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Report No. 13

Summary Technical Report No. 3

March 31, 1966, to July 15, 1967

A STUDY OF BONDING BETWEEN GLASS AND PLASTIC IN GLASS-REINFORCED PLASTICS: PHASE III

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NASr-49(14)

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA



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SUMMARY

The general objective of this research project was to evaluate the effect of deliberate and known bonding between glass and plastic on the physical properties of a composite material.

During this report period, the effect on mechanical properties of direct chemical bonding between glass fibers and resin matrix was evaluated on experimental laminates of E-glass fabric (181 weave) and Epon 825 resin. Two laminates were prepared from alkylated glass fabric, two from fabric having the Al100 silane finish, and two from fabric without a finish.

Mechanical test data show the flexural modulus of surface-modified samples to be at least equal to that for samples prepared with Al100 finish. Flexural strength, however, was somewhat lower than for the Al100 samples. Retention of strength after a two-hour boil was very good, approaching that of the well-known Al100 treatment. Retention of modulus after a two-hour boil was equal to that for Al100 samples. The results are discussed in relation to bonding mechanisms and degradation reactions at the glass-plastic interface.

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INTRODUCTION

This investigation was undertaken to evaluate the effect of deliberate and known bonding between glass and plastic on the physical properties of the composite material and to gain knowledge of the degradation mechanisms that occur at the glass-plastic interface.

Current practice in preparation of glass-reinforced plastics includes treatment of the glass fibers (or fabrics) with a "finish" to ensure adhesion or "bonding" of the subsequently applied plastic. The bonding that may result is supposedly due to the formation of a silicon-oxygen-agent (Si-O-A) linkage between the glass surface (Si-O) and the finishing agent (A), where A may be Si (as in commercial silane finishes) or chromium (as in certain other commercial finishes). For example:

$$\begin{array}{c} | \\ \text{-Si-OH} \\ | \end{array} + \text{X-SiR}_3 \longrightarrow \begin{array}{c} | \\ \text{-Si-O-Si-R}_3 \\ | \end{array} + \text{HX}, \text{ where } \begin{array}{c} | \\ \text{-Si} \\ | \end{array} \text{ is a silicon atom bonded to three oxygen atoms in the glass surface, X is chlorine (Cl) or alkoxy (-OR'), and R is an organic group such as vinyl, allyl, etc.}$$

The true function of glass-fiber finishes is not understood. Some evidence has been obtained to show that there is not a true chemical bond between glass and plastic in those laminates which have been prepared with conventional finishing agents. For example, McGarry¹ discusses the evidence for the complete absence of chemical bonding between plastic and glass, and for the function of glass "finishes" to be the improvement of wetting of the fiber with the polymer during the impregnation process. Other work, however, has shown that A-1100 and 801 finishes interfere with the wetting of glass fibers by epoxy resins.^{2,3}

If the assumption is made that silane-type finishes do indeed effect a chemical link between the glass and plastic phases, the question of the hydrolytic stability of such an $\text{Si}_{\text{(glass)}}\text{-O-Si}_{\text{(finish)}}$ bond must be considered. Though Si-O-Si bonds are not easily hydrolyzed in the bulk, they do undergo an acid- or base-catalyzed redistribution reaction. This redistribution reaction has been shown to be responsible for stress-relaxation and compression-set processes in silicone polymers.^{4,5}

The role of water in the finish layer at the glass-plastic interface is not understood, but it may be very important.

This project is concerned with other types of bonding between glass and organic phases which are not dependent upon the Si-O-A linkage, and particularly with systems in which a direct silicon-carbon bond has been produced between glass and plastic. The objective of Phase I was to investigate methods for the halogenation of glass and/or silica surfaces in order to form reactive silicon-chlorine or silicon-fluorine groups. These groups would serve as intermediates for the production of silicon-carbon bonds by suitable alkylation reactions. The objective of Phase II was to study methods for converting reactive intermediate surface groups to surface-based organic groups that would provide a direct covalent bond between silicon atoms in the glass surface and polymer molecules in the resin matrix.

In Phase I methods were developed for the chlorination of glass and silica with phosgene and for the fluorination with gaseous fluorine. The "population" of these reactive intermediate groups was found to be as high as 6.5 per 100 Å² (a theoretical maximum is about 7.8). The feasibility of the final alkylation step was established by conversion of surface-based silicon-chlorine groups to silicon-phenyl groups. In Phase II methods were developed for the conversion of reactive intermediate groups to surface-modifying organic groups. Methods were also developed to measure the effects of surface modification upon properties of siliceous surfaces.

The objectives of Phase III were to prepare experimental glass fiber reinforced laminates using the procedures developed in Phases I and II, to determine the mechanical properties of these laminates, and to compare these properties with the same properties of conventional laminates.

RESULTS

General

Two configurations were considered for experimental composite samples: multi-ply woven fabric laminates and filament-wound NOL rings. The woven fabric laminates were chosen because of the lower cost of preparing limited numbers of samples, and for the fewer experimental difficulties involved in preparing surface-modified fabrics by a batch process, as compared with preparing surface-modified roving on a continuous basis.

Flexural strength was selected as the most informative measure of interfacial bonding (or integrity), and sample preparation and testing were carried out in accordance with ASTM Flexural Test D790-63.

The reaction scheme chosen for preparing surface-modified E-glass fabric (181 weave) was: preparation of reactive intermediate Si-F groups; reaction of the Si-F intermediate groups with the di-Grignard of 1,5-dibromopentane; and finally, stepwise oxidation and hydrolysis of the Grignard product to produce the surface-modifying group

$$-\underset{|}{\overset{|}{\text{Si}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}.$$

The resin system chosen for laminates was Epon 825^{*}-Nadic Methyl Anhydride,[†] cured with benzyldimethylamine. Epon 825 is an epoxy resin of narrow molecular weight range based on Bis-Phenol A. The terminal alcoholic hydroxyl groups on the alkyl surface-modified glass should have undergone reaction with epoxy and anhydride groups in the resin, resulting in strictly covalent chemical linkages between the glass and resin phases.

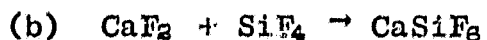
Fluorination of Glass Fabric

Fluorination rather than chlorination was chosen as the procedure for generating reactive intermediate groups on the surface of fibers in

* Shell Chemical Co. tradename

† Allied Chemical Co. tradename

a glass fabric, because the lower temperature (200°C) required for fluorination would result in less thermal damage to the glass. A disadvantage of fluorination is the probability that complex metal fluorides may be deposited on the glass surface. This is illustrated by the reaction with a simple calcium silicate:



The insoluble fluorosilicates would contribute to the fluorine content of the glass, but may reduce the number of sites available for establishing interfacial bonding. A further disadvantage is that extensive fluorination causes some chemical degradation of the mechanical properties of the fiber. Careful control of the fluorination process keeps this degradation to a minimum.

The deposition of fluoride is illustrated in Table I, which shows the population of fluorine atoms per 100 Å² of surface area. Fluorine gas at 18 psig at 200°C for three hours resulted in an average of 1117 F atoms per 100 Å². Fluorine gas, 4% in dry nitrogen, at a total pressure of 2 psig and at 200° for 5 minutes resulted in 38 F atoms per 100 Å². This latter value is about 10 times the calculated 7 to 8 F atoms required for complete conversion of surface silicon atoms to Si-F groups on crystalline quartz. The difference between 88 and 8 is probably due to metal fluorides and their SiF₄ complexes. There may also be some contribution from silicon atoms in the surface layer which bear two fluorine atoms instead of the ideal single atom.

Complex fluorides on the surface also make it impossible to know the concentration of useable fluorine atoms and may block, or cover, some sites that would otherwise be available for bonding. A practical measure of the number of these reactive intermediate sites is the number of surface-modifying organic groups that are found on the final treated glass.

Alkylation of Fluorinated Glass Fabric

The effectiveness of surface modification is shown in Table II. The efficiency of gaseous fluorine as a cleaning agent for glass is also demonstrated. Heat-cleaned glass, after vacuum-thermal desorption, had 64 ppm of carbon, by weight. After fluorination the carbon concentration had dropped to 45 ppm. This residual carbon is believed to be present within the glass rather than on the surface. Adsorbed carbon compounds corresponding to 19 ppm of carbon was removed by fluorination.

The amount of finish present on the Al100 treated glass fabric is also shown in Table II. The chemically cleaned (fluorinated-hydrolyzed) cloth had an average of 34 Al100 groups per 100 Å², while the cloth that received only the heat cycle had only 26 Al100 groups/100 Å². In both cases the silane was present in a multimolecular layer.

In contrast to the Al100 treated fabric, the two surface modified fabric samples contained only 0.7 and 0.1 pentanol groups per 100 Å². This coverage corresponds to about 9% and 1.3% of the calculated 7.5 groups per 100 Å² that are possible on a silica surface. These should be substituent groups bonded to silicon atoms in the glass surface. The method of preparation and the rigorous cleaning procedure practically preclude these groups as adsorbed species.

The function of terminal hydroxyls on the surface-modifying groups is to react with anhydride, acid, or epoxide groups in the epoxy resin phase of a laminate.

Preparation of Experimental Laminates

The quality of experimental laminates must be unusually high if confidence is to be placed in the results of physical property measurements. The conventional laboratory layup methods for producing experimental laminates were evaluated. A modified method, described in the Experimental section of this report, was developed. The technique was practiced until sufficient skill was acquired to produce laminates of desired and reproducible color, clarity, and density.

The clarity of the light-amber-colored laminates is illustrated in Fig. 1, which is a photograph of strips placed on a printed page. The density and resin contents of the laminates are summarized in Table III. The observed densities are equal to the calculated densities except for the heat-treated specimen and one alkylated specimen. In these two cases, the 1.6% density difference indicates a void content of about 1.3%, although visual inspection did not reveal significant differences between the various samples.

Flexural Testing of Experimental Laminates

The results of flexural tests on experimental laminates showed that surface modification of glass fibers (as an alternate to the use of a "finish" or "coupling agent") was definitely beneficial.

