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

Prepared for:

NATIONAL AERONAUTICAL AND SPACE ADMINISTRATION
WASHINGTON 25, D.C.

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SRI Project FRU-4525

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POLYMER & PROPULSION SCIENCES DIVISION

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INTRODUCTION

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

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. Such "bonding" as may result is supposedly due to the formation of an 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 Cr (as in certain other commercial finishes). For example: $\begin{array}{c} | \\ -\text{Si}-\text{OH} \\ | \end{array} + \text{X}-\text{SiR}_3 \rightarrow \begin{array}{c} | \\ -\text{Si}-\text{O}-\text{Si}-\text{R}_3 \\ | \end{array} + \text{HX}$, where $\begin{array}{c} | \\ -\text{Si} \\ | \end{array}$ is a silicon atom bonded to three oxygen atoms in the glass surface, X is chlorine 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. Recent 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 $\begin{array}{c} \text{Si} \text{-----} \text{O} \text{-----} \text{Si} \\ \text{(glass)} \quad \quad \quad \text{(finish)} \end{array}$ bond must be considered. Though Si-O-Si bonds are not 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 interface between glass and plastic 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 I was accomplished. 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 Si-Cl groups to Si-phenyl groups.

The objective of Phase II is to study methods for the production of an organic "finish" on glass or silica that will be bonded directly to the surface via silicon-carbon bonds.

SUMMARY

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Four methods for the evaluation of bonding between plastic materials and an inorganic substrate were studied: peel tests, contact angle measurements, dilatometric measurements, and sonic measurements. The first three methods were found to yield useful information. Evaluations were made, by all three methods, on clean glass and silica surfaces, and on these surfaces modified by n-butyl groups. For the peel tests a modified apparatus and procedure were developed.

Author

Surface modification was applied to macroscopic surfaces such as microscope slides and 2-inch by 1.7-inch OD cylinders, as well as to particulate materials.

Alkoxylation was evaluated as a method for the preparation of reactive intermediate surfaces. This method has potential for replacing chlorination or fluorination in the preparation of reactive Si - X groups for subsequent alkylation. Alkoxylation has the advantages of lower corrosion of the glass surface, lower temperature than for chlorination, and potentially lower cost.

DISCUSSION

Materials

The two materials used in this work are glass and silica. Silica was chosen for early work because of its simpler structure. Early work was also confined to finely divided materials because of the desirable high surface-to-weight ratio. As methods for surface treatment were developed, macroscopic materials such as flat plates and cylinders were used to evaluate the effects of surface treatment. As progress was made, silica was replaced with glass. All materials used, except glass powder, behaved in a straightforward manner.

The difficulty with glass powder became apparent when attempts were made to correlate specific surface (surface area of one gram of material) with the "population" (surface concentration) of halogen atoms on halogenated materials. Surface area was measured by nitrogen adsorption. The difficulty appeared to lie in the change in measured surface area with change in the temperatures of initial desorption. This effect may be attributed to the presence of fractures in the glass particles. These fractures may be completely filled with adsorbed gases at low temperatures. The desorption of these gases at higher temperatures would result in higher measured surface areas, as shown in Table I. With this situation, quantitative correlation between measured surface area and the concentration of surface groups could not be made.

Attempts to obtain fire-polished glass beads of comparable specific surface were unsatisfactory. None were found in Pyrex or E-Glass composition. Superbrite spherical glass beads (Minnesota Mining and Manufacturing Company) are available in diameters as small as 29 microns, but they are of a high sodium content and leach severely in water. Therefore, silica was chosen for all subsequent work with fine particulates.

Halogenation and Alkoxylation Reactions

Chlorination

Chlorination reactions proceeded smoothly on finely divided materials. A modified reactor, shown in Fig. 1, was very effective; with a silica tube it can be operated to 1000°C in a tube furnace. The effect of temperature upon the chlorination of low-iron silica with phosgene is shown in Table II. The data at 500°C and higher agree well with previous results. The erratic results at 335 and 400°C may be explained by the observed variability of surface area with desorption temperature. Thus, at higher temperatures, the rate of desorption (and of increase in surface area) may be rapid and reproducible, while at lower temperatures, the rate may be much slower and much less reproducible.

Chlorination of glass and silica rings was accomplished in the apparatus shown in Fig. 2. However, difficulties arose in maintaining a 500°C temperature at the surface of the inner jacket. These difficulties must be overcome before the apparatus can be useful for chlorination of glass rings with phosgene. The outer surface of the inner tube was halogenated, the tube removed for alkylation, and finally the tube was cut into 1.5-inch lengths for use in peel tests.

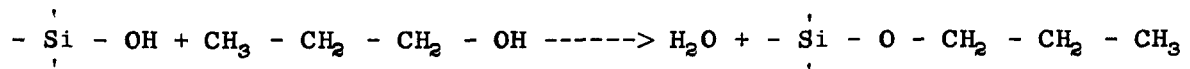
Fluorination

Fluorination of rings for peel tests was conducted at 200°C in the apparatus shown in Fig. 2. No problems were encountered in heating to 200°C.

Fluorination of glass microscope slides for contact angle studies was carried out in the apparatus described previously.⁶ The presence of metallic ions, or other differences between glass and silica, resulted in an interesting temperature effect: Fluorination at low temperatures, ca. 100°C, resulted in severe and non-uniform etching of the surface; at 150°C, a clear surface was obtained, but a thin, transparent film of nonvolatile metal fluorides could be peeled from the glass surface. Optimum conditions for this reaction have not yet been found.

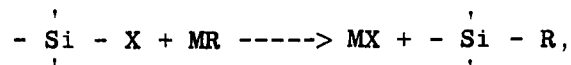
Alkoxylation

Alkoxylation of surface-based SiOH groups offers an alternative to chlorination or fluorination as a route to reactive surface groups. This reaction was carried out on glass powder and microscope slides using n-propyl alcohol, according to the method of Iler.⁷ Analyses on the powdered glass are not complete, but the wettability of the product indicates the reaction was successful. Alkoxylation offers advantages of fewer possible side effects (such as etching) and greater safety of operation.



Alkylation

A generalized alkylation reaction can be written as



where X is chlorine, fluorine, or alkoxy, M is lithium or other metal, and R is an organic group such as butyl, phenyl, etc.

The alkylation of chlorinated, fluorinated, or alkoxyated materials was accomplished in a straightforward fashion with the appropriate organolithium compound. In the case of glass rings for peel tests, the apparatus (Fig. 2), after halogenation, was flushed

with nitrogen and the inner jacket was quickly removed and immersed in a solution of the organolithium compound. After alkylation, the tube was carefully cut into 1.5-inch lengths for use with the peel test apparatus.

Analytical

Analysis of particulate material for halogen content was readily accomplished by methods described in Phase I of this work.⁶

Analysis of particulate material for the concentration of alkyl (or aryl) groups on the surface presented a problem. Of the few possible methods considered, analysis for carbon seemed the most promising. The Leco Combustion Apparatus, for the determination of carbon in steel, was evaluated for the determination of carbon on glass and silica particulate materials. The data for this evaluation are shown in Table III. The three runs 65A, 65B, and 84 show that the carbon content of silica powder can be reduced to a low and reproducible value, and that the adsorption of organic vapors from laboratory air does not seem to be a major source of error. On the other hand, chlorination with phosgene (Sample 71A) results in appreciable carbon residue, even after rigorous desorption. This residue surely must have a structure related to phosgene or carbon monoxide, and it seems unusual that it would resist desorption at 200°C and 10^{-6} mm Hg. Further, relatively high values for sample 71C indicate that washing with water and redrying does not dislodge the residual carbon species. The carbon content of run 80C indicates that the treatment of a "clean" surface with an alkylating agent results in some residual carbon. Whether this is present as chemically bound carbon or strongly adsorbed species is not known.

The carbon analysis for the remaining (Table III) pairs of surface-treated samples are in good agreement, indicating good reproducibility in both the chlorination and alkylation reactions.

On the basis of a surface area of 0.19 meter²/g, the chloride "population" for sample 71 is 2.6 atoms per 100 Å², and for sample 75 it is 3.6 atoms per 100 Å². These values are below the values of 5 to 6.5 obtained in early development of the chlorination procedure,⁶ but they do not represent an attempt to obtain an optimum degree of chlorination.

