves the flexural strength after 200 hours exposure to 500°F.

TABLE No. 61

Ultimate Flexural Strength and Modulus of Elasticity
Vibrin 135 - 181-301 Cloth with Overlay 9526 Asbestos

Resin No.	Room Temperature Strength Tested at 75°F		High Temperature Strength Tested at 500°F	
	After Postcure	After Aging	After Postcure	After Aging
	24 Hrs-400°F	200Hrs-500°F	24Hrs-400°F	200Hrs-500°F
V-135, 1% DTBP				
9526 Asbestos				
1	52,656	38,604	17,002	31,309
2	51,802	38,179	22,101	29,560
3	52,220	35,643	21,673	32,036
4	50,144	32,809	17,920	23,691
5	55,571	36,132	19,477	32,468
Average	52,479	36,274	19,635	29,813
Mod. of Elasticity	2.5	2.3	1.8	1.8

TABLE NO. 62

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Weight Aged at 400°F		% Loss in Weight Aged at 500°F		% Resin in Panel
	24Hrs	48Hrs	24Hrs	48Hrs	
V-135, 1% DTBP					
9526 Asbestos					
Surface Overlay	1.4	2.1	1.7	2.3	38.2

TABLE NO. 63

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F		Average Percent Water Absorption After 48Hrs Aging at 500°F	
V-135, 1% DTBP				
9526 Asbestos				
Surface Overlay		2.4		3.2

G. Investigation of Anti-Oxidants and Postcuring in Inert Atmospheres

Previous work has shown that polyester laminates, heat aged in sealed glass tubes, lose little strength. This data suggests the problem of oxidation of polyester resins may be analogous to the degradation of rubber by oxygen at elevated temperatures. This indicates that the use of anti-oxidants, similar to those used in rubber, might stabilize triallylcyanurate-alkyd copolymers against oxidation.

One of these, Agerite, which is chemically N, N'-di-B-naphthyl-p-phenylenediamine, was tried in castings of Laminac 4232, Vibrin 135 and Selectron 5000-468-53. In castings 0.5 percent of benzoyl peroxide with 0.5 and 1.0 percentages of Agerite were used. This anti-oxidant initially caused a rapid polymerization with a high exotherm. The cured resin was found to be soft and rubbery with a Barcol Hardness of less than 10. Since most of the commercially available anti-oxidants were similar amine compounds, they were not tested further.

Use of the normal type anti-oxidants, hydroquinone, etc. was not considered in this investigation, since these compounds are employed generally to inhibit autoxidation or polymerization and, in the latter instance, their use would lead to difficulties in the curing of the laminate. It was believed that at 400-500°F these compounds would decompose and lose their usefulness.

One anti-oxidant, Wingstay S (a styrenated phenol), was obtained from the Goodyear Tire & Rubber Company. Since this material was not an amine, it was considered worth evaluating. Initially, investigations using this material were confined to resin castings of Laminac 4232 and V-135. The various percentages used were 0.5, 1.0, 3.0 and 5.0.

After curing, the cast specimens were examined for cracking and hardness. All samples had Barcol Hardnesses in the range of 40-60 as compared to 60-70 for straight resin samples, although cracking was reduced slightly.

Two laminates were then prepared, one from Laminac 4232 and one from V-135, each containing two percent Wingstay S by weight of the resin. No difficulty was encountered in the curing of these laminates. Heat deterioration and water absorption tests were carried out. The heat loss was slightly less than with the clear resin and the water absorption values slightly higher. Cracking was not improved however.

A laminate was prepared from V-135, 5 percent Paraplex G-60, 5 percent Wingstay S with 9526 Asbestos sheet surface overlay. The heat loss and water absorption values were considerably reduced when compared to the other laminates. No cracking was observed. Flexural strengths were found to be satisfactory. The flexural strength after 200 hours at 500°F was very good. Further work with Wingstay S appears to be desirable.

The data obtained on the Vibrin 135 with G-60, Wingstay S, with surface overlay of 9526 Asbestos, such as water absorption, heat loss and flexural strength, are given in Tables 64, 65 and 66.

It is well known that the unsaturated alkyd portion of the polyester resins is readily attacked by oxygen. This oxidation probably results in rupture of the alkyd chain and the formation of short chain reaction products which probably accounts for the heat degradation of the laminate and loss of strength.

To check this theory on triallylcyanurate copolymer laminates, a method of aging the samples in an inert atmosphere of nitrogen was investigated. An air tight stainless steel box was obtained having an inlet and outlet tube for the flow of nitrogen. A slotted metal plate was placed in the bottom of the box to hold the 1/8" x 1" x 4" laminate specimens in an upright position so the nitrogen would flow around the specimens.

The box was placed in a circulating air oven at 500°F and kept at this temperature for 200 hours with a constant flow of nitrogen being maintained through the air tight box. At the end of this period, specimens were removed and tested for flexural strength and modulus of elasticity.

The theory that the loss in strength is due to oxidation seems to be verified by comparing flexural strength data of samples, heat aged in air and in nitrogen. Ultimate flexural strengths of the nitrogen aged samples of both clear and pigmented resins were considerably higher in every case when tested at room temperature and at 500°F after 200 hours at 500°F. The data obtained are outlined in Tables 68 through 72.

With the exception of samples prepared from Selectron 5016, flexural strengths of samples which were cured for 200 hours at 500°F under nitrogen were higher than those which had been cured for only 24 hours in air at 400°F, when tested at 500°F. The problem of cracking was not reduced when the specimens were aged in nitrogen but the resin degradation and charring off of the surface resins, as normally experienced after 200 hours at 500°F in air, were not apparent after 200 hours at 500°F in nitrogen.

To determine how the loss in strength progresses in a typical triallylcyanurate copolymer laminate when it is aged at 500°F, in an inert atmosphere, the following test was carried out.

A 1/8" x 22" x 22" 181-301 glass cloth laminate impregnated with Laminac 4232 was cured in the press for 3 hours at 220°F, then put into an air circulating oven at 500°F for 3 hours at which time the laminate was thought to have reached full cure and strength. The panel was removed from the oven and held flat between aluminum caul plates until it cooled to room temperature.

TABLE NO. 64

Ultimate Flexural Strength and Modulus of Elasticity
Cloth: 181 with surface plies of 9526 Asbestos

Resin No.	Room Temperature Strength		High Temperature Strength	
	Tested at 75°F		Tested at 500°F	
	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°	After Postcure 24Hrs-400°F	After Aging 200Hrs-500°
V-135, G-60 5%				
5% Wingstay S				
1	51,641	33,350	9,410	24,152
2	55,518	35,656	9,440	22,647
3	56,076	34,196	10,169	22,150
4	52,783	33,290	10,260	26,194
5	51,152	34,600	10,878	25,287
Average	53,434	34,258	10,031	24,086
Mod. of Elasticity	2.0	1.5	1.2	1.2

TABLE NO. 65

Heat Deterioration - Average Weight Loss in Percent

Resin No.	% Loss in Wgt. Aged at 400°F		% Loss in Wgt. Aged at 500°F		% Resin in panel
	24Hrs	48Hrs	24Hrs	48Hrs	
V-135 2% Wing S	1.8	2.8	2.7	3.8	34.6
4232 2% Wing S	2.5	3.9	3.7	5.5	36.8
V-135 G-60 5%	0.9	1.1	1.5	2.1	37.2
5% Wingstay S					
9526 Asbestos Overlay					

TABLE NO. 66

Water Absorption After 24 Hours Immersion

Resin No.	Average Percent Water Absorption After 48Hrs Aging at 400°F	Average Percent Water Absorption After 48Hrs Aging at 500°F
V-135 2% Wing S	4.9	5.3
4232 2% Wing S	5.8	6.6
V-135 G-60 5%	2.8	2.0
5% Wingstay S		

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Seventy-five specimens 1" x 4" were cut from the panel. Three specimens were saved for flexural tests, and the seventy-two remaining specimens were put into a stainless steel box in a perpendicular position. The air tight box was put into an oven at 500°F, and nitrogen flowed through the box during the aging of the specimens. After each hour, for twenty-four hours, three specimens were removed. The ultimate flexural strength and the modulus of elasticity were then determined at room temperature. The data given in Table 67 are the average for three specimens. Figure 19 shows how the loss in strength progresses when aged at 500°F in nitrogen.

Based upon these tests, it can be stated that the optimum properties of a typical triallylcyanurate copolymer are obtained after three to four hours exposure at 500°F. After further exposure to this temperature in an inert atmosphere, the laminate strength is slowly reduced as shown in Figure 18. Further checking of aging in an inert atmosphere for periods from 24 to 200 hours, indicates that the curve becomes approximately asymptotic to a line at a flexural strength of 32,000 psi.

TABLE NO. 67

Heat Aging of Laminac 4232 Laminate at 500°F Under Nitrogen
(38% Resin)

Time Aged(Hrs)	Ultimate Flexural Strength PSI at 75°F	Modulus of Elasticity - PSI at 75°F
0	51,000	2.7
1	49,000	2.7
2	47,000	2.6
3	46,000	2.6
4	45,000	2.6
5	49,000	2.6
6	48,000	2.7
7	46,000	2.7
8	46,000	2.7
9	42,000	2.7
10	42,000	2.6
11	45,000	2.8
12	42,000	2.7
13	43,000	2.4
14	43,000	2.5
15	43,000	2.5
16	43,000	2.7
17	41,000	2.5
18	40,000	2.7
19	40,000	2.7
20	40,000	2.7
21	36,000	2.1
22	33,000	2.2
23	39,000	2.3
24	37,000	2.3

TABLE NO. 68

VIBRIN 135 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Vibrin 135 Cloth: 181-301

	Tested at 75°F		Tested at 500°F	
	Postcured 24Hrs-400°F	Aged 200Hrs-500°F	Postcured 24Hrs-400°F	Aged 200Hrs-500°F
Vibrin 135 Clear No Pigment				
Average Flexural Strength Modulus of Elasticity	52,292 2.8	25,416 2.2	34,471 2.4	17,353 1.2
			8,505 2.1	29,452 1.9
Vibrin 135 40% Surfex MM				
Average Flexural Strength Modulus of Elasticity	52,286 2.6	40,855 2.7	42,508 3.0	21,862 1.5
			18,764 1.9	32,340 2.1
Vibrin 135 40% Kalite				
Average Flexural Strength Modulus of Elasticity	52,499 3.1	15,762 1.6	41,181 2.6	16,052 1.3
			13,432 1.9	31,353 2.2
Vibrin 135 20% Mica				
Average Flexural Strength Modulus of Elasticity	43,746 3.0	8,379 1.6	25,718 2.4	7,838 0.7
			5,965 0.7	16,707 1.4
Vibrin 135 10% Asbestos				
Average Flexural Strength Modulus of Elasticity	61,629 2.5	10,591 1.8	56,592 2.6	12,495 1.0
			10,062 1.3	38,515 2.0

TABLE NO. 69
LAMINAC 4232 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity

	Tested at 75°F			Tested at 500°F		
	Postcured 24Hrs-400°F	Aged 200Hrs-500°F	Aged 200Hrs-500°F	Postcured 24Hrs-400°F	Aged 200Hrs-500°F	Aged 200Hrs-500°F
Laminac 4232 No Pigment						
Average Flexural Strength	44,286	21,816	28,971	18,658	18,953	30,166
Modulus of Elasticity	2.0	2.0	2.6	1.6	1.3	1.6
Laminac 4232 40% Surfex MM						
Average Flexural Strength	45,267	29,453	40,310	20,202	14,736	30,689
Modulus of Elasticity	2.7	2.3	2.6	1.9	1.4	1.9
Laminac 4232 40% Kalite						
Average Flexural Strength	42,077	19,799	34,573	17,922	19,305	30,169
Modulus of Elasticity	2.7	2.0	3.0	1.8	1.3	2.1
Laminac 4232 20% Mica						
Average Flexural Strength	45,861	15,866	38,992	11,405	12,788	36,314
Modulus of Elasticity	2.1	1.9	2.5	1.2	1.1	2.0
Laminac 4232 10% Asbestos						
Average Flexural Strength	51,024	23,087	44,998	20,677	21,170	33,960
Modulus of Elasticity	2.4	2.3	2.3	1.6	1.6	1.9

TABLE NO. 71

SELECTION 5016 LAMINATES

Ultimate Flexural Strength and Modulus of Elasticity
Resin: Selection 5016 Cloth: 181-301

Selection 5016 No Pigment	Tested at 750F			Tested at 5000F		
	Postcured 24Hrs-400°F	Aged 200Hrs-500°F	Aged 200Hrs-500°F	Postcured 24Hrs-400°F	Aged 200Hrs-500°F	Aged 200Hrs-500°F-N2
1	40,274	No load	22,106	7,574	918	4,103
2	44,246	"	24,402	8,786	356	5,371
3	44,735	"	24,071	9,055	578	5,360
4	43,279	"	22,854	9,064	3,059	4,652
5	46,813	"	24,059	8,072	-	4,647
Average	43,869	-	23,498	8,510	1,228	4,826
Modulus of Elasticity	2.4		2.5	1.5	-	0.5
Selection 5016 40% Surfex MM						
1	44,984	No load	37,168	12,296	4,323	8,826
2	44,141	"	36,770	10,883	2,906	8,127
3	46,687	"	38,016	10,721	3,536	8,844
4	45,512	"	35,426	10,896	5,203	8,438
5	46,066	"	38,052	11,257	5,025	8,513
Average	45,478	-	37,086	11,211	4,199	8,550
Modulus of Elasticity	2.7		2.8	1.9	-	1.1
Selection 5016 40% Kalite						
1	46,785	28,246	20,176	12,967	7,779	9,015
2	42,371	29,060	35,558	10,497	7,518	8,142
3	46,970	32,131	33,241	10,719	6,680	7,618
4	44,014	24,451	39,215	14,067	7,689	7,222
5	44,368	30,949	22,361	12,054	6,258	8,600
Average	44,902	30,110	30,110	12,061	7,185	8,119
Modulus of Elasticity	2.8	2.2	2.2	1.8	0.7	0.7

H. Comparative Evaluation of Triallylcyanurate Laminates

In addition to the data obtained in Section A on the commercially available triallylcyanurate resins, the following data were determined on laminates of these resins, to compare with the better resins formulated during this investigation.

1. Tensile strength
2. Compressive strength
3. Wet and dry flexural strength at room temperature
4. Water absorption after thirty days immersion
5. Water absorption after two hours immersion in boiling water.

In all cases, the resins used in the preparation of these test laminates were catalyzed with 0.5 percent of benzoyl peroxide and 0.5 percent of di-tertiary butyl peroxide. In some cases, one set of the laminates was cured for 24 hours at 400°F and another set at 500°F for 3 hours. The comparative results obtained are outlined in Tables 73 through 76 on the following pages.

If the electrical properties are satisfactory, resin 152 should be made on a pilot plant basis and examined further and evaluated for conformance to Specification MIL-R-25042 (Resin Polyester, High Temperature Resistant, Low Pressure Laminating).

TABLE NO. 73

Ultimate Flexural Strength at 75°F - PSI
Dry and After 30 days Immersion in Water
Average of 5 Specimens Postcured 24 Hours at 400°F

Resin No.	Dry	Wet	Percent Retention Strength
Vibrin 135	56,100	50,400	90
Laminac 4232	51,500	47,300	92
Selectron 5000 468-53	46,200	43,000	93
X-1068	58,500	46,800	80
137	58,200	49,500	85
143-ACN	52,700	50,000	95
152	49,600	45,300	91

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TABLE NO. 74

Ultimate Tensile and Compressive Strength After 200 Hours Aging at Test
Temperature - Average of 5 Specimens

Resin	Test Temperature °F	Tensile Strength PSI	Compressive Strength PSI
Vibrin 135	400	28,600	24,800
Laminac 4232	400	34,900	20,900
Selectron 5000 468-53	400	26,200	11,000
X-1068	400	29,800	18,100
141	400	25,200	12,200
137	400	28,300	13,900
143-ACN	400	25,800	15,800
152	400	29,000	17,300
Vibrin 135	500	22,400	16,400
Laminac 4232	500	23,300	13,300
Selectron 5000 468-53	500	18,500	8,200
X-1068	500	26,800	9,300
141	500	13,200	7,200
137	500	17,400	9,100
143-ACN	500	16,100	8,000
152	500	18,500	9,800

Note: All these laminates were postcured for 24 hours at 400°F before aging 200 hours.