Test data are summarized in Tables IV-VII. The actual stress-strain curves are shown in Figs. 2-7.

The cloth that received the least treatment (the heat cycle only) produced the laminate that had the highest initial dry strength (78,000 psi) but suffered the greatest loss of strength (16.4%) after a two-hour boil. The cloth that received the heat cycle plus fluorination and hydrolysis produced a laminate that had a lower initial dry strength (74,300 psi) but lost only 11% of its strength after the two-hour boil.

The cloth that received the A1100 finish produced a laminate with high initial dry strength (77,500 psi), and which showed a slight gain in flexural strength after two hours in boiling water. The cloth that received the A1100 finish following fluorination and hydrolysis produced a laminate with a substantially lower initial dry strength (64,250 psi). This laminate, however, lost only 3% of its strength after a two-hour boil.

The two samples of surface-modified cloth (which received fluorination and alkylation) produced laminates that had initial dry strengths of 57,300 psi for the sample with 0.7 groups per 100 Å², and 69,150 psi for the sample with 0.1 groups per 100 Å². After the two-hour boil these laminates lost 8.7% and 4.4% respectively of their initial dry strength.

Before these values are discussed the additional data on the flexural modulus should be presented. These data are summarized in Table V. The first data column gives the modulus of the dry specimen taken at the initial part of the curve. The second data column gives the modulus of the specimen after it had received a two-hour period in boiling water, was air-dried, and finally conditioned at controlled temperature and humidity. Under each value, in parentheses, is the standard deviation for each series of five measurements.

The dry modulus for the heat-treated specimen was surprisingly high, but this value dropped the most (19%) after a 2 hour boil. The modulus for each of the other three control samples is about the same but is lowest for the heat-cleaned All00-finished sample. The deviation on the latter sample is also high. These three control samples also performed very much alike on the two-hour boil, with a drop in modulus of 3.0 to 3.8%.

For the two alkylated samples, the dry modulus was higher than for all other samples. Likewise the drop in modulus after boiling was the lowest for these two: 1.6% and 1.5%, respectively.

In Table VI is shown the flexural modulus of the laminates calculated from the portion of the stress-strain curve just prior to rupture, before and after the two-hour boil. Here again, the alkylated samples compared quite favorably with those samples that received the commercial All00 finish.

Finally, in Table VII, the modulus at break is compared with the modulus initially, for both dry and boiled series. The alkylated samples compare quite well with those samples which received the All00 finish. Small differences may be ignored, but the great differences between the boiled, untreated samples (the first two) on the one hand, and the boiled All00 and alkylated samples on the other hand, show plainly that the surface-modification process, making use of only a fraction of the available sites for reaction, produces laminates with properties significantly improved over those receiving no treatment and closely approaching the properties of laminates made with the commercial All00 finish.

DISCUSSION

Alkyl-substituted chlorosilanes and alkoxy silanes have become "standard" finishing or coupling agents for use on glass fibers in fiber-reinforced resins. The popularity of these finishes resulted from their ability to protect a composite material from loss of strength due to aging, especially in a wet or humid environment.

The mechanisms by which these agents provide protection against degradation of a laminate are not known. There is some evidence that the silanes form Si-O-Si bonds with silanol groups (Si-OH) on the glass surface. There is other evidence that chemical bonds are not formed at all, and that the silane is present as a separate homopolymer phase adsorbed into the glass surface.

Regardless of the nature of the adhesive bond, there are two important mechanisms for loss of strength in a fiber-reinforced composite: loss of strength (degradation) of the reinforcing fibers; and loss of adhesion between the reinforcing fiber and the supporting matrix. (This statement assumes that the primary function of the matrix is to transfer applied loads to the reinforcing phase, and that good interfacial adhesion (lack of slippage) is necessary for this transfer.) Therefore the function of finishes (coupling agents) must be either one of protecting the glass fiber from attack by water vapor and other degrading environments, or maintaining good adhesion in the presence of degrading environments such as heat and water. Some silane finishes may serve both purposes.

Whatever the protection mechanisms and the type of interfacial bonding, silane finishes are less effective at higher temperatures. Adhesion due to physical forces rapidly decreases as temperature increases. Though their thermal stability is very well known, Si-O-Si bonds are very susceptible to an acid- or base-catalyzed redistribution reaction shown to be responsible for stress-relaxation and compression-set processes in silicone polymers.^{4, 5} This reaction, while it produces

no observable chemical change in a material, should be available as a stress-relief (slippage) mechanism at a glass-resin interface where a silane coupling agent had been used.

Against this background, the objectives of this investigation were to study the methods for obtaining covalent chemical bonding at glass-plastic interfaces, to evaluate the properties of laminates based upon this type of interface, and to infer from these data the mechanisms operating to degrade the properties of laminates. Methods of preparing covalent chemical bonding at interfaces were investigated in Phases I and II of the project.^{6,7} Before proceeding with the discussion of the final phase of this research, it would be pertinent to evaluate the benefit which might come from purely covalent chemical bonding at a glass-resin interface.

The potential for obtaining strong adhesive strength from purely chemical bonding at a glass-plastic interface may be estimated from the strength (60 kcal/mole) of silicon-carbon bonds. Assume that only one silicon-carbon bond is formed per 100 Å² of interface, and that a separation of 4 Å is required for complete bond breakage. The conversion factors used in this calculation are:

$$1 \text{ mole} = 6 \times 10^{23} \text{ chemical bonds}$$

$$1 \text{ Å} = 10^{-8} \text{ cm} = 3.94 \times 10^{-9} \text{ in.}$$

$$1 \text{ kcal} = 3.09 \times 10^3 \text{ ft. lbs.}$$

$$S(\text{lbs./in.}^2) = \frac{1 \text{ bond}}{(10 \text{ Å} \times 10 \text{ Å})} \times \frac{10^8 \text{ Å} \times 10^8 \text{ Å}}{\text{cm}^2}$$

$$\frac{1 \text{ mole}}{6 \times 10^{23} \text{ bonds}} \times \frac{60 \text{ kcal}}{\text{mole}} \times \frac{3.09 \times 10^3 \text{ ft. lbs.}}{\text{kcal}}$$

$$\times \frac{1}{4 \text{ Å}} \times \frac{1 \text{ Å}}{3.94 \times 10^{-9} \text{ in.}} \times \frac{12 \text{ in.}}{\text{ft.}} \times \frac{(2.54)^2 \text{ cm}^2}{\text{in.}^2}$$

$$S = 152,000 \text{ lbs./in.}^2$$

Thus, the calculated adhesive strength for chemical bonding that utilizes only 13% of the maximum available bonding sites is 150,000 psi. This value is far greater than the cohesive strength of the polymeric phase, and of the calculated maximum bond strength obtained from the usual physical forces of adhesion.

An additional benefit, which cannot be estimated numerically, should be derived from the superior resistance of interfacial bonding to hydrolysis, thermal cleavage, and displacement by polar molecules.

In Table IV, the flexural strength data are summarized for two laminates prepared with interfacial chemical bonding, for two laminates prepared with the standard All00 silane finish, and for two laminates prepared without finish. In each of the last two pairs one laminate was prepared from heat-treated glass cloth and the other laminate was prepared from cloth that was fluorinated and then hydrolyzed. This fluorination-hydrolysis treatment served dual purposes of chemically cleaning the surface and of chemically preparing surface silanol groups. Indeed, the concentration of these groups should be at a maximum as a result of fluorination and hydrolysis. The following discussion is based upon the flexural strength data of Table IV and the modulus data of Table VII.

Of the six samples, the heat-treated sample had the highest dry strength, the lowest strength after two-hour boil, and the greatest drop in modulus from the dry to the boiled state. From its appearance it was obvious that loss of interfacial adhesion occurred after boiling due to the loss of physical adhesion caused by water. Probably the glass fiber was also degraded.

The laminate prepared from fluorinated-hydrolyzed glass cloth had a flexural strength 4,000 psi lower than the heat treated sample, but its strength loss and modulus loss after boil were much less. Thus, one may conclude that the fluorination step may have caused some degradation of strength of the fabric. On the other hand, better wetting resulting from a cleaner, more polar glass surface gave more protection to the glass resin interface.

Similar reasoning applies to the heat-treated All100-finished laminate and the fluorinated-hydrolyzed All100-finished laminate. The dry strength of the former was high. After boiling, the strength had increased slightly. If this increase is real and significant, the only explanation for it is an increase in the adhesion between the two phases, possibly by the introduction of additional bonding sites at the interface. This conclusion is tentative but it is supported by the modulus data in Table VII. The modulus of the dry sample at break was 14.6% lower than it was initially, while the modulus of the boiled sample at break was only 13.3% lower. It may therefore be construed that the laminate became stiffer as a result of the boiling water treatment. This could have resulted, it seems, only from an increase in the number of bonding sites at the interface.

The results of tests on the fluorinated All100-finished laminate shows that fluorination probably caused, as in other instances, a slight decrease in the strength of the glass fabric. However, a cleaner surface with an increased number of bonding sites must have resulted from the fluorination treatment, since the deviation in flexural strength for these five samples was only 2.0%, compared to 3.5% for the heat-treated All100-finished samples. This observation was made for the boiled samples as well. Further, the fluorinated series of samples appeared to be stiffer than the heat-treated series since the difference between modulus at break and initial modulus is less.

The data for the alkylated No. 1 samples show an initial flexural strength of 57,300 psi, compared to 64,200 psi for the fluorinated hydrolyzed All100 samples. This value fell to 52,300 psi (an 8.7% loss) after a two-hour boil. However, the modulus data for the alkylated No. 1 samples show them equal to or perhaps a bit stiffer than the fluorinated-hydrolyzed All100 samples, and noticeably stiffer than the heat-treated All100 samples. This stiffness may be ascribed to lack of slippage at the interface, which in turn is a consequence of interfacial bonding that is resistant to attack by boiling water.