The corresponding populations of organic groups, per 100 Å² are: sample 72, 1.9 butyl groups; sample 74, 1.3 undecyl (11 carbon atom) groups; and sample 80A, 1.6 phenyl groups. Thus, the chlorine conversion was as follows: to butyl, 73% yield; to undecyl groups, 35%; and to phenyl groups, 45%.

Evaluation of the Effects of Surface Modification

Modification of a glass or silica surface with a monolayer, or less, of organic groups bonded to surface silicon atoms should cause a noticeable decrease in the surface free energy of the material. This decrease will be accompanied by corresponding changes in surface properties. Contact angles between the surface and polar liquids should be increased, and the work of adhesion to such modified surfaces should be decreased. Under certain circumstances, however, the work of adhesion may be increased, due to autohesion. If the surface has been modified by a long chain group, e.g. dodecyl, the intertwining of diffusion of the long chains into the bulk of the adhesive layer (the process of autohesion) should result in increased adhesion even though the surface free energy has been reduced.

In the case of the four-carbon butyl groups used in the initial surface modification studies reported here, it is doubtful that autohesion plays a significant role.

Four methods were chosen for evaluating the effects of surface modifications of glass and silica materials: peel tests, contact angle measurements, dilatometric measurements, and sonic measurements.

The results presented are the initial ones in a program to evaluate the effect of a systematic change in the nature of the organic group attached to surface silicon atoms.

Peel Tests

Peel Tests were carried out on the apparatus shown in Fig. 3a, b, and c. This apparatus is of a modified design, chosen for simplicity of construction and operation.

The data for surface-modified samples are summarized in Table IV. Data are given for commercially available tapes, a 1.0-inch-wide cloth-backed tape and a 0.75-inch-wide glass filament-reinforced tape. A control series for each tape was prepared using a "standard" reproducible clean surface. This clean surface was prepared by fluorination of the glass at 200°C, a process which completely removes a surface layer of SiO₂ and leaves surface SiF groups, followed by hydrolysis to a hydroxyl-rich silica surface. The alkylated samples were prepared by treatment of a fluorinated surface with butyl lithium.

It is seen from Table IV that the butylated samples require a consistently lower peel force than do the hydroxyl-rich samples, which is consistent with the expectations for this surface treatment.

It is further seen that the peel force required for the 0.75-inch tape is somewhat greater than for the 1.0-inch tape. No explanation is available for this difference; however, two variables are present which undoubtedly contribute. All tapes were applied with a constant 12-pound load on the drum, so that the pressure at point of contact of drum and tape during application was nominally 25% greater for the 0.75-inch tape. The second variable is the type of adhesive used on each of these tapes. Although no data are known for this factor, it is probable that the adhesives used on the two tapes are different.

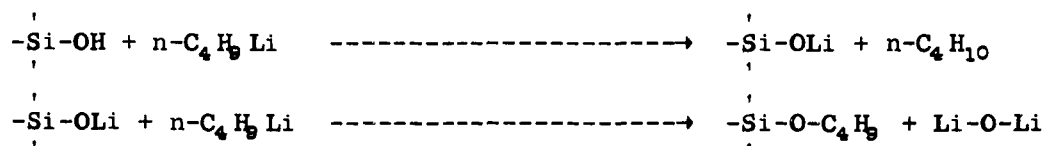
Figure 4 shows the peel-test record for sample 7494-29-15. This record is typical of all samples run. The erratic nature of the trace is explained in part by the presence of defect areas in the adhesive layer of the tape. Of the many different tapes evaluated in preliminary

work, some had very pronounced translucent areas clearly visible through the transparent tape. These areas remained after the tape was rolled on the glass rings, and coincidence between these areas and breaks in the recorder trace were easily observed.

The data in Table IV were derived from the area under the curve measured with a planimeter.

Contact Angle Measurements

For a clean glass surface, the contact angle for water and organic liquids should be zero (i.e., the glass should be completely wetted.) The predicted effect of butylation of a glass surface upon the contact angle between that surface and polar liquids, as discussed earlier, is lowering the surface free energy of the glass, and increasing the contact angle for water and other polar liquids. (This prediction is verified by the data in Table V and Figs. 5a, b, c, and d.) Contact angles between several liquids of decreasing polarity (or surface tension) and glass were measured for a series of surface-modified glass microscope slides. For all liquids, the contact angles with clean glass slides (for reference) were zero (complete wetting). For a control series, in which clean glass surfaces received the same treatment (with n-butyl lithium, etc.) as the halogenated surfaces, contact angles were zero for all liquids except water. The 32° angle for water is probably due to surface contamination, or possibly to a slight reaction between n-butyl lithium and surface -Si-O-Li groups to produce butoxy groups.



Three methods of surface modification were evaluated: a surface modified by n-propoxy groups was prepared by esterification of hydroxyl groups with n-propyl alcohol; a surface modified with n-butyl groups was prepared by reaction of a propoxylated surface with n-butyl lithium;

and a surface modified by n-butyl groups was prepared by reaction of a fluorinated surface with n-butyl lithium. The contact angles of the five liquids with each of the three surfaces were comparable. Theoretically, one would expect the n-butyl-modified surface to exhibit a higher contact angle than a propoxylated surface assuming equal coverages. Experimentally, the fluorinated-butylated surfaces exhibited higher contact angles than the propoxylated ones. However, this result includes any differences that may have existed in the extent of coverage of propoxy vs. butyl groups.

The slightly lower values for the propoxylated-butylated samples, compared with the propoxylated-only sample, may be ascribed to the incomplete conversion of propoxy groups ($-\text{Si}-\text{O}-\text{C}_3\text{H}_7$) to butyl groups ($-\text{Si}-\text{n}-\text{C}_4\text{H}_9$). Groups that escaped alkylation were ultimately hydrolyzed to $-\text{Si}-\text{OH}$ groups, resulting in a surface of higher free energy and therefore lower contact angles.

Figures 5a, b, and c show the plot of the data in Table V. The abscissa, $\cos \theta$, is the cosine of the measured contact angle; the ordinate, γ_{LV} , is the surface tension of the liquid at 20°C in contact with its saturated vapor. The plot of such data usually gives a straight line.⁸ The surface tension corresponding to the point on the curve at $\cos \theta = 1.0$ is the critical surface tension for that solid surface. Figure 5d shows a similar plot, from Fox and Zisman,⁹ of contact angles of a series of liquids with a polyethylene surface. The data for the surface-modified glass parallel those for polyethylene.

Dilatometry

The dilatometric method for evaluation of adhesion is based upon the change in volume of a filled elastomer due to void formation at filler-polymer interfaces as the composite material is elongated. The sample consists of a rectangular prism of an elastic polymer which is filled with the desired solid in the form of fine particles. As the sample is slowly stretched in a constant volume system, the difference in pressure between sample and reference cells is continuously recorded. This pressure difference is measured as change in volume on the strip chart.

The dilatometric method, in one form or another, has been used for some years as a research tool. (For example, see T. L. Smith¹⁰ and references therein.) The apparatus and procedure used in this work are described in detail by Fishman and Rinde.¹¹

The method requires an elastic polymer with sufficient cohesive strength to undergo an elongation of 50% or more. Initial experiments were carried out with General Electric RTV-615, room-temperature vulcanizing silicone rubber. The cohesive strength of this rubber was insufficient for our purpose. Subsequent experiments were conducted with a polyurethane rubber, prepared from a polypropylene glycol and tolylene-2,4-diisocyanate, crosslinked with 1,1,1-trimethylolpropane. Composites of this formulation containing 55 wt % of particulate matter underwent elongations of 50% or more. The corresponding volume increase of these samples fell in an easily and accurately measurable range.

Two sets of three samples each in the polyurethane formulation have been evaluated in the dilatometer. Triplicate samples of cleaned silica powder embedded in the rubber served as control samples. Triplicate test samples were prepared from silica powder which had been chlorinated, then butylated (with n-butyl lithium). The stress vs. extension and the volume vs. extension curves for control and test samples shown in Fig. 6 are very similar for both sets of samples. The average curve for butylated silica shows a slight tendency for greater volume change (corresponding to a greater degree of debonding) at a given extension, relative to the cleaned silica. In these dilatometry experiments, as in the peel tests, two opposing effects may come into play. Butylation of the surface should lower the surface free energy of silica, causing a lower energy of adhesion. However, any autohesion effect (diffusion of hydrocarbon chains on the silica surface into the bulk polymer) should result in a higher energy of adhesion.