TABLE NO. 75

Water Absorption in Percent of Laminates 181-301 Fabric
Average of 3 Specimens

Resin No.	30 day Immersion		2 Hour Boil	
	Postcured 24Hrs-400°F	Postcured 3Hrs-500°F	Postcured 24Hrs-400°F	Postcured 3Hrs-500°F
Vibrin 135	2.5	3.6	2.4	3.8
Laminac 4232	3.6	4.2	3.5	4.2
Selectron 5000 468-53	3.6	4.4	3.4	4.5
X-1068	3.5	4.3	3.1	4.3
141	0.7	0.9	0.9	1.1
137	6.5	7.1	5.9	6.9
143-ACN	0.4	0.5	0.6	0.8
152	0.5	0.7	0.6	0.8

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TABLE NO. 76

Ultimate Tensile and Compressive Strength After 0.5 Hours at Test
Temperature - Average of 5 Specimens

Resin	Test Temperature °F	Tensile Strength PSI	Compressive Strength PSI
Vibrin 135	75	41,800	36,000
Laminac 4232	75	36,900	29,900
Selectron 5000-468-53	75	34,000	27,500
X-1068	75	41,500	32,000
141	75	32,500	26,400
137	75	36,200	34,900
143-ACN	75	34,000	27,000
152	75	35,600	30,100
Vibrin 135	400	29,800	16,300
Laminac 4232	400	36,600	17,900
Selectron 5000-468-53	400	27,300	11,900
X-1068	400	29,500	19,900
141	400	26,000	10,800
137	400	32,800	15,700
143-ACN	400	29,700	14,200
152	400	32,400	16,000
Vibrin 135	500	26,300	14,600
Laminac 4232	500	32,000	13,200
Selectron 5000-468-53	500	21,500	10,300
X-1068	500	26,200	13,000
141	500	16,800	8,000
137	500	19,900	11,800
143-ACN	500	19,200	11,000
152	500	21,700	12,600

Note: all these laminates were postcured for 24 hours at 400°F before testing

IV. SUMMARY AND CONCLUSIONS

The tendency of commercially available triallylcyanurate resins to crack upon postcure and to become thermally degraded after exposure to 500°F for periods up to 200 hours was investigated. These studies indicate that the cracking of these resins is severe. The cracking of the laminates can be attributed to the crosslinking of the triallylcyanurate monomer. No correlation between the amount of cracking and water absorption was found.

While the degradation of the laminates was greatly reduced when they were cured and heat aged in an inert atmosphere of nitrogen, it was found that the cracking was not eliminated or significantly reduced.

A study of the influence of inert pigments as fillers to reduce the cracking showed that although the cracking was not eliminated, it was materially reduced with forty percent of pigment. In general, the flexural strength of laminates using 40 percent of carbonate fillers, based upon the weight of the resin, was comparable to the unfilled laminates. The most satisfactory pigment of those investigated was Surfex MM, a treated calcium carbonate filler.

The use of a .010" thick overlay of asbestos felt on both surfaces of of a 1/8" thick 181-301 glass reinforced laminate, eliminated cracking and reduced the thermal degradation as well as the water absorption. This system appeared to be the most practical solution to the problem of cracking.

The use of external plasticizers was found to reduce cracking but they also tend to reduce the strength properties after exposure to 500°F for 200 hours.

In the investigation of new alkyd triallylcyanurate copolymers for laminating, several resins (137 and 143 ACN) were developed that had lower water absorption and better resistance to thermal degradation upon exposure to 500°F for 200 hours with reduced tendency to crack.

The cracking was eliminated and generally satisfactory physical properties were obtained with two resins developed (141, 152). These resins both contained benzoyl acrylic acid.

Further pilot plant runs of these resins should be more extensively evaluated.

1. Preparation of Alkyd Resins

In the laboratory preparation of the alkyd resins described in this report, a standard one or two liter flask with 3 ground glass necks was used. Through the center opening, a stirrer was run and this was sealed off with a stuffing box. The other opening accommodated a thermometer and an inlet for nitrogen gas. This inert gas was bubbled through the resin during esterification. The other opening was attached to a condenser and a Deane Starke trap for collecting the water. The heating was carried out using an electric Glas-Col heater, the amount of heat being regulated by a Variac.

An excess of glycol, usually ten percent, was charged into the flask and the stirrer started and a slow stream of nitrogen introduced. The glycol was heated to about 85°C at which time the acid or anhydride was added. After this has dissolved, the temperature was slowly increased to 200°F.

The water was collected and samples of the resin taken and the acid number determined. The reaction was usually continued until the acid number was close to 50. The resin was then cooled to 100°C at which time the triallylcyanurate and/or other monomer was added and thoroughly mixed till the resin reached room temperature.

2. Preparation of Laminates

In order to obtain comparable data on glass reinforced laminates using the triallylcyanurate copolymer resins, discussed in this report, all samples were prepared under similar conditions. The same technician made all laminate panels in the same press by the following procedure:

The glass fabric used was 181 cloth, conforming to Specification MIL-F-9084. This fabric is usually employed for reinforcing structural aircraft plastic components. Finish 301 was selected on the basis of the studies carried out by Naugatuck Chemical for Wright Air Development Center (Reference 3) in which they found that laminates made with 181 glass fabric having 301 finish maintained greater strength after exposure to elevated temperature. One thousand yards of 181 glass cloth with 301 finish from the same batch of treated cloth was obtained from United Merchants Industrial Fabrics Corporation, so that in so far as possible, the treated 181 cloth was uniform.

The glass fabric was cut into 18" x 19" pieces and laid up so that all plies were parallel. The 18" length of the laminates was made parallel to the warp to prevent cross layup and for easy identification of the panels for cutting, i.e. all test specimens were cut parallel to the warp or

parallel to the 18" length of the panel. Twelve plies of 181-301 glass cloth were used which gave flat test panels nominally 1/8" thick. The layup was made on a large sheet of cellophane laid over metal caul plates. The triallyl-cyanurate resins were poured on the center of the cloth and spread out with a spatula. The cellophane was then folded over the layup and a caul plate was laid on top. The resin was allowed to soak into the fabric for 15 minutes, so that the glass fabric was thoroughly impregnated.

After the soaking period, the top plate was removed and the excess resin and entrapped air are worked out by wiping with a rigid, flat piece of plastic over the cellophane surface.

The laminate was then cured between aluminum caul plates in a hydraulic press equipped with steam-heated platens. The layup was placed in the press and a pressure of 15 ± 2 pounds per square inch was applied. The pressure was kept constant by turning on the hydraulic pump and adjusting the by-pass valve so as to keep a constant pressure during cure. The only variable that could not be controlled was the viscosity of the resin during polymerization in the press.

The final resin content of the laminates ranged from 32 to 40 percent in the laminates that used clear resin. The percentage of the pigment plus resin in the filled laminates ranged from 35 to 40.

The steam was then turned on and the platen temperature was raised from room temperature to a temperature ranging from 170° to 220°F in 30 minutes. Generally the laminates were cured for 1 hour at this temperature, however, some laminates had to be cured for periods up to three hours. After the laminates became rigid, cooling water was run through the platens and the laminate was cooled while remaining under pressure. The panel was then removed from the press and put in an air circulating oven at 250°F. The temperature was then raised in 50°F increments, each half hour, to 400° or 500°F. In most instances the postcure for 24 hours at 400°F was equivalent to 3 hours at 500°F.

It was noted that most triallylcyanurate alkyd copolymer glass reinforced laminates had a tendency to blister when cured for 3 hours at 500°F. This phenomenon was not observed when the same laminate was cured for 24 hours at 400°F.

The commercially available triallylcyanurate polyester resins in general are very "hot", i.e. they produce a very high exothermic heat upon copolymerization. It has been observed in this investigation that if the impregnated laminates were brought up to 170° - 220°F too rapidly in the press, the exotherm reached caused the resin retained in the cellophane outside of the press to start smoldering. To reduce the amount of cracking

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and a build-up of a large amount of exothermic heat, it was found desirable to use a slow stepwise cure, as noted below. For simplicity, the postcures and heat aging cycles used will be defined for this report as follows:

Condition "A"	Initial cure: 170°-220°F in press for 1/2 to 2 hours, in oven at 250°F, raised to 400°F in 1-1/2 hours, held at 400°F for 24 hours.
Condition "B"	Initial cure: 170°-220°F in press for 1/2 to 2 hours, in oven at 250°F, raised to 500°F in 2-1/2 hours, held at 500°F for 3 hours.
Condition "C-A"	Heat aged at 400°F for 1/2 hour in addition to initial cure of Condition "A".
Condition "C-A1"	Heat aged at 400°F for 24 hours in addition to initial cure of Condition "A"
Condition "C-A2"	Heat aged at 400°F for 48 hours in addition to initial cure of Condition "A"
Condition "C-A3"	Heat aged at 400°F for 200 hours in addition to initial cure of Condition "A"
Condition "D-A"	Heat aged at 500°F for 1/2 hour in addition to initial cure of Condition "A"
Condition "D-A1"	Heat aged at 500°F for 24 hours in addition to initial cure of Condition "A"
Condition "D-A2"	Heat aged at 500°F for 48 hours in addition to initial cure of Condition "A"
Condition "D-A3"	Heat aged at 500°F for 200 hours in addition to initial cure of Condition "A"
Condition "E-B"	Heat aged at 400°F for 24 hours in addition to initial cure of Condition "B"
Condition "E-B1"	Heat aged at 400°F for 48 hours in addition to initial cure of Condition "B".
Condition "E-B2"	Heat aged at 400°F for 200 hours in addition to initial cure of Condition "B".
Condition "D-B"	Heat aged for 1/2 hour at 500°F in addition to initial cure of Condition "B".

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- Condition "D-B1" Heat aged for 24 hours at 500°F in addition to initial cure of Condition "B"
- Condition "D-B2" Heat aged for 48 hours at 500°F in addition to initial cure of Condition "B"
- Condition "D-B3" Heat aged for 200 hours at 500°F in addition to initial cure of Condition "B"

3. Methods of Testing

Except as noted below, the test methods used in the evaluation of the laminates were in accordance with Specification LP-406 as follows; Compressive strength, Method 1021; Water absorption, Method 7031; Tensile strength, Method 1011.

The flexural strength and modulus of elasticity were determined on all specimens according to Federal Specification LP-406b, Amendment 1, Method 1031.1. Specimens were approximately 1/8" x 1" x 4". Normally five specimens were evaluated. Thickness dimensions were measured to 0.001", the span length of 2" was measured to 0.01".

The condition of the specimens was as follows:

- (a) One set of five specimens from each of the postcured laminated panels prepared were set aside with no further heat aging. (Condition A or Condition B)
- (b) Another set from each laminate was aged an additional 200 hours at 500°F in an air circulating oven. (Condition D-A3 or Condition D-B3)

Upon completion of postcuring and heat aging, five specimens in each group were tested at 75°F, and five specimens at 500°F. The specimens tested at 500°F were exposed to a one-half hour conditioning period at this temperature.

The loss in flexural strength during the 200 hours heating at 500°F was found to vary with the method of holding the specimens in the oven. The specimens that were supported perpendicularly to the shelf in the circulating air oven generally lost more strength than the specimens that were laid flat on pieces of Transite.

In these tests, the specimens were set in a slotted plate and held perpendicularly to the shelf in the oven so that the heated air flowed around the test specimens.

4. Loss of Weight on Heating at 400°F and 500°F

To observe the surface cracking of the laminates and to determine the heat stability of the resins with and without fillers in glass reinforced laminate systems, the following tests were carried out, after the laminates had been brought to full cure by postcuring for 24 hours at 400°F or 3 hours at 500°F.

Sets of three test specimens from each laminate, nominally 1/8" x 1" x 3", were conditioned and weighed. One set was exposed to 400°F and one set was exposed to 500°F, in addition to the original postcure, for 24 hours and 48 hours exposure. The specimens were then weighed and the amount of weight lost due to heat degradation determined.

5. Water Absorption After Heat Aging at 400°F and 500°F

Specimens 1/8" x 1" x 3" were cut from test laminates after the laminates had been brought to full strength by postcuring at 400°F for 24 hours or 500°F for 3 hours. One set of these specimens was heat-aged in a circulating oven for 48 hours at 400°F and one set for 500°F for 48 hours. After cooling to room temperature in a dessicator, the weight of each sample was recorded. Specimens were then placed in distilled water for 24 hours at 75°F. At the completion of the immersion, samples were wiped dry of excess water and weighed again as outlined in Specification L-P-406B. This procedure was used since this heat aging usually resulted in greater cracking of the laminate with subsequent greater water absorption.

6. Thirty Day Water Absorption Tests

For this test, three specimens, 1/8" x 1" x 3", were taken from each laminate. These specimens were conditioned in an air circulating oven at 122° + 4°F. (50° + 2°C) for 24 hours. After conditioning, the specimens were cooled in a desiccator and weighed. The specimens were then completely immersed in distilled water maintained at a temperature of 73.5° + 4°F (23° + 2°C) for 30 days. At the end of 30 days immersion, each specimen was removed, the surface moisture quickly absorbed by a dry cloth, and the specimen reweighed.

The percentage increase in weight during immersion was calculated to the nearest 0.1 percent as follows:

Increase in weight, percent =

$$\frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

7. Water Absorption After Two Hours in Boiling Water

Five specimens, 1/8" x 1" x 4", were taken from laminates made of fully cured triallylcyanurate resins (Condition A or B). These specimens were conditioned in a circulating air oven at 122° + 4°F (50° + 2°C) for 24 hours. After

conditioning, the specimens were cooled in a dessicator and weighed. The specimens were then completely immersed in boiling distilled water for two hours. At the end of this time, the specimens were removed, the surface moisture quickly absorbed on a dry cloth and the specimen reweighed.

The percentage increase in weight during immersion was calculated to the nearest 0.1 percent as follows:

Increase in weight, percent =

$$\frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

8. Equipment for Elevated Temperature Testing

For testing of specimens at 400°F and 500°F in flexure and compression, an insulated transite air circulating oven was used as shown in Figure 19. The oven had interior dimensions as follows; 12" x 14" x 12". The source of heat was a 6000 watt heater connected to a 220 volt power source. Temperature was controlled to within + 5°F of the desired temperature by means of two 110 volt Variacs connected in series.

Tensile strength tests were conducted in a resistance wound tube furnace with a 2" inside diameter. Temperature of this furnace was controlled to + 5°F of the desired temperature by means of a variac and thermocouples.

