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HEAT RESISTANT POLYESTER LAMINATING RESINS

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FOREWORD

This report was prepared by the Naugatuck Chemical, Division of United States Rubber Company under USAF Contract No. AF 33(600)16825. The contract was initiated under Research and Development Order No. 614-12, "Structural Plastics", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. D. Rosato acting as project engineer.

ABSTRACT

The heat resistance of Vibrin X-1047 laminates is notably influenced by the finish on the glass cloth employed. The heat resistance of such laminates is a more searching test of cloth quality than the measurement of green flexural strengths. A 301-finish is generally satisfactory for use with heat resistant polyesters.

Two monomers, triallyl aconitate and diallyl Δ^4-3,6-methanotetrahydrophthalate, in combination with Alkyd X-1038 provide two new resins which show good retention of flexural strength at 300-400°F. With the triallyl aconitate resin, a flexural strength of 27,000 psi is maintained through 408 hours at 300°F. At 400°F the flexural strength is still 26,500 psi after 408 hours exposure. The resin derived from diallyl Δ^4-3,6-methanotetrahydrophthalate is still increasing in strength between 192 and 408 hours at 300°F (38,900 to 42,100 psi) and does not lose strength in the same interval at 400°F (38,000 psi level.).

It has been demonstrated that a cured foam of 10 lbs./cu.ft. density can be prepared from Vibrin X-1047 using the technique developed under Bu. Ships Contract Nobs-54183 (1773).

A modified poly (bismethylolxylene maleate) alkyd is superior to the modified poly (ethylene maleate) used in Vibrin X-1047 where resistance to long term exposure to 500°F is involved. Using a mixed triallyl cyanurate - diallyl Δ^4-3,6-methanotetrahydrophthalate monomer system, rather than triallyl cyanurate alone, affords a superior heat resistant polyester. At the same time the materials cost of the resin is reduced.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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I INTRODUCTION

This research was undertaken to provide a more thorough evaluation of the high temperature properties of Vibrin X-1047 and if necessary to improve upon this resin so that longer exposures to 500°F (>192 hours) and relatively short exposures to temperatures up to 650°F could be tolerated.

The work may be divided into five categories:

(1) evaluation of the newer glass cloth finishes with Vibrin X-1047

(2) evaluation of this resin for short term exposures to 650°F, and longer (408 hours) exposures to 500°F

(3) study of alkyd variations

(4) study of monomer variations

(5) investigation of mixed monomer systems.

The investigation of alkyd structure encompassed studies of alkyds of lower acid number, fumarate vs. maleate unsaturation, incorporation of potential antioxidant structures, and reinvestigation of alkyds based on glycols having no beta hydrogens. The last approach was most fruitful. A modified poly (bis-methylolxylene maleate) was found to confer superior long term aging properties (408 hours at 500°F). This phase of the work is incomplete but the data at hand suggest that substantial improvements can be realized by using an alkyd based on a bismethylol derivative of an aromatic ring.

Since triallyl cyanurate was known to be outstanding as a heat resistant monomer, the research in this area was directed toward a definition of the reasons for its superiority. This effort lead to no conclusions but was productive in that several new resin systems suitable for service at temperatures up to 400°F were discovered. Moreover the use of one of several new monomers studied, diallyl 4-3,6-methanotetrahydrophthalate, in a mixed monomer system with triallyl cyanurate, revealed a synergistic monomer effect which permitted the realization of a substantial improvement in heat resistance as compared to Vibrin X-1047.

Laminates prepared from the improved resin have flexural strengths at 500°F, after 192 hours at 500°F, as high as 30,000 psi (Vibrin X-1047: 20,000 psi, at best 23,000 psi). With an exposure of 408 hours to 500°F, the strength at 500°F of the new system is 16,000 psi compared to 10,000 psi for Vibrin X-1047 laminates. It seems quite possible that the full potentialities of the new system have not been realized in the relatively short time that it has been known.

Foams of 10 lbs./cu.ft. were prepared from Vibrin X-1047 using the method developed under Bu. Ships Contract Nobs 54183 (1773).

II CONCLUSIONS

1. Glass cloth finish is an important consideration in heat resistant laminates. The 301 finish is generally satisfactory in these applications with the Vibrin X-1047 resin.

2. A notable improvement in heat resistance is realized when the alkyd structure is based on bismethylolxylene as the glycol.

3. Triallyl aconitate, triallyl carballylate and diallyl Δ^4-3,6-methanotetrahydrophthalate, when blended separately with Alkyd X-1038, provide three new resins suitable for service at temperatures up to 400°F.

4. A Vibrin X-1047 laminate on 181-301 cloth which has an average flexural strength after 192 hours at 500°F of 23,000 psi (measured at 500°F) is reduced to a strength of 8,000 psi when the aging period is extended to 408 hours at 500°F.

5. A similar laminate, which in one test had a 192 hour at 500°F strength of 18,000 psi, is reduced to a flexural strength of 17,000 psi in a second test (measured at 600°F) by an exposure of 3 hours at 500°F (postcure) and 3 hours at 600°F. When the exposure to 600°F is extended to 24 hours the strength (measured at 600°F) is 5,400 psi.

6. Wet strength retentions of 90% or better are realized with Vibrin X-1047 laminates prepared with 181-301 cloth.

7. The optimum compressive strength (36,000 psi) of Vibrin X-1047 laminates involving 181-301 cloth is realized when the resin content is 35±2%.

8. Use of diallyl Δ^4-3,6-methanotetrahydrophthalate in conjunction with triallyl cyanurate and Alkyd X-1038 gives a resin which heat ages notably better than Vibrin X-1047.

9. Vibrin X-1047 can be foamed to a cured density of 10 lbs./cu.ft.

III DISCUSSION

A. Evaluation of Various Glass Cloth Finishes with Vibrin X-1047 (Table I)

The decision was made at the start of the work on this contract to use 181-136 glass cloth throughout. Comparison of a roll of this cloth received from Supplier A with a sample obtained previously from Owens-Corning revealed that the new roll was decidedly stiffer and required 27.5 rather than 10 psi to produce a Vibrin X-1047 laminate having 37±2% resin content. Large (23" x 23") laminates made with the stiff 181-136 cloth failed to exhibit a flexural strength of 30,000 psi or greater at 500°F after 24 hours at 400°F postcure and 1/2 hour exposure to 500°F. This unexpectedly poor laminate quality was traced to the stiff 136-finished cloth by elimination of other possible causes and by preparation of a test laminate. (UR, Table I). The heat aging of this panel is seen to be generally poor compared to a laminate prepared from 181-114 cloth (VV) whereas previous experience in these laboratories had indicated that

136-finished cloth (i.e. from Owens-Corning) affords Vibrin X-1047 laminates surpassing in heat resistance those containing 114-finished fabric.