Sonic Tests

The sonic method for evaluation of bonding between particulate glass and a polymer matrix was evaluated on 7.5-mm-thick by 25-mm-O.D. buttons containing 50 wt % of glass powder in G. E. RTV-615 elastomer. These buttons were placed in contact with a barium titanate transducer, which served both as a source of sound and as a receiver for the sound not absorbed by the sample. While this method was successful in principle, it was discarded because of the difficulties in obtaining reproducible measurements upon the same sample. This difficulty, while not investigated, appeared to be due to the extreme sensitivity of the system to contact between transducer and sample.

EXPERIMENTAL

Materials

Glass Powder

Glass powder (Fisher Scientific Company, Cat. No. G-17) was used for initial attempts to prepare composites for dilatometric evaluation of bonding. The raw material was washed and sized by wet screening between 150 mesh and 325 mesh U. S. Standard sieves. Use of this material was discontinued when it was found that surface area, as measured by the flow method of Nelson and Eggertsen,^{1,2} became greater with increased temperature of initial desorption. This effect is shown in Table I.

Low-Iron Silica

Low-iron silica (International Minerals and Chemical Corporation) was sized by screening. The fraction passed through a 150 mesh U. S. Standard sieve and retained on a 325 mesh sieve was collected. This fraction was washed with water and cleaned with freshly prepared sulfuric acid-potassium dichromate cleaning solution at 100°C for four hours. The material was then rinsed with distilled water until the washings were of neutral PH. The silica was dried in air at 200°C and stored.

Specific surface, measured by the flow method, was found to be 0.170 meter²/gram. The particle size, as measured on a Fisher Subsieve Sizer (Fisher Scientific Co.) was 25.6 microns (average diameter, assuming spherical shape. This value gives a surface area, calculated from the expression $S = \frac{6}{\rho D}$, of 0.09 meter²/gram. The actual shape of these particles is very irregular, which probably accounts for the discrepancy between the two methods of determining surface area.

Other Materials

Other materials used in this work are described as they are referred to in the experimental section.

Chlorination

Chlorination of particulate silica was accomplished with phosgene in the reactor shown in Fig. 1. This reactor may be used at temperatures as high as 1000^oC. The charge, sufficient to cover the end of the thermocouple well, was put into the reactor tube and the apparatus was assembled. The tube was flushed with a slow, continuous stream of dry nitrogen, the rotation was started, and the reactor was heated and maintained at 500^oC.

The nitrogen stream was replaced by a stream of phosgene which had been purified by passage through a linseed oil scrubber (to remove chlorine) and finally through a concentrated sulfuric acid scrubber. A flow of 20 ml phosgene per minute was maintained, at 500^oC, for 2.5 hours. The phosgene flow was stopped, and the reactor was evacuated to about 1 mm Hg. After 30 minutes at 500^oC and 1 mm pressure, the system was allowed to cool at the low pressure. The reactor was filled with dry nitrogen and opened. The material was alkylated immediately.

The effect of temperature on the chloride content of chlorinated silica is shown in Table II. The low values for surface chloride concentrations obtained at higher temperatures (600^o-800^oC) may be attributed to the more rapid disproportionation of intermediate surface-based structures to silicon tetrachloride.

Chlorination of glass and silica rings (for peel test evaluation) was carried out at 500°C in the apparatus shown in Fig. 2. Chlorination in this apparatus was discontinued due to difficulties of heating the inner (sample) jacket. The well in the inner jacket was heated with a silica-sheathed immersion heater surrounded with 80 mesh alumina. The heating element failed after one run because of the high filament temperature required to maintain 500°C at the surface of the jacket.

After chlorination, the system was flushed with dry nitrogen and the inner jacket removed for further treatment. Finally the treated glass tube was carefully cut into cylinders (or sleeves), 1.25 inches long, for use with the peel test apparatus.

Fluorination

Fluorination of glass rings for peel tests was carried out with elemental fluorine at 200°C, in the apparatus shown in Fig. 2, using sodium chloride as a heat-transfer agent around a Calrod heater. No difficulty was experienced with corrosion, etching, or inorganic fluoride residues.

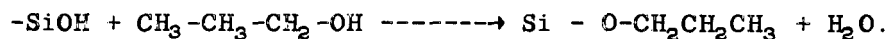
Fluorination of standard microscope slides was carried out in the fluorination apparatus described previously.⁶ Whereas the fluorination of silica (which produces volatile products exclusively) was smooth, the fluorination of glass was complicated by the formation of nonvolatile fluorides. At low temperatures deep etch lines approximately perpendicular to the four edges of the plate were formed. Examination under a microscope revealed that they probably were initiated at notches, resulting from the cutting operation, along the edges of the glass slides.

Fluorination of glass microscope slides at 150°C for 0.25 hour produced a transparent surface that was not etched with lines, but which was covered with a thin transparent layer of metal fluorides. This film was easily peeled from the glass substrate. Its thickness was governed by the length of time of exposure to fluorine gas. Control of time and temperature of fluorination resulted in unmarred fluorinated

surfaces. Optimum conditions have not been established for this reaction. These plates were used for contact angle measurements.

Alkoxylation

Alkoxylation of surface-based SiOH groups on glass was accomplished according to the reaction



The reaction was carried out at 180°C with n-propyl alcohol, in a pressure vessel, as recommended by Iler.⁷ Glass powder and glass microscope slides were alkoxyated for subsequent use.

Alkylation

Alkylation of glass and silica samples was accomplished by causing the appropriate chlorinated, fluorinated, or alkoxyated sample to react with the desired organolithium compound. n-Butyllithium and phenyllithium were prepared from n-butyl bromide and lithium metal or were purchased from Foote Chemical Company. Undecyllithium was prepared from undecyl bromide.

As a specific example, butylated silica was prepared by adding a many-fold excess, based on the chlorine content of the silica, of n-butyllithium (in hexane solution) to 50 grams of chlorinated silica. The mixtures were stirred vigorously, stoppered tightly, and allowed to stand for about 20 hours. The supernatant solution was decanted, and the silica was washed three times with hexane, three times with acetone (reagent grade), three times with distilled water, and three times with 0.1 N hydrochloric acid. The acid was removed with distilled water, and the sequence of washing with organic solvents was repeated. Finally, the product was washed exhaustively with distilled water. The product was collected on a filter and dried in an oven at 140°C. The product was subjected to a temperature of 160°C at a pressure of $5-8 \times 10^{-6}$ mm Hg for 18 to 20 hours in order to desorb volatile organic materials.

Analytical

The analysis of noncarbonaceous inorganic particulate material for carbon content was accomplished with a Leco Model No. 516-000 Combustion Apparatus. This apparatus is commercially available and widely used in the analysis for carbon in steel. A sample of about 1.5 grams, and containing at least 3 micrograms of carbon, is oxidized with oxygen at high temperature. The carbon dioxide is trapped in a dilute sodium hydroxide solution. The change in conductivity of the solution is a measure of the amount of carbon dioxide absorbed. Data on analysis of various samples are given in Table III.

Adhesion Evaluation

Final evaluation of the effect of surface modification must be done on a finished laminate or other end-use product. However, experiments on suitable model systems provide a less expensive and much more rapid screening procedure. To this end, four methods for studying the effect of surface treatment upon surface properties were examined: peel tests, contact angle measurements, dilatometric measurements, and sonic measurements.

Peel Tests

The apparatus for carrying out peel tests is shown in Fig. 3. It was designed to evaluate the effect of surface modification of glass adherends upon the peel strength of pressure-sensitive tapes.

The roller-stirrup design was chosen for simplicity of construction, reproducibility of operation, and ease of surface preparation of cylindrical samples. The preparation of samples may, in some cases, be more time-consuming than other peel test methods.¹³ Particular advantages of this method for peel testing are: the apparatus is self-aligning; the angle of peel is always (essentially) 90° ; and the configuration of cylindrical glass adherend is such that it is readily halogenated and alkylated.