Contrails
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APPENDIX

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Contrails

TABLE NO. 77

FORMULATION OF EXPERIMENTAL RESINS - MOLS

RESIN	EG	PG	DEG	CMA	CPA	MA	CA	OTHER	MONOMER	DAM	TAC
100-1	1.0					1.0	0.5	ADA PA GLY	0.2 0.2 0.5		
101-1		1.0				1.0	1.0	HET GLY ADA	0.5 1.0 0.5		
102-1	1.0	1.0				2.0				0.2	0.5
103-1		2.0				1.5	0.5	HET	0.2	0.3	0.7
104-1		2.0				1.2	0.7	HET	0.4	0.3	0.7
105-1			2.0			2.0				0.2	0.5
106-1			2.0			1.8	0.1	HET	1.2	0.3	0.7
107-1			2.0			1.8	0.1	PA	0.2	0.2	0.6
108-1	0.3		1.0			1.3	0.2	ADA PA GLY	0.9 0.1 0.2	0.1	1.5
109-1		2.0				1.1	1.0	HET	0.4	0.2	0.8
110-1		1.5				0.8		TCPA	0.7	0.2	0.5
111-1						1.5	0.5	HET	0.2	MMA 0.7 HTO 1.3	0.2 1.0
112-1	2.0					1.0		DCPA	1.0	0.2	0.3
113-1		2.0				1.5	0.5	CPA	0.2	MMA 0.9	0.2 0.7
113-2		2.0				1.5	0.5	CPA	0.2	MMA 0.9	0.2 0.7
114-1		2.0		1.5			0.5	CPA	0.2	MMA 1.0	0.2 0.7
114-2		2.0		1.5			0.5	CPA	0.2	MMA 1.0	0.2 0.7
115-1		2.0		1.5			0.5	HET	0.2	0.2	0.7
116-1	3.0					1.0		PA PDIAc	0.5 1.0	0.2	0.33
117-1	2.0					1.0		DCPA TA	0.8 0.3	0.1	0.33
118-1	2.0				0.5	1.0		TA	0.5	0.1	0.66
119-1	2.0				0.5	1.0		TCPA	0.5	0.1	0.33
120-1	2.0			1.0	0.25			TCPA	0.8	0.1	0.33
120-2	2.0			1.0	0.25			TCPA	0.8	0.1	0.66
121-1	2.0			1.0				TCPA	1.0	0.1	0.33
121-2	2.0			1.0				TCPA	1.0	0.1	0.33
122-1	2.0			1.5	0.25		0.5			MMA 0.5	0.1 0.67
123-1					0.25	1.5	0.5	DEG	2.0	0.1	0.67
124-1					0.25	1.5	0.5	BUDIOl	2.0	0.1	0.67
125-1		2.2			1.0	1.0				ACN 2.1	0.1 1.3
126-1		2.2			1.0	1.0				MMA 1.1	0.1 1.3
127-1		2.2				1.0		PIDIAc		MMA 0.8	0.1 1.0
128-1		2.0			0.25	1.5	0.5			ACN 1.8	1.1
129-1		2.0			0.25	1.5	0.5			MMA 1.0	1.1
130-1					0.25	1.5	0.5	BUDIOl	2.0	ACN 1.9	1.2
131-1					0.25	1.5	0.5	BUDIOl	2.0	MMA 1.0	1.2
132-1	2.0					2.0					1.2
133-1		2.0				2.0					1.3
134-1						2.0		GLY	2.0		GELLED
135-1						2.0		BD	2.0		1.4
136-1			2.0			2.0					1.6
137-1	2.0			2.0							1.5
137-2	2.0			2.0							1.1
137-3	2.0			2.0						ACN 1.7	1.1
137-4	5.0			5.0						MMA 2.2	2.6
138-1			2.0	2.0							1.9
139-1	2.0					2.0		HTO TA	1.0 0.5	MMA 1.2	0.3 1.4
140-1	2.0			1.0			1.0	TA	0.5	MMA 1.1	1.3
141-1		2.0			0.25	1.5		BAA	0.5	MMA 1.0	1.2

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TABLE NO. 77 (cont)

FORMULATION OF EXPERIMENTAL RESINS - MOLS

RESIN	EG	PG	DEG	CMA	CPA	MA	CA	OTHER	MONOMER	DAM	TAC
141-2		2.0			0.25	1.5		BAA 0.5	MMA 1.0		1.2
141-3		2.0			0.25	1.5		BAA 0.5	MMA 1.0		1.2
142-1		2.0			0.25	1.5	0.5	DBE 0.4			1.1
143-1		5.7			0.71	4.3	1.4				3.2
143-2 NM		2.0			0.25	1.5	0.5				1.1
143-2 MMA		2.0			0.25	1.5	0.5		MMA 1.0		1.1
143-2 ACN		2.0			0.25	1.5	0.5		ACN 1.8		1.1
143-3 NM		2.0			0.25	1.5	0.5				1.6
143-3 DAC		2.0			0.25	1.5	0.5	DAC 0.7			0.8
143-3 DATP		2.0			0.25	1.5	0.5	DATP 0.8			0.8
143-3 MMA		2.0			0.25	1.5	0.5		MMA 1.0		1.1
143-3 IBMA		2.0			0.25	1.5	0.5	IBMA 0.7			1.1
144-1	3.0							PA 0.4 FA 2.6			1.9
145-1	3.0			1.3				FA 1.3 PA 0.4			2.0
146-1		3.0						FA 2.6 PA 0.4			2.0
147-1		3.0		1.3				FA 1.3 PA 0.4			2.2
148-1			2.0					FA 1.7 PA 0.3			1.6
149-1			3.0	1.3				FA 1.3 PA 0.4			2.5
150-1		2.0			0.25	1.5	0.2	BAA 0.2	MMA 1.0		1.2
150-2		2.0			0.25	1.5	0.2	BAA 0.2	MMA 1.0		1.2
151-1	2.0				0.25	1.5	0.5		MMA 0.8		1.1
151-2	2.0				0.25	1.5	0.5	5% G-50	MMA 0.8		1.1
152-1	2.0				0.25	1.5	0.2	BAA 0.2	MMA 0.9		1.1
153-1	3.0			1.3				FA 1.3 PA 0.4	MMA 1.2		1.5
154-1	3.0			1.3				FA 1.3 PA 0.4	DAC 0.9		1.0
155-1	3.2			1.3				FA 1.3 PA 0.4 BAA 0.5	MMA 1.5		1.8
156-1	3.2			1.3				FA 1.3 PA 0.4 BAA 0.5	DAC 1.1		1.2
157-1	2.0				0.25	1.6	0.2	BAA 0.1	MMA 0.9		1.0
158-1	2.0				0.37	1.5	0.2	BAA 0.1	MMA 0.9		1.1
159-1		2.0			0.25	1.5	0.4	BAA 0.1	MMA 0.9		1.1
160-1	2.0				0.25	1.5	0.4	BAA 0.1	MMA 0.9		1.1
161-1	2.0				0.25	1.5	0.4	BAA 0.1 5% G-50	MMA 0.9		1.1
162-1	2.0				0.25		0.2	BAA 0.2 FA 1.5			1.1
163-1	2.5				0.50		0.2	BAA 0.2 FA 1.7			1.3
164-1	2.2			2.0				BAA 0.5			1.8
165-1	2.2			2.0				BAA 0.5			1.3
166-1	2.2			2.0				BAA 0.5	DAC 0.9		0.9
167-1	2.2			2.0				BAA 0.2		0.7	1.3

LIST OF ABBREVIATIONS.

ACN ACRYLONITRILE
ADA ADIPIC ACID
BAA BENZOYL ACRYLIC ACID
BD BUTANEDIOL-1,4
CA CINNAMIC ACID
CMA CHLOROMALEIC ANHYDRIDE
CPA CHLOROPHTHALIC ANHYDRIDE
DAC DIALLYL CARBATE
DAM DIALLYL MALEATE

DATP DIALLYL TETRAHYDROPHthalATE
DBE DIBENZOYL ETHYLENE
DCPA DICHLOROPHTHALIC ANHYDRIDE
DEG DIETHYLENE GLYCOL
EG ETHYLENE GLYCOL
FA FUMERIC ACID
GLY GLYCEROL
G-50 PARAPLEX PLASTICIZER
HET HEXACHLOROENDOMETHYLENE
TETRAHYDROPHthalIC ACID

HTO 1,2,6-HEXANETRIOL
IBMA ISOBUTYLMETHACRYLATE
MA MALEIC ANHYDRIDE
MMA METHYL METHACRYLATE
NM NO SECOND MONOMER-TAC ONLY
PA PHTHALIC ANHYDRIDE
PG PROPYLENE GLYCOL
TA TARTARIC ACID
TAC TRIALLYLCYANURATE
TCPA TETRACHLOROPHTHALIC ANHYDRIDE
PDIAc PHENYLENEDIACETATE

**ULTIMATE FLEXURAL STRENGTH AND MODULUS OF ELASTICITY
RESIN: EXPERIMENTAL CLOTH: 181-301**

RESIN NO.	TESTED AT 75°F		TESTED AT 500°F	
	AGED 24 HR-400°F	AGED 200 HR-500°F	AGED 24 HR-400°F	AGED 200 HR-500°F
<u>128-1</u>				
AVG. FLEXURAL STRENGTH	78,413	11,377	27,805	21,287
MODULUS OF ELASTICITY	2.3	3.2	2.4	1.9
<u>129-1</u>				
AVG. FLEXURAL STRENGTH	67,202	13,187	49,880	16,910
MODULUS OF ELASTICITY	3.1	3.4	3.0	3.5
<u>130-1</u>				
AVG. FLEXURAL STRENGTH	74,270	7,981	23,731	19,047
MODULUS OF ELASTICITY	3.0		2.2	1.6
<u>131-1</u>				
AVG. FLEXURAL STRENGTH	66,339	15,322	47,576	12,161
MODULUS OF ELASTICITY	2.7	4.0	2.6	1.2
<u>132-1</u>				
AVG. FLEXURAL STRENGTH	46,700	23,000	22,050	17,100
MODULUS OF ELASTICITY	3.3	2.4	4.0	1.4
<u>133-1</u>				
AVG. FLEXURAL STRENGTH	46,900	24,800	18,250	19,750
MODULUS OF ELASTICITY	2.4	2.3	3.8	1.5
<u>135-1</u>				
AVG. FLEXURAL STRENGTH	48,300	22,650	17,050	14,950
MODULUS OF ELASTICITY	3.1	2.5	3.7	0.9
<u>136-1</u>				
AVG. FLEXURAL STRENGTH	59,150	24,300	10,850	18,050
MODULUS OF ELASTICITY	4.1	2.9	1.4	2.3
<u>137-1</u>				
AVG. FLEXURAL STRENGTH	61,900	39,050	18,200	29,250
MODULUS OF ELASTICITY	3.0	2.7	2.7	2.4
<u>137-2</u>				
AVG. FLEXURAL STRENGTH	54,586	33,151	6,081	37,513
MODULUS OF ELASTICITY	2.9	2.5		2.9
<u>137-3 ACN</u>				
AVG. FLEXURAL STRENGTH	53,557	34,829	14,167	25,475
MODULUS OF ELASTICITY	2.6	2.0	1.2	1.5
<u>137-4</u>				
AVG. FLEXURAL STRENGTH	58,222	31,498	8,971	27,660
MODULUS OF ELASTICITY	2.5	1.9	1.7	1.7
<u>138-1</u>				
AVG. FLEXURAL STRENGTH	54,975	26,760	14,943	27,880
MODULUS OF ELASTICITY	2.9	2.4	1.5	2.0
<u>141-2</u>				
AVG. FLEXURAL STRENGTH	65,160	38,517	4,601	17,211
MODULUS OF ELASTICITY	2.6	2.3		1.5
<u>143-2 NM</u>				
AVG. FLEXURAL STRENGTH	53,180	34,401	13,163	18,900
MODULUS OF ELASTICITY	2.3	2.3	1.5	1.6
<u>143-2 MMA</u>				
AVG. FLEXURAL STRENGTH	58,341	46,225	7,638	15,631
MODULUS OF ELASTICITY	2.4	2.3	1.0	1.4
<u>143-2 ACN</u>				
AVG. FLEXURAL STRENGTH	56,771	34,518	5,997	24,202
MODULUS OF ELASTICITY	2.4	2.1		1.7
<u>143-3 NM</u>				
AVG. FLEXURAL STRENGTH	48,619	30,241	16,681	22,993
MODULUS OF ELASTICITY	1.8	2.0	1.1	2.5
<u>143-3 MMA</u>				
AVG. FLEXURAL STRENGTH	70,303	25,744	13,290	10,536
MODULUS OF ELASTICITY	2.7	1.5	1.4	1.0
<u>143-3 DAC</u>				
AVG. FLEXURAL STRENGTH	69,268	33,762	21,241	19,425
MODULUS OF ELASTICITY	2.6	2.5	1.6	2.3

Contrails

TABLE NO. 78 (cont)

ULTIMATE FLEXURAL STRENGTH AND MODULUS OF ELASTICITY RESIN: EXPERIMENTAL CLOTH: 181-301

RESIN NO.	TESTED AT 75°F		TESTED AT 500°F	
	AGED 24 HR-400°F	AGED 200 HR-500°F	AGED 24 HR-400°F	AGED 200 HR-500°F
<u>143-3 DATP</u>				
AVG. FLEXURAL STRENGTH	70,874	37,651	12,584	21,153
MODULUS OF ELASTICITY	2.8	2.2	1.1	2.6
<u>143-3 IBMA</u>				
AVG. FLEXURAL STRENGTH	69,159	27,184	11,243	18,007
MODULUS OF ELASTICITY	3.4	2.1	1.0	2.4
<u>144-1</u>				
AVG. FLEXURAL STRENGTH	40,698	29,343	29,102	22,453
MODULUS OF ELASTICITY	2.5	2.3	1.9	2.1
<u>145-1</u>				
AVG. FLEXURAL STRENGTH	55,963	37,857	13,567	22,930
MODULUS OF ELASTICITY	2.8	2.6	1.4	2.0
<u>146-1</u>				
AVG. FLEXURAL STRENGTH	42,539	21,220	12,171	13,488
MODULUS OF ELASTICITY	2.2	2.0	1.3	2.0
<u>147-1</u>				
AVG. FLEXURAL STRENGTH	49,625	32,918	7,451	19,821
MODULUS OF ELASTICITY	2.6	2.6	0.8	2.0
<u>148-1</u>				
AVG. FLEXURAL STRENGTH	49,625	32,918	7,451	19,821
MODULUS OF ELASTICITY	2.6	2.6	0.8	2.0
<u>149-1</u>				
AVG. FLEXURAL STRENGTH	49,777	36,405	7,713	22,092
MODULUS OF ELASTICITY	2.5	2.4	0.9	1.8
<u>150-1</u>				
AVG. FLEXURAL STRENGTH	59,614	10,163	6,764	7,208
MODULUS OF ELASTICITY	2.5	1.1	0.6	-
<u>151-1</u>				
AVG. FLEXURAL STRENGTH	53,242	26,219	11,422	26,716
MODULUS OF ELASTICITY	2.3	2.3	1.0	2.1
<u>151-2</u>				
AVG. FLEXURAL STRENGTH	72,720	41,122	8,891	23,160
MODULUS OF ELASTICITY	2.8	2.2	1.1	1.7
<u>152-1</u>				
AVG. FLEXURAL STRENGTH	52,616	42,917	8,038	15,744
MODULUS OF ELASTICITY	2.6	2.4	0.6	1.8
<u>154-1</u>				
AVG. FLEXURAL STRENGTH	33,714	28,001	18,227	23,714
MODULUS OF ELASTICITY	2.0	2.2	1.3	1.8
<u>155-1</u>				
AVG. FLEXURAL STRENGTH	59,704	47,360	8,144	15,131
MODULUS OF ELASTICITY	2.6	2.1	0.8	1.8
<u>157-1</u>				
AVG. FLEXURAL STRENGTH	48,214	15,732	12,132	13,094
MODULUS OF ELASTICITY	2.6	1.8	1.4	1.4
<u>158-1</u>				
AVG. FLEXURAL STRENGTH	53,846	13,694	11,686	11,168
MODULUS OF ELASTICITY	2.6	1.7	1.4	1.1
<u>159-1</u>				
AVG. FLEXURAL STRENGTH	68,241	14,143	8,848	9,051
MODULUS OF ELASTICITY	-	-	-	-
<u>160-1</u>				
AVG. FLEXURAL STRENGTH	58,676	9,028	7,148	7,120
MODULUS OF ELASTICITY	-	-	-	-
<u>161-1</u>				
AVG. FLEXURAL STRENGTH	58,011	22,600	7,094	17,297
MODULUS OF ELASTICITY	-	-	-	-
<u>162-1</u>				
AVG. FLEXURAL STRENGTH	52,481	14,482	7,732	12,100
MODULUS OF ELASTICITY	2.3	1.3	0.9	0.9
<u>163-1</u>				
AVG. FLEXURAL STRENGTH	59,833	31,647	7,187	13,877
MODULUS OF ELASTICITY	2.4	1.8	0.9	0.8