Further testing of 181-136 cloth from Supplier A (including several samples from other rolls) demonstrated that this failure to attain heat resistance in Vibrin X-1047 laminates in the measure indicated by experience with Owens-Corning 136 cloth was a general phenomenon. Moreover, the flexural strength of such laminates after all exposure periods was found to fluctuate widely. This meant that investigation of resin variations using this cloth would be impossible since there would be no assurance that the cloth was not responsible for all (or part) of the differences from a Vibrin X-1047 panel used as a control. Since one of the objectives of the contract was to evaluate the newer cloth finishes with Vibrin X-1047, a program was set up which would include a study of the uniformity of various cloth finishes in their contribution to heat resistance as well as their average level of performance in this respect. It was anticipated that at least one type of cloth would show a uniform contribution to the heat resistance of Vibrin X-1047 laminates thereby permitting the start of resin variation studies.

Three rolls of each type of cloth were purchased and color coded. Laminates were prepared from the outer, inner and middle sections of each roll. A complete study of a second silane-finished cloth obtained from Supplier B (Table I) showed an appreciable inter- and intra- roll variation and a general inferiority to 114-finished cloth after 192 hours exposure to 500°F. The variations are such as to preclude the use of this cloth in a study of resin composition. These results were transmitted to Supplier B. They prepared and tested a Vibrin X-1047 laminate using our layup techniques, with the following results:

Resin Content	Flex.Str.x10^{-3} (Room Temp.)	Flex Str. x 10^{-3} at 500°F after aging at 500°F 3 hrs.	24 hrs.	72 hrs.	192 hrs.
39%	61.9	44.9	39.1	33.7	24.1

Using a second sample of cloth furnished by them, we prepared a laminate at 37.5 psi which contained only 28% resin rather than 35-40% obtained with the same pressure using the previous sample of this cloth. This indicates a considerable difference in the two samples.

A less detailed study of another silane finish (Supplier C) revealed a similar lack of uniformity and essentially the same contribution to heat resistance.

Through the courtesy of Mr. F. W. Dennen of Owens-Corning, we were furnished with a sample of 136-finished cloth which was considered by them to be typical. Laminate VS (Table I) prepared from this cloth showed resistance to heat on the level which we had previously observed with Owens-Corning 136-finished cloth. At the same time there was made available to us a sample of 301 finished cloth. A panel prepared from this cloth and Vibrin X-1047 (VT, Table I) showed an even greater heat-resistance particularly after 192 hours exposure to 500°F when a flexural

strength of more than 30,000 psi was obtained. Three additional rolls of this 181-301 cloth were obtained and tested (Table I). The high level of heat-resistance conferred by the original sample was not maintained in these rolls but the uniformity was reasonably good and the level of heat resistance was uniformly better than had been experienced with other finishes. An unusual feature of the results is a large variation in the flexural strengths at 500°F after 3 hours at 500°F. However the laminates which show up poorly at three hours (particularly WX, XB and XG) all show an increase in strength between 3 and 24 hours such that an overall uniformity in 24-hour and 192-hour values was attained. The heat aging data on the large panel (YG) is consistent with that obtained on the small test panels showing that no complications need be expected in scaling up laminate size with this cloth.

Three hour boil tests on seven laminates prepared with 181-301 fabric show six cases where 90% or better retention of strength was realized. There seems to be little question that the use of the 301 finish involves no sacrifice of resistance to humidity.

B. Alkyd Variations (Table II)

Before the uniformity of 181-301 cloth was established, the study of resin variations was started using 181-114 fabric. This was dictated by the fact that this finish had been shown to introduce no large variations in the heat resistance of Vibrin X-1047 laminates and by the necessity of activating this phase of the program without further delay if any progress was to be realized in the time available. This accounts for the use of both 114 and 301 cloth types in the work to be described. In some cases the more promising resin developments obtained with the use of 114 cloth have been duplicated using the 301 finish. Limitations of time have prevented this being done in all cases.

Relatively small departures from the Vibrin X-1047 system were involved in reducing the acid number of the alkyd from ca. 40 to 11 (laminate YD, Table II) and in substituting fumaric acid for maleic anhydride in the alkyd formula (panel YL). Comparison of the heat aging data for these systems with that of Vibrin X-1047 on the same cloth (VV, Table I) show that the changes are both disadvantageous. Poly (ethylene maleate) had been shown to be a good alkyd for heat resistant resins in work carried on by Air Force Contract 733(038)-11821, but suffers the disadvantage of yielding mixtures with triallyl cyanurate which are pasty at room temperature and are therefore, difficult to use in lamination. Poly (propylene maleate) does not have this characteristic but is relatively poor in its contribution to heat resistance (laminate WM, Table II). The Atlac 362A alkyd* was studied since it is presumed to have a structure quite distinct from those heretofore used in heat resistant polyesters. In order to obtain a reasonable resin viscosity it was necessary to use a relatively large proportion of triallyl cyanurate monomer. The failure of the laminate (XQ) to heat age as well as VV (Vibrin X-1047, Table I) probably reflects a low percentage of maleic unsaturation in the Atlac alkyd.

*Product of the Atlas Powder Company, Wilmington, Delaware

The substitution of dimethylol-p-cresol for 5% of the ethylene glycol of Alkyd X-1038 used in Vibrin X-1047 was prompted by the known antioxidant action of phenolic substances. It was hoped that oxidative attack on the cured structure would be retarded by the p-cresol portion of the alkyd. Comparison of the heat aging data (panel XN Table II) with that for the Vibrin X-1047 control (VV, Table I) shows that contrarily, the phenolic alkyd has less resistance to heat.

The undesirable crystalline properties of poly (ethylene maleate) were eliminated by cooking into the alkyd a small proportion of 2-butene-1, 4-diol. This modifying agent was chosen on the basis that its allylic unsaturation would be available for crosslinking during cure. The resulting alkyd (0.1 moles butenediol/2.3 moles maleic anhydride) was given the notation Alkyd X-1318. Evaluation of a 50:50 blend with triallyl cyanurate on 301 cloth (panel ZM Table II) revealed that the new system was comparable to Vibrin X-1047 in heat resistance (compare laminates WX, WY, XA, XB, XY, XZ, YG of Table I.) Use of larger amounts of butenediol in the alkyd (up to 0.5 moles/2.3 moles maleic anhydride) gave essentially the same results.

Work carried out on Navy Contract N-8-onr-504 demonstrated that the poly-maleate of bismethylolxylene, when blended with styrene, gave a composition which heat aged better than conventional alkyds. A blend of a dicyclopentadiene-modified version of this alkyd gave a laminate which heat aged better than Vibrin X-1047. The 3-hour and 24-hour strengths were low but the 192-hour strength was high (20,000 psi) and the panel suffered no loss between 24 and 192 hours and still had a flexural strength of 10,000 psi after 408 hours exposure to 500°F (laminate XE, Table II). Unfortunately the bis(chloromethyl) xylene which is an intermediate in the preparation of this alkyd proved to be a vesicant and capable of producing extreme allergic sensitization in individuals coming in contact with it. The related methoxymesitylene-α,α'-diol alkyd does not involve the use of vesicant intermediates and it was hoped that the presence of the additional methoxy group in this structure will not detract from the heat resistance of the structure. Time limitation has prevented its evaluation.

