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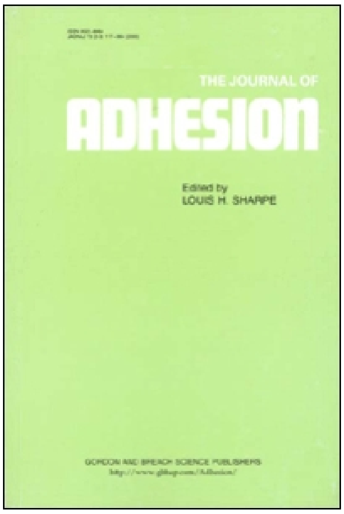

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Radioisotopic Studies of Bonding at the Interface

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ABSTRACT

The use of radioisotopic and complementary surface chemical techniques in characterizing the nature of coupling agent films on glass surfaces is reviewed. The heterogeneous nature of the coupling agent film, and the effects of method of application are described. These are correlated with adhesive joint resistance to hydrolytically induced failure under static load. New data are presented yielding evidence that glass-resin joint failure in hot water occurs as a result of hydrolysis of bonds within the coupling agent structure.

Chemical Bonding Theory

Application of chemical finishes to glass fibers used in reinforced plastics results in improved laminate properties. This improvement has been most notable in the ability of the laminate to retain its strength under conditions of severe exposure to moisture. While no completely satisfactory explanation has been offered for this phenomenon, the chemical bonding theory has proved to be a useful working hypothesis for research in the field. This theory states that the finish forms a chemical bond with the surface of glass through one functional group, while another functional group on the same molecule chemically bonds to the resin. Adhesion of the resin to glass is therefore strengthened through a bridge of chemical bonds connecting the two phases.

This view of the mode of action of a typical coupling agent would suggest that a film of the coupling agent applied to a glass substrate consists of a monolayer, with each molecule individually chemisorbed to the surface through the glass-reactive functional group, while another functional group on each molecule remains free to ultimately react with the resin.

Coupling Agent as Multilayer

Sterman and Bradley[10] first conducted a physicochemical investigation of the characteristics of a film of coupling agent adsorbed to a glass surface. Using a technique developed by D. E. Bradley[2] for replication of fibers, they applied the electron microscope to an investigation of the amount and state of aggregation of various silane coupling agent films applied to E glass fibers. The first and most striking feature of their findings was that the commercial method of applying coupling agents resulted in deposition of a thick (in terms

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of molecular dimensions) non-uniform layer of the material, which tended to form agglomerates in the cavities between the fibers. Furthermore, upon extracting the treated fibers in a Soxhelet for 4 hours, about 80% of the deposited coupling agent was removed, with the remainder present in the form of islands. The technique was not sensitive enough to determine whether the space between the islands was bare glass or contained an ultra-thin film of the order of a monolayer. A comparison of the material present in the islands as estimated by electron microscopy with the total amount present (on the extracted surface) as determined by chemical analysis did not necessarily require the postulating of coupling agent in between the islands to obtain a material balance. In short, the nature of the surface layer of coupling agent as seen by the electron microscope was far different than the simple picture of a monolayer of neatly oriented molecules required by the chemical bonding theory. The authors concluded that the film consisted mainly of easily removable outer layers but with a "tightly bonded polymer close to the glass". To obtain optimum performance from the coupling agents, the authors found it necessary to apply from 8 to 70 monolayer equivalents to the glass surface. They explained the need for high loadings on the basis of the uneven distribution of coupling agent on application.

Heterogeneous Nature of Multilayer: Three Fractions

Schrader, Lerner, and D'Oria[8] utilized radioisotope techniques in combination with electron microscopy in an attempt to further examine the nature of a coupling agent film on glass. Of special interest was the question of the possible existence of a monolayer, which could not be detected with the electron microscope, in between the islands observed by Sterman and Bradley after Soxhelet extraction. The coupling agent chosen for investigation was gamma-aminopropyltriethoxysilane (Union Carbide's A1100), with a C-14 label placed in the hydrocarbon chain alpha to the amino group. The coupling agent was deposited on the surface of polished Pyrex blocks from benzene solution, and the surface of the blocks, excluding the edges, was then counted for radioactivity. The blocks were then extracted in water at room temperature and the radioactivity on the block determined as a function of time of extraction. Following this the blocks were placed in boiling water and the residual radioactivity determined periodically. It was found that the deposit of A1100 could be regarded as consisting of three fractions with respect to tenacity when subjected to extraction procedures (Fig. 1). The major fraction, called Fraction One, which was as much as 98% of the total, depending on the amount deposited, consisted of the hydrolyzate of the silane (ethoxy groups replaced by hydroxyls) physically adsorbed to the surface. It could consist of as much as 270 monolayer equivalents, and although insoluble in benzene, was rapidly removed by the cold water rinse. Fraction Two was a chemisorbed polymer of the coupling agent, consisting of about 10 monolayer equivalents. This fraction required about 3 to 4 hours extraction