Controls

TABLE NO. 79

WATER ABSORPTION AFTER 24 HOURS IMMERSION

EXPERIMENTAL RESIN NO.	AVG. % WATER ABSORP. AFTER 48 HRS. AGING 400° F.	AVG. % WATER ABSORP. AFTER 48 HRS. AGING 500° F.	EXPERIMENTAL RESIN NO.	AVG. % WATER ABSORP. AFTER 48 HRS. AGING 400° F.	AVG. % WATER ABSORP. AFTER 48 HRS. AGING 500° F.
103-1	2.9	12.2	141-2	0.3	0.5
103-1 MMA	2.7	7.4	143-2 NM	1.6	2.5
104-1	3.0	15.4	143-2 MMA	0.3	1.0
105-1	4.5	12.3	143-2 ACN	0.5	0.6
106-1	4.1	12.3	143-3 NM	0.9	1.2
107-1	5.2	8.8	143-3 MMA	0.4	0.7
108-1	4.0	7.9	143-3 DAC	1.2	1.4
109-1	2.0	4.8	143-3 DATP	0.4	1.0
110-1	3.5	8.6	143-3 IBMA	1.0	2.0
112-1	1.3	3.3	144-1	5.6	5.8
113-2	2.8	3.6	145-1	3.8	4.4
115-1 A	6.1	8.4	146-1	6.1	5.3
115-1 B	3.8	10.4	147-1	4.7	6.6
116-1	-	-	148-1	5.5	5.4
117-1	1.44	8.29	149-1	3.4	6.7
118-1	1.78	8.40	150-2	0.5	1.9
119-1	1.13	4.91	151-1	0.6	1.1
120-2	0.95	6.75	151-2	0.4	1.8
121-2	1.20	3.38	152-1	0.3	0.4
122-1	2.75	11.47	153-1	**	*
123-1	2.24	8.53	153-2	*	*
124-1	3.36	11.90	154-1	2.5	3.3
125-1	1.63	5.51	155-1	1.1	1.2
126-1	1.58	8.73	156-1	*	*
127-1	-	-	156-2	*	*
128-1	0.43	0.70	157-1	0.4	0.7
129-1	0.44	0.80	158-1	0.4	0.6
130-1	0.97	3.04	159-1	0.8	1.9
131-1	0.48	2.84	160-1	1.0	2.8
132-1	5.6	8.1	161-1	0.6	2.1
133-1	5.0	7.0	162-1	0.8	1.1
135-1	6.0	9.3	163-1	0.8	1.4
136-1	5.8	7.7	164-1	*	*
137-1	3.6	5.1	165-1	*	*
137-2	5.1	3.7	166-1	*	*
137-3 ACN	6.3	7.5	167-1	*	*
137-4	3.7	4.7			
138-1	3.7	3.0			
139-1	2.3	3.6			
141-1	3.0	3.2			

* DELAMINATION OCCURRED ON CURING
NO TESTS CONDUCTED

WADC TR 55-342

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HEAT DETERIORATION OF 181-301 REINFORCED LAMINATES
AVERAGE WEIGHT LOSS IN PERCENT

RESIN	% LOSS IN WGT. 400° F.		% LOSS IN WGT. 500° F.		% RESIN IN PANEL
	24 HRS.	48 HRS.	24 HRS.	48 HRS.	
103-1	2.30	3.60	12.2	14.3	32.6
103-1 MMA	1.30	2.30	9.60	11.1	35.4
104-1	2.20	3.10	11.10	13.40	35.8
105-1	4.00	5.90	11.70	14.30	23.0
106-1	4.15	6.30	14.00	15.80	25.5
107-1	5.30	8.10	12.40	15.30	40.5
108-1	3.80	5.80	11.30	14.30	49.7
109-1	1.9	3.0	13.7	16.8	44.0
110-1	5.35	7.2	16.4	20.4	43.5
112-1	1.03	1.88	7.25	12.7	38.0
113-2	3.00	3.86	6.73	9.10	45.0
115-1 A	5.83	8.08	15.5	17.5	35.7
115-1 B	8.06	10.18	16.8	19.2	37.7
116-1	-	-	-	-	-
117-1	5.51	7.03	21.23	25.99	49.7
118-1	6.25	7.41	14.25	16.43	31.8
119-1	4.26	5.55	19.08	24.21	52.7
120-2	6.14	8.31	11.56	12.89	30.5
121-2	7.69	10.08	13.90	15.83	31.5
122-1	9.34	11.61	20.98	21.13	51.8
123-1	3.32	5.02	12.94	16.78	51.8
124-1	2.92	4.86	14.57	19.43	50.0
125-1	1.89	2.60	6.36	9.31	40.5
126-1	3.75	4.89	12.70	14.98	38.5
127-1	-	-	-	-	-
128-1	0.58	0.93	1.81	2.54	34.4
129-1	0.50	0.84	1.57	2.43	34.2
130-1	1.04	2.20	3.56	4.81	35.3
131-1	0.45	0.78	1.93	4.69	38.2
132-1	2.0	3.0	5.9	8.0	40.0
133-1	2.2	3.1	5.8	7.9	45.0
135-1	2.6	3.7	7.1	9.5	36.2
136-1	2.7	3.9	5.3	6.9	34.5
137-1	4.2	5.1	7.6	8.5	42.0
137-2	2.8	4.0	8.8	5.2	42.3
137-3 ACN	2.2	2.8	3.3	4.2	32.8
137-4	2.4	3.3	4.8	6.0	36.0
138-1	8.1	9.4	11.9	12.6	39.6
139-1	2.9	3.7	5.2	6.6	39.3
141-1	2.9	4.9	2.7	4.7	33.0

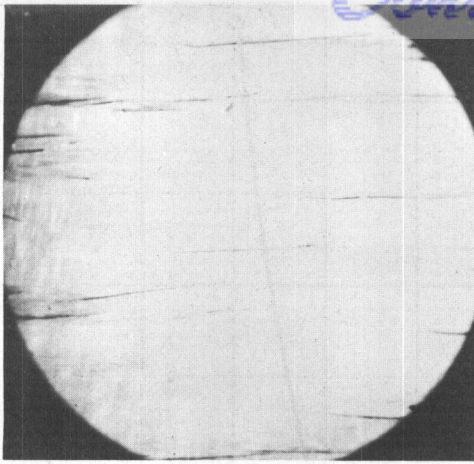
TABLE NO. 80 (cont)

HEAT DETERIORATION OF 181-301 REINFORCED LAMINATES AVERAGE WEIGHT LOSS IN PERCENT

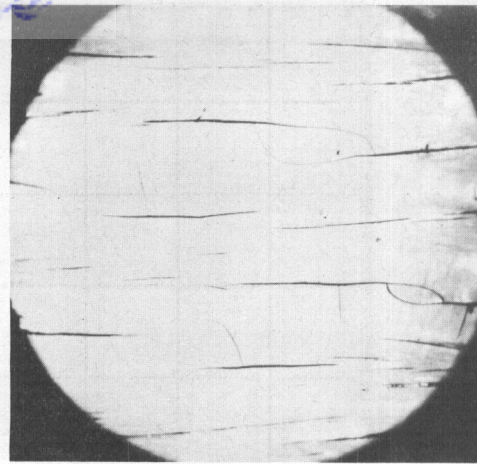
RESIN	% LOSS IN WGT. 400° F.		% LOSS IN WGT. 500° F.		% RESIN IN PANEL
	24 HRS.	48 HRS.	24 HRS.	48 HRS.	
141-2	0.7	1.0	2.3	2.7	38.6
143-2 NM	1.0	1.5	3.8	5.1	38.8
143-2 MMA	0.6	1.0	2.7	3.8	37.3
143-2 ACN	0.8	1.1	1.2	2.1	38.9
143-3 NM	0.7	1.1	2.4	3.7	38.9
143-3 MMA	0.4	0.8	1.8	3.0	36.6
143-3 DAC	0.4	0.8	1.4	2.5	38.4
143-3 DATP	0.5	0.8	1.9	3.1	38.3
143-3 IBMA	0.8	1.2	2.2	3.4	36.4
144-1	3.5	5.2	3.8	5.2	42.3
145-1	7.8	8.8	7.5	8.9	40.2
146-1	5.4	7.0	4.4	6.3	38.4
147-1	10.1	11.6	13.6	15.0	40.6
148-1	5.4	7.2	5.6	7.5	43.2
149-1	10.3	10.9	13.6	14.4	41.5
150-2	0.5	0.7	1.8	3.4	37.0
151-1	0.5	0.8	1.3	2.3	35.8
151-2	0.6	0.9	1.5	2.8	34.5
152-1	0.5	0.8	1.0	1.6	31.5
153-1	*				*
153-2	*				*
154-1	1.9	2.7	5.1	6.6	40.0
155-1	1.7	2.4	3.7	5.0	37.1
156-1	*				*
156-2	*				*
157-1	0.8	1.4	1.2	2.0	36.6
158-1	0.8	1.2	1.1	1.8	38.0
159-1	1.9	2.5	3.1	4.7	37.7
160-1	1.3	1.8	2.7	4.4	35.3
161-1	1.4	1.9	3.1	5.1	38.5
162-1	0.8	2.9	1.9	2.8	36.3
163-1	0.7	2.7	2.4	3.7	38.1
164-1	*				*
165-1	*				*
166-1	*				*
167-1	*				*