Glass cylinders, after treatment, were wound with tape as follows: a suitable length of tape was placed, adhesive side up, on a smooth flat surface which was cushioned with a smooth sheet of rubber; the glass cylinder to be tested was slipped on the aluminum roller; the roller was centered on the tape, the leading edge of the tape fixed to the roller, and the tape wound by pushing the roller over the tape. Uniformity in winding was achieved by providing a guide and a 12-pound weight for the roller.

Small variations in the inside diameter of the glass rings were accommodated by wrapping the roller with one or more turns of a cloth-backed adhesive tape.

Peel-test rings and tape were conditioned and wound in a constant temperature, constant humidity chamber. The chamber was a plastic dry box fitted with a thermostat, heater, and blower. A constant relative humidity of 50% (at 81-82^oF) was maintained with a large shallow tray of saturated calcium nitrate solution.¹³ Relative humidity and temperature were recorded with a Bendix Hygro-Thermograph.

Peel test samples were pulled on an Instron tensile testing machine, at a rate of 2 inches/min, and with a load cell that measured 4 pounds pull at full-scale chart deflection. The data for surface-modified samples and for control samples are shown in Table IV. Preliminary data, obtained on a nonrecording Baldwin-Lima tester,¹⁴ are not shown.

Figure 4 shows a typical peel-force vs. time recording for these samples. In Table IV are tabulated the data for control and surface-modified samples. These data were derived from the areas under recorder traces. These areas were measured with a planimeter, over a 5-inch length of chart (equivalent to 5 inches of tape). The fifth column in Table IV shows peel force in pounds per inch width of tape. The values for 0.75-inch tape are converted to 1.0-inch width.

The data obtained during evaluation of various types of tape, wrapping procedures, etc., are not included in this report. However, they consistently agreed with the data in Table IV as to reproducibility within a given set of samples.

Contact Angle Measurements

Contact angle measurement was used to evaluate the effect of surface treatment of glass. Standard glass microscope slides were used for this work. Five sets of three slides each were prepared: blank samples of glass plates were cleaned with dichromate cleaning solution; control samples of glass plates were cleaned with dichromate cleaning solution, washed, dried, and treated with butyl lithium; test samples of glass plates were cleaned as above and alkoxyated by treatment at 180°C for two hours with a large excess of purified n-propyl alcohol. (The anticipated reaction was $-\text{Si}-\text{OH} + n\text{-C}_3\text{H}_7\text{OH} \rightarrow \text{H}_2\text{O} + -\text{Si}-\text{O}-\text{C}_3\text{H}_7$.) This was done in a high-pressure autoclave. After cooling, the slides were removed, air-dried, and then desorbed under vacuum); another set of test samples was alkoxyated as above, followed by alkylation with n-butyl lithium.

Contact angles were measured by photographing the drop of liquid on the plate through a microscope. Tangents were drawn on the enlarged images, and angles were measured with a protractor. The data are shown in Table V. Data for the three treated slides are plotted in Figures 5a, b, and c. Figure 5d shows, for comparison, the results of Fox and Zisman⁶ regarding the contact angles of a series of liquids on a polyethylene surface.

Dilatometry

A polyurethane elastomer, similar to those used in propellant formulations, was prepared according to the following recipe:

38.8 wt. %	Polypropylene glycol (MW = 2025), elastomer grade
0.616	1,1,1-Trimethylol propane
0.483	Tergitol TMN, non-ionic wetting agent (polyglycol ethers)
55.3	Silica powder
4.67	Tolylene diisocyanate (2,4-isomer)
0.0725	Ferric acetylacetonate

The mixing was done almost entirely under vacuum of <1 mm Hg, with a stainless steel ribbon blender having inner and outer helical blades which were wound in opposite directions. The blender fitted

loosely into a cylindrical glass mixing vessel of 5 cm ID. A vacuum-tight connection was obtained with a greased rubber ring which fit tightly on the shaft and turned smoothly against the face of the bronze shaft bushing. The polypropylene glycol, trimethylol propane, and Tergitol were degassed by evacuation, in the mixer, at 100°C for 4 hours. During the last hour the flask containing the silica powder was attached by means of a side arm, in order to expose the silica to the mixer atmosphere. The silica was slowly added under vacuum. The tolylene diisocyanate, saturated with ferric acetylacetonate, was added under vacuum at 0°C. The mixture was cast under vacuum into vertical Teflon molds of $\frac{1}{2}$ -inch by $\frac{1}{2}$ -inch cross section and 4-inches deep. The specimens were cured at 60°C for 48 hours. The ends of the silica-elastomer bars were carefully cut to 3-inch lengths with a band saw. T-shaped aluminum tabs with sandblasted $\frac{1}{2}$ -inch-square faces were glued onto the ends of the bars with Rubbaseal (Rubba, Inc.) or Eastman "910" adhesive. The elastomer-metal junction was reinforced with Rubbaseal to prevent failure when pulled. The specimens were stretched, at a rate of 2 inches/min, in a dilatometer.¹¹ The instrument measures volume change in the specimen being extended by means of the differential pressure between the sample cavity and a reference cavity. The pressure in sample and reference cavities was equalized and the apparatus was conditioned to 100°F (38°C) for each measurement. The constant extension rate was 2.0 inches/min.

Three specimens containing cleaned silica and three containing n-butylated silica were extended in the dilatometer. They extended on the order of $1\frac{1}{2}$ inches (50% of original length) before breaking; at the breaking point the volume increase ranged from 0.0083 to 0.112 inch³ (1.1 to 15.2% of original volume.) The results of the tests are shown graphically in Fig. 6.

Sonic Method

The sonic method for evaluation of bonding has been successfully employed in a variety of circumstances. The possibility that the method could be adapted to at least the qualitative measurement of

bonding between a finely divided filler and a polymeric matrix was explored. The method depends on the absorption of sound waves at the interfaces between phases of a composite material. The apparatus used was a barium titanate transducer placed upon a "button" of glass powder-filled elastomer 7.5 mm thick and 25 mm O.D. General Electric RTV-615 silicone polymer was used for the elastomer, because of its ease of formulation and fabrication. Buttons were fabricated with 50% (by weight) of glass powder.

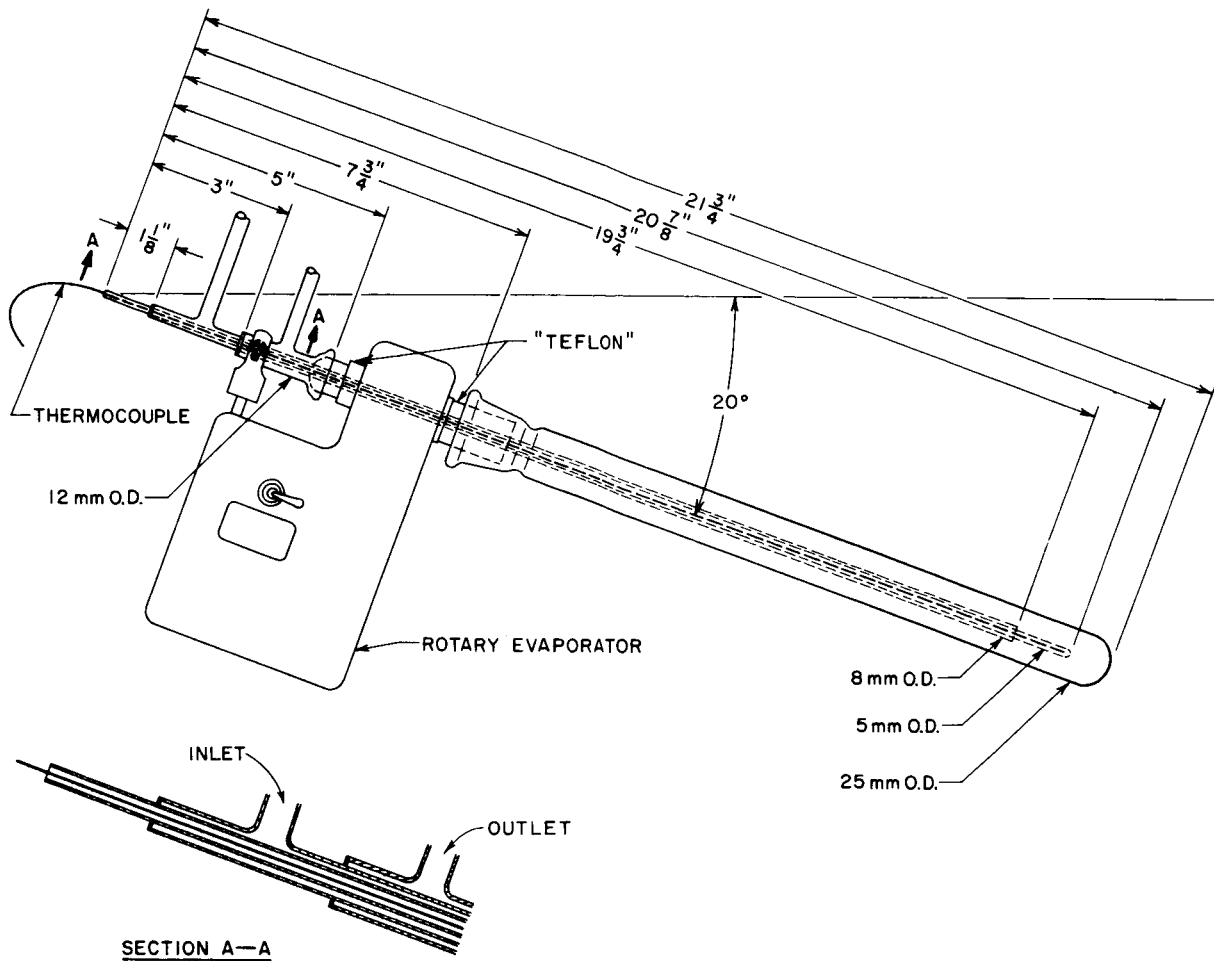
The sonic method, as used, was unsatisfactory, due to the poor reproducibility of results from sample to sample and between successive measurements upon the same sample. Effort in this direction was discontinued.