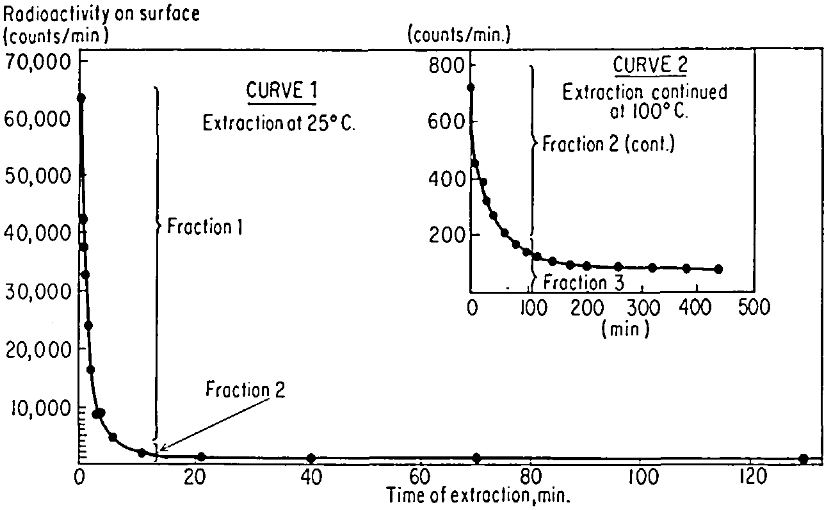

Figure 1. Amount of radioactive A1100 remaining on polished Pyrex surface after extraction with water (Schrader, Lerner, and D'Oria).

in boiling water for essentially complete removal. Electron miscroscope pictures of this fraction taken in parallel experiments after one hour boiling water extraction showed the presence of islands. Assuming that the one hour water boil is roughly equivalent to a four hour Soxhelet extraction, these islands can be identified with those observed by Sterman and Bradley, supporting their findings of a tightly bound polymeric layer. Now, upon complete removal of this Fraction Two, defined by the complete tapering off of the curve of radioactivity versus time obtained during the boiling water extraction, Schrader *et al* found that the electron microscope now indicated a completely bare surface, the islands having all disappeared. However, a radioisotope count of this apparently bare surface indicated that the equivalent of a monolayer (or substantial fraction thereof) of the previously undetected coupling agent still remained. This residue was called Fraction Three. It was apparently more tenaciously held to the surface than Fraction Two, the bulk of the chemisorbed polymer, and the authors speculated that this resulted from multiple bonding of the molecules (perhaps as monomers, perhaps as dimers or trimers) to the glass surface. In this connection, it should be noted that it has been suggested that silanol groups on glass are too far apart to allow multiple bonding of a monomeric silane to the glass surface. It is well known, however, that silanols are usually present in pairs. In fact, Hair and Hertl[3] have recently obtained kinetic evidence supporting studies of Peri[6] and Armistead and Hockey[1] that silicon tetrachloride, trichloromethylsilane, and dichloromethylsilane molecules each react with two freely vibrating hydroxyl groups on a silica surface, even though these hydroxyl groups are too far apart to hydrogen bond with each other. The surface studied (Hair and Hertl)[3] had an average of 1.4 hydroxyl groups per 100A^2.