* DELAMINATED

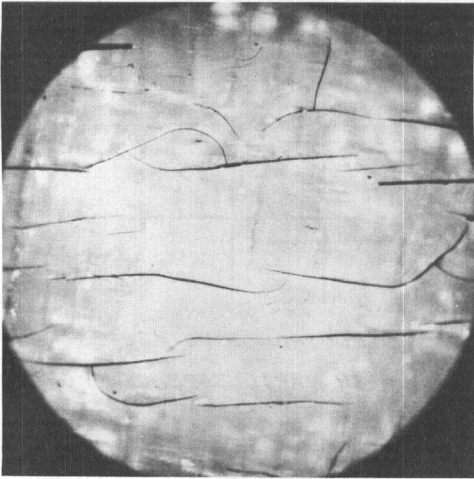
Contrails



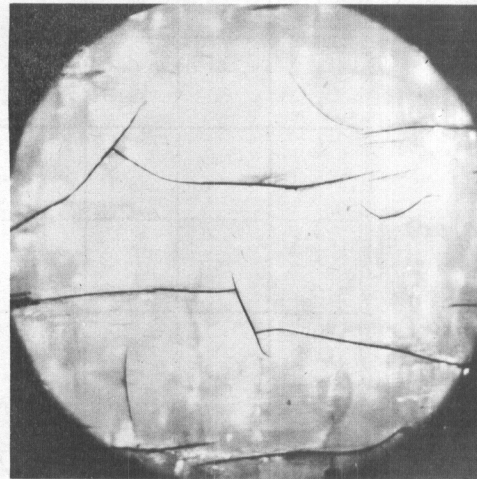
POSTCURE - NONE



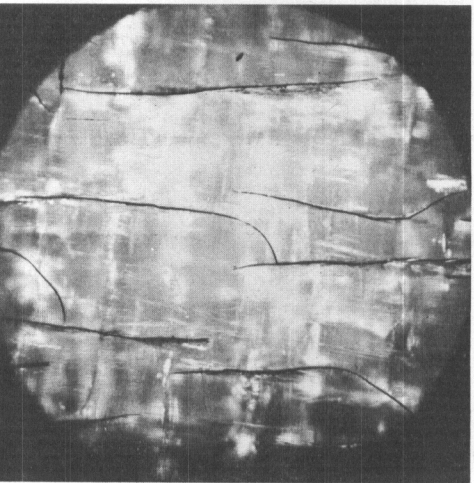
POSTCURE - 1 HR - 500°F



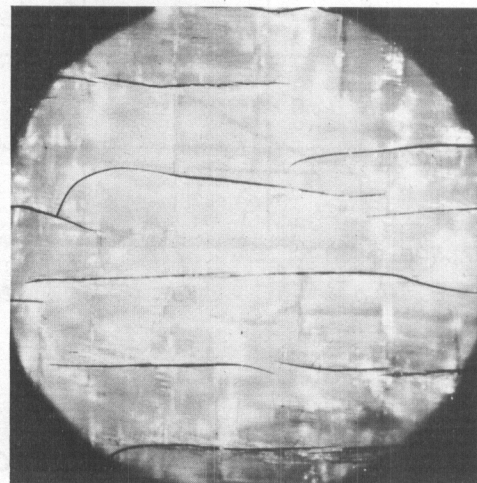
POSTCURE - 2 HRS - 500°F



POSTCURE - 3 HRS - 500°F



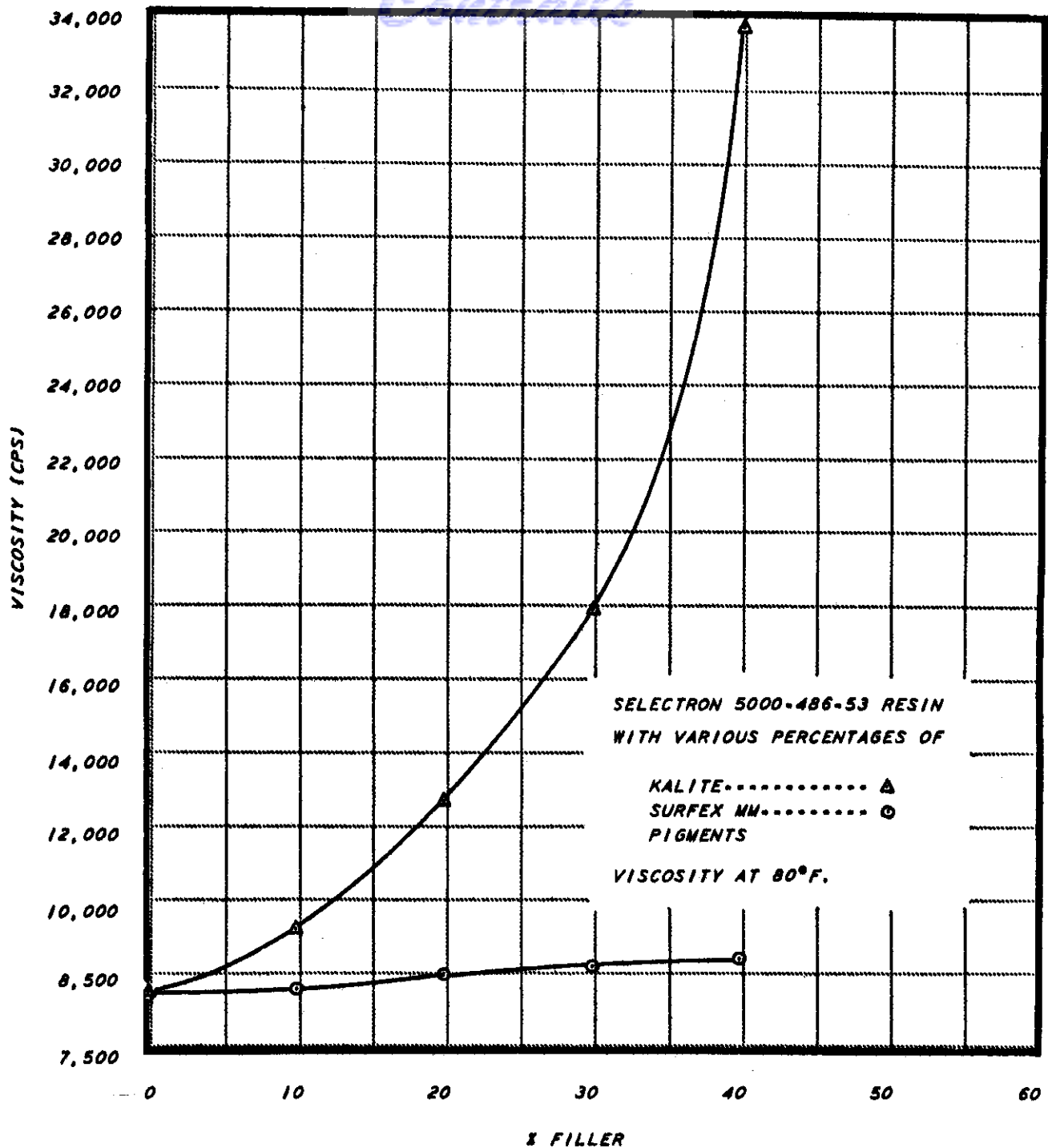
POSTCURE - 4 HRS - 500°F



POSTCURE - 5 HRS - 500°F

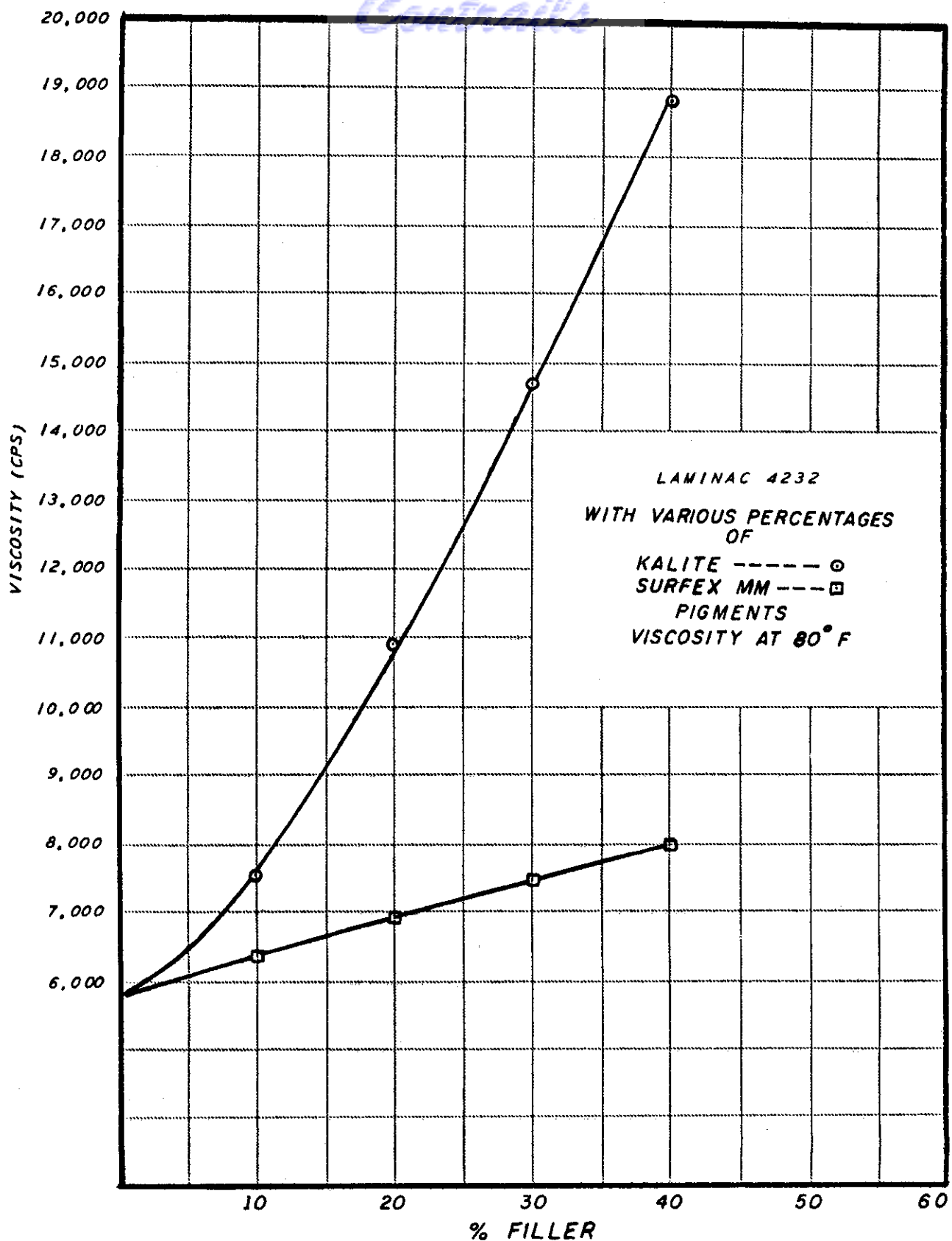
PHOTOMICROGRAPHS - 25X OF TYPICAL COMMERCIAL TRIALLYLCYANURATE
POLYESTER 181-301 LAMINATES AFTER 2 HOURS CURE IN PRESS AT
220°F AND POSTCURES NOTED.

FIGURE 1



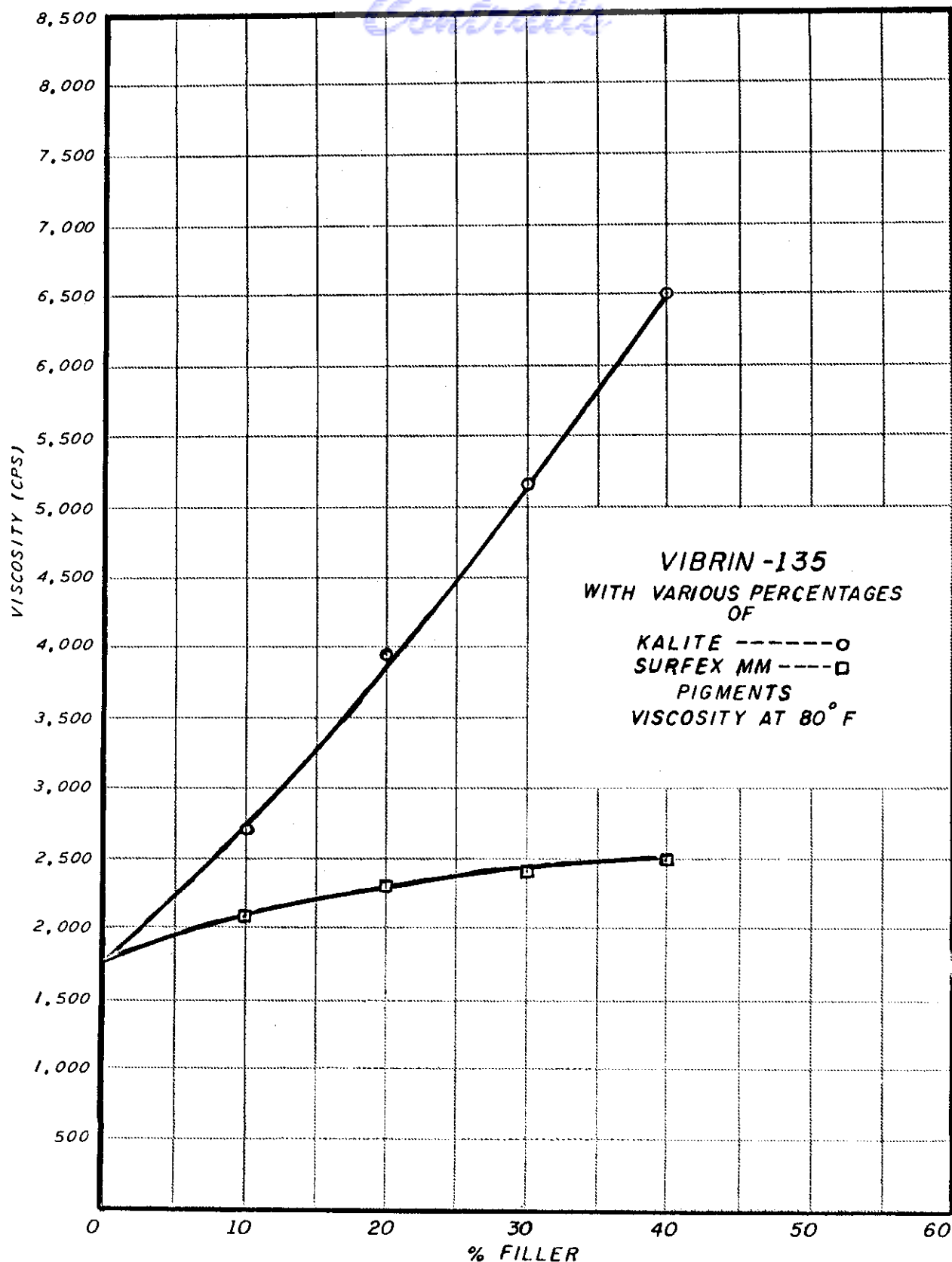
INFLUENCE OF PIGMENTS ON VISCOSITY
SELECTION 5000-468-53 RESIN

Figure 2



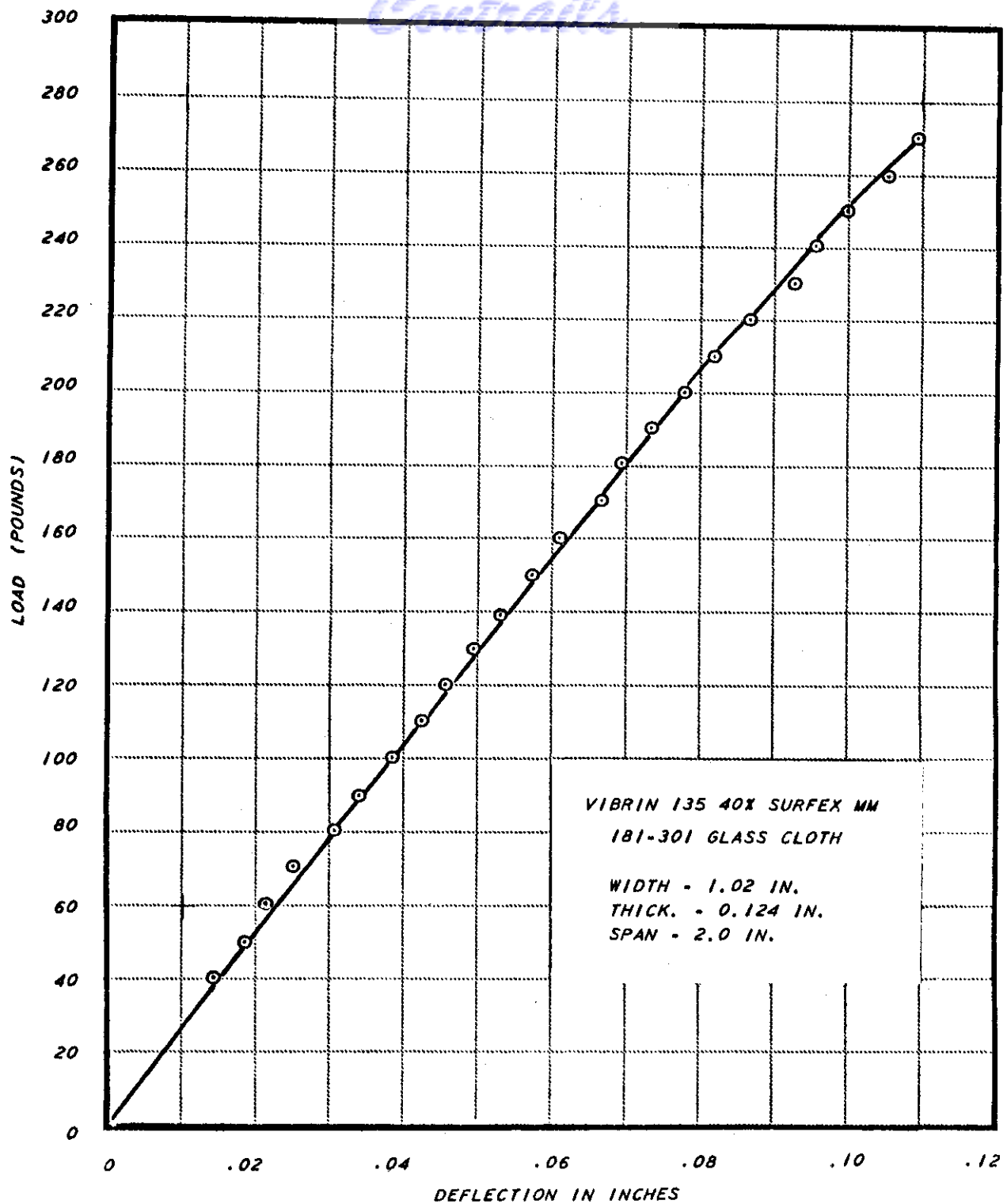
INFLUENCE OF PIGMENTS ON VISCOSITY
LAMINAC 4232

Figure 3



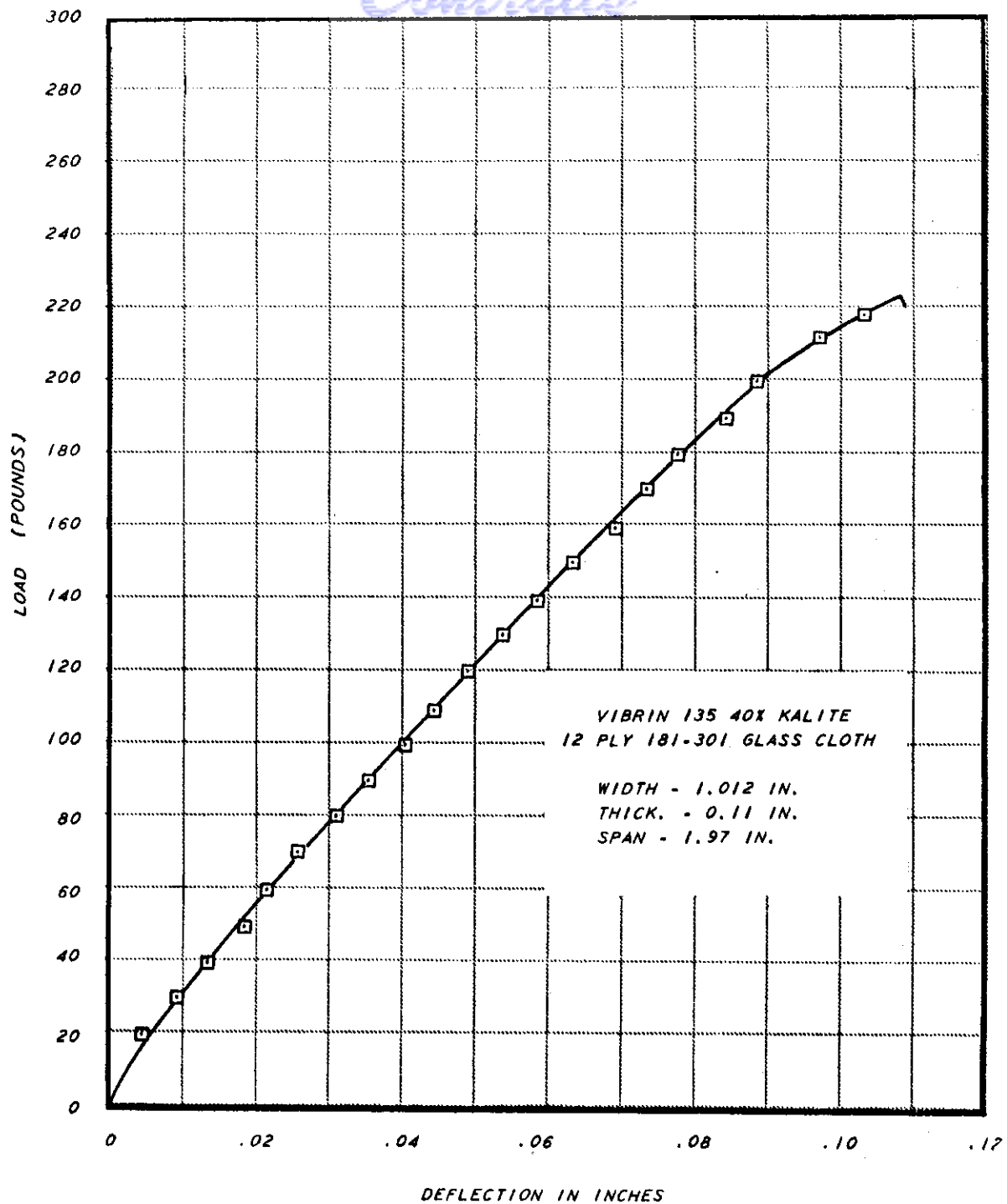
INFLUENCE OF PIGMENTS ON VISCOSITY
VIBRIN 135

Figure 4



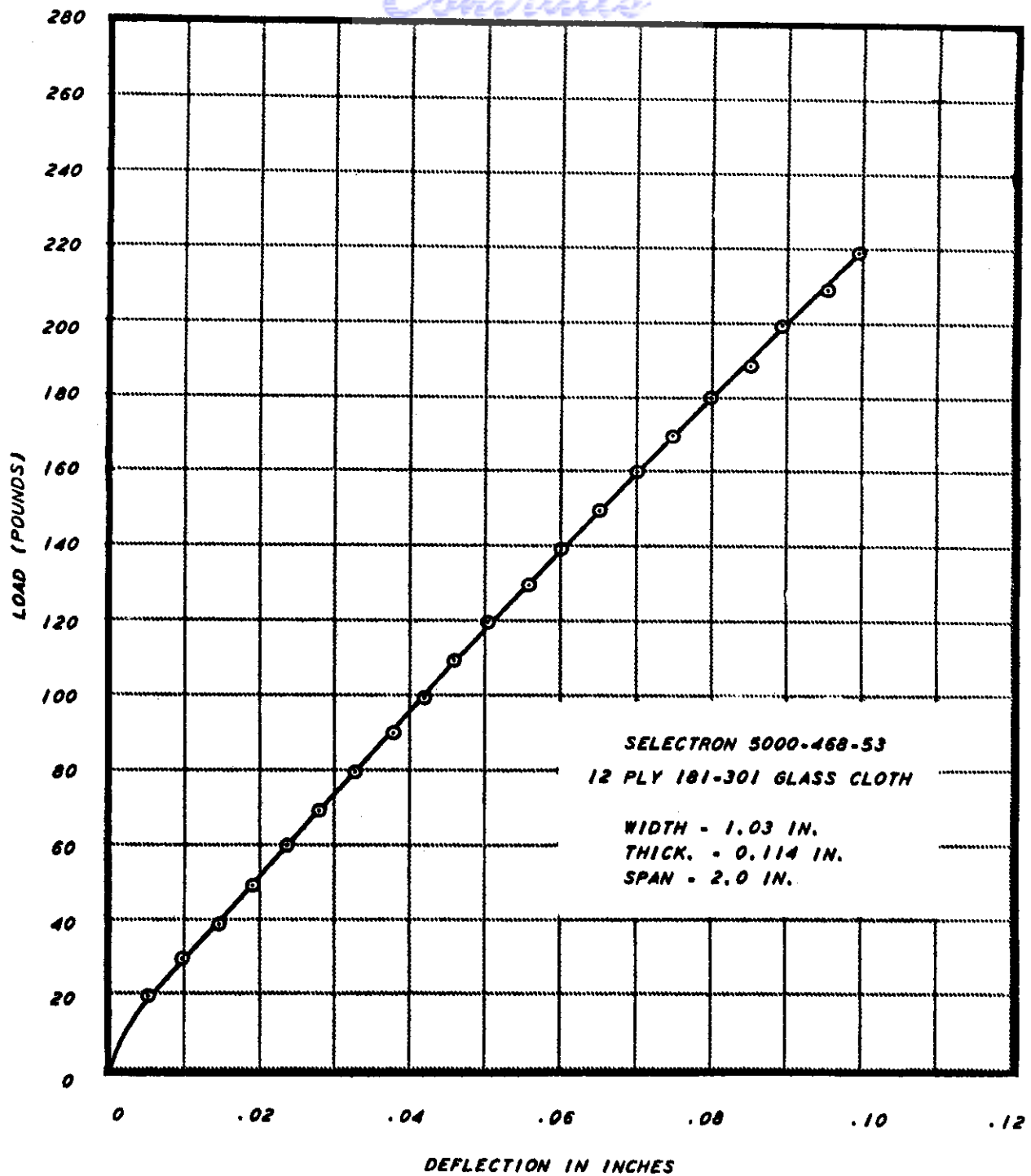
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
VIBRIN 135 PLUS SURFEX MM LAMINATES - TESTED AT 75°F.