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The bulk of this work was conducted by Mrs. Fern Jantzeff and Mr. Michael Bertolucci. Contact angle measurements were made by Mr. John Saunders; surface area and particle-sized measurements were made by Dr. Harold Eding and Mr. Charles Lapple; sonic measurements were made by Mr. John Martner; Mr. Norman Fishman was a consultant for the dilatometry, and Mr. James Rinde performed the dilatometric measurements.

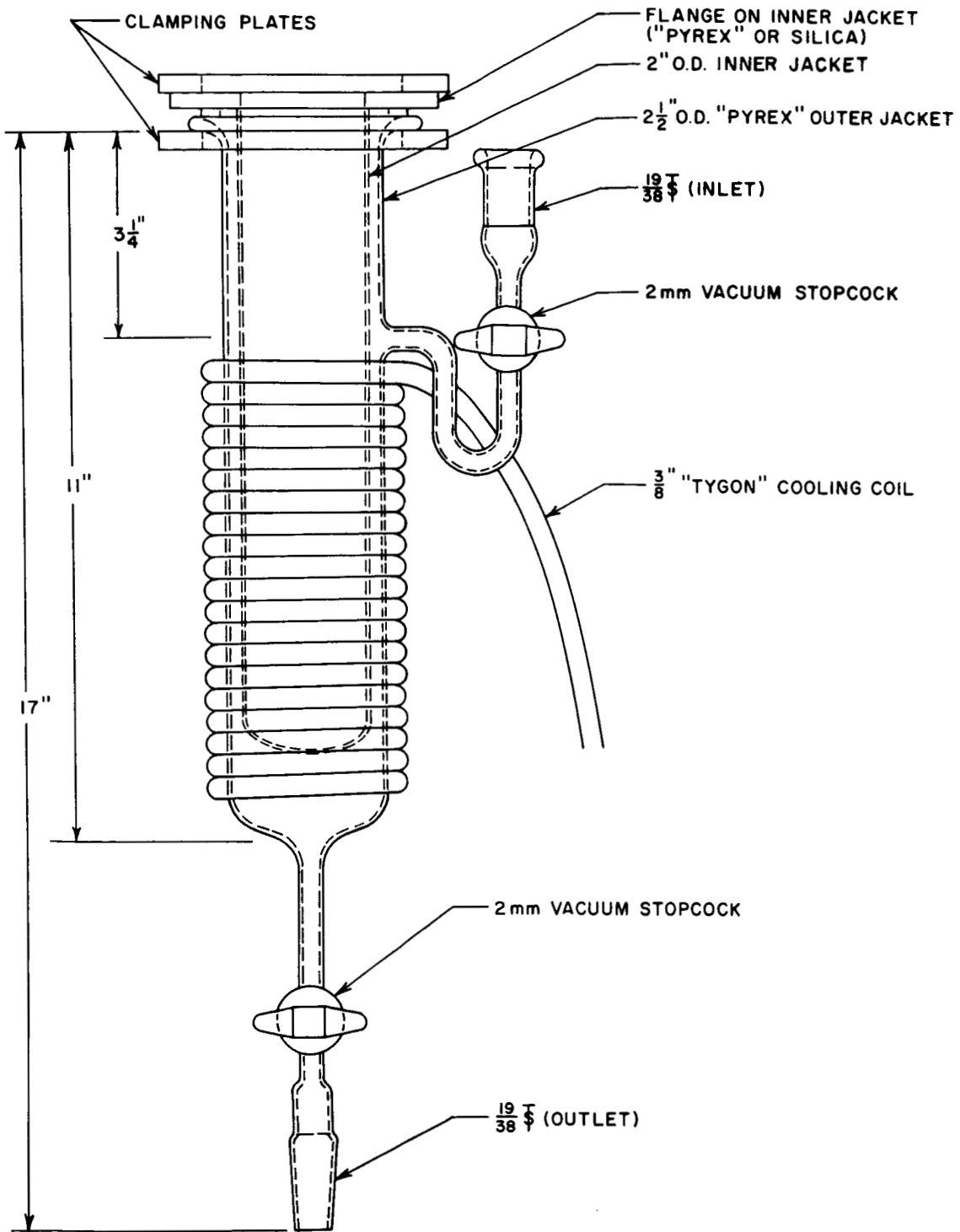
REFERENCES

1. F. J. McGarry, "Properties of Glass-Fiber Reinforced Plastics," Proceedings of the Sixth Sagamore Ordnance Materials Research Conference, August 18-21 (1959).
2. J. O. Outwater and Oguzcan Ozaltin, "Surface Effects of Various Environments and of Thermosetting Resins on the Strength of Glass," SPE Transactions, 2, 321 (1962).
3. T. G. Roskos, H. R. Radloff, and F. M. Young, SPE Transactions, 2, 326 (1962)
4. C. Eaborn, Organosilicon Compounds, Butterworth's Scientific Publications, London, 1960, p. 255
5. R. C. Osthoff, A. M. Bueche, and W. T. Grubb, J. Am. Chem. Soc., 76, 4659 (1954)
6. D. L. Chamberlain, Jr., Summary Technical Report, Contract No. NASr-49(14), June 1, 1963 to July 31, 1964.
7. R. K. Iler, Method of Esterifying the Surface of a Silica Substrate Having a Reactive Silanol Surface, and Product Thereof, U. S. Patent No. 2,657,149 (Oct., 1953)
8. W. A. Zisman, "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution," p. 13, Chapter 1 in Contact Angle, Wettability and Adhesion, Advances In Chemistry Series No. 43, American Chemical Society, Washington, D. C., 1964.
9. H. W. Fox and W. A. Zisman, J. Colloid Sci., I, 428 (1952).
10. T. L. Smith, "Volume Changes and Dewetting in Glass Bead-Polyvinyl Chloride Elastomeric Composites Under Large Deformations," Transactions of the Society of Rheology, III, 113-116 (1959)
11. Norman Fishman and James A. Rinde, Solid Propellant Mechanical Properties Investigations, Final Report, Contract No. AF 04(611)-9559, Dec. 2, 1964.
12. F. Nelson and F. T. Eggertsen, Anal. Chem., 30, 1387 (1958).
13. 1964 Book of ASTM Standards, Part 16, Structural Sandwich Constructions; Wood; Adhesives, American Society for Testing Materials, Philadelphia, 1964. (a) ASTM Peel Test D903-49, (b) ASTM Climbing Drum Peel Test D1781-62.
14. D. L. Chamberlain, Jr., Quarterly Report No. V, Contract NASr-49(14) May 26, 1965.