Differences in Adsorption Behavior Among Coupling Agents

Johannson *et al* [5] utilized C-14 labeled silane type coupling agents in an investigation of the nature of the adsorbed film of these agents on E glass fibers. The coupling agents used were 3-aminopropyltriethoxysilane (Union Carbide's A1100), 3-methacryloxypropyltrimethoxysilane (Dow Corning's Z 6030 or Union Carbide's A174), and 3-(2′, 3′ -epoxypropoxy) propyltrimethoxysilane (Dow Corning's Z6040 or Union Carbide's A187). The authors obtained data on adsorption as a function of solution concentration by immersing heat-cleaned E glass fibers in solutions of varying concentrations of each coupling agent. Each immersion, on a separate sample of fibers, took place for one minute, after which the supernatant solution was removed by aspiration. In one experiment in which the immersion time was varied from 30 seconds to 48 hours it was found that rapid adsorption took place within 30 seconds followed by a very slow further build up of coupling agent. It is to be emphasized that the amount adsorbed after one minute for each solution concentration was not the result of temporary adsorption-desorption equilibrium between the solution and substrate, but rather a function of the manner in which the nature of the resulting irreversibly chemisorbed film was influenced by the kinetics of formation or by any other variables influenced by the coupling agent concentration in solution. The authors report about 10 monolayer equivalents (on the basis of their assumption of 1 molecule per 100 A^2) remaining on the surface, yielding a smooth appearance to the electron microscope. These results are essentially in accord with those of Sterman and Bradley[10] and of Schrader *et al*[3] if allowance is made for differences in solution concentration and method of application (i.e., the method of Johannson *et al* minimizes the presence of Fraction One).

An interesting difference is found in the graph of surface coverage *vs* solution concentration (Fig. 2) among the three coupling agents investigated

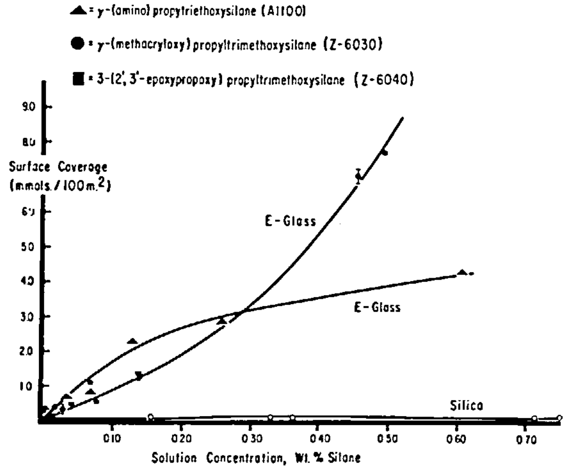

Figure 2. Adsorption of three different coupling agents (Johannson, Stark, Vogel, and Fleischman).

by these authors (Johannson *et al*)[5]. Z6030 and Z6040 fall on on the same curve, with coverage increasing convex to the concentration axis with increasing solution concentration of silane in the region 0—0.6 wt. % of silane. The curve of A1100, on the other hand, is steeper initially but tapers off rapidly in this solution concentration region. The authors point out that while Z6030 and Z6040 will interact with the surface through their silanol groups, A1100 contains both silanol and amino functional groups which can interact with the surface. It is interesting, in this connection, to note the work of Tutas, Stromberg and Passaglia[12] on the thickness of adsorbed layers of vinyl tris (2-methoxyethoxy) silane and A1100 on glass from aqueous and MEK solutions. Unlike the A1100, the surface layer of the vinyl silane continued to increase in thickness with the time during the observation period of 300 to 400 minutes. The authors point out that this may be due to continuous surface polymerization, caused by the vinyl groups, taking place after initial adsorption of coupling agent polymer from solution.

Nature of Desorption by Boiling Water

Johannson *et al*[5] also investigated the stability of coupling agents they deposited on the surface of E glass to the action of boiling water. They report the following:

1. "The amount of coupling agent remaining on the surface after a given time of immersion is proportional to the initial loading on the surface".
2. a) Upon boiling a gram of E glass treated with coupling agent in 50 ml. of water the pH of the water increases.
   b) An electron micrograph of an untreated E glass fiber which was boiled in water for 2 hours shows evidence of surface destruction.
3. An electron micrograph shows that boiling water has "destroyed the integrity of the coupling agent film".
4. When coupling agent is adsorbed to the surface of an "aersoil" silica gel (surface area 410 m^2/g), an "insignificant amount of displacement occurred in boiling water during a 2 hour immersion".