Figure 5



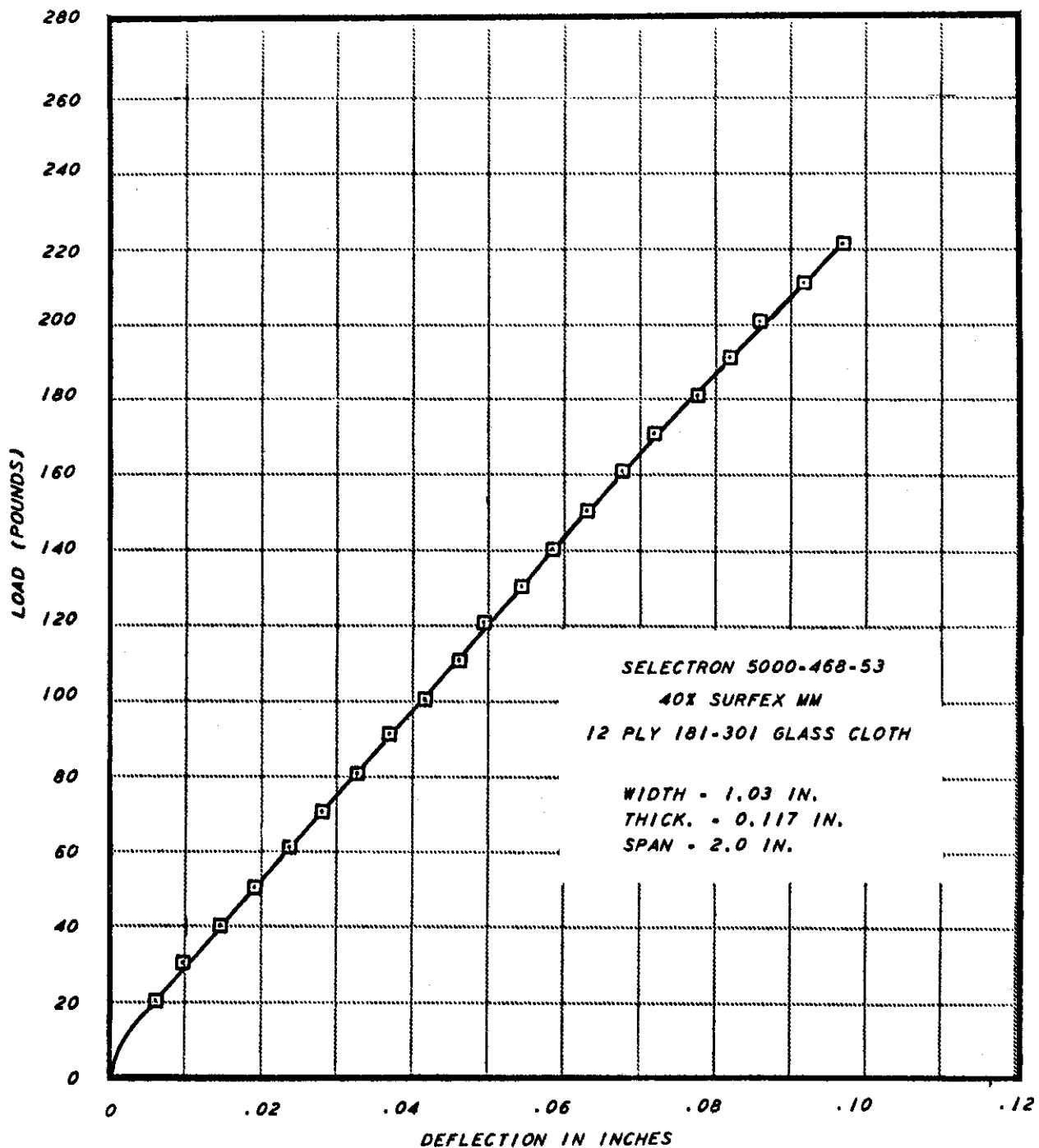
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
VIBRIN 135 PLUS KALITE LAMINATES - TESTED AT 75°F.

Figure 6



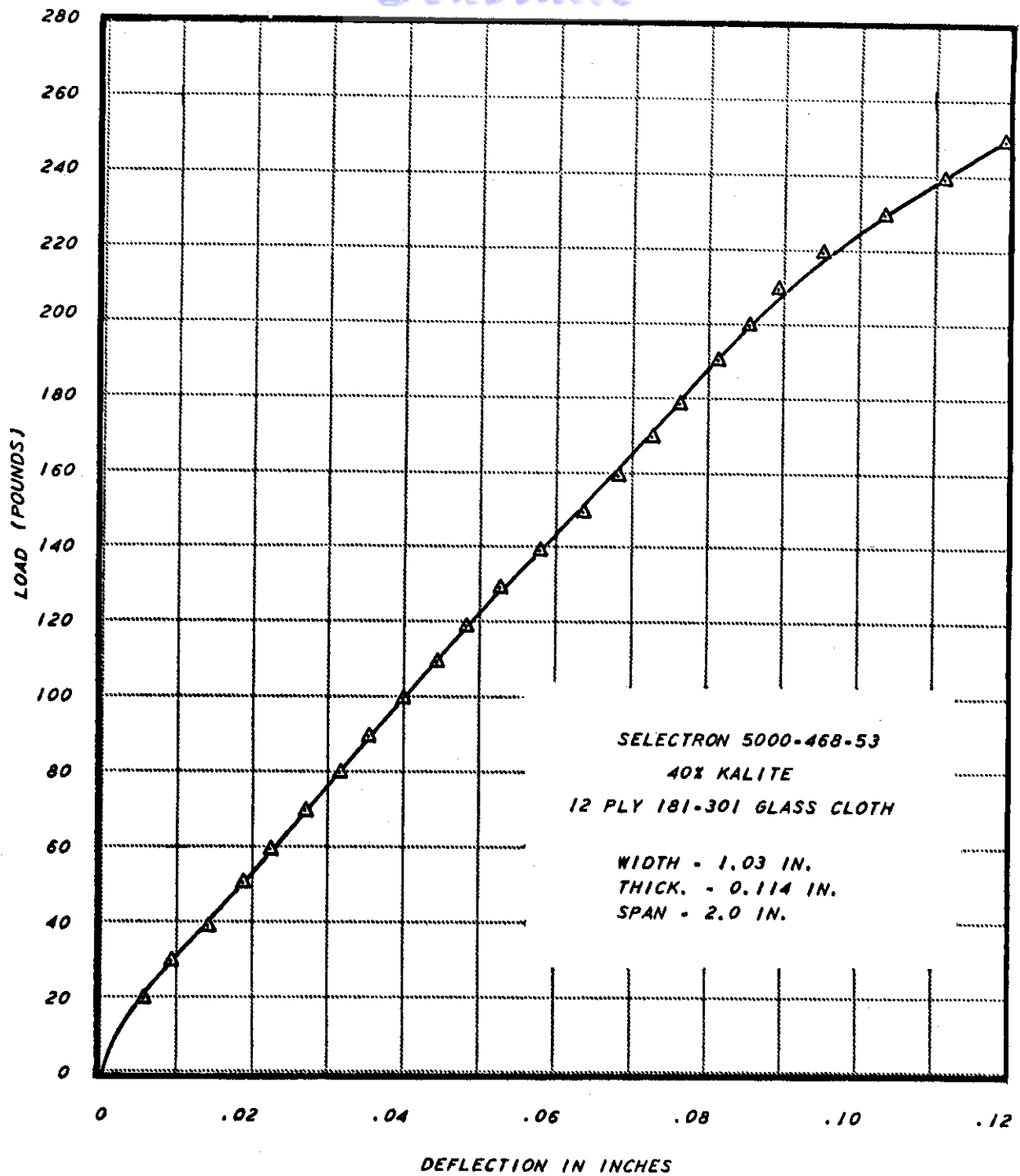
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
SELECTION 5000-468-53 LAMINATES - TESTED AT 75°F.

Figure 7



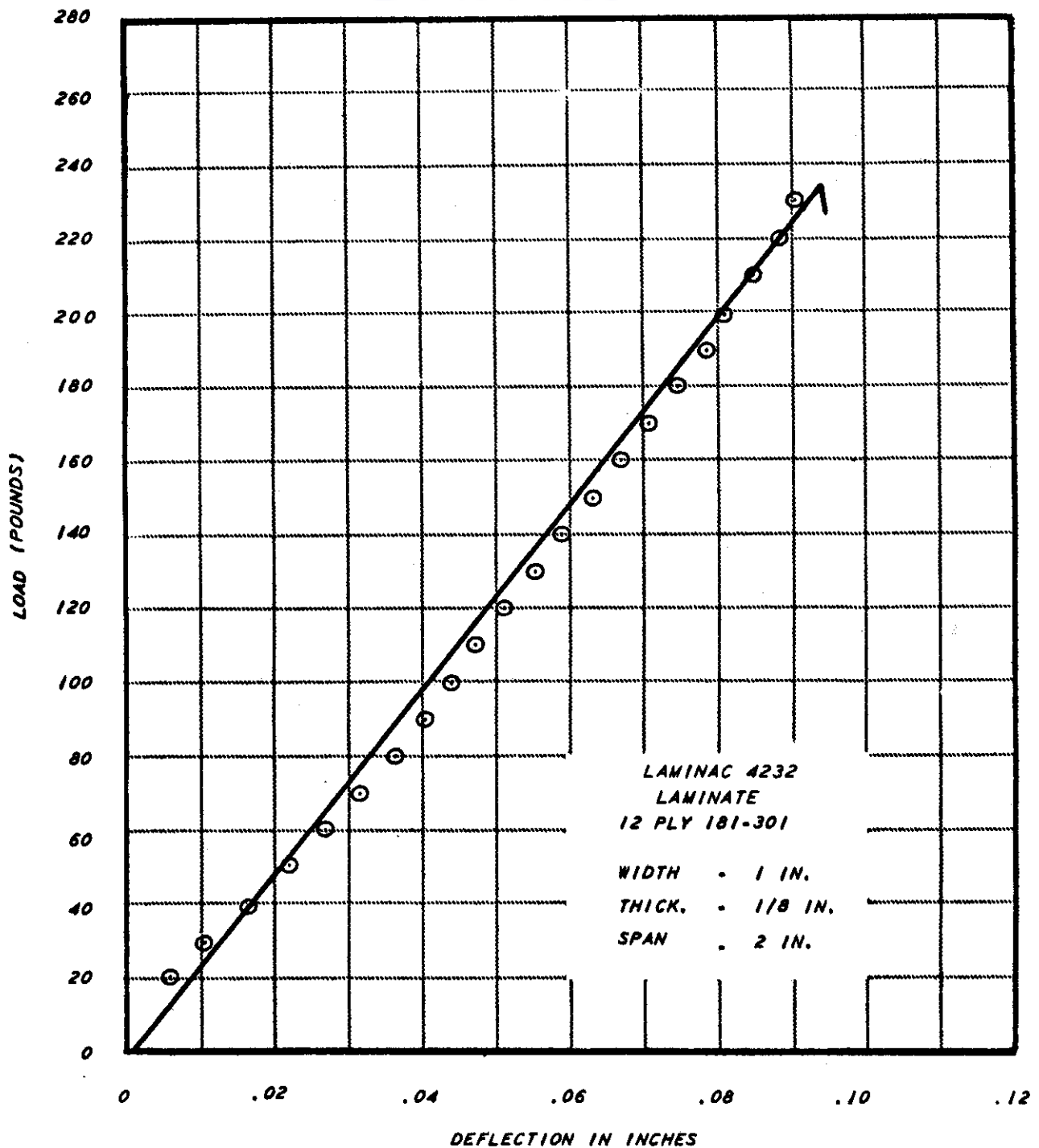
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
SELECTRON 5000-468-53 PLUS SURFEX MM-LAMINATES - TESTED AT 75°F.

Figure 8



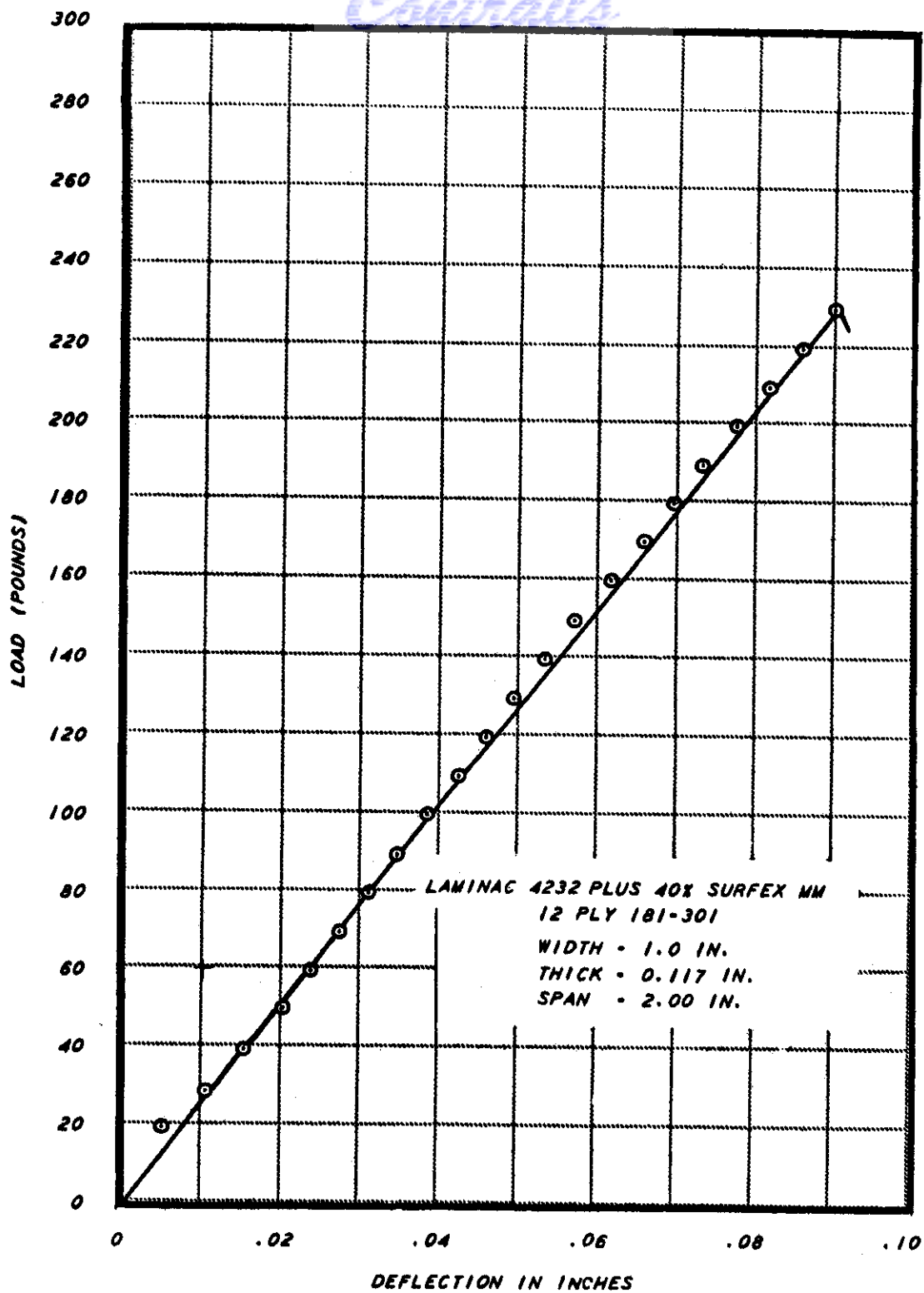
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
SELECTRON 5000-468-53 PLUS KALITE LAMINATES - TESTED AT 75°F.