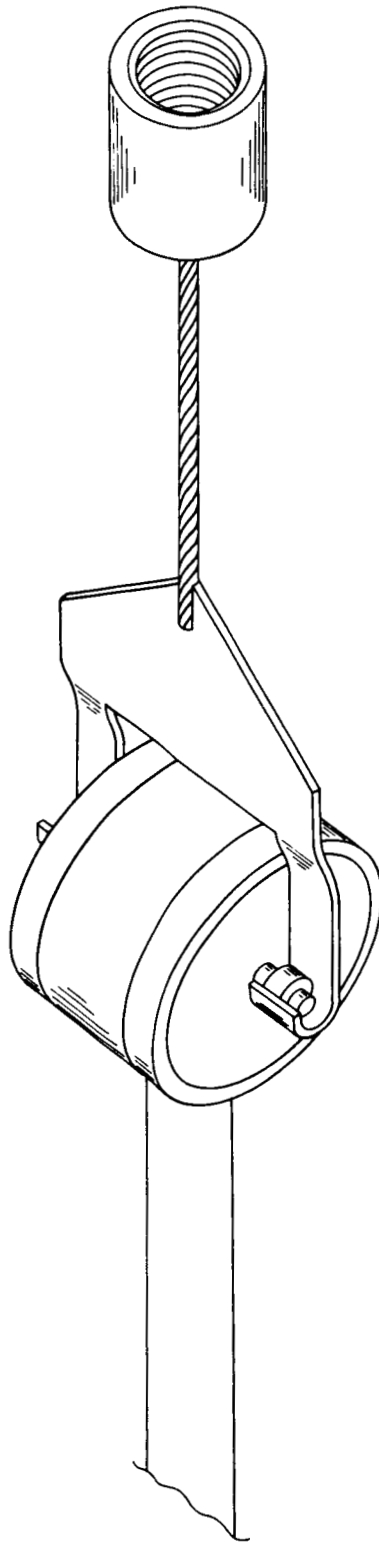
TB-4525-5

FIG. 1 APPARATUS FOR HALOGENATION OF PARTICULATE MATERIALS



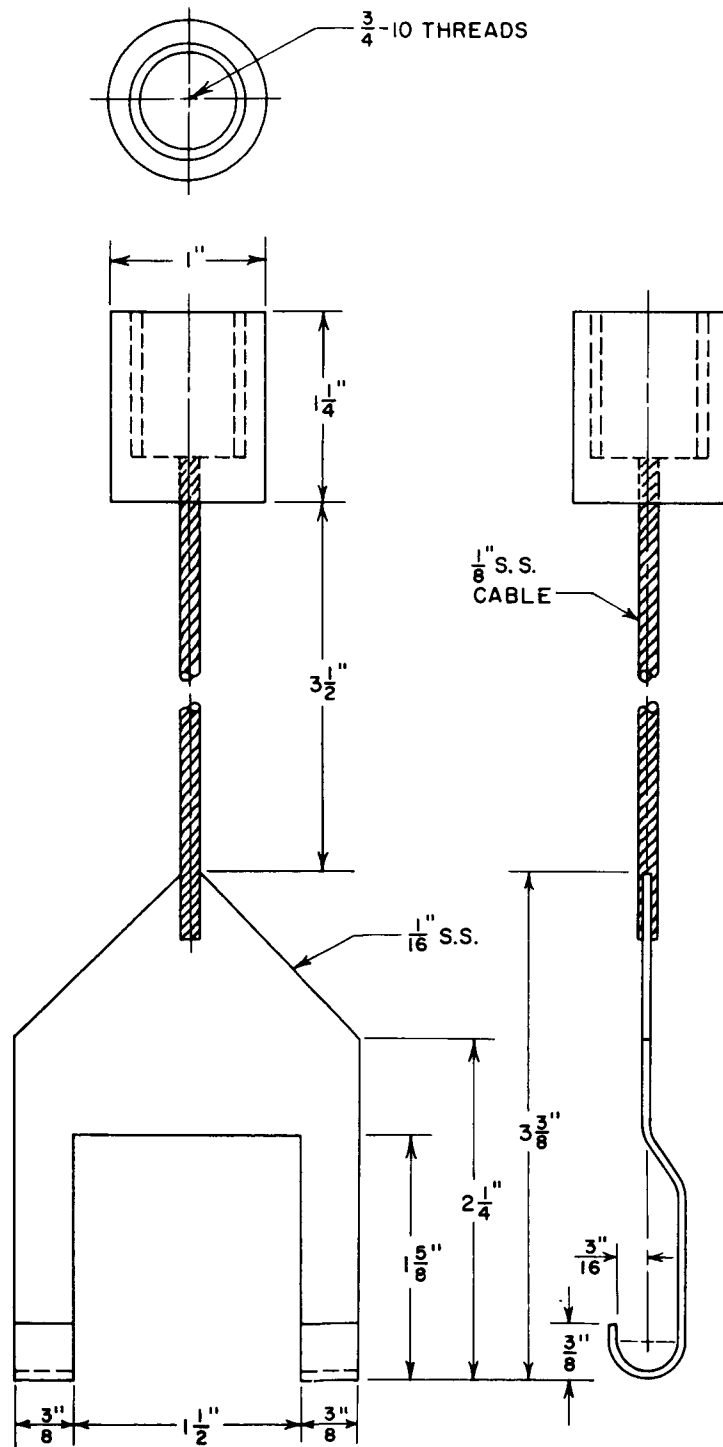
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FIG. 2 APPARATUS FOR HALOGENATION OF RINGS FOR PEEL TESTS