The data for the alkylated No. 2 samples, when taken alone and when compared to the All00 samples, allow about the same conclusions as for the alkylated No. 1 samples. However, a comparison between the two alkylated sets of samples is a bit puzzling. Alkylated No. 2 samples, with an initial flexural strength of 69,100 psi, were prepared from glass cloth for which the measured concentration of 5-hydroxypentane groups was only 0.1 per 100 Å². Alkylated No. 1 samples, with an initial flexural strength of only 57,300 psi, were prepared from glass cloth with 0.7 reactive alkyl groups per 100 Å². We have no explanation for this apparent discrepancy, for it was expected that the strength of the laminate should be directly proportional to the number of interfacial bonds. The cause of this apparent discrepancy is probably simple, however, and may become obvious when more data are available. Analytical error is a possible but not a probable explanation.

When the modulus data for the two sets of alkylated samples are compared, there is no longer a discrepancy. Modulus values are definitely and consistently lower for the alkylated No. 2 samples. From this fact it is evident that the alkylated No. 1 samples, with a higher concentration of bonding groups at the interface, are definitely stiffer. Further, this stiffness (or interfacial bonding) is not greatly affected by the two-hour boil test.

In summary, it may be said that the All00 finished samples were resistant to loss of strength during the two-hour boil while at the same time they suffered a noticeable drop in modulus. In contrast, the alkylated samples, with a very low conversion of available sites for alkylation, were not as resistant to loss of strength during the two-hour boil, but were much more resistant than samples with no interfacial treatment. Further, the alkylated samples were observably more resistant to loss in modulus during the two-hour boil than were the All00 samples; and they were much more resistant than the untreated samples.

From these observations (loss of strength but retention of modulus), it may be concluded that the mechanism of damage to the surface-modified samples by boiling water was chemical degradation of the glass fiber

by water, enhanced perhaps by basic ions in the glass surface. Further, it may be concluded that loss of flexural strength in a composite may occur without loss of bonding at an interface. Still another conclusion is that the All00 finish probably functions by protecting the interface against entry by water, thereby preventing chemical attack on the glass fiber member of the composite.

Other conclusions which may be drawn from the foregoing data are that fluorination of glass fibers is an effective cleaning procedure; fluorination of glass fibers, as carried out in this study, causes noticeable loss of strength of the glass cloth; and that the low initial strength of the alkylated samples is probably caused by the extra handling required to accomplish the processing.

EXPERIMENTAL

Preparation of Laminate Samples

Fluorinated Glass Fabric

The fluorination of IP81 glass fabric was accomplished by hanging two 6 in. x 7 ft. sections of fabric on the fabric support rack (Fig. 8). The points at which the fabric crossed the stainless steel support bars were marked by razor blade cuts. These marks would be used to cut the fabric into its final 6 in. x 6 in. configuration.

The rack and its contents were placed in the fluorine reactor (Fig. 9) at room temperature. The reactor, flushed with N_2 and well insulated with aluminum foil, glass wool, and vermiculite, was heated to $200^\circ C$. Heating was manually controlled, and the required temperature was achieved in approximately 15 minutes. Temperature was monitored via a thermocouple and a potentiometer. At $200^\circ C$ the reactor was flushed three times with nitrogen by filling to 20 psig and venting. While the reactor was heating, a mixture of fluorine (F_2) and N_2 was prepared by filling the hold tank and mixing chamber (initially filled to 0 psig with N_2) to 8 psig with F_2 . A schematic diagram of the N_2 and F_2 lines is shown in Fig. 10. The pressure was then brought to 20 psig with N_2 . Mixing of the N_2 and F_2 gases in the small chamber continued during the reactor heating cycle.

The N_2 -flushed reactor was maintained at $200^\circ C$ for 5 minutes to insure thermal equilibrium. The N_2 - F_2 mixture was admitted rapidly. The mixing chamber was flushed three times by filling to 20 psig with N_2 . Each time the gas was added to the reactor. The reaction mixture was approximately 4% F_2 . The fluorination reaction was allowed to proceed for 8 minutes before heating of the reactor was terminated. The sample chamber was repeatedly filled with N_2 to 20 psig and vented until the exhaust gases showed no trace of F_2 when tested with moistened starch-iodide paper. The reactor, now at approximately $150^\circ C$, was allowed to

cool to room temperature; the rack was removed and the fluorinated fabric was used immediately.

Alkylating Agent

The alkylating agent chosen for this study was pentane-1,5-dimagnesium bromide prepared in the following manner: 2 moles (48 g) of magnesium metal turnings were placed in a 2 l, three-neck, round-bottom flask fitted with a 3 ft. condenser, ground glass stirrer shaft (with teflon blade), and a 250 ml dropping funnel with N₂ inlet. This system was dried with a heat gun while N₂ was bled through the system and vented through a CaCl₂ drying tube. When the system had cooled, 1 l of tetrahydrofuran (THF) rigorously dried over sodium hydride was placed over the magnesium. One-half mole (115 g) of 1,5-dibromopentane was dissolved in 200 ml of dry THF and this solution was put into the dropping funnel. The system was heated to reflux temperature (69°C). The dibromopentane solution was admitted dropwise over a 3 hour period with vigorous stirring for reaction with the magnesium turnings. An N₂ atmosphere was maintained at all times.

Alkylated Glass Fabric

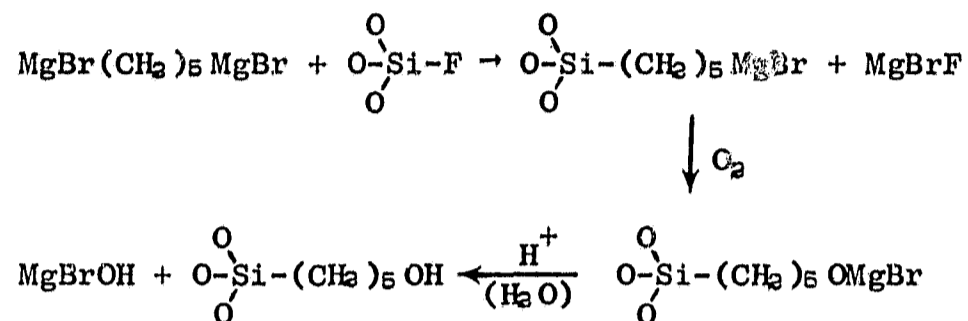
The prepared pentane-1,5-dimagnesium bromide solution was transferred to the thoroughly dried, N₂-flushed, 2 l alkylation reactor (Fig. 11). The volume of the Grignard solution in the reactor was brought to approximately 2 l with dry THF.

A 6 in x 7 ft. section of fluorinated glass fabric was removed from the fabric support rack and loosely rolled around the outside of the cylindrical baffle (Fig. 11). The baffle and fabric were slowly lowered into the alkylation reactor containing the 2 l of Grignard solution. The design of this system allowed for the movement of solution without abrasion of the fabric by the stirrer blades.

The alkylation reaction was carried out for 18 hours at room temperature, with continuous stirring. The fabric, still rolled, was removed from the Grignard solution and placed in 1 l of dry THF. Oxygen was bubbled in and around the plies of the roll. The oxidation was

continued for 30 minutes. The fabric was removed from the THF and hydrolyzed in 1 l of dilute hydrochloric acid (~ 1%) for 15 minutes.

The reaction scheme was:



where $\begin{array}{c} \text{O} \\ | \\ \text{Si}-\text{O} \\ | \\ \text{O} \end{array}$ is a surface silicon atom joined to three oxygen atoms in the glass fiber.

The alkylated fabric was removed from the acid solution and was washed with 1 l quantities of distilled water until a neutral pH was attained. The cloth was then soaked in THF to remove residual organics and washed with three 1 l portions of water to remove THF. Next the fabric was soaked in an ammonium chloride solution to remove magnesium salts, and finally was washed with distilled water to remove ammonium chloride. The total wash volume was approximately 4 gallons of distilled water.

The alkylated fabric was oven dried at 80°C for 20 hours, wrapped in aluminum foil, and stored in a desiccator until used.

Fluorinated-Hydrolyzed Glass Fabric.

Fluorination was carried out on sufficient fabric for two test laminates. Subsequently half was alkylated; the other half of the fluorinated fabric was washed in dilute sodium hydroxide (1%) to effect surface hydrolysis, and rinsed repeatedly with water to a neutral pH. The remainder of the washing and drying cycle was the same as the alkylated fabric. The hydrolyzed portion was used as a control.

Heat-Treated Glass Fabric

Two 6 in. x 7 ft. pieces of glass fabric were hung on the fabric support rack and placed in the N₂-flushed fluorine reactor (Fig. 9) at

room temperature. These samples were subjected to the same heating and cooling cycle given fluorinated glass fabric. The environment was dry nitrogen instead of fluorine.

The fabrics were removed from the cooled reactor and washed with dilute sodium hydroxide (~ 1%) and then water-washed to a neutral pH. The remainder of the washing and drying procedure was the same as for the other fabric samples.

All100-Treated Glass Fabric

All100 silane finish (gamma-aminopropyltriethoxysilane) was used as a treatment for heat-treated and fluorinated-hydrolyzed fabrics. The finish was applied to these samples by the method recommended by the manufacturer.⁸ The concentration of silane in the finishing solution was 0.5% by weight of cloth. The fabrics were allowed 1 hour contact with the aqueous silane solution. They were then drip dried for 1 hour at room temperature and oven dried for 4 hours at 80°C.

Glass-Fabric Laminates

The resin system used for the production of laminates was as follows: Epon 825, Nadic Methyl Anhydride 91 phr, benzyldimethylamine 0.57 phr. The Epon 825 and Methyl Nadic Anhydride were combined and brought to 50-60°C. The benzyldimethylamine was then added and the resin thoroughly mixed. The resin was poured into a 6½ in. x 6½ in. sheet metal pan lined with 12 in. x 13 in. x 0.001 in. FEP fluorocarbon film. The pan and contents were maintained at 50° to 60°C.