C. Monomers Variations (Table III)

As an approach to a monomer exhibiting heat-resistance superior to triallyl cyanurate it was of interest to compare a number of monomers which were structurally related to the triazine derivative. β-Chloroallyl cyanurate was found to have very low resistance to heat. A blend of this substance with X-1038 alkyd made into a laminate with 114 cloth was entirely destroyed by 24 hours exposure to 500°F (panel XT, Table III). Presumably the cured monomer structure suffers dehydrohalogenation at 500°F producing olefinic regions which are loci for rapid oxidative attack at this temperature. This observation makes it doubtful that any new monomer having the grouping -CHX-CH- (X=Cl, Br, I) will be useful as a heat resistant monomer.

The evaluation of vinylpyridine (laminate XM, Table III) was undertaken for comparison with styrene. It was hoped that the difference

would be a measure of the value of hetereocyclic nitrogen in the monomer. It appears doubtful however that the comparison is valid since the curing conditions were necessarily quite different. Moreover the assumption that the copolymerization of the two monomers with the alkyd is identical is open to question.

Triallyl aconitate and triallyl carballylate were made available to us by Dr. L. F. Martin of the Southern Regional Research Laboratories. A comparison of the latter monomer with triallyl cyanurate was instructive since both are trifunctional allyl monomers differing only in the structure connecting the polymerizable groups. On the assumption that the difference in activity of the allyl groups of the two monomers in polymerization was so small as to give the same degree of cure, the difference between the two laminates (YP, Table III and VV, Table I) can be ascribed to the different heat stability of the connecting structures. The Barcol hardness of the two panels was the same (75-80). Accordingly the considerable superiority of the triazine monomer may well be ascribed to the superior heat stability of the structure connecting the allyl groups.

It has been supposed that the ability to cure "tightly" is a valuable feature of a heat resistant monomer. It was therefore to be expected that triallyl aconitate, by virtue of its additional (α,β) unsaturation, would show some superiority to triallyl carballylate. Actually the carballylate seems to be marginally superior (the standard deviation in our measurement of flexural strength being 2000 psi). This result indicates either that the additional unsaturation does not have the value that was suspected for it, or that it is incompletely involved in polymerization and thus serves as a locus for oxidative degradation. A comparison with diallyl itaconate might clarify this point.

The superiority of (50:50) X-1038 Alkyd-triallyl aconitate polyester (Vibrin X-1064) to conventional styrene-based analogs in resistance to 500°F, coupled with its considerable cost advantage in comparison with Vibrin X-1047, suggested an evaluation at 300°F and 400°F (laminates XR and 2A, Table III). The results indicate that Vibrin X-1064 will maintain a flexural strength of 27,000 psi at 300°F through 408 hours exposure to this temperature. With the use of 301 cloth rather than 114, this level would undoubtedly be raised. This is indicated by the results of 400°F aging where the test laminate (2A) was prepared with the 301 cloth. The level of flexural strength maintained at the higher temperature is 36,000 psi. Since one would expect greater losses of strength at 400°F than 300°F, the difference is probably another example of the advantage in using the 301 rather than the 114-treated cloth in heat resistant laminates.

Vinyl crotonate was evaluated because the monomer is cheaper than triallyl cyanurate and because a comparison with the other ester monomers might suggest new lines of investigation. The 500°F aging results, in comparison with a triallyl aconitate system on the same cloth (panels YI and XS, Table III), show that the crotonate system has lost more strength after 24 hours exposure than the aconitate. This suggests that the

crotonate system is approaching complete failure at a faster rate. A comparison of vinyl crotonate with allyl crotonate would be of interest in evaluating allyl vs vinyl unsaturation in heat resistant systems.

Acrylonitrile was investigated as a monomer primarily to provide background information for mixed monomer studies. Because of the low boiling point of this monomer, a prolonged low temperature curing cycle had to be employed in order to obtain a satisfactory laminate (YE, Table III). A high green strength (82,000 psi) was drastically reduced by 3-hours exposure to 500°F. This was followed by a notable increase at 24 hours and complete failure in some time less than 192 hours. These results indicate that acrylonitrile has no unusual virtue as a monomer in heat resistant resins.

The best heat-resistant monomer, other than triallyl cyanurate, was discovered when heat aging of a 50:50 Alkyd X-1038-diallyl Δ^4-3,6-methano-tetrahydrophthalate laminate was carried out. As shown in Table III, the panels prepared with 301 glass cloth retained a higher strength during exposure to 500°F, 400°F or 300°F than any of the other new resins investigated. The 500°F aging (laminate YW) is noteworthy in that this is the first example of a non-cyanurate laminate that will retain a measurable flexural strength (10,000 psi) at 500°F after 192 hours exposure to 500°F. The strength at 300°F is seen to be increasing between 192 and 408 hours and to have leveled off at ca. 38,000 psi during the same period at 400°F (panel 1A).

D. Mixed Monomer Systems (Table IV and V)

The dilution of triallyl cyanurate with a cheaper monomer in a blend with a suitable alkyd could possibly be accomplished with little or no loss in heat resistant properties of the cured resin. When this was tried with acrylonitrile it was found that heat resistance did not suffer appreciably when 25% of the triallyl cyanurate of Vibrin X-1047 was replaced, and that the loss (except for a low 3 hour value) was not too great even with a 50% substitution (compare laminate VV of Table I and YH and YF of Table IV). In the case of dilution with triallyl aconitate, 25 and 50% dilutions resulted in much greater losses in 24 hour values and total failure at 192 hours (panels YO and YN, Table IV). The trend of the data suggests that the loss in heat resistance increases with the relative amount of triallyl aconitate and this is born out by the aging of laminate YM (75% aconitate).

This experience with mixed monomer systems provided no basis for anticipating the remarkable improvement in heat resistance encountered when diallyl Δ^4-3,6-methanotetrahydrophthalate (DAC) was employed as the second monomer, (Table V). Two of the first three blends investigated (ZC, ZY and ZZ corresponding to TAC-DAC ratios of 1:3, 1:1, and 3:1) gave laminates on 181-301 cloth which had flexural strengths at 500°F after 192 hours at 500°F of 36,000-37,000 psi and the third exceeded 31,000 psi. Moreover two of these survived 408 hrs. at 500°F with strengths in the 16,000-17,000 psi range. All three showed excellent wet strength retention. A laminate which was a duplicate of ZX except that it was

made with spacers, and therefore had a lower resin content (36% rather than the 40% of ZX), had a much lower 192 hour strength (17,000 rather than 36,000 psi).

E. Further Evaluation of Vibrin X-1047 (Table VI)

One of the objects of this contract was to evaluate Vibrin X-1047 for resistance to 500°F for periods longer than 192 hours and to temperatures above 500°F for shorter periods. Table VI contains the pertinent data. Typical laminates on 301 cloth were chosen for the study, one (XB) having a low resin content and the other WX having a relatively high percentage of resin. The loss in flexural strength at 500°F of laminate XB is seen to be roughly linear with time after 24 hours. Extrapolation of the data indicate that the laminate would fail completely after about 500 hours exposure.