The authors conclude that these results strongly indicate that displacement of the coupling agent has resulted from corrosive removal of the glass itself from the fiber. With respect to this conclusion, the following should be noted:

1. a) The quotation indicates first order kinetics, which is consistent with a mechanism involving desorption of rod-like slivers of coupling agent through failure of the glass substrate. However, first order kinetics are equally consistent with a mechanism involving desorption of rod-like slivers of the coupling agent through failure of the coupling agent to glass bonds, or of the coupling agent to coupling agent bond closest to the glass.
   b) An analysis of the data the authors present does not indicate a first order rate dependence during a given run with respect to the amount

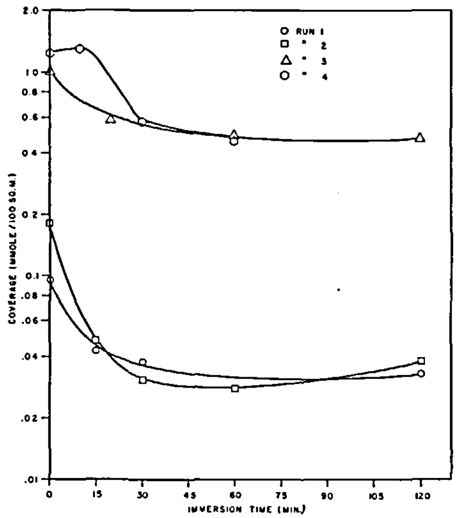

Figure 3. Semi-log plot of data in Table 4 of Johannson *et al:* Z6030 remaining on E glass *vs* time of immersion in boiling water.

initially present on the surface. In Fig. 3 their data is plotted as the logarithm of the amount on the surface *vs* time, which should yield a straight line for a first order reaction. The actual shape of the curve implies the possibility of some degree of random scission in rod-like slivers combined with increased resistance to desorption as the extraction proceeds. This is consistent with the findings of Schrader *et al*[8] that the adsorbed coupling agent is heterogeneous with respect to stability during hydrolytic desorption.

2. Alkali cations can be leached out of siliceous glassy surfaces, leaving behind a porous silica structure. Coupling agent molecules chemisorbed to the silica should remain. If it is postulated that hydrolysis of the silica structure should then be enhanced by the increased pH of the solution, this should also hold true for hydrolysis of the siloxane bonds formed by the coupling agent to each-other and to the glass surface.
3. Schrader *et al*[8] have reported electron micrographs of Pyrex which was treated with radioactive A1100 and then boiled in water. The micrographs reported by Johannson *et al*[5] for water-boiled coupling agent-treated E glass are quite similar in appearance. They also resemble those obtained by Sterman and Bradley[10] on coupling agent-treated E glass extracted with hot water. No important pit formation was observed. Rather, removal down to a common base plane is observed, leaving behind islands of finish. While the possibility that the base plane is created by the uniform removal of a thin layer of glass from the substrate should be considered, it would seem that hydrolysis of glass to coupling agent bonds, or of coupling agent to coupling agent bonds close to the glass is a more likely interpretation of the electron micrographs.

4. The nature of an extremely high surface area silica gel is considerably different from that of a relatively low surface area fiber. Differences in adsorption or desorption behavior between E glass fibers of specific surface area 0.2 m^2/g and a bed of silica gel of specific surface area 410 m^2/g are not necessarily attributable to the difference in glass composition. Schrader and Lerner[7] investigating the adsorption of a sample of low specific activity A1100 (obtained from A.O. Smith, Inc.) on very high purity abraded silica flats, found that nearly all the chemisorbed polymeric coupling agent was removed in a few hours by boiling water (Fig. 4). This behavior was similar to that subsequently observed by Schrader *et al*[8] on Pyrex flats, and is consistent with the behavior reported by Johansson *et al*[5] for coupling agents on E glass fibers.

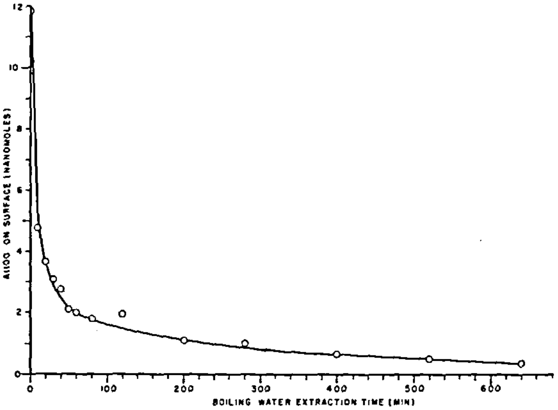

Figure 4. A1100 remaining on silica flat (geometric surface area = 3 sq. cm.) during boiling water extraction which followed preliminary rinses in benzene and cold water (Schrader and Lerner).