Figure 9



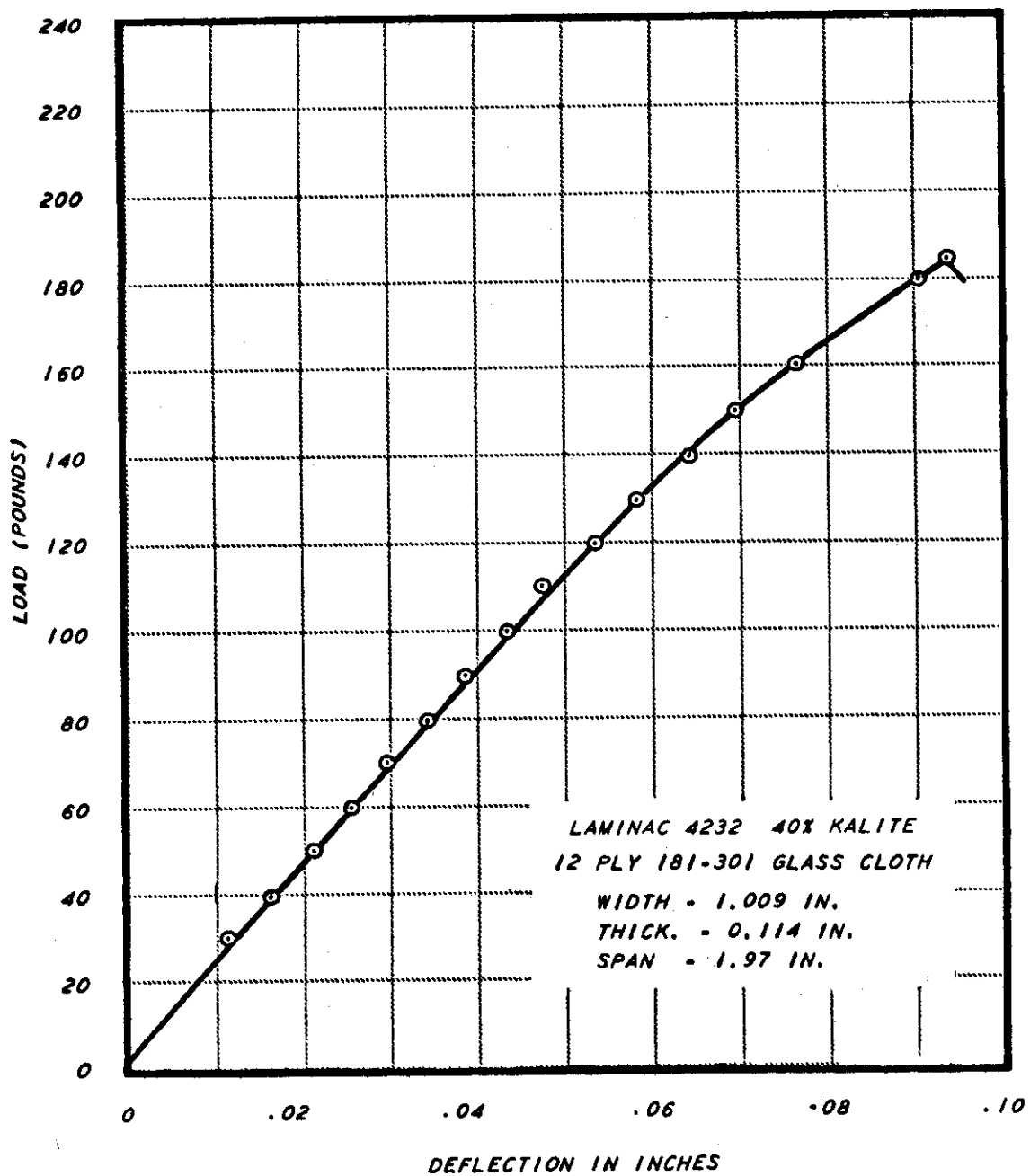
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF
181-301 LAMINAC 4232 LAMINATES - TESTED AT 75°F.

Figure 10



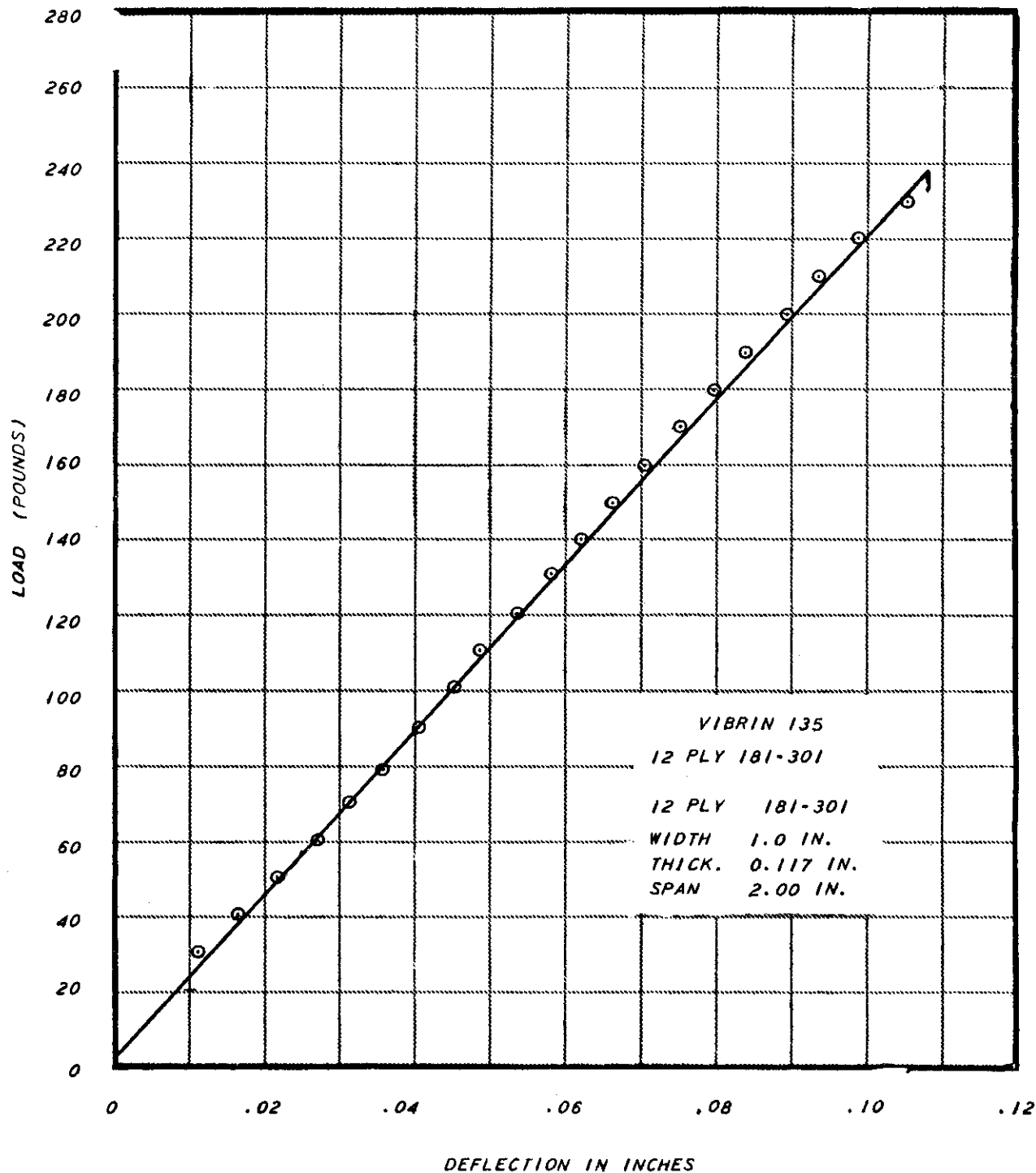
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301
LAMINAC 4232 PLUS SURFEX MM LAMINATES - TESTED AT 75°F

Figure 11



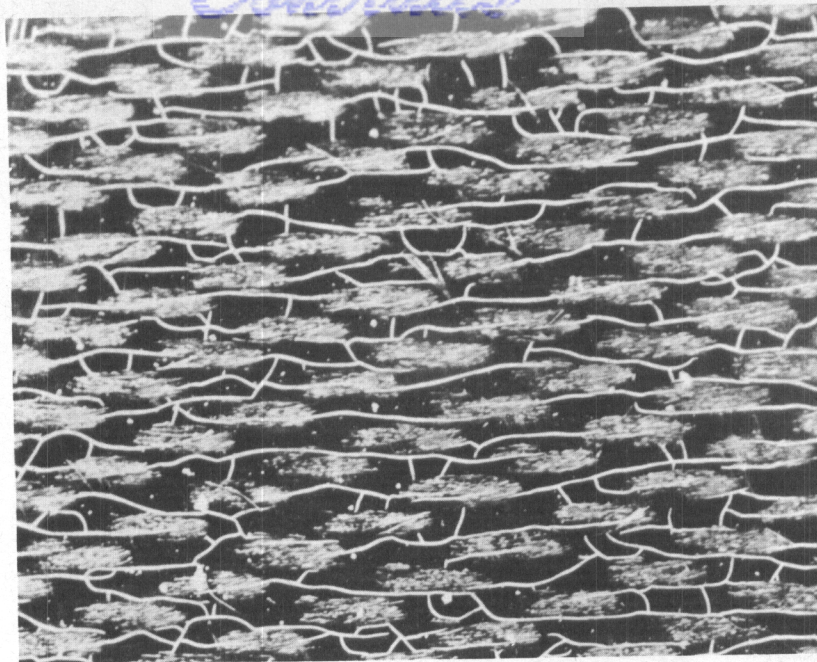
AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF 181-301 LAMINAC 4232 PLUS KALITE LAMINATES TESTED AT 75°F.

Figure 12

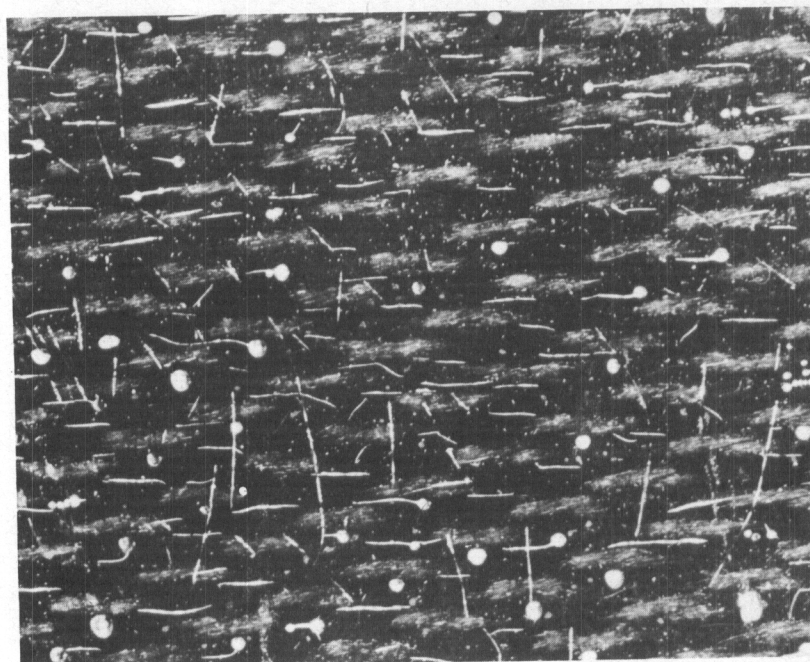


AVERAGE LOAD DEFLECTION CURVE FOR SIX SPECIMENS OF
181-301 VIBRIN 135 LAMINATES - TESTED AT 75°F.

Figure 13



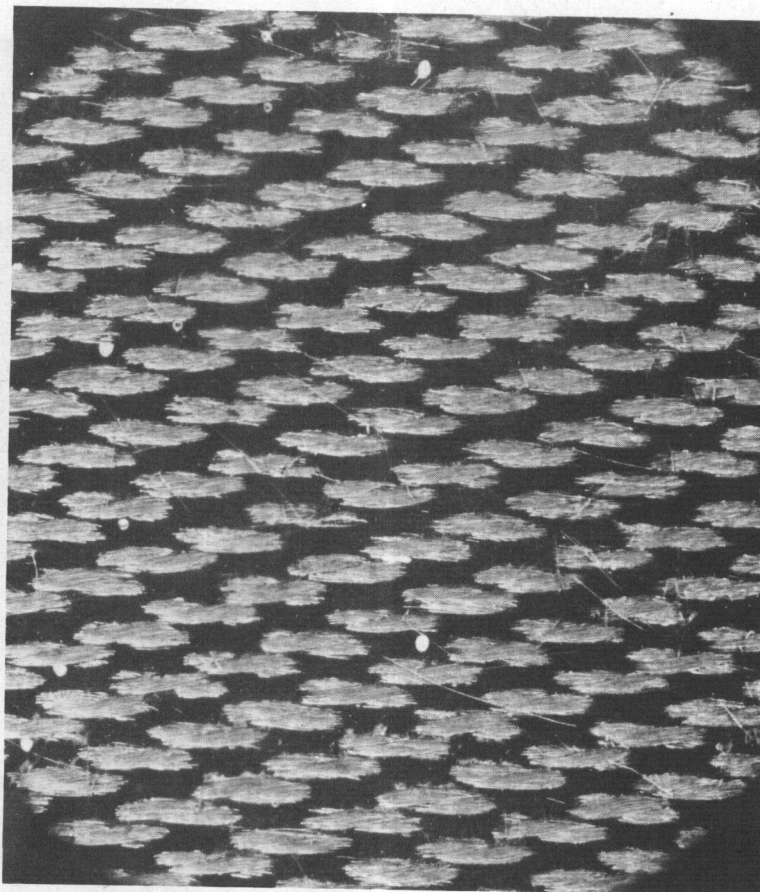
LAMINAC 4233



C.A.L. RESIN 141-1

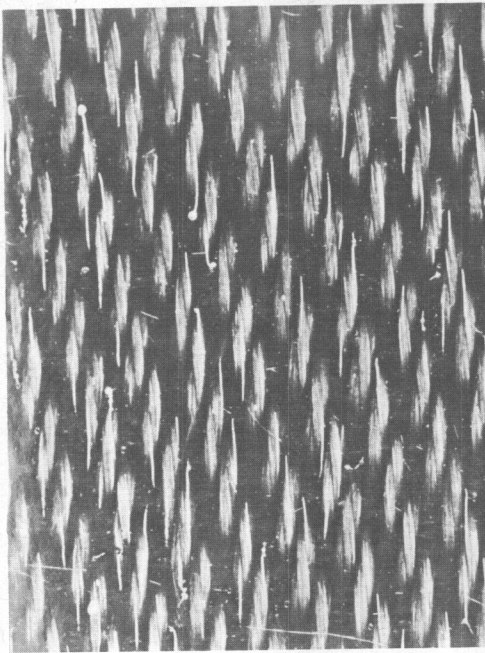
PHOTOMICROGRAPHS - 10X TRIALLYLCYANURATE POLYESTER
181-301 LAMINATES AFTER 2 HOURS CURE IN PRESS AT
220° F AND AGED 48 HOURS AT 500° F.