The 600°F exposure tests on laminate WX indicate that 3 hours at this temperature is equivalent to 192 hours at 500°F. The necessity of a postcure is greater when exposure to 600°F rather than 500°F is involved since a non-postcured test strip averaged 10,400 psi in flexure after 3 hours at 600°F whereas a preliminary 3 hour at 500°F postcure raises this value to 17,000 psi.

A series of laminates were prepared from Vibrin X-1047 and 181-301 cloth at cure pressures varying between 5 and 15 psi. The resin contents determined by area calculation and by combustion were consistently different (the combustion values being assumed to be more reliable). Compressive strengths at room temperature were determined on this series. The data (Table VII) and Fig. 1 show that the maximum strength (36,000 psi) is associated with a resin content of 35%. The plot (Fig. 1) suggests that the range 33-7% (corresponding to cure pressures of 8-15 psi) will give optimum compressive properties for this system since the differences within this range are of the order of the precision of measurement.

F. Foaming of Vibrin X-1047

The preparation of a low density (approximately 10 lbs. per cubic foot) cellular plastic material from Vibrin X-1047 resin for use, at elevated temperatures, as a core material in sandwich constructions with glass fabric-Vibrin X-1047 resin laminate faces, as outlined in the objectives of the subject contract, has been accomplished.

A chemical method (essentially that developed on Bu. Ships Contract Nobs-54183(1773)) utilizing maleic anhydride, ammonium bicarbonate and water as the gassing system was used to foam the Vibrin. The following formulation yielded foams of approximately 10 lbs. per cubic foot.

	Parts
Vibrin X-1047	100
Benzoyl peroxide	2
Maleic Anhydride	5
Diethylene glycol monooleate	0.25
Aluminum tristearate	1

	Parts
Magnesium oxide	2
Kaolin	3
Ammonium bicarbonate	4
Diethylaniline	1.026
Water	1.0

The Vibrin is catalyzed with the benzoyl peroxide (which was first wet with a minimal amount of styrene). The maleic anhydride (coarsely ground), aluminum tristearate, magnesium oxide, kaolin and ammonium bicarbonate (finely ground) are weighed into one container and are added all together, with stirring, to the catalyzed Vibrin. The diethylene glycol monooleate is then added. After sufficient stirring to produce a homogenous suspension, the promoter (diethylaniline) is added from a calibrated dropping pipette. After the promoter is thoroughly blended into the mix, the water is added dropwise and very thoroughly dispersed. The mix is then ready to be poured into the mold or cavity to be filled. The expansion of the resin, or the "blow" starts approximately 2-3 minutes after the dispersion of the water in the mix. The foam gels at the height of the "blow" and partially cures to a light tan, essentially unicellular, semi-hard, moderately friable mass.

Experimental mixtures were foamed in cellophane bags made to fit a hollow glass form 2 1/8" x 4" x 14". The foams prepared in the cellophane bag reached the height of their expansion and cured simultaneously in approximately 8-9 minutes and at 60-70°C. (internal temperature during height of exotherm). The surface texture of the foams produced in cellophane is characteristic, i.e., they presented a cheese-like appearance of multiple, non-uniform, connecting ruptured cells. However, the entire internal texture is excellent, presenting a uniform, fine unicellular structure completely free of voids. The foam produced utilizing the formula listed, and using 100 grams of Vibrin, produced approximately 600 cubic centimeters of foam.

It should be noted that thorough mixing is necessary to produce proper foaming. Greatest care should be exercised in making certain the water is completely dispersed throughout the mixture as the water is the triggering agent which sets off the gas-producing reaction of the maleic anhydride and ammonium bicarbonate.

Several foams of varying sizes were prepared in glass fabric-Vibrin X-1047 laminate-faced sandwich molds. The material was foamed in place forming the core material of the sandwich without difficulty. The laminate foam sandwiches were trimmed so as to examine the internal structure. In each instance the foam structure appeared excellent throughout. The cells were essentially uniform and unicellular. One of the foams seemed harder and possessed greater compressive strength than the others but the reason for this variation has not been established.

It may be necessary to set up a post-curing schedule to overcome some of the physical shortcomings of the non-postcured foams, such as lack of compressive strength, lack of sufficient hardness and friability. However, the time element prevented us from expending any further effort in this direction.

IV EXPERIMENTAL

A. Preparation of Monomers

1. Triallyl Aconitate a mixture of aconitic acid (2262 grams) allyl alcohol (2498 grams) toluene (2600 ml.) and p-toluenesulfonic acid monohydrate (26 grams) was refluxed with removal of water of esterification as the lower layer of the toluene-allyl alcohol-water azeotrope in a Dean and Stark trap. Stirring was used throughout - the aconitic acid did not completely dissolve until some 3 hours after the start of refluxing. After 31.5 hours, no more water layer was separating. Calcium carbonate (624 grams) was added and the mixture stirred and filtered. Concentration and vacuum-topping of the filtrate gave 3774 grams (96.4%) of a brown oil which polymerized as rapidly in the presence of 2% benzoyl peroxide as distilled material obtained from the Southern Regional Research Laboratories.

2. Diallyl Δ^4-3,6,-methanotetrahydrophthalate (DAC) a mixture of Δ^4-3,6,-methanotetrahydrophthic anhydride (1554 grams) allyl alcohol (1653 grams) toluene (1900 ml.) and p-toluenesulfonic acid monohydrate (19 grams) was refluxed for 24 hours with stirring until a homogeneous solution was obtained. During this time 188 ml. of lower azeotrope layer was collected in a Dean and Stark trap. Toluene-allyl alcohol azeotrope and toluene were distilled from the mixture until the pot temperature reached 150°C. The remaining solvent was removed in vacuo and the residue distilled. The main fraction (2127 grams or 85.6%, b.p. 153-70° at 3-5 m.m.) was diallyl Δ^4-3,6,-methanotetrahydrophthalate; a second fraction (111 grams, b.p. 170-182°C at 4-4.5 m.m.) has not been identified. The refractive indices n_D^{25} = 1.4955, and 1.4997 respectively show the two fractions to be different.

B. Preparation of Alkyds

1. Alkyd X-1318 a mixture of maleic anhydride (678 grams) ethylene glycol (427.5 grams) and 2-butene-diol-1,4 (26.4 grams) was stirred and heated under a nitrogen blanket according to the following schedule:

97 min.	to 100°C
5 min.	at 100°C (exotherm)
50 min.	to 150°C
192 min.	at 150°C
26 min.	to 200°C
17 min.	at 200°C

The alkyd was then cooled and hydroquinone (0.072 grams) added with stirring giving 963 grams of product.