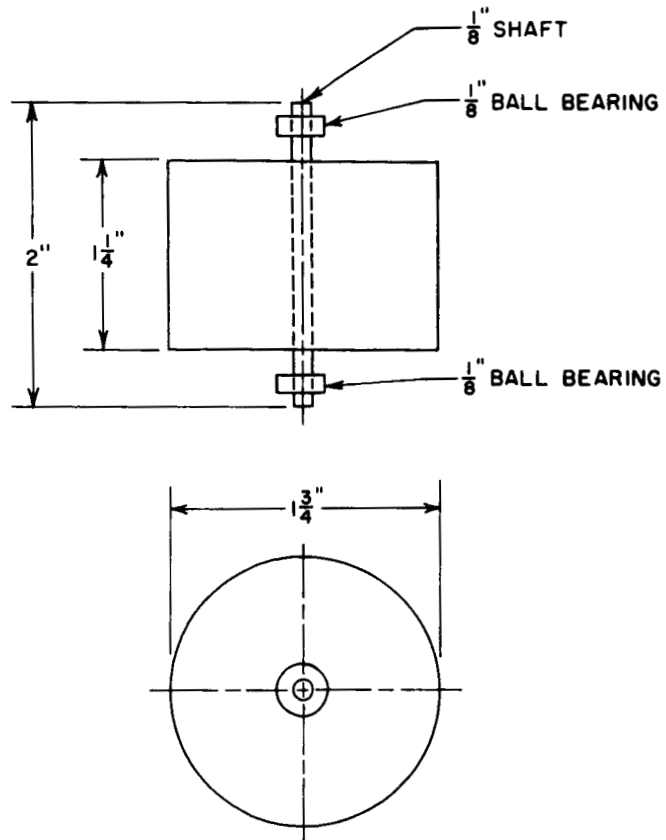
TB-4525-3

FIG. 3(a) APPARATUS FOR PEEL TEST



TB-4525-1

FIG. 3(b) APPARATUS FOR PEEL TEST — DETAIL OF STIRRUP CONSTRUCTION



TA-4525-2

FIG. 3(c) APPARATUS FOR PEEL TEST — DETAIL OF ROLLER CONSTRUCTION

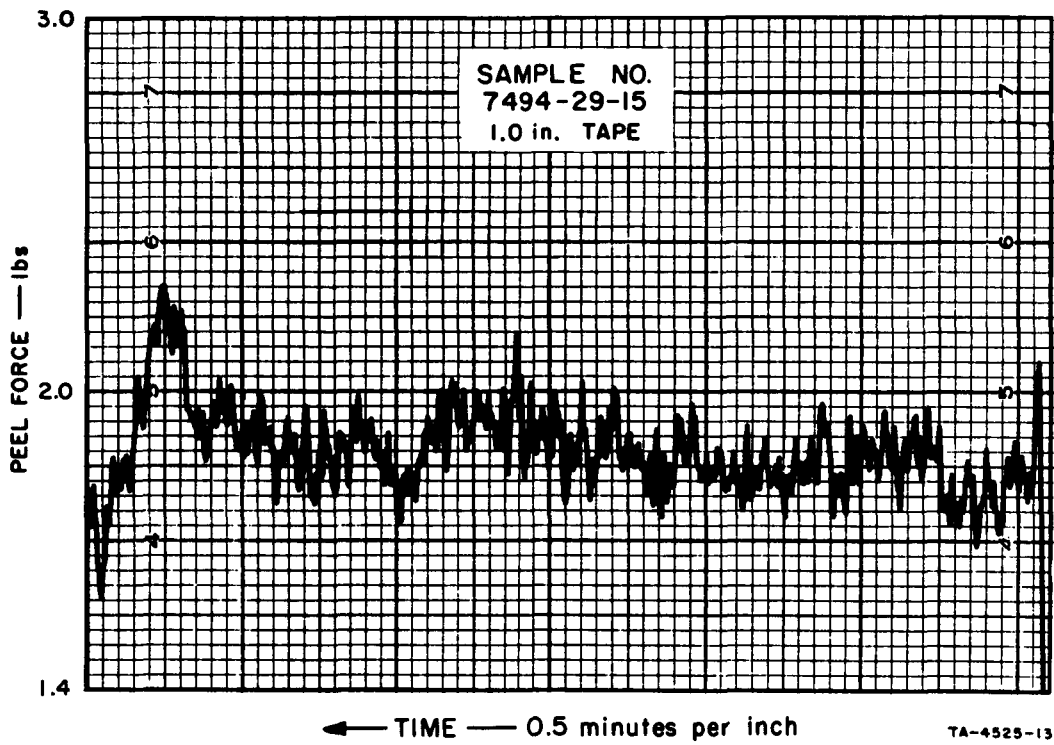
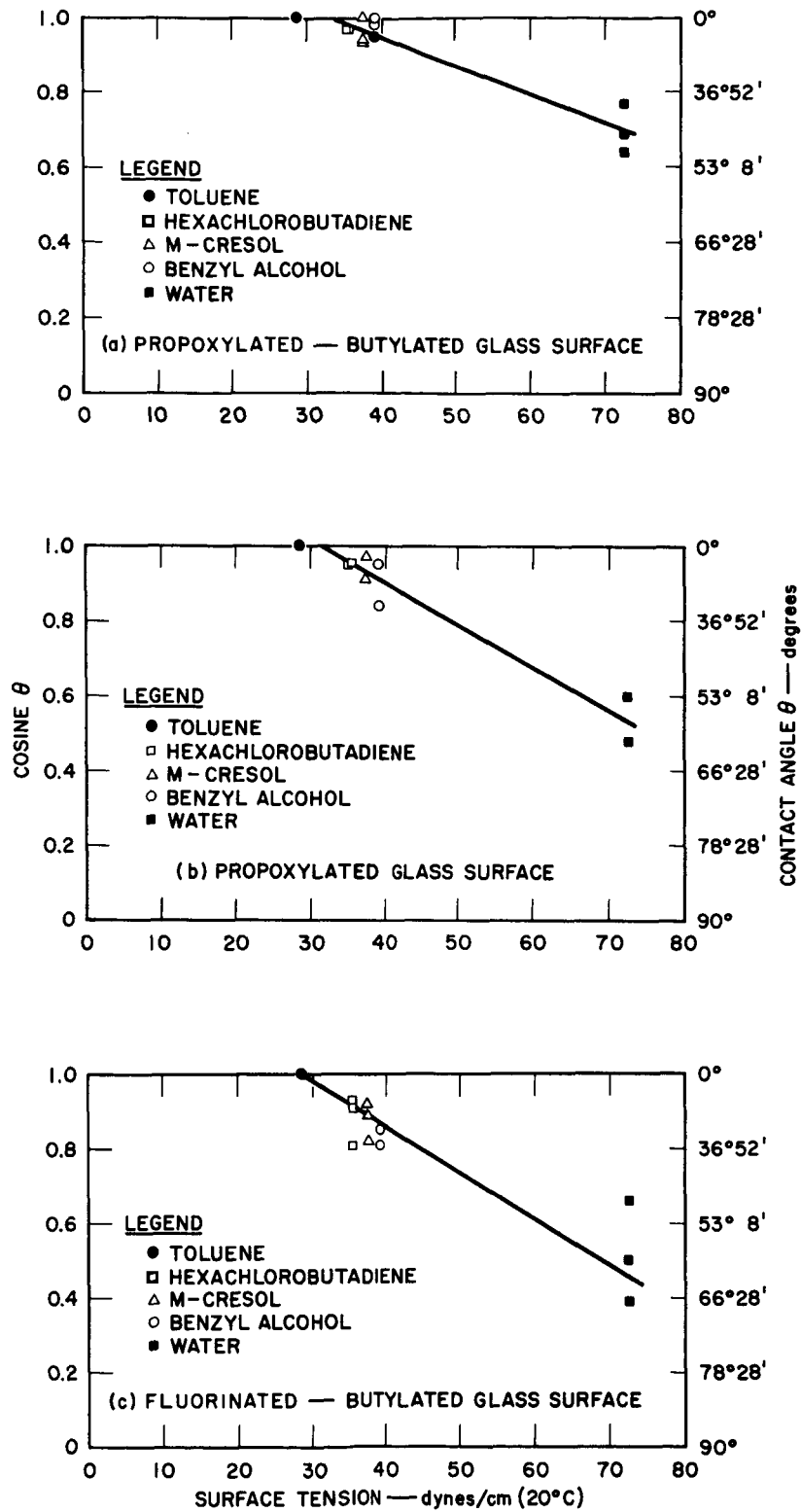


