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The Wettability of Ethyl- and Vinyltriethoxysilane Films Formed at Organic-Liquid/Silica Interfaces

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ABSTRACT

Critical surface tensions γ_c and water contact angles θ_{H_2O} have been determined for adsorbed films of ethyltriethoxysilane and vinyltriethoxysilane on silica and α-alumina. The films were formed by retraction from hydrocarbon solution. Studies were also made of film resistance to desorption and alteration when in prolonged contact with water. The vinyltriethoxysilane films were generally more oleophobic (low γ_c values) and more hydrophobic (high θ_{H_2O} values) than the films formed by the ethyl analog. The vinyltriethoxysilane films were also more resistant to disruption and desorption when contacted with water. Neither vinyl- nor ethyltriethoxysilane formed strongly held films on α-alumina. The addition of low-molecular-weight organic acids or bases to the adsorbate solutions resulted in both the ethyl- and vinyltriethoxysilane forming hydrophobic and water resistant films on silica and α-alumina. The results suggest that the adsorption process involves the adsorbate molecules reacting with silanol groups on the silica to form siloxane linkages to the surface and reacting with themselves to form adsorbed siloxane polymer. The properties of the resulting film will depend upon the number of surface attachments and the extent of crosslinking between adsorbate molecules.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE WETTABILITY OF ETHYL- AND VINYLTRIETHOXYSILANE FILMS FORMED AT ORGANIC-LIQUID/SILICA INTERFACES

INTRODUCTION

Various trialkoxysilanes have been found to improve the adhesion of organic polymers to glass and other inorganic solids, especially when the bond is to be exposed to high relative humidities. For example, glass-filament-resin-composite materials are seriously degraded by water (1), the attack presumably occurring at the glass/resin interface. However, this water sensitivity can be reduced by applying certain trialkoxysilanes as finishing agents to the glass fiber. Little is known about the mechanism by which the trialkoxysilanes improve the wet strength of adhesive bonds. It is generally assumed that the mechanism involves the adsorption of the trialkoxysilane at the resin/substrate interface to form a "bridge" between adhesive and adherend (2). It would appear from available evidence that alkoxysilanes can be specifically adsorbed at liquid/glass interfaces (3) and that this adsorption involves an interaction with the silanol groups, $\equiv$ Si—OH, on the substrate surface (4,5).

The present report describes the adsorption of ethyltriethoxysilane (ETES) and vinyltriethoxysilane (VTES) at various organic-liquid/silica interfaces. Films formed by these compounds on silica and glass from solution in nonpolar organic liquids were found to be oleophobic and so could be isolated by retraction; that is, the substrate on which the films had been formed emerged dry from the solution, thus allowing direct examination of the adsorbed layer. Another reason for choosing to study these particular trialkoxysilanes is that the vinyl compound is a useful finishing agent for glass-resin composites, whereas ethyltriethoxysilane is not (2). Differences in their adsorption behavior might be expected to give an insight into the function of finishing agents.

EXPERIMENTAL PROCEDURES

Materials

The adsorbates studied, ethyltriethoxysilane (bp = 159-161°C at 760 mm Hg; n_D^{20} = 1.3912) and vinyltriethoxysilane (bp = 160°C at 760 mm Hg; n_D^{20} = 1.4257), were obtained from Union Carbide Corp., Silicones Division. They were distilled and stored in desiccators over molecular sieves. The solvents from which these materials were adsorbed, α-chloronaphthalene and isopropylbicyclohexyl, and the organic liquids used for contact angle measurements were reagent-grade chemicals from which polar contaminants had been removed by percolation through activated adsorbents. The organic acids and bases listed in Tables 1 and 2 were obtained as reagent-grade chemicals and were used without further purification.