2. Modified (Poly bismethylolxylene Maleate)

The required diol was prepared in three steps from xylene. Bischloromethylation of C.P. Xylene was carried out by stirring a mixture of

37% formalin (848 grams), xylene (424 grams) conc. hydrochloric acid (2120 grams) and zinc chloride (400 grams) for 8.5 hours at 65±5°C while passing in a stream of hydrogen chloride. After adding 800 grams salt and chilling, the crude product crystallized. It was filtered off and recrystallized from alcohol, mp. 84-6°C. Yield: 335 grams or 41%. The chlorine analysis indicated an impure product

calcd. for $C_{10} H_{12} Cl_2$: Cl, 31.2%;
found: Cl, 34.9%

A solution of bis (chloromethyl) xylene (10.1 grams) and fused potassium acetate (9.8 grams) in acetic acid (50 ml.) was refluxed for 4 hours and poured over 150 grams of ice. The organic layer was separated and added to a benzene extract of the aqueous layer. Distillation gave 9.2 grams (73.5%) of bis-(acetoxymethyl) xylene. b.p. 165-8°C at 5 m.m.

calcd. for $C_{14} H_{18} O_4$: C, 67.2; H, 7.25
found: C, 66.9, 67.2; H, 7.32, 7.45

This diacetate was hydrolyzed by refluxing a solution of 18.5 grams of the compound in 50 ml. alcohol and 20 ml. water containing 6.1 grams sodium hydroxide for 7 hours. When cooled, the mixture deposited 8.0 grams (65%) of bismethylolxylene, m.p. 146-150°C. The analytical sample was recrystallized from alcohol, m.p. 150-151.5°C.

calcd for $C_{10} H_{14} O_2$: C, 72.5; H, 8.49
found: C, 72.1, 72.2; H 8.65, 8.47

The alkyd was prepared by heating maleic anhydride (65.6 grams), bismethyolxylene (111.0 grams) and dicyclopentadiene (26.4 grams) to 150±5°C for 2.5 hours with stirring under a nitrogen blanket and removal of evolved water in a Dean and Stark trap. On raising the temperature to 190°C gelation seemed imminent. Heating was discontinued and hydroquinone (0.072 grams) added at 165°C followed by triallyl cyanurate (175 grams) at 160°C.

3. Modified Poly (methoxymesitylene-$\alpha\alpha'$-diol Maleate)

The required diol was prepared from p-cresol in two steps. Bismethylolation of the phenol was accomplished by treatment of a solution of 324 grams of p-cresol in water (600 ml) containing sodium hydroxide (150 grams) with 37% formalin (645 grams). After several days at room temperature a thick slurry of the sodium salt was obtained. Water (2000 ml.) was added, followed by dimethyl sulfate (378 grams) in small portions with stirring and cooling. The slurry became a clear solution which deposited an oil during 2.5 hours. After destroying excess methylating agent with 25 ml. conc. ammonium hydroxide, the mixture was cooled to -10°C. causing the oil to crystallize. The solid was filtered off and air dried. Yield 370 grams or 67.8%. The analytical sample was recrystallized from

toluene, m.p. 102-5°C.

calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.74
found: C, 65.9, 66.1; H, 7.81, 7.69

The alkyd was prepared from maleic anhydride (98 grams), diol (182 grams) and dicyclopentadiene (39.6 grams). After heating to 100°C with stirring under nitrogen, an exotherm to 105°C occurred. The temperature was then brought to 150±5°C and maintained there for 2 hours. After cooling to 140°C, hydroquinone (0.036 grams) was added followed by triallyl cyanurate (430 grams) at 140°C. Acid number of the alkyd was 116.5. Viscosity (disc) of the blend at 25°C, 50.4 poises. Catalyzed stability of the blend at 25°C. (1.5% benzoyl peroxide): OK 17 hours, N.G. 25 hours.

C. Laminate Preparation - Large (23" x 23") and Small (7" x 13")

Glass Cloth:

After cutting the glass cloth to the desired size, each ply is carefully cleaned of loose threads. The warps of the plies are always kept parallel. 14 plies are required for 1/8" laminate and 28 plies for 1/4" laminate.

Vibrin:

The preparation of a 7" x 13" x 1/8" laminate requires 600 grams Vibrin X-1047; a 23" x 23" x 1/8" - 2400 grams: a 23" x 23" x 1/4" - 4500 grams.

Catalyzing the Vibrin:

Benzoyl peroxide (2%) is weighed into a dry wide mouth jar, and is then wet with an equal weight of styrene and mulled to a smooth paste. The Vibrin is then weighed into the jar and is agitated until all the catalyst is in solution. The catalyzed Vibrin is then evacuated to completely remove suspended air.

Laminate Layup:

Wooden frames, inside dimensions 8" x 14" x 1-1/2" deep for the 7" x 13" laminates, and 25-1/2" x 25-1/2" x 1-1/2" deep for the 23" x 23" laminates are used as the support for a cellophane lining. This lining is one-half of a piece of cellophane, which when folded over on itself and the edges sealed, forms the bag in which the curing of the laminate is carried out. The form is placed on a smooth hard surface (e.g. a steel plate) and the catalyzed resin is poured through one layer of cheese cloth into the cellophane-lined cavity. All the plies of glass cloth are added at once to the pool of resin and are permitted to stand (covered) overnight to insure complete wetting of the cloth by the resin.

The following morning the layup is removed from the frame and the bag formed by sealing the end and sides with scotch tape.

Any air trapped between the plies is removed by use of a metal bar squeegee, working from the center towards the edges.

Curing the Laminate:

The layup is placed between two ferrotype plates and is placed in a press, the platens of which are preheated to 175-195°F. The required pressure (to give desired resin content) is applied to the platens for thirty minutes causing excess resin to be squeezed out. This excess resin is manipulated into that portion of the cellophane bag hanging away from the platens. Curing as evidenced by hardening of the edges, usually occurs within twelve minutes and when this is complete the portion of the bag containing the excess resin may be cut off with a pair of scissors.

In the case of 7" x 13" laminates, after the 30 minute press cure (during which the temperature is not permitted to exceed 195°F), the press is opened and the laminate allowed to cool in place to prevent warpage. The bag is then trimmed to the edges of the laminate and after suitable marking, the laminate is placed in an oven at 248°F for 2 hours to complete the cure.

In the case of 23" x 23" laminates the same procedure is used with the exception that the entire cure is carried out in the press.

D. Laminate Testing

Each laminate was subjected to a standard flexural strength screening test. The panels were cut with a one-sixteenth inch thick Alundum cut-off wheel into test strips approximately 3" x 1/2". Four strips were tested at each of the following times and temperatures: unaged at room temperature; and at 500°F after 3, 24 and 192 hours at 500°F.

The flexural strength measurements were made on an Olsen Lo Cap Universal Testing Machine (using the 1,000 pound scale) equipped with an oven having a temperature range from room temperature to 600°F at a head speed of 0.05 inches per minute. The method was comparable to that of ASTM D790-45T. At 300°F, the temperature control was approximately ±2°F and at 500°F the range was about ±5°F. The aging was done in circulating air ovens and about one-half hour before the testing time the specimens were transferred to the testing machine oven in a preheated insulated box. The 300°F aging was carried out in a Fries Precision Scientific Co. oven, Serial number 821-598, type A. An American Instrument Co. circulating air oven (No. 4-148C; Serial D-15508) was used for the 500°F aging. The 400°F and 600°F aging was carried out in a Desptach Oven, Style CF-26, equipped with an Aminco "Quickset" Thermoregulator of the appropriate temperature range. This gave control of ±3°F at 400°F and ±5°F at 600°F.