FIG. 4 PEEL TEST DATA FOR FLUORINATED-BUTYLATED GLASS



TC-4525-7

FIG. 5(a,b,c) CONTACT ANGLES OF LIQUIDS ON GLASS SURFACES

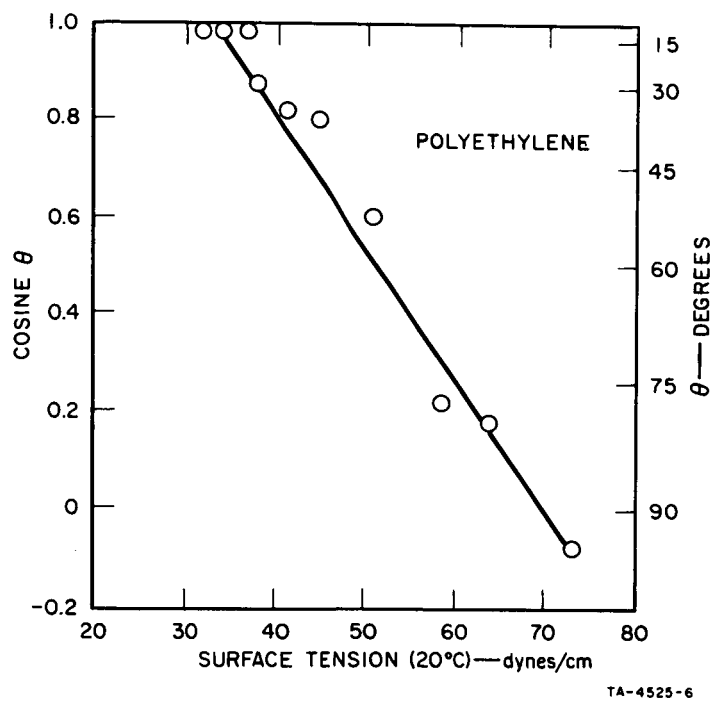
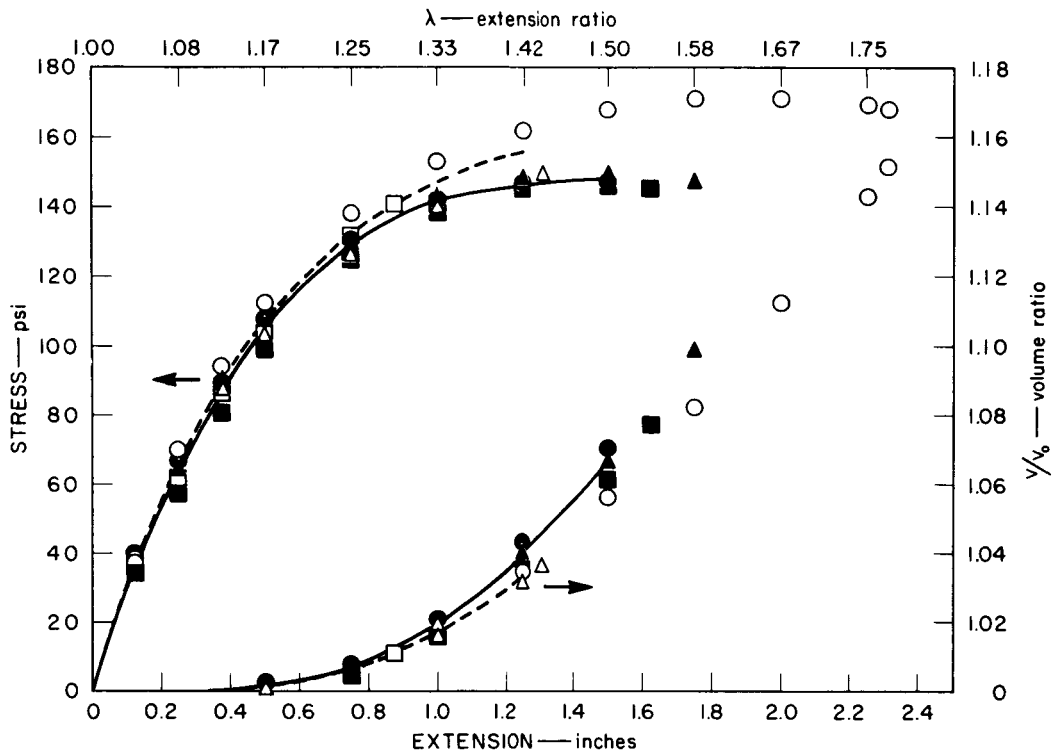


FIG. 5(d) CONTACT ANGLES OF LIQUIDS ON POLYETHYLENE (See Ref. 3)



TB-4525-16

LEGEND

- , ▲, ■ BUTYLATED SILICA ○, △, □ CLEANED SILICA
- AVERAGE VALUES FOR CLEANED SILICA
- AVERAGE VALUES FOR BUTYLATED SILICA

FIG. 6 DILATOMETER DATA FOR POLYURETHANE — SILICA COMPOSITES

Table I

THE EFFECT OF INITIAL DEGASSING TEMPERATURE
ON SURFACE AREA
AS MEASURED BY NITROGEN ADSORPTION

Notebook Reference	Material	Surface Area (Meters ² per Gram)	
		Calculated from Particle Size	Measured by N ₂ Adsorption following Desorption at the Indicated Temperature
7452-25	Powdered Glass		240 ^o C - 0.04
			335 ^o - 0.10
7452-25	Low-Iron Silica		160 ^o - 0.04
			200 ^o - 0.06
			260 ^o - 0.07
			335 ^o - 0.08
7452-69	Powdered Glass	0.053*	155 ^o - 0.11

*Calculated on the basis of spherical particles of the minimum size
(4.3 x 10⁻³ cm) retained by a 325 mesh screen.

TABLE II

THE EFFECT OF TEMPERATURE ON THE
CHLORINATION OF LOW-IRON SILICA WITH PHOSGENE

Notebook Reference	Temperature °C	Chloride Concentration (mg Cl/g SiO ₂)
7452-20	800	0.0021
-17	700	0.0054
-16	600	0.0060
-15	500	0.077
-22	500	0.077
-24A	400	0.016
-24B	400	0.024
-26	400	0.010
-27A	335	0.020
-27B	335	0.015

Table III

ANALYSIS OF PARTICULATE SILICA FOR SURFACE CARBON

Sample No. (Notebook Reference)	Sample History	Chlorine Content (ppm)	Carbon Content (ppm)
7494-65A	Acid washed, rinsed, dried, degassed at 200°C and 10 ⁻⁶ mm for 18 hrs ¹	---	2.3
7494-65B	Portion of 65A exposed to laboratory air for 18 hrs instead of degassing procedure	---	4.6
7494-84	Acid-washed, rinsed, and dried at 200°C at atmospheric pressure, overnight	---	2.0
7494-71A	Portion of 65A, chlorinated with COCl ₂ , and degassed at 132°C, <1 mm, 24 hrs ²	28.5	21, 7.0 ³
7494-71C	Portion of 71A, hydrolyzed, dried at 200°C, and degassed at 170°C 10 ⁻⁶ mm, 44 hrs	---	14
7494-72	Portion of 71A, alkylated with n-butyllithium, washed, dried, degassed ⁴	---	27, 29 ³
7494-74	Portion of 71A, alkylated with undecyllithium, washed, dried, degassed ⁴	---	53, 53 ³
7494-75	Portion of 65A, chlorinated with COCl ₂ , and degassed at 130°C, <1 mm, overnight	40.4	----
7494-83	Portion of 75, hydrolyzed, dried at 200°C, degassed at 170°C, 10 ⁻⁶ mm, 44 hrs	---	18
7404-80A	Portion of 75, arylated with phenyllithium, washed, dried, degassed ⁴	---	35, 39 ³
7494-80C	Portion of 75, hydrolyzed, dried, treated with phenyllithium, washed dried, degassed (This was a control run for 7494-80A)	---	7, 13 ³

¹Low-iron silica, specific surface (Ref. 13) about 0.16 meter²/gram

²After chlorination, specific surface was about 0.19 meter²/gram

³Duplicate analyses

⁴Degassing done at 160°C and 10⁻⁶ mm for 22 hrs.

Table IV

PEEL TEST DATA ON 2-INCH OD PYREX GLASS RINGS

Notebook Reference and Sample Number	Tape Designation	Prewrap Treatment	Postwrap Treatment	Peel Force	Average Peel Force lbs/in ²	Maximum Deviation from Average
7494-29 C D E F	1-inch Scotch No. 0300 cloth-backed tape	Fluorinated, hydrolyzed, dried, solvent-cleaned, humidified 16 hrs at 76°F, 58% R.H.	Aged 22 hours at 76°F and 58% R.H.	2.31 2.25 2.20 1.98	2.19	9.6
12	Same as above	Fluorinated, butylated, treated as above	Same as above	1.86 1.90 1.92 1.83 1.76	1.85	4.9
7494-30 C D E F	3/4-inch Scotch Glass-filament reinforced	Fluorinated, hydrolyzed, dried, solvent-cleaned, humidified 5 days at 50% R.H. and 81°F	Aged 25 hours at 76°F and 58% R.H.	2.45 2.43 2.23 2.47	2.40	7.1
12 13 14 15 16	Same as above	Fluorinated, butylated, and treated as above	Same as above	1.69 2.05 2.34 2.14 2.10	2.07	18.0

Table V

CONTACT ANGLES IN DEGREES FOR LIQUIDS ON SURFACE-MODIFIED GLASS

Notebook No. and Page	Type of Surface Modification	Liquids (γ_{LV} , dynes/cm @ 20°C)*				
		Water (γ_{LV} = 72.8)*	Benzyl Alcohol (γ_{LV} = 39.0)	M-Cresol (γ_{LV} = 38.4)	Hexachloro-butadiene (γ_{LV} = 36.3)	Toluene (γ_{LV} = 28.4)
7494; pp. 3-11	Blank: Cleaned in acid-dichromate solution	0°	0°	0°	0°	0°
	Control: Cleaned and treated with n-butylolithium	32°	0	0	0	0
	Propoxylated	53, 61	33, 18	25, 15	18, 18	0
	Propoxylated and alkylated with n-butylolithium	40, 46, 50	4, 19, 10	4, 22, 22	14, 14	0
	Fluorinated and alkylated with n-butylolithium	67, 60, 49	36, 32	23, 27, 35	22, 24, 26	0

*Figures in parentheses are surface tension in dynes/cm for liquids in contact with saturated vapor at 20°.

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