The glass fabric sample, previously cut into thirteen 6 in. x 6 in. squares, were placed into the resin in the following manner. One corner of one fabric square was grasped with forceps and the opposite corner was put into the resin at one corner of the pan. The fabric was slowly lowered at the same rate as the resin wet the fabric. Thus the slowly moving glass-resin interface effectively displaced air that might have become trapped in the weave or between plies of the fabric. This sequence was repeated, alternating the warp and fill directions for 13 plies.

The layup was lifted from the pan with the FEP film, and another 12 in. x 13 in. section of film was placed over it. Three sides of the film were rolled and taped so that resin would flow out in one direction only. This assembly was placed directly into the laminating press with a U-shaped 0.125 in. gauge block around it. Pressure was slowly increased until 125 psig was applied against the gauge block. The press platens were heated to 225°F, and this temperature and pressure were maintained for 2 hours.

Six laminates were made using this procedure: two were alkylated, one was fluorinated-hydrolyzed, one was heat treated, one was fluorinated-hydrolyzed and All100 finished, and one was heat treated and All100 finished. All six laminates were post cured, simultaneously, for 4 hours at 300°F and 4 hours at 400°F.

Flexure Test Samples

Flexure test samples were cut with a precision diamond saw, using a 7 in. OD x 0.027 in. thick blade. Each 6 in. x 6 in. laminate was cut into ten 6 in. strips 0.500 ± 0.0005 in. wide. The device used for clamping the laminates for cutting was a 1" thick wood block with eleven $\frac{1}{4}$ in. x $\frac{1}{4}$ in. steel straps set 0.525 in. center to center and bolted at either end. The laminate was placed on $\frac{1}{4}$ in. thick plate glass and clamped beneath the retaining straps. The laminate was cut between adjacent straps; the depth of cut was approximately 1/16 in. into the plate glass. This arrangement held the work rigidly while cuts were made.

Five of the ten $\frac{1}{2}$ in. x 6 in. strips from each laminate sample were later cut in half giving ten $\frac{1}{2}$ in. x 3 in. test specimens.

Physical Testing of Laminates

Conditioning

Five $\frac{1}{2}$ in. x 3 in. test specimens from each of five laminates were placed in boiling water for two hours, removed, and wiped dry. These, along with five unboiled samples from each laminate, were put into a

desiccator and immersed in a constant temperature bath at $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 48 hours, as specified by ASTM D-618. Humidity within the desiccator was controlled by a saturated solution of calcium nitrate, which yields 50% relative humidity at this temperature.

The sixth laminate, designated alkylated No. 2, made from alkylated glass fabric was aged differently. Five $\frac{1}{2}$ in. x 3 in. strips of this specimen were given a two-hour boil. These along with five unboiled samples were allowed to sit at ambient room temperature and humidity for 12 hours before testing.

Flexural Testing

The laminate samples were tested in flexure using a Baldwin-Tate-Emery test machine, type PTE. The specimens were run using a 2 in. span and a deflection rate of 0.05 in. per minute, according to ASTM D-790.

Calculation of Flexural Strength and Modulus of Laminates

Laminate flexural strength was calculated using the following equation:⁹

$$S = \frac{3PL}{2bd^2}$$

where S = flexural strength
P = load at break, in pounds
L = span, in inches
b = width of beam tested, in inches
d = depth of beam tested, in inches

The modulus of elasticity was calculated by measuring the slope of the tangent to the load-deflection curve over the first 50 lbs. of applied load. The following equation was used to calculate the modulus of elasticity (E_B , lbs./in.²):⁹

$$E_B = \frac{L^3m}{4bd^3}$$

where L = span, in inches
 m = slope of tangent to the load-deflection curve,
 in pounds per inch
 b = width of beam tested, in inches
 d = depth of beam tested, in inches

The modulus of elasticity at break was calculated by measuring the slope of the tangent of the load-deflection curve over the last 25 lbs. of applied load prior to break.⁹ The value of m (slope) was substituted in the preceding equation for the modulus of elasticity.

The standard deviation for all calculated values was obtained by using the equation:⁹

$$S = \frac{\sum X^2 - n\bar{X}^2}{n-1}$$

where S = standard deviation
 X = value of single observation
 n = number of observations
 \bar{X} = arithmetic mean of the set of observations

Analytical Studies

Determination of Laminate Density and Resin Content

Laminate densities were determined by water displacement. The apparatus used was an analytical balance positioned above a constant temperature bath and specifically modified to weigh samples immersed in water. The laminate test strips were weighed in air, then in distilled in water at 25°C. The difference between the two weights is the weight of displaced water. From this value and the density of water at 25°C, the volume of the test strip may be calculated. The sample density was directly and accurately obtained in this manner.

The resin content was calculated by measuring the densities of samples of glass fabric and of cured resin by water displacement, and applying the following equations:

$$X\rho_{\text{resin}} + (1-X)\rho_{\text{glass fabric}} = \rho_{\text{laminates}}$$

where X = resin-to-glass-fabric weight ratio, and $X(\rho_{\text{resin}})$ (test strip volume) = wt. resin in test strip. The densities of glass fabric and cured resin were found to be 2.554 g/cm³ and 1.227 g/cm³ respectively.

Test strip densities were also calculated from independently measured values of ρ_{resin} , $\rho_{\text{glass fabric}}$, experimentally measured weight per unit area of glass fabric, and the length and width of the test strips. These data provide an independent check on density and some indication of void content for the laminates. The following equation was used:

$$\rho = \frac{W}{\frac{13S(3.003 \times 10^{-2} \text{ g/cm}^2)}{2.554 \text{ g/cm}^3} + \frac{W-13S(3.003 \times 10^{-2} \text{ g/cm}^2)}{1.227 \text{ g/cm}^3}}$$

where W = weight of test strip
 S = surface area of test strip
 $3.003 \times 10^{-2} \text{ g/cm}^2$ = weight to surface area of glass fabric
 13 = no. of plies of fabric in laminate

Carbon Analyses

Carbon on inorganic solid substrates was determined with a precision of ± 2 ppm of carbon. This was done with the Leco analyzer, which consists of the Leco Model 521 high-frequency induction furnace and the Leco Model 515 conductometric carbon analyzer. The apparatus was standardized with carbon standards in the 30 to 210 ppm range.

Fluoride Analysis

Fluoride analyses were carried out using an Orion fluoride-ion electrode and a Corning Model 12 expanded-scale pH meter. The glass-cloth sample was hydrolyzed in 2N NaOH. An equal volume of 2N H₂SO₄ was added, and the electrode response to the solution is read in millivolts. The corresponding F⁻ concentration is determined from a standard curve for fluoride ion in 1N Na₂SO₄ solution.

ACKNOWLEDGMENT

Surface area measurements were performed by Dr. Harold Eding.