The flexural strength measurements were made with a two-inch span, giving a span-depth ratio of 16:1 or greater, and the calculations of the strengths were made with the simple beam formula.

A series of five laminates were subjected to a standard compressive strength test comparable to Federal Specification L-P406b, Method 1021.

The panels were cut with a one-sixteenth inch alundum cut off wheel into test strips approximately 3" x 1/2". Great care was exercised to make certain the ends were smooth and parallel to each other and perpendicular to the axis of the specimen. Five strips were tested for each laminate. A standard jig was used to hold the specimen so that the loading is truly axial and applied through surfaces which are flat and parallel to the ends of the specimen.

The compressive strength measurements were made on a Tinius Olsen Plastiversal Testing Machine (using the 1,000 pound scale). The rate of head travel was at no time greater than 0.05 inches per minute.

TABLE I

Evaluation of Various Glass Cloth Finishes with Vibrin X-1047

The laminates were prepared using 14 plies 181-weave cloth (7" x 13") and 600 g. Vibrin X-1047 catalyzed with 2% benzoyl peroxide. Press cure 0.5 hour at 170-190°F. Oven Cure: 2 hours at 250°F

Laminate Code	Cloth Finish	Cure Pressure (psi)	% resin area[a]	Flex. Str. x 10^{-3} (room temperature) Dry	Wet[b]	% retention	Flex. Str. x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.
UR	136 (Supplier A)	27.5	36	hi 54.8			32.5	20.2	8.11
				low 52.5			29.3	16.2	6.10
				ave. 53.3			30.8	19.4	6.82
VV	114	15	38	hi 44.7			25.9	34.2	15.2
				low 43.3			24.4	30.1	13.8
				ave. 44.2			25.1	31.9	14.7
VJ	Silane (Supplier B) (red outer)	37.5	35	hi 55.4				31.8	8.97
				low 55.0			19.4	27.6	8.56
				ave. 55.2				29.7	8.86
VM	Silane (Supplier B) (red middle)	37.5	38	hi 45.5			23.6	31.5	16.7
				low 41.1			20.2	26.6	15.3
				ave. 44.0			22.4	28.7	16.0
VO	Silane (Supplier B) (red inner)	37.5	41	hi 59.0			37.8	30.2	9.97
				low 56.0			32.8	27.4	8.86
				ave. 57.6			34.8	28.8	9.35
VI	Silane (Supplier B) (blue outer)	37.5	35	hi 58.0			23.3	29.3	9.51
				low 53.3			17.7	26.2	7.51
				ave. 55.9			19.4	27.4	8.60
VL	Silane (Supplier B) (blue middle)	37.5	35	hi 49.1			32.7	26.3	9.20
				low 46.1			26.4	21.4	8.70
				ave. 48.0			29.2	24.5	9.02

TABLE I - continued

Evaluation of Various Glass Cloth Finishes with Vibrin X-1047

The laminates were prepared using 14 plies 181-weave cloth (7" x 13") and 600 g. Vibrin X-1047 catalyzed with 2% benzoyl peroxide. Press cure 0.5 hour at 170-190°F. Oven Cure: 2 hours at 250°F

Laminate Code	Cloth Finish	Cure Pressure (psi)	% resin area[a]	Flex. Str. x 10^{-3} (room temperature)			% retention	Flex. Str. x 10^{-3} at 500°F after aging at 500°F		
					Dry	Wet[b]		3 hr.	24 hr.	192 hr.
VN	Silane (Supplier B) (blue inner)	37.5	36	hi	60.2			32.8	23.7	9.75
				low	55.7			29.9	20.3	9.13
				ave.	58.1			31.3	22.2	9.50
VU	Silane (Supplier B) (green outer)	37.5	41	hi	51.5			36.7	31.2	13.3
				low	45.0			30.8	29.4	11.0
				ave.	47.3			32.6	30.3	12.5
VX	Silane (Supplier B) (green middle)	37.5	41	hi	50.0			26.5	30.8	10.1
				low	47.4			22.5	24.6	9.43
				ave.	49.0			25.0	29.3	9.77
VY	Silane (Supplier B) (green inner)	37.5	40	hi	55.3			28.0	29.2	9.73
				low	43.4			25.6	24.1	8.93
				ave.	49.3			26.6	27.1	9.40
VP	Silane (Supplier C) (red outer)	15	35	hi	60.4			29.4	30.1	16.4
				low	54.4			28.2	25.4	14.5
				ave.	56.7			28.6	27.3	15.7
VQ	Silane (Supplier C) (blue outer)	15	41	hi	54.3			31.0	22.8	10.3
				low	53.1			28.7	20.3	9.04
				ave.	53.5			30.2	21.7	9.85
VR	Silane (Supplier C) (green outer)	15	40	hi	53.2			31.0	24.1	12.7
				low	51.9			28.5	22.5	10.7
				ave.	52.6			30.0	23.3	11.8
VS	136 (Owens Corning)	15	33	hi	68.7	58.1		34.6	39.3	25.0
				low	59.7	56.4	90	30.5	35.4 c.	21.2
				ave.	63.6	57.3		32.2	36.5	22.6

TABLE I - continued

Evaluation of Various Glass Cloth Finishes with Vibrin X-1047

The laminates were prepared using 14 plies 181-weave cloth (7" x 13") and 600 g. Vibrin X-1047 catalyzed with 2% benzoyl peroxide. Press cure 0.5 hour at 170-190°F. Oven Cure: 2 hours at 250°F

Laminate Code	Cloth Finish	Cure Pressure (psi)	% resin area[a]		Flex. Str. x 10-3 (room temperature) Dry	Wet[b]	% retention	Flex. Str. x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.
VT	301 (original sample)	15	35	hi	66.0			33.5	37.8	31.2
				low	64.6			30.0	32.9 d.	30.3
				ave.	65.6			31.3	36.1	30.7
WX	301 (blue outer)	15	41	hi	53.8	51.6		20.9	36.4	18.5
				low	50.6	48.1	97	18.9	33.1	17.5
				ave.	52.1	50.4		19.8	34.5	18.0
WY	301 (blue inner)	15	31	hi	59.8	53.3		33.9	42.7	15.4
				low	55.4	51.7	91	30.4	41.3	14.2
				ave.	57.6	52.5		33.0	42.2	14.9
XA	301 (green outer)	15	32	hi	65.5	54.1		27.6	42.4	23.1
				low	64.1	51.4	82	23.6	41.4	21.8
				ave.	64.9	53.0		25.8	41.9	22.4
XB	301 (green inner)	15	31	hi	53.5	47.4		24.8	39.3	24.8
				low	51.2	45.7	90	21.2	35.7	21.6 e.
				ave.	52.2	46.7		22.6	37.4	23.1
XY	301 (orange)	15	32	hi	59.8	55.5		36.0	39.4	18.6
				low	56.7	51.7	93	31.8	29.1	17.3
				ave.	58.3	53.9		34.4	39.3	18.0
XZ	301 (purple)	15	33	hi	60.7	57.2		33.9	41.6	20.4
				low	57.0	52.6	92	30.4	30.6	18.0
				ave.	58.9	54.5		32.0	36.6	18.9