Identity of Coupling Agent Fraction Responsible for Wet-Strength Retention

The presence of coupling agents on the surface of glass in the form of a heterogeneous film raises the question as to which of the components of this film are responsible for its effectiveness in protecting the resin-glass interface from degradation by exposure to water; what is the minimum, in terms of the surface chemical structure and amount of a component or components, necessary to provide this protection; and, what combination of conditions yields maximum protection. Schrader, Lerner, and D'Oria[8] and then Schrader and Block[9] determined the efficacy of each of the fractions of the heterogeneous film by separately measuring the effectiveness of each in protecting glass-epoxy adhesive joints from the effect of moisture. Pyrex glass block surfaces containing selected components of the heterogeneous film, in varied amounts, were prepared by varying the nature of extraction with solvent following deposition of the coupling agent. The treated blocks were then crossed, in pairs, and cemented together with epoxy resin. Each glass-epoxy-glass adhesive joint was then immersed under a 50 lb. load in hot water, and the time for failure of the joint ("joint life") automatically recorded. After a few preliminary results were reported, Schrader and Block[9] investigated the entire range of coupling agent coverage utilizing radioactive A1100 on all Pyrex blocks which were used to form the adhesive joints. This allowed direct determination of the residual A1100 on the block prior to preparing the joint. It was found that joint lives of equal duration were obtained with or without the presence of Fraction One (physically adsorbed hydrolyzate which is removed by cold water) in the heterogeneous coupling agent film. In fact, too large an excess of Fraction One sometimes caused bond deterioration. Maximum joint lives were obtained with maximum amounts of Fractions Two and Three (chemisorbed polymeric A1100). With depletion of Fraction Two by extraction with boiling water before preparing the adhesive joint, there was a linear decrease in joint life.

Effect of Method of Coupling Agent Application on Lifetime of Adhesive Joint

In another set of experiments, (Schrader and Block)[9] the glass blocks were immersed in a very dilute benzene solution of radioactive A1100, then withdrawn, drained, and room temperature cured. The amount of coupling agent adsorbed on the surface was regulated by the time of immersion. When applied under these conditions, the near maximum joint life of 1100 hours was obtained with two monolayer equivalents of coupling agent, whereas approximately 8 monolayer equivalents were required to obtain this joint life when the coupling agent was applied by the deposition-evaporation technique followed by cure at 110° C.

Mechanism of Hydrolytic Failure of Adhesive Joint

The question of the mechanism of hydrolytic failure of a glass-coupling agent-resin adhesive joint is entirely different, of course, from that of the mechanism of extraction of coupling agent from bare glass in hot or boiling water. Firstly, the more complicated interface has additional components which may become a weak link, such as, for example, the coupling agent to resin bond. Secondly, the nature of the coupling agent may change as a result of its interaction with the resin. Thirdly, and perhaps most importantly, is the protection the resin, in combination with the coupling agent, gives with respect to the entrance of water into the interfacial region. A resin-coupling agent-glass adhesive joint can take weeks or months to fail in hot water, even under load, as compared to hours required to remove nearly all the coupling agent from bare glass immersed in hot water. Interestingly, James, Norman, and Stone[4] have found evidence that with coupling agent present in a laminate water migrates to the interface as a vapor, rather than as liquid water. It is clear then, that the mechanism for failure at the resin-coupling agent-glass interface must be separately determined.

The possible loci for homogeneous debonding in the interface region may be listed as follows:

1. In the resin near the interface
2. At the resin-coupling agent subinterface
3. In the coupling agent structure at the interface
4. At the coupling agent-glass subinterface
5. In the glass near the interface

It is obvious that if the disposition of a radioactively labelled coupling agent after debonding of a single epoxy-coupling agent-glass joint could be determined, this list of possibilities could be narrowed down considerably. For example, if all the coupling agent remained on the glass, then either 1. or 2. is true. If coupling agent remained on glass and resin, the implication is that 3. is the mechanism, if the debonding is homogeneous. If all the coupling agent remained on the resin, 4. or 5. would be indicated. In nearly all the bond life tests performed by Schrader and Block[9] the failure appeared to be cleanly interfacial so that the resulting glass surface, and often the debonded resin, could be examined for radioactivity. The results for the amount of radioactivity remaining on glass which was debonded from glass-coupling agent-epoxy resin adhesive joints are given in Fig. 5, where the amount of A1100 on a glass block surface after failure of a joint is plotted *vs* the amount that was on that surface prior to making up the joint. It can be seen that throughout this entire range of surface coverage by adsorption (approximately two monolayer equivalents based on one molecule per $33Å^2$), half the coupling agent remains on the surface after joint failure, and half has been removed. This must be taken as strong evidence that siloxane bonds linking one coupling agent molecule to another have been broken. The constant 50% residue observed can be explained most easily by assuming that the A1100 molecules adsorbed from benzene solution to the glass surface as dimers, with one end of each dimer chemisorbed to the glass surface, so that a double monolayer equivalent is actually a monolayer of dimers, while a monolayer equivalent is