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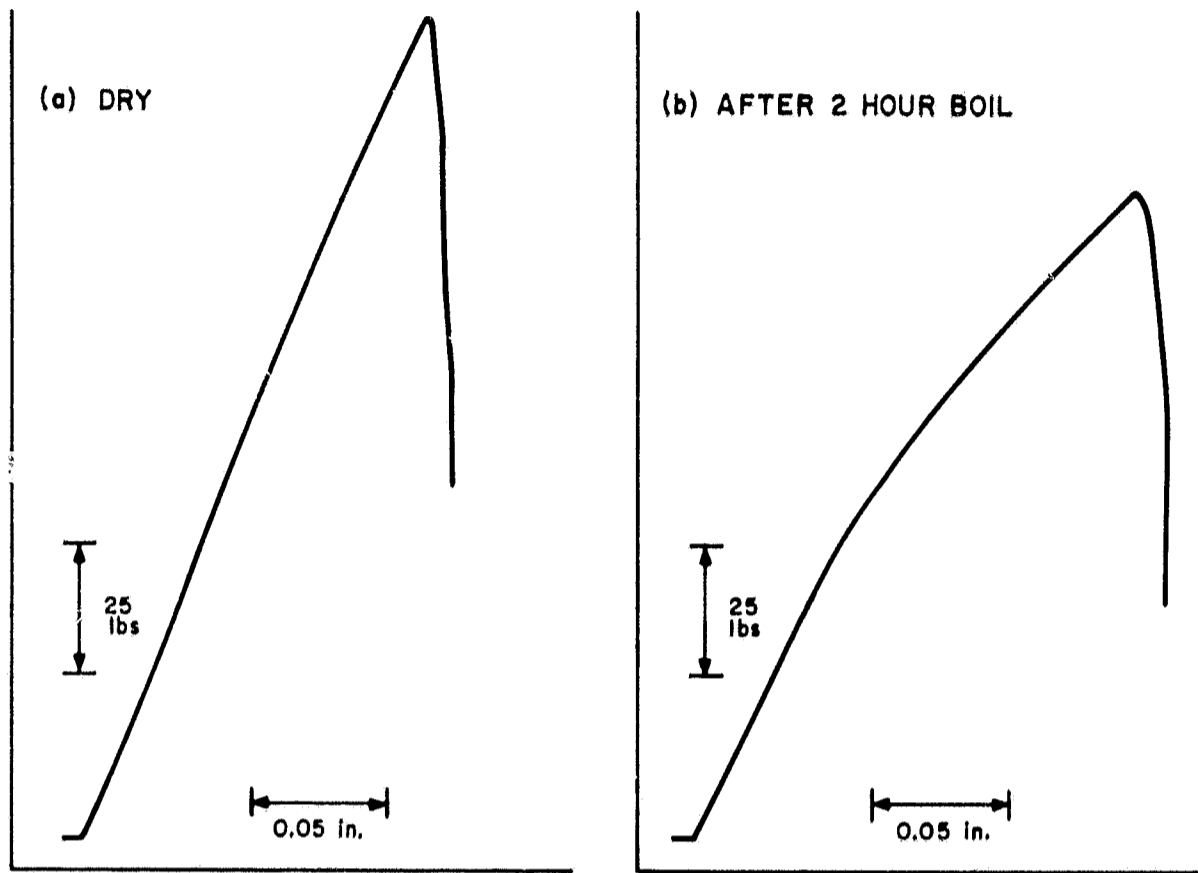
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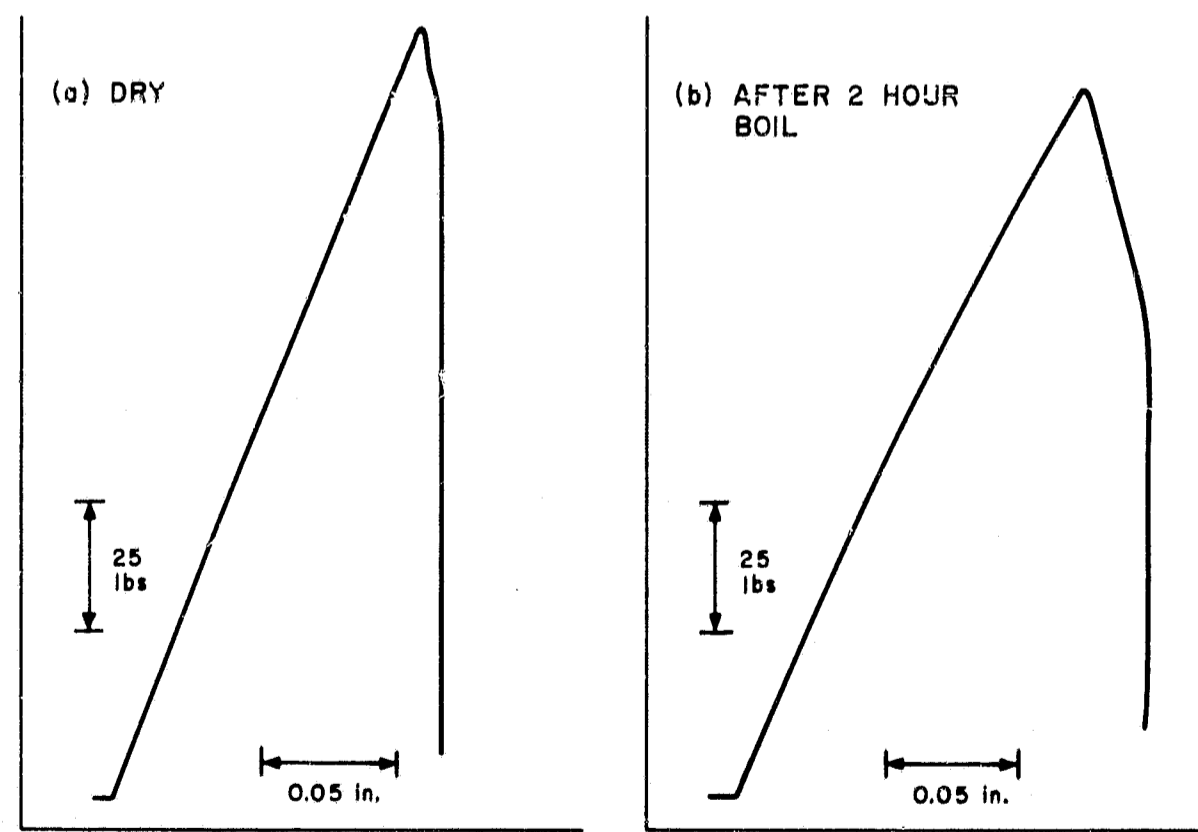
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FIG. 1 TRANSPARENCY OF EXPERIMENTAL LAMINATES



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FIG. 2 LOAD-DEFLECTION CURVES FOR HEAT-TREATED FABRIC LAMINATES



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FIG. 3 LOAD-DEFLECTION CURVES FOR FLUORINATED-HYDROLYZED FABRIC LAMINATES