TABLE I - continued

Evaluation of Various Glass Cloth Finishes with Vibrin X-1047

The laminates were prepared using 14 plies 181-weave cloth (7" x 13") and 600 g. Vibrin X-1047 catalyzed with 2% benzoyl peroxide. Press cure 0.5 hour at 170-190°F. Oven Cure: 2 hours at 250°F

Laminate Code	Cloth Finish	Cure Pressure (psi)	% resin area[a]		Flex. Str. x 10^{-3} (room temperature) Dry	Wet	% retention	Flex. Str. x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.
YG	301 (green) (23"x23" Laminate)	15	34	hi	56.5	51.7		21.4	40.4	20.8
				low	49.3	45.8	94	17.2	32.4	18.1
				ave.	51.5	48.1		19.6	36.5	19.0

Footnotes to Table I:

a. resin content calculated from planar density of the cloth (0.0302 g./cm.^{2}) and laminate weight and area.
b. after 3 hour boil
c. after 72 hours: 26.4
24.3
25.2
d. after 72 hours: 36.8
32.4
33.7
e. after 408 hours: 8.14
7.45
7.75
f. delamination

TABLE II

Heat Aging of Triallyl Cyanurate Polyester Resins Involving Variations in Alkyd

Laminate	Alkyd	Cloth	Resin % Alkyd	Resin % TAC[a]	Cure pressure psi	% resin	Flex. Str. x 10^{-3} (room temperature)		Flex. Str. x 10^{-3} at 500°F after aging at 500°F: 3 hr.	24 hr.	192 hr.	408 hr.
UN	propylene maleate	114	51	49	15	38	hi	44.7	16.1	26.2	b.	
							low	43.7	14.5	23.7		
							ave.	44.1	15.4	24.7		
XE	modified bis-methylol xylene maleate	114	47	53	15	39	hi	44.9	20.2	21.8	21.4	11.31
							low	40.1	14.1	20.4	19.3	8.70
							ave.	43.1	16.2	20.9	20.2	9.77
ZM	X-1318	301	47	53	10	35	hi	57.8	36.3	42.2	20.2	
							low	40.4	35.6	33.7	18.3	
							ave.	55.4	35.7	37.2	19.1	
XQ	Atlac 362A	114	32	68	15	38	hi	31.7	25.5	30.5	7.01	
							low	30.8	24.4	27.4	5.75	
							ave.	31.3	24.8	29.0	6.30	
XN	X-1038 with 5% dimethylol-p-cresol cooked in	114	50	50	15	42	hi	45.6	23.2	34.4	11.6	
							low	39.5	21.6	32.2	10.4	
							ave.	43.0	22.6	33.4	11.0	
YD	X-1038, acid # = 11 (vs. 40 in Vibrin X-1047)	114	50	50	15	38	hi	39.0	34.3	30.0	11.7	
							low	37.2	33.0	27.4	10.2	
							ave.	38.1	33.7	29.7	11.1	
YL	fumarate analog of Alkyd X-1038	114	49	51	15	41	hi	39.6	34.2	25.2	7.23	
							low	34.0	30.0	23.6	6.82	
							ave.	37.0	32.2	24.2	6.96	

a. TAC = triallyl cyanurate
b. delaminated

TABLE III

Heat Aging of Polyesters Prepared from Alkyd X-1038 and Various Monomers

Laminate Code	Monomer	Test Temp.	% Alkyd	Cloth 181-	Cure psi	% resin	Flex. Str. x 10^{-3} (room temperature)	Flex Str. x 10^{-3} test temp. after aging at test temp. 3 hr.	24 hr.	192 hr.	408 hr.
XT	-chloroallyl cyanurate	500°F	40	114	15	43	40.7	11.2			
							37.4	10.9	a.		
							38.9	11.1			
XM	2-vinylpyridine	500°F	62	301	10	34	42.9	4.99	5.55		
							39.2	4.77	5.10	a.	
							40.3	4.85	5.37		
YI	vinyl crotonate	500°F	55	301	b	34	61.3	18.2	16.9		
							55.5	16.4	15.1	a.	
							57.4	17.1	15.9		
XS	triallyl aconitate	500°F	50	301	10	38	63.8	21.5	25.8		
							56.8	17.9	22.9	a.	
							60.0	19.5	24.3		
WF	triallyl aconitate	500°F	50	114	15	35	36.0	19.5	15.7		
							34.9	18.1	14.8	a.	
							35.5	18.7	15.4		
XR	triallyl aconitate	300°F	50	114	15	40	39.6		27.5	27.4	27.8
							36.7		27.1	26.4	27.3
							38.4		27.3	26.9	27.6
2A	triallyl aconitate	400°F	50	301	10	39	44.6		35.6	38.7	27.3
							44.0 c.		32.8	35.2	25.9
							44.4		34.5	36.7	26.5
YP	triallyl carballylate	500°F	50	114	b	32	39.0	22.9	20.2	a.	
							38.0	22.4	18.5		
							38.6	22.7	19.4		

TABLE III - continued

Heat Aging of Polyesters Prepared from Alkyd X-1038 and Various Monomers

Laminate Code	Monomer	Test Temp.	% Alkyd	Cloth 181-	Cure psi	% resin	Flex. Str. x 10^{-3} (room temperature)	Flex Str. x 10^{-3} test temp. after aging at test temp. 3 hr.	24 hr.	192 hr.	408 hr.
YW	Δ^4-4,6-methano-tetrahydro-phthalate	500°F	50	301	10	36	64.5 57.0 d. 60.3	25.3 21.8 23.7	31.0 29.4 30.1	10.5 9.35 10.2	
1A	Δ^4-4,6-methano-tetrahydro-phthalate	400°F	50	301	10	35	54.8 51.2 e. 52.9		36.3 32.5 34.2	43.2 31.7 39.3	40.5 35.8 38.1
IA	diallyl Δ^4-3,6-methanotetra-hydrophthalate	300°F	50	301	10	35	54.8 51.2 52.9		31.7 24.0 28.6	39.8 38.2 38.9	42.6 41.5 42.1
YE	acrylonitrile	500°F	64	114	b	32	82.7 81.8 82.3	14.7 13.0 13.7	26.2 21.8 24.6	a.	

a. delaminated
b. spacers used
c. 3 hr. boil: 41.7, 32.0, 37.1 — 84% retention
d. 3 hr. boil: 68.4, 64.9, 63.6 — 105% retention
e. 3 hr. boil: 47.5, 41.7, 44.6 — 83% retention

TABLE IV

Heat Aging of Polyesters Prepared from Alkyd X-1038 and Triallyl Cyanurate plus a Second Monomer