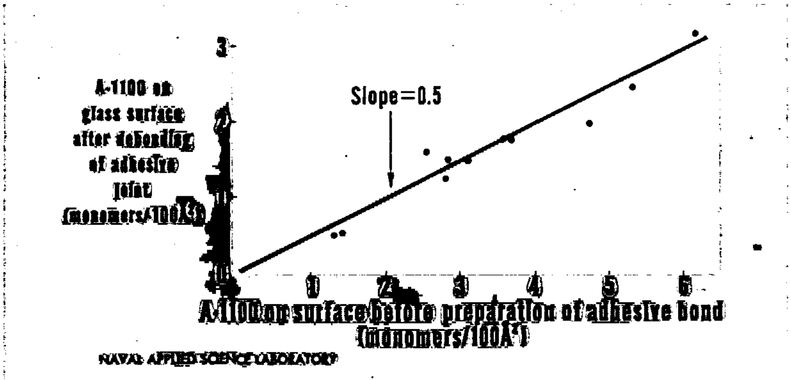

Figure 5. Location of radioactive A1100 after debonding of adhesive joint. (Schrader and Block).

one half a monolayer of dimers etc. It is further assumed that the resin reacts only with the amino group of the molecule (half dimer) that is not chemisorbed directly to the glass surface. Failure of the joint then results from hydrolysis of the siloxane linkage at the midpoint of each dimer which has reacted with both the resin and glass. Half of each dimer remains on the glass and the other half is removed, resulting in the observed constant 50% residue of radioactivity after joint failure.

Chemical Bonding to Resin

While chemical bond formation between silane functional groups and the surface of glass is fairly well established, the attaining of evidence bearing on the assumed formation of chemical bonds between coupling agents and resins has been more elusive. Sterman and Marsden(1966)[11] determined the extractibility with benezene and trichloroethylene respectively, of polystyrene and polyethylene from composites with unfinished E glass and E glass finished with A174 coupling agent. For the case of both polymers, residual carbon analysis indicated that a thin layer of polymer was retained on the surface through long periods of extraction, as a result of the presence of the coupling agent. Johannson *et al*[5] utilized carbon-14 labeled methylmethacrylate-styrene copolymer to determine the extractibility with tetrahydrofuran of that resin from its composite with E glass in the presence and absence of coupling agent. They found that the presence of coupling agent resulted in retention of a sizeable residue of resin after the extraction procedure. The results of both of these investigations favor the theory of chemical bond formation between resin and coupling agent.

SUMMARY

1. Coupling agents deposited on glass surfaces are usually heterogeneous layers consisting of physisorbed and chemisorbed fractions. The chemisorbed fraction consists of polymerized coupling agent, about 5 to 10 monolayer equivalents thick.
2. Most of the chemisorbed polymeric coupling agent can be removed from the bare glass by boiling in water for a few hours. The residue appears to be especially strongly bound to the surface.
3. The polymerized coupling agent chemisorbed to the glass surface is responsible for wet strength retention in glass-resin laminates. The physisorbed hydrolyzate of the coupling agent is either ineffective or deleterious.
4. Although coupling agent can be removed from bare glass by hot water in a few hours, when resin is applied to finished glass to form a proper glass-coupling agent-resin adhesive bond, the interface can remain stable in the presence of boiling water for many weeks, even under load.

5. Near maximum bond life of a glass-resin adhesive joint can be obtained with only two monolayer equivalents of coupling agent when the latter is applied by slow adsorption from very dilute benzene solution followed by room temperature cure.
6. Evidence obtained from radioisotopic examination of debonded Pyrex-A1100-epoxy adhesive joints indicates that failure is caused by hydrolysis of siloxane bonds in the coupling agent structure. This may be the failure mechanism for all properly bonded glass (borosilicate)-reinforced plastics utilizing silane finishes.
7. Experiments performed utilizing organic solvents to extract thermoplastic or thermosetting resins from glass fibers treated with coupling agent yield evidence supporting the existence of chemical bonding between the resin and coupling agent.

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