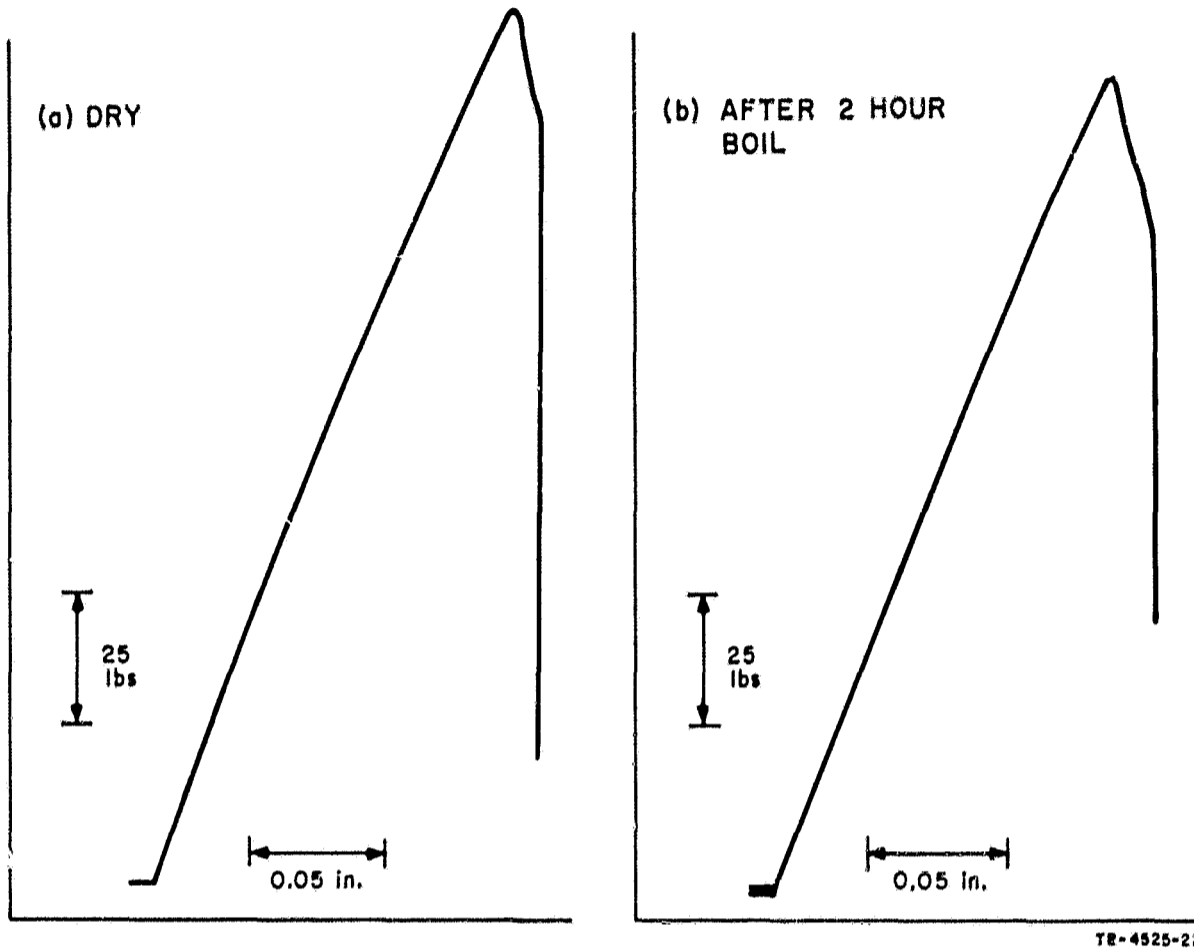


FIG. 4 LOAD-DEFLECTION CURVES FOR HEAT-TREATED, A1100-FINISHED FABRIC LAMINATES

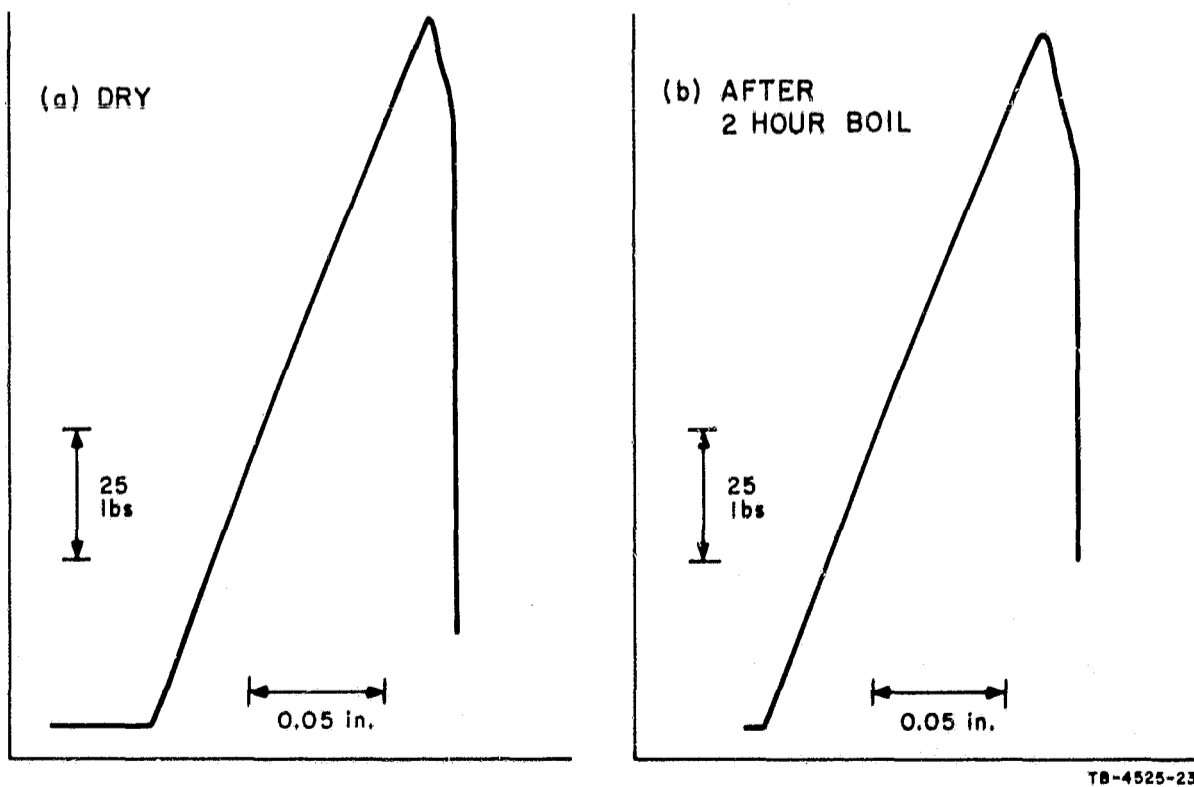


FIG. 5 LOAD-DEFLECTION CURVES FOR FLUORINATED-HYDROLYZED, A1100-FINISHED FABRIC LAMINATES

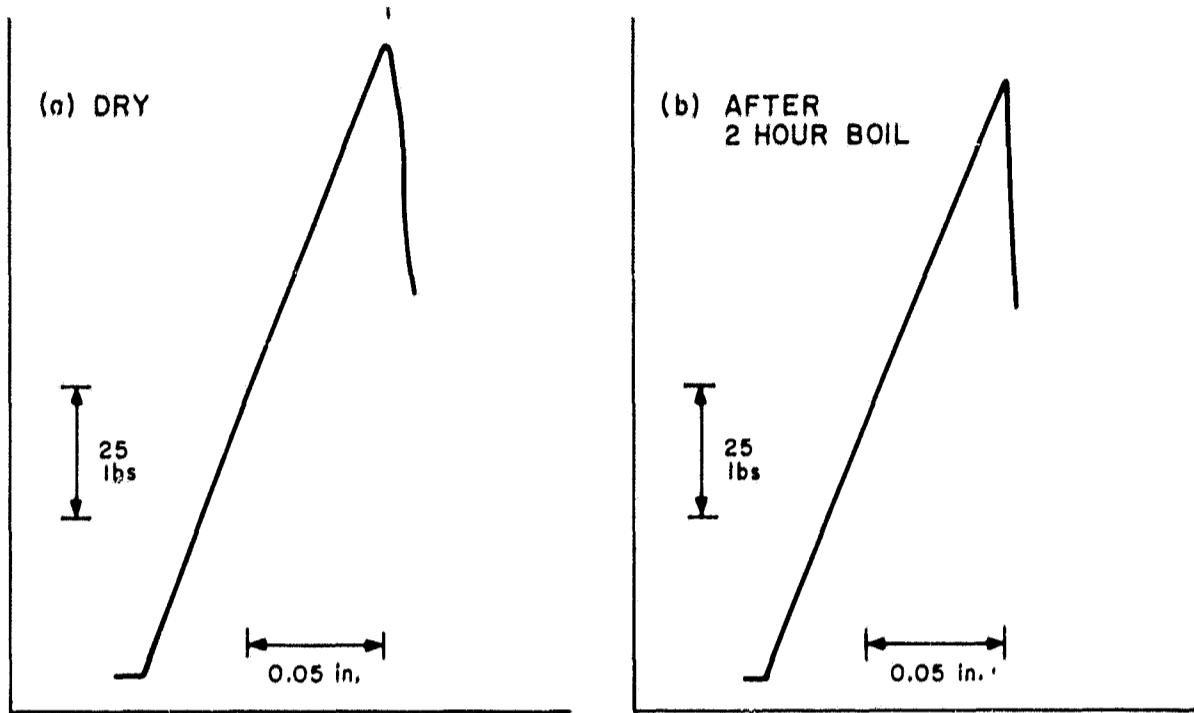


FIG. 6 LOAD-DEFLECTION CURVES FOR ALKYLATED FABRIC LAMINATES (0.7 Pentanol groups/100 Å²)

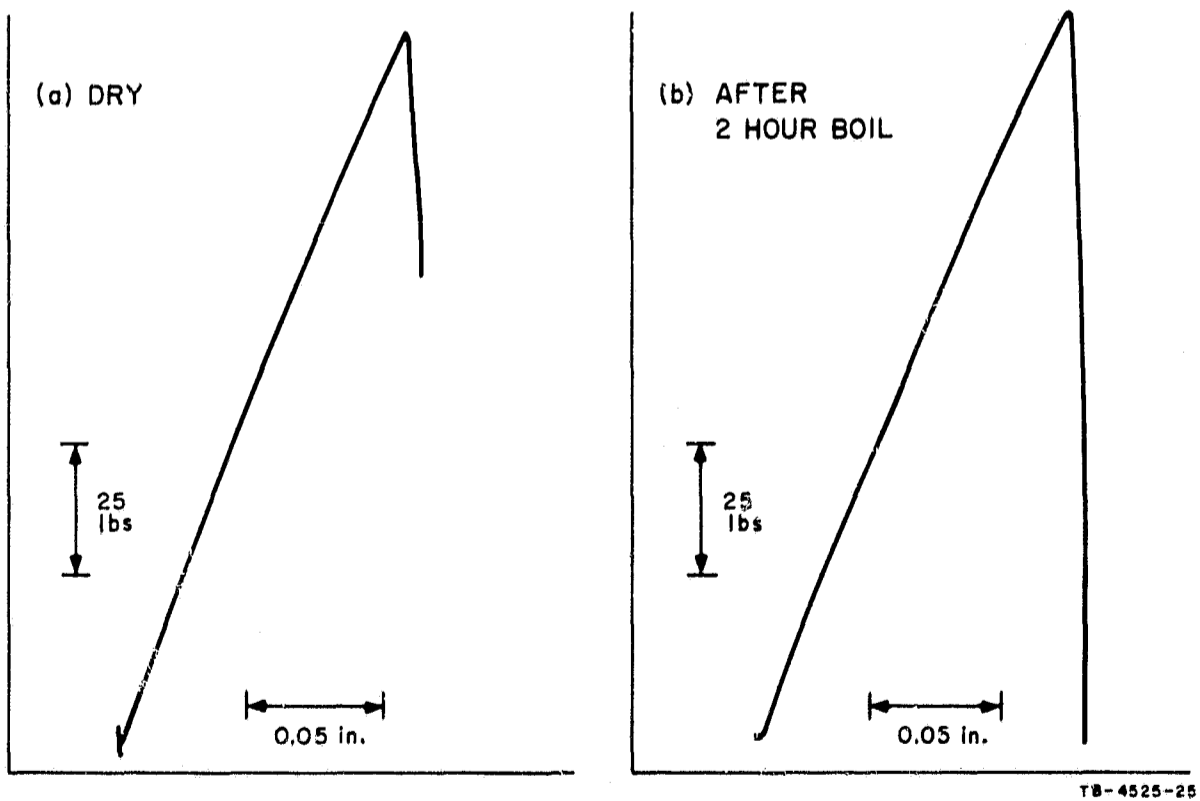


FIG. 7 LOAD-DEFLECTION CURVES FOR ALKYLATED FABRIC LAMINATES (0.1 Pentanol groups/100 Å²)