Laminate Code	% X-1038	% TAC[a]	% Comonomer	Cloth 181	Cure psi	% resin	Flex. Str. x 10^{-3} (room temperature)	Flex. Str. x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.
YH	50	37.5	12.5A[d]	114	b.	36	62.8 54.5 58.9	26.0 23.0 24.8	36.4 30.4 34.2	13.1 11.5 12.1
YF	50	25	25A	114	b.	32	75.9 70.8 73.2	11.8 10.2 11.3	29.3 26.0 27.2	15.4 13.4 14.2
YO	50	37.5	12.5 TAA[e]	114	b.	32	37.6 37.4 37.5	29.4 27.8 28.6	23.8 22.9 23.6	c.
YN	50	25	25 TAA	114	b.	32	35.8 34.4 35.2	25.0 24.0 24.4	20.7 19.6 20.1	c.
YM	50	12.5	37.5 TAA	114	b.	32	35.0 34.2 34.5	21.4 20.8 21.2	17.9 17.4 17.6	c.

a. TAC = triallyl cyanurate
b. spacers used
c. delaminated
d. A = acrylonitirle
e. TAA = triallyl aconitate

TABLE V

Heat Aging of Laminates Involving Alkyd X-1038 and Triallyl Cyanurate (TAC)-Diallyl Δ^4-3,6-Methanotetrahydrophthalate (DAC) Mixed Monomers (181-301 Cloth)

Laminate Code	% alkyd	Monomer %TAC[a]	Monomer %DAC[b]	% resin area[c]	% resin comb.[d]	Cure psi	Flex. Str. x 10^{-3} Room Temp	Flex. Str. x 10^{-3} 3 hr. Boil	% retention	Flex. Str. x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.	408 hr.
ZX	50	12.5	37.5	36	40	10	62.7	60.8		24.3	33.6	39.2	17.7
							57.3	58.0	98	20.8	31.8	28.9	14.4
							60.3	59.1		23.2	32.7	36.1	15.8
ZY	50	25	25	39	43	10	58.0	60.7		26.2	38.2	33.1	20.5
							53.6	56.2	104	24.1	37.2	29.9	15.8
							56.2	58.7		25.1	37.7	31.3	17.6
ZZ	50	37.5	12.5	36	37	10	63.0	70.0		27.8	37.6	38.8	10.9
							60.5	66.6	109	23.1	31.8	32.8	9.5
							62.0	67.7		24.9	35.6	36.8	10.1

a. TAC = triallyl cyanurate
b. DAC = diallyl Δ^4-3,6-methanotetrahydrophthalate
c. See footnote a to Table I
d. by method except that samples were square (no grooves cut)

TABLE VI

408 Hour at 500°F and 600°F Aging of Vibrin X1047 Laminates (181-301 cloth)

Laminate Code	Cure psi	Resin % a.		Flex.Str.x 10^{-3} (room temp.)		% Retention	Flex. Strength x 10^{-3} at 500°F after aging at 500°F 3 hr.	24 hr.	192 hr.	408 hr.	Flex.Str.x10^{-3} at 600°F after aging at 600°F 3 hr.	24 hr.
XB	15	30.9	hi	53.6	47.4		24.8	39.3	24.8	8.14	22.1[d]	
			low	51.2	45.7		21.2	35.7	21.6	7.45	20.4	
			ave.	52.2	46.7	90.0	22.6	37.4	23.1	7.75	21.3	
WX	15	40.5	hi	53.8	51.6		20.9	36.4	18.5		17.8[e]	6.46[c]
			low	50.6	48.1		18.9	33.1	17.5		16.7	4.19
			ave.	52.1	50.4	97.0	19.8	34.5	18.0		17.0	5.41

a. by area calculation - see footnote a. to Table I
b. all test strips for 600°F tests were postcured 3 hours at 500°F before exposure to the higher temperature
c. due to failure of the oven control these test strips were at 640-645°F for ca. 2 of the 24 hours
d. two tests only
e. without a 3 hour at 500°F pretreatment the corresponding values were 11.3
9.65
10.4

TABLE VII

Compressive Strength of Vibrin X1047 Laminates with 181-301 Cloth as a Function of Resin Content

Laminate Code	Cure psi	% resin area[a.]	% resin combustion[b.]	Compressive Strength x10^{-3}	Modulus x10^{-6}
ZC	5	41	43	33.2	2.5
				29.2	2.1
				31.4	2.3
ZD	7.5	36	40	39.3	2.8
				29.1	2.5
				31.6	2.7
ZE	10	34	37	35.6	2.9
				27.1	2.7
				32.2	2.8
ZF	12.5	32	35	38.0	3.0
				33.1	2.6
				35.8	2.8
ZG	15	32	34	35.4	3.2
				33.6	2.7
				35.2	3.0

a. see footnote a. to Table I
b. see footnote d. to Table V

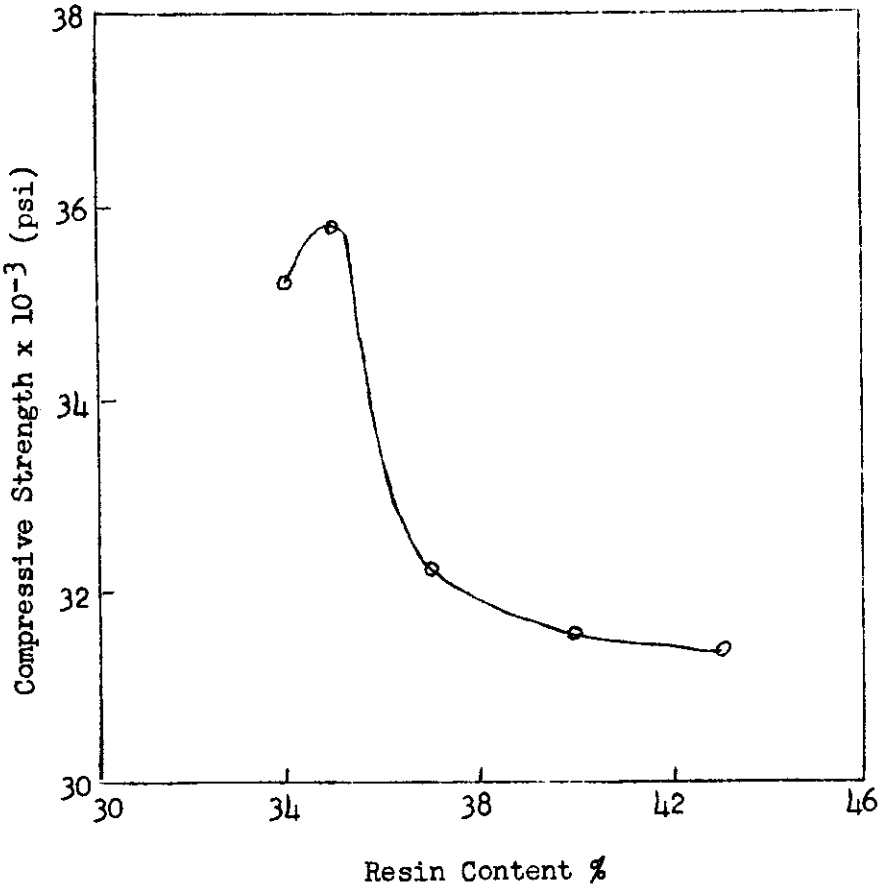

Fig. 1. Compressive Strength of Vibrin X-1047 Laminates (181-301 Cloth) as a function of resin content.