FIGURE 14

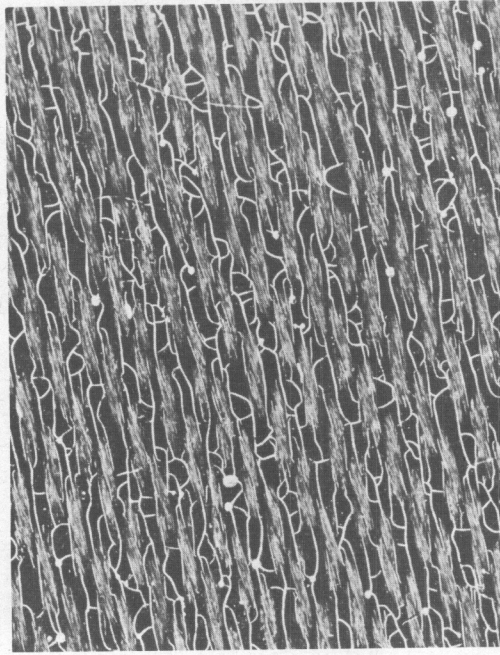


*PHOTOMICROGRAPH - 10X OF LAM-
INATE OF 181-301 CLOTH, 152 RESIN
AFTER 24 HOURS POSTCURE AT
400°F AND HEAT AGED FOR 48 HOURS
AT 500°F*

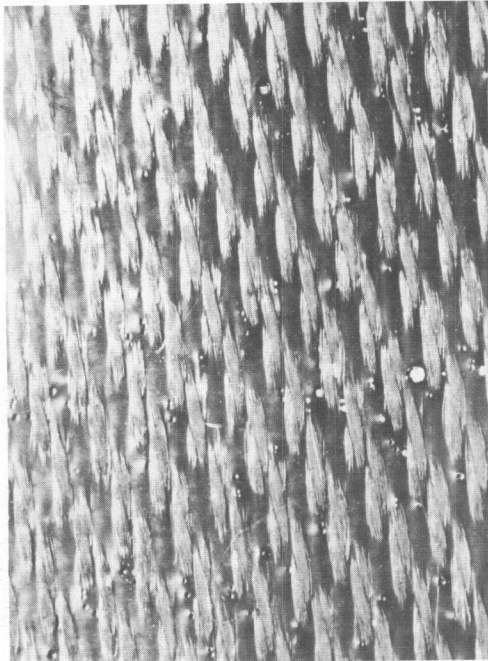
FIGURE 15



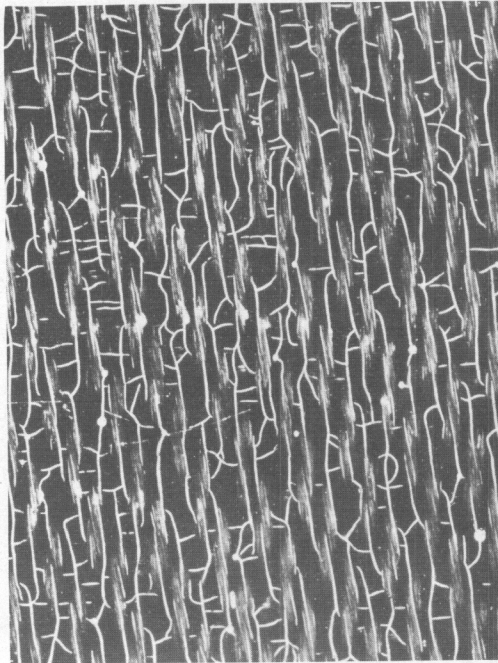
LAMINAC 4232 5% PARAPLEX G-60



VIBRIN 135 5% PARAPLEX G-50



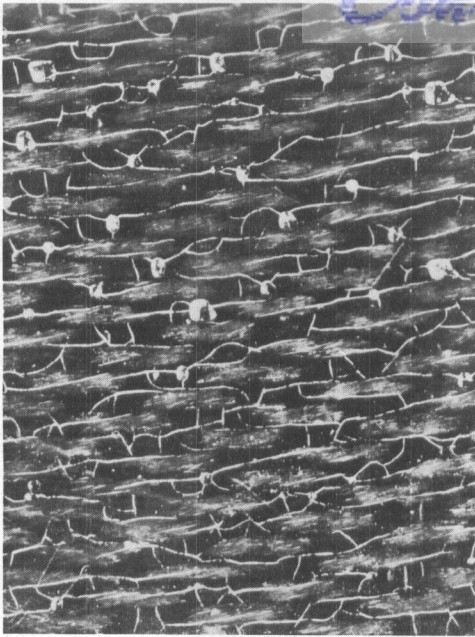
LAMINAC 4232 5% PARAPLEX G-50



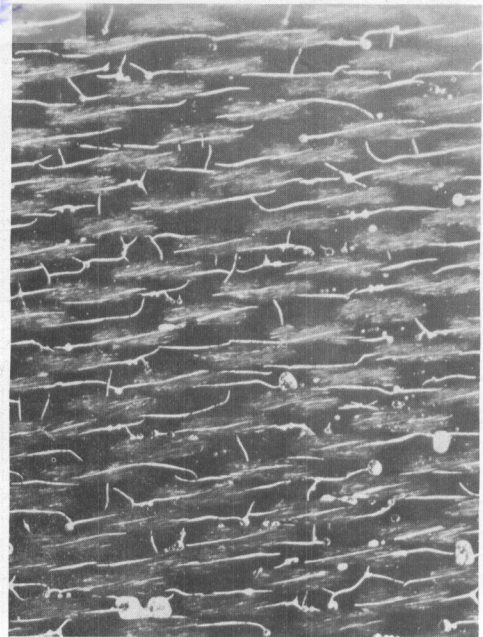
SELECTION 5900 603-4 5% PARAPLEX G-50

PHOTOMICROGRAPHS - 10X PLASTICIZED TRIALLYLCYANURATE POLYESTER 181-301
LAMINATES AFTER 2 HOURS CURE IN PRESS AT 220°F AND AGED 48 HOURS AT 500°F

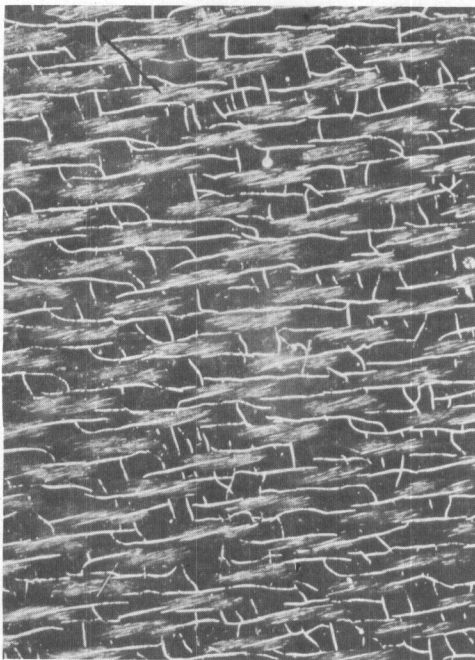
FIGURE 16



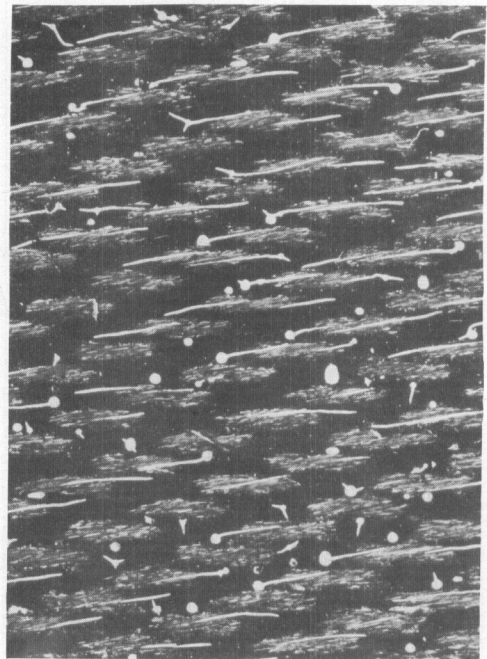
SELECTRON 5000-468-53
POSTCURED 3 HOURS AT 500 °F



SELECTRON 5000-603-28
POSTCURED 3 HOURS AT 500 °F



SELECTRON 5000-603-26
POSTCURED 3 HOURS AT 500 °F



SELECTRON 5000-603-27
POSTCURED 24 HOURS AT 400 °F

SELECTRON TRIALLYLCYANURATE RESINS
WITH VARIOUS CROSSLINKING DENSITIES

FIGURE 17

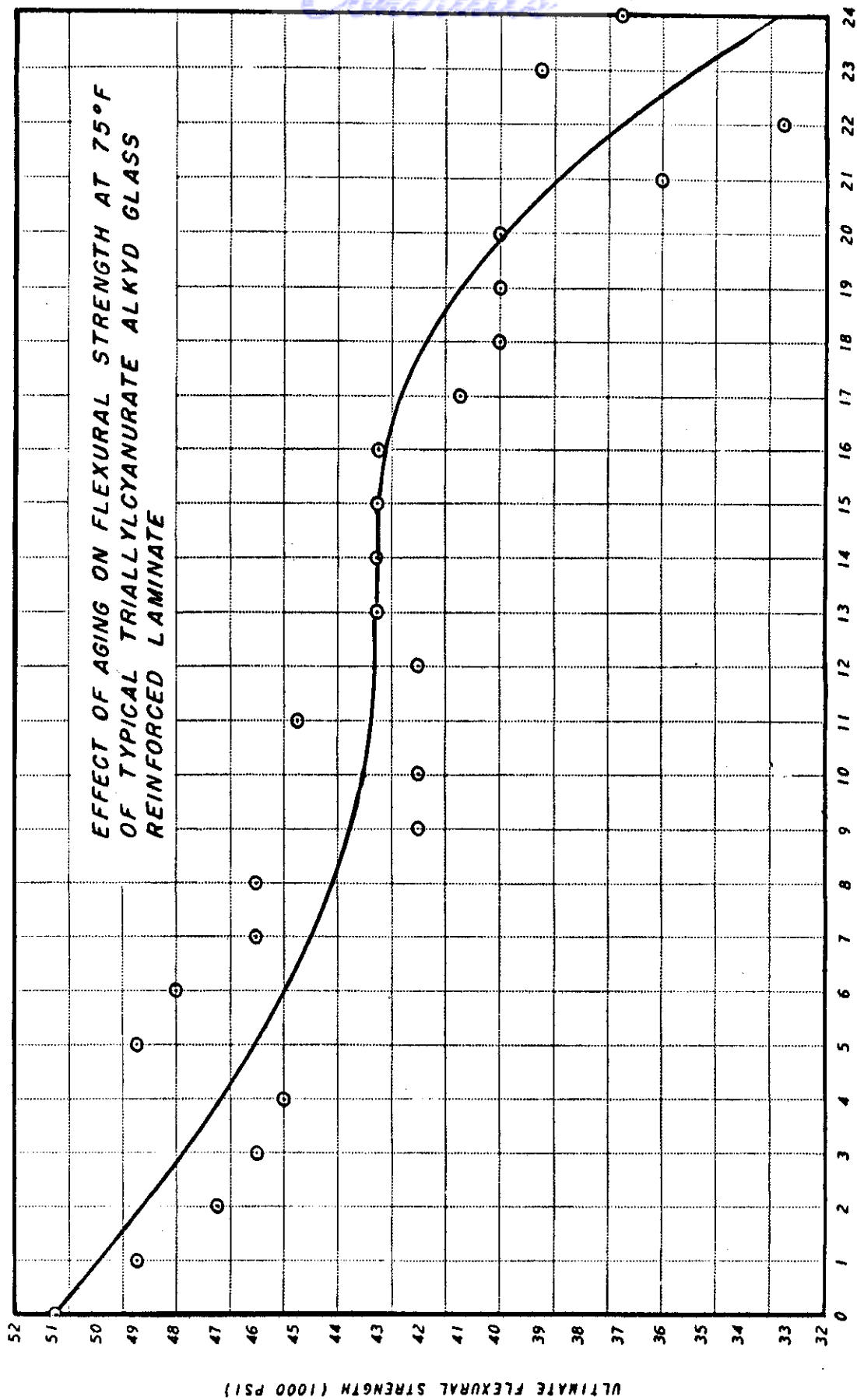


FIGURE 18

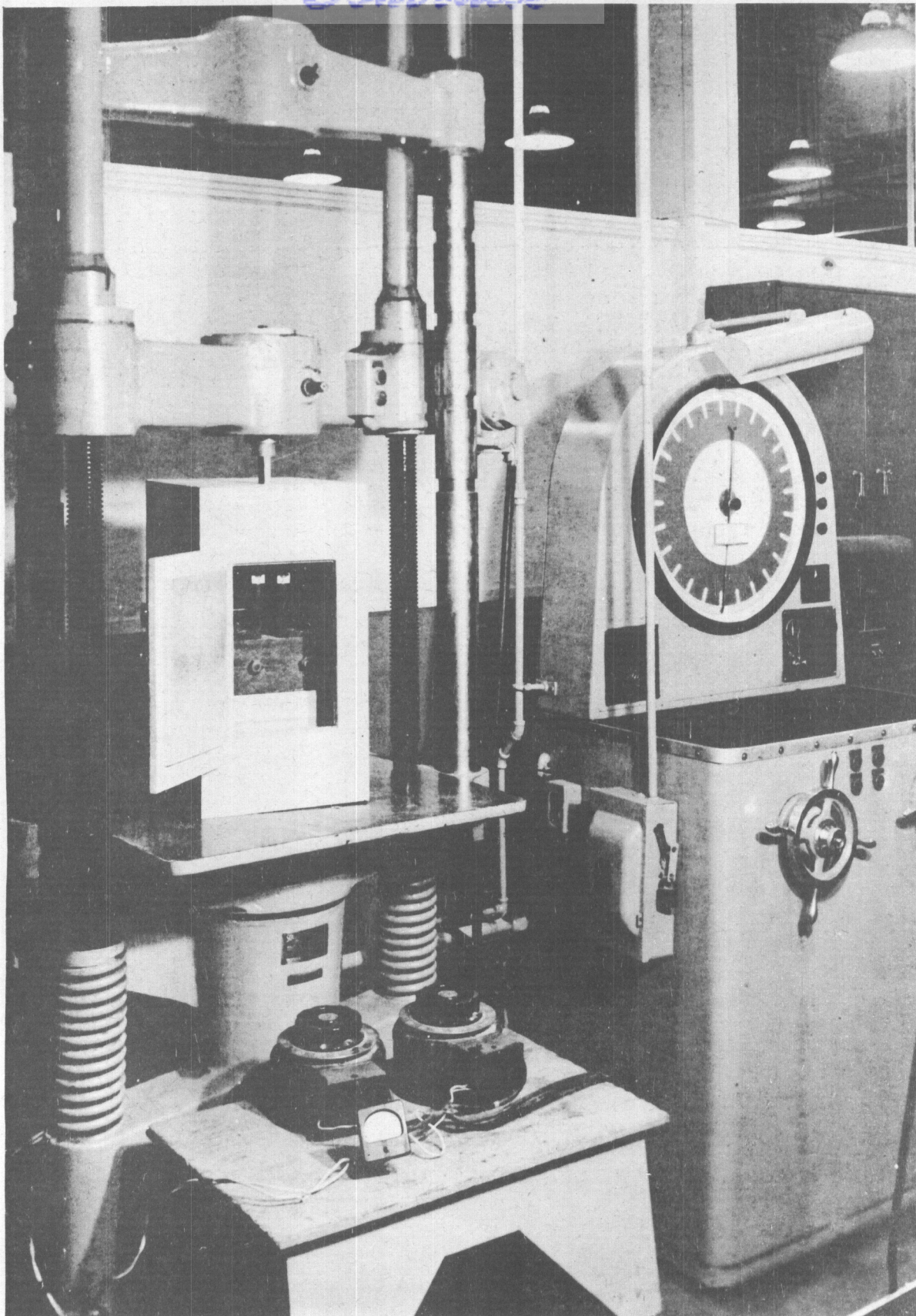


FIGURE 19