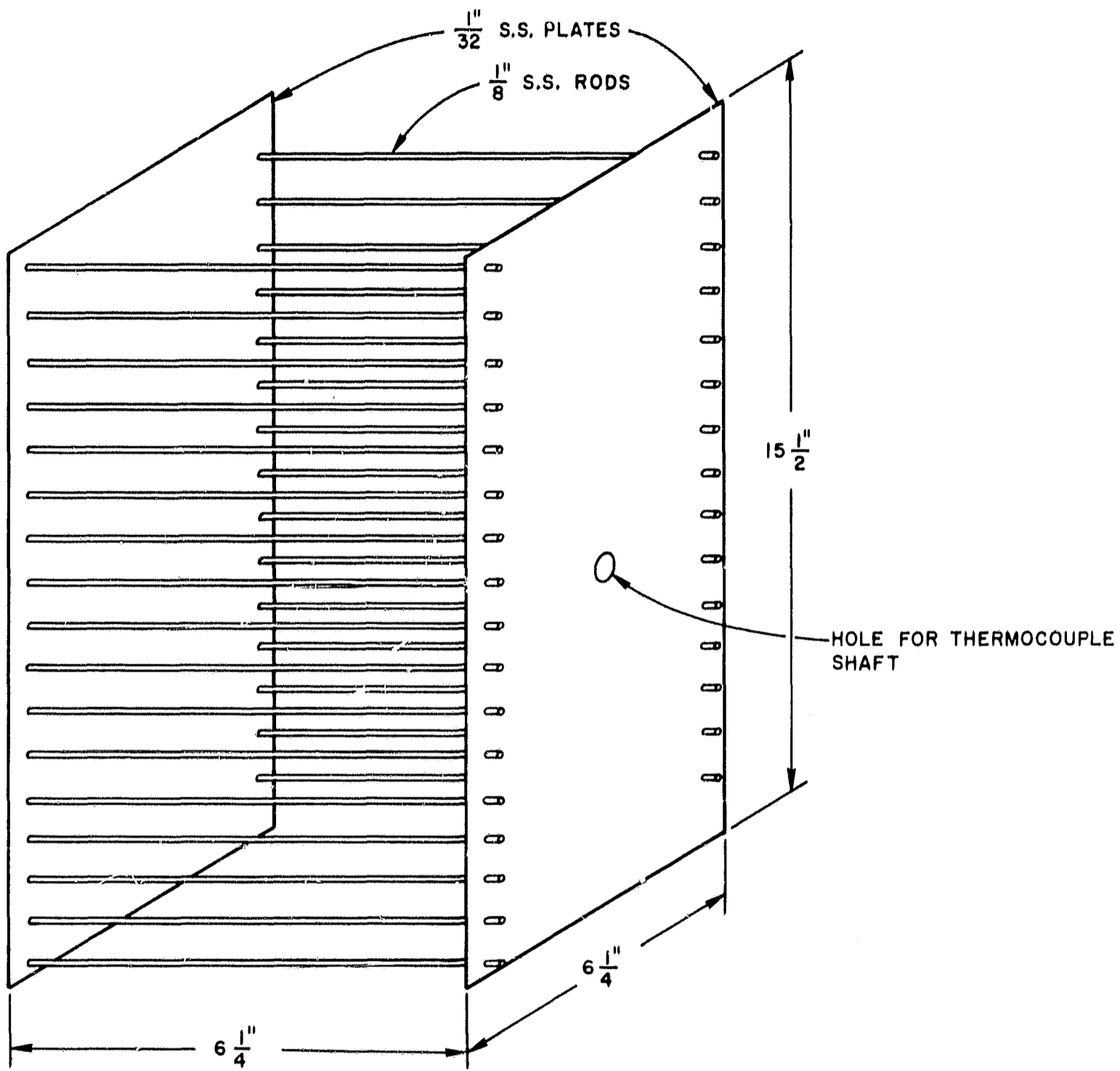


FIG. 8 FABRIC SUPPORT RACK

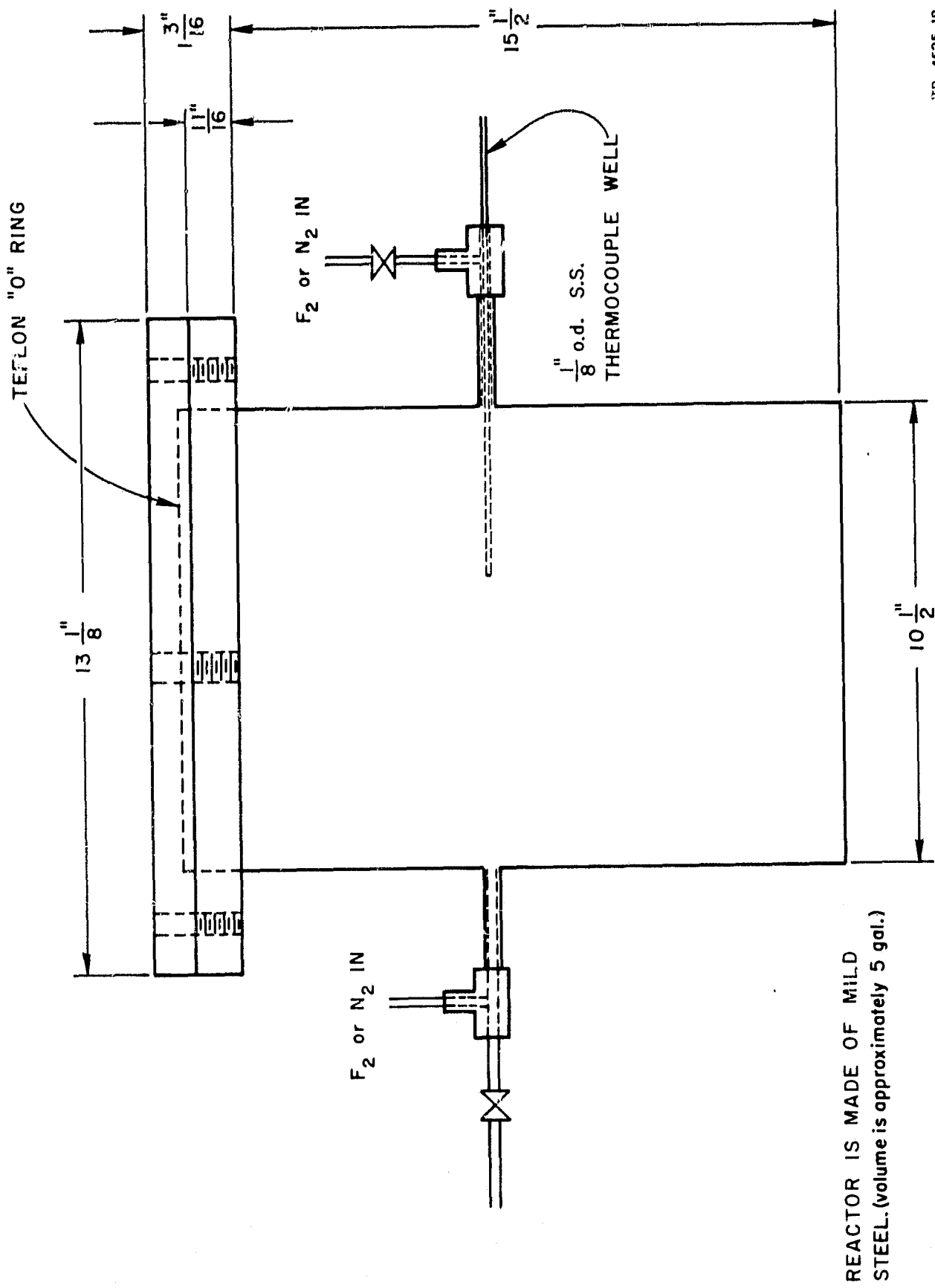
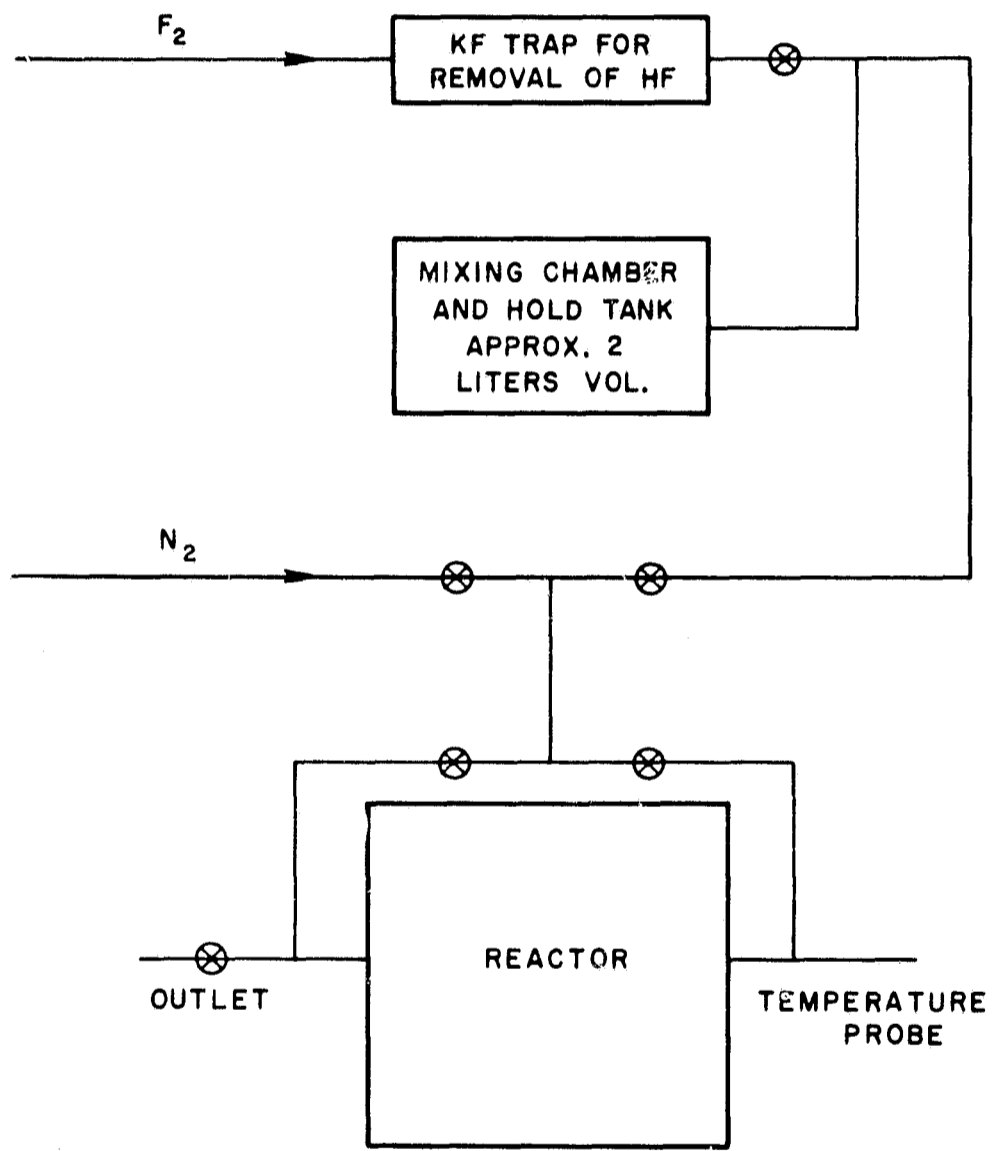
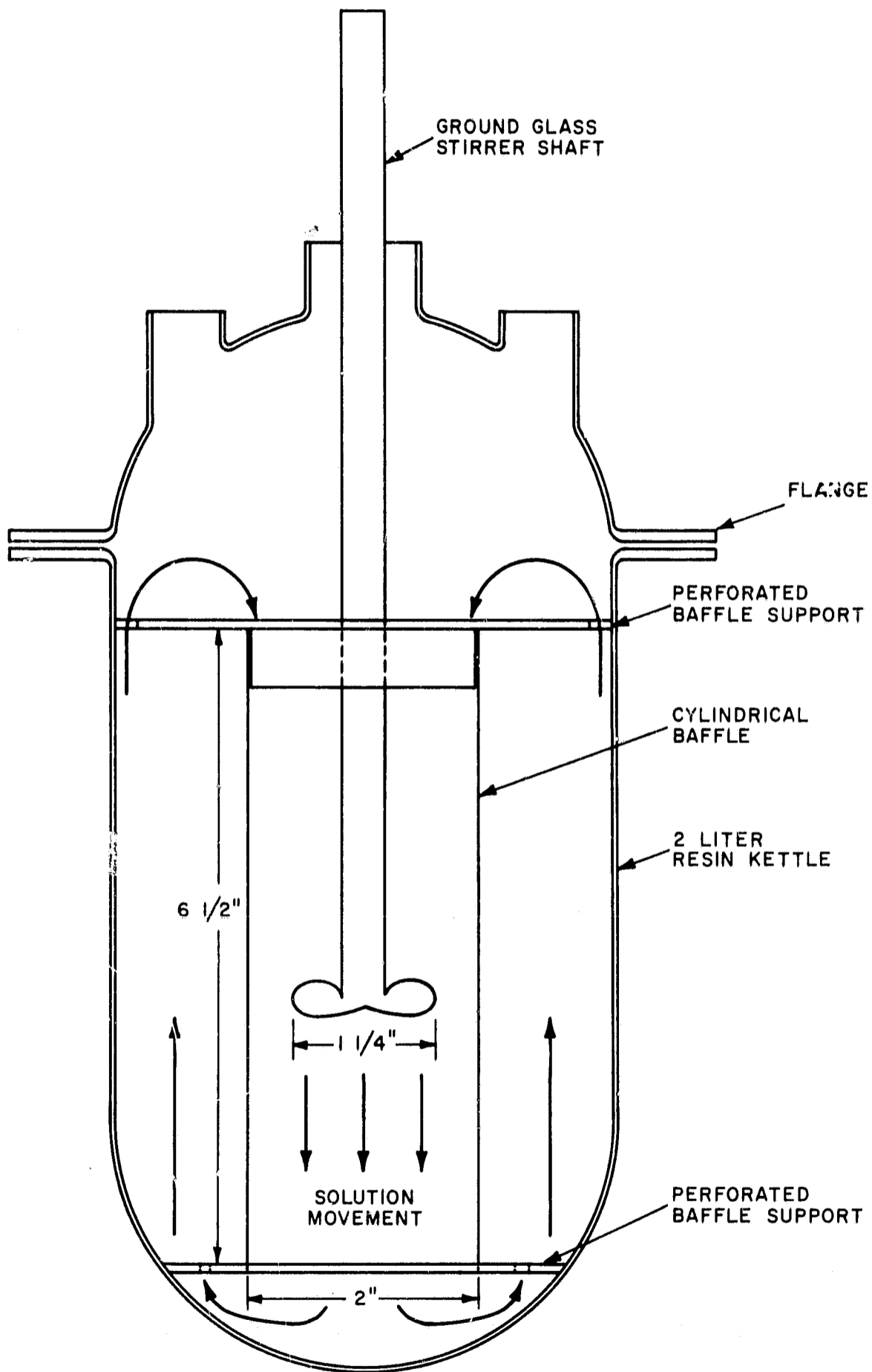


FIG. 9 FLUORINE REACTOR



TA-4525-17

FIG. 10 FLUORINE SYSTEM



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FIG. 11 ALKYLATION REACTOR

Table I
 FLUORINATION OF SILICA AND GLASS FABRIC

Glass Sample	F ₂ Treatment	Analysis (F/100 Å ²)
Cab-O-Sil (silica)	F ₂ , 20 psig, 200°C, 2 hr.	4.04
1P81 Glass Fabric	F ₂ , 18 psig, 200°C, 3 hr.	1117
1P81 Glass Fabric	4% F ₂ in N ₂ , 2 psig, 200°C, 30 min.	220
1P81 Glass Fabric	4% F ₂ in N ₂ , 2 psig, 200°C, 5 min.	88
1P81 Glass Fabric	4% F ₂ in N ₂ , 2 psig, 200°C, 8 min.	101

Table II
 CARBON ANALYSES ON 1P81 E-GLASS^(a) FABRIC
 FOR EXPERIMENTAL LAMINATES

Sample	Total Carbon (ppm, by wt.)	Net Carbon from alkyl or A1100 groups (ppm)	Groups/100 Å ²
Heat-treated ^(b)	64 (residual)	-	-
Fluorinated- hydrolyzed ^(c)	45 (residual)	-	-
Heat-treated, A1100-finished ^(b)	584	520	26 A1100 groups
Fluorinated- hydrolyzed, A1100- finished ^(b)	712	667	34 A1100 groups
Alkyl No. 1 (Fluor- inated-alkylated)	67	22	0.7 pentanol groups
Alkyl No. 2 (Fluor- inated-alkylated)	48	3	0.1 pentanol groups

(a) 1P81 E-Glass fabric was supplied by Coast Manufacturing and Supply Co. as heat-cleaned and washed to neutral pH. All samples for carbon analysis were desorbed at 100°C and 10⁻⁶ mm Hg for 24 hours.

(b) "Heat-treated" means that control samples received the same thermal treatment as the test samples.

(c) The concentration of F-atoms in the fluorinated glass was 101 per 100 Å².

Table III

DENSITY AND RESIN CONTENT OF EXPERIMENTAL LAMINATES

Laminate Sample	Density, by Water Displacement at 25°C Corrected for Temperature (g/cm ³)	Calculated Density ^(a) (g/cm ³)	$\Delta\rho$ (%)	Resin Content (wt. %)
Heat-treated	1.88	1.91	1.6	33.5
F ₂ -Treated, hydrolyzed	1.89	1.89	0	32.8
Heat-treated, A1100-finished	1.89	1.89	0	32.3
F ₂ -treated, hydrolyzed, A1100-finished	1.89	1.89	0	32.4
Alkyl-treated 0.7 pentanol groups/100 Å ²	1.87	1.90	1.6	33.7
Alkyl-treated 0.1 pentanol groups/100 Å ²	1.89	1.89	0	32.8

(a) See Experimental section for detailed calculation.

Table IV
 FLEXURAL STRENGTH OF EXPERIMENTAL LAMINATES
 (Average of 5 Separate Samples)

Laminate Sample	Dry (psi)	After 2-hour boil (psi)	Loss in Flexural Strength (%)
Heat-treated	78,100 ± 2300 (2.9%)	65,300 ± 7000 (10.7%)	16.4
Fluorinated- hydrolyzed	74,300 ± 4200 (5.7%)	66,400 ± 3100 (4.7%)	10.7
Heat-treated, A1100-finished	77,500 ± 2700 (3.5%)	78,000 ± 3700 (4.8%)	0.6 (gain)
Fluorinated- hydrolyzed, A1100-finished	64,200 ± 1300 (2.0%)	62,300 ± 1500 (2.4%)	3.0
Alkylated No. 1 0.7-(CH ₂) ₅ OH groups/100 Å ²	57,300 ± 3300 (5.8%)	52,300 ± 3200 (6.2%)	8.7
Alkylated No. 2 0.1-(CH ₂) ₅ OH groups/100 Å ²	69,100 ± 3600 (5.2%)	66,100 ± 5,300 (8.0%)	4.4

Table V
 MODULUS OF ELASTICITY OF EXPERIMENTAL LAMINATES
 (Average of 5 Separate Samples)

Laminate Sample	Dry (psi x 10 ⁻⁶)	After 2-hour boil (psi x 10 ⁻⁶)	Loss in Modulus of Elasticity (%)
Heat-treated	3.44 ± 0.11 (3.3%)	2.78 ± 0.15 (5.4%)	19.1
Fluorinated- hydrolyzed	3.37 ± 0.19 (5.8%)	3.25 ± 0.15 (4.7%)	3.6
Heat-treated, A1100-finished	3.32 ± 0.23 (7.0%)	3.22 ± 0.16 (5.1%)	3.0
Fluorinated- hydrolyzed, A1100-finished	3.43 ± 0.09 (2.5%)	3.30 ± 0.19 (5.8%)	3.8
Alkylated No. 1 0.7-(CH ₂) ₅ OH groups/100 Å ²	3.49 ± 0.05 (1.5%)	3.43 ± 0.11 (3.3%)	1.6
Alkylated No. 2 0.1-(CH ₂) ₅ OH groups/100 Å ²	3.58 ± 0.31 (8.7%)	3.53 ± 0.28 (7.9%)	1.5

Table VI
 MODULUS OF ELASTICITY OF EXPERIMENTAL LAMINATES PRIOR TO BREAK^(a)

Laminate Sample	Dry (psi x 10 ⁻⁶)	After 2-hour boil (psi x 10 ⁻⁶)	Loss of Modulus at Rupture (%)
Heat-treated	2.73 ± 0.19 (6.9%)	1.48 ± 0.12 (7.9%)	45.9
Fluorinated- hydrolyzed	3.19 ± 0.11 (3.4%)	2.26 ± 0.11 (4.8%)	29.2
Heat-treated, A1100-finished	2.84 ± 0.12 (4.2%)	2.79 ± 0.19 (6.8%)	1.6
Fluorinated- hydrolyzed, A1100-finished	3.02 ± 0.12 (4.0%)	3.04 ± 0.19 (6.2%)	0.56
Alkylated No. 1 0.7-(CH ₂) ₅ OH groups/100 Å ²	3.25 ± 0.11 (3.4%)	3.16 ± 0.11 (3.3%)	2.7
Alkylated No. 2 0.1-(CH ₂) ₅ OH groups/100 Å ²	3.02 ± 0.13 (4.1%)	2.91 ± 0.19 (6.6%)	3.6

(a) Slope of tangent measured over last 25 lbs. of applied load on load-deflection curve.

Table VII
CHANGE IN MODULUS WITH DEFLECTION

Laminate Sample	Dry			2-Hour Boil		
	Initial Modulus (psi x 10 ⁻⁶)	Modulus at Rupture (psi x 10 ⁻⁶)	Loss in Modulus (%)	Initial Modulus (psi x 10 ⁻⁶)	Modulus at Rupture (psi x 10 ⁻⁶)	Loss in Modulus (%)
Heat-treated	3.44	2.73	20.8	2.78	1.48	47.1
Fluorinated-hydrolyzed	3.37	3.19	5.3	3.25	2.26	30.5
Heat-treated, A1100-finished	3.32	2.84	14.6	3.22	2.79	13.3
Fluorinated-hydrolyzed, A1100-finished	3.43	3.02	11.8	3.30	3.04	7.9
Alkylated No. 1 0.7-(CH ₂) ₅ OH groups/100 Å ²	3.49	3.25	6.8	3.43	3.16	8.0
Alkylated No. 2 0.1-(CH ₂) ₅ OH groups/100 Å ²	3.58	3.02	15.7	3.53	2.91	17.5