A solution containing both the ethyltriethoxysilane monomer and its polymeric hydrolysis products was prepared by shaking a 1-wt-% solution of the distilled monomer in α-chloronaphthalene with an aqueous 0.01N HCl solution. The two phases were shaken intermittently for about 4 weeks until a finely divided precipitate -- presumably polymeric material -- appeared in the aqueous phase. The two phases were then separated. The organic phase was washed first with 0.1N $NaHCO_3$ solution, then washed with distilled water until the washings were neutral, and finally centrifuged to remove dispersed water.

Table 1
The Wettability of Films Produced by Ethyltriethoxysilane with Organic Acids and Bases

Added Catalyst	ETES-Catalyst Mole Ratio	Substrate	Film Wettability			
			Initial		After 1 hr Water-Desorption Test	
			γ_c* (dynes/cm)	θ_{H_2O} (deg)	γ_c* (dynes/cm)	θ_{H_2O} (deg)
None	—	Silica, air-dried	33	63	—	41
None	—	Silica, flamed	34	70	—	50
Propionic acid	20	Silica, air-dried	24	71	—	70
Propionic acid	4	Silica, air-dried	26	73	26	62
Bromopropionic acid	4	Silica, air-dried	26	73	25	63
Acetic acid	10	Silica, air-dried	30	81	—	70
Acetic acid	10	Silica, flamed	32	96	—	104
n-Propylamine	10	Silica, air-dried	30	97	32	90
n-Propylamine	4	Silica, air-dried	36	104	36	105
n-Propylamine	4	Silica, flamed	38	105	38	105
n-Propylamine	4	α-Alumina, air-dried	35	101	35	101
Piperidine	4	Silica, air-dried	30	89	31	91
Pyridine	4	Silica, air-dried	27	76	30	63

Table 2
The Wettability of Films Produced by Vinyltriethoxysilane with Organic Acids and Bases

Added Catalyst	VTES-Catalyst Mole Ratio	Substrate	Film Wettability			
			Initial		After 1 hr Water-Desorption Test	
			γ_c* (dynes/cm)	θ_{H_2O} (deg)	γ_c* (dynes/cm)	θ_{H_2O} (deg)
None	—	Silica, air-dried	30	80	—	44
None	—	Silica, flamed	24	80	—	72
Acetic acid	10	Silica, air-dried	30	78	—	63
Acetic acid	10	Silica, flamed	36	90	34	80
n-Propylamine	4	Silica, air-dried	No retraction		35	103

The silica surfaces used were fused-silica microscope slides (1 by 2 by 1/16 inch, A. H. Thomas and Co.), and the alumina surfaces were 3/4-inch-diameter, 1/8-inch-thick, synthetic α-alumina disks (synthetic sapphire, Linde Division, Union Carbide Corp.). The specimens were cleaned by heating in a mixture of equal parts of sulfuric and nitric acid, given a preliminary rinse in hot tap water, and then soaked in three successive baths of hot distilled water. After the wash and rinse operations, the specimens were freely wet by water, indicating that the surfaces were not contaminated with organic material. The specimens were then dried in a clean glass oven at about 100°C for

15-30 min. Surfaces prepared in this fashion are referred to in this report as "air-dried." Flamed surfaces were prepared by playing the flame of an oxyhydrogen torch over the surface of an air-dried specimen, holding the flame at each position until the area showed white heat.

Methods

The adsorption studies were carried out by immersing the clean substrate specimen in the adsorbate solution for a specified time, withdrawing it slowly, and allowing the solution to retract from the film-coated surface. The solvents were selected so as to have high enough surface tensions γ_{LV} to retract from the majority of the adsorbed films encountered in the experiments. All solution preparations and adsorption experiments were conducted in glove bags maintained at 25°C and 400-800 ppm of water vapor by a positive pressure of air that had been passed over Drierite and molecular sieves.

The adsorbed films were characterized by determining their critical surface tension γ_c by the method of Zisman (6), which consists of determining the slowly advancing contact angle exhibited on the adsorbed film by each member of a series of wetting liquids. The cosines of the contact angles (cos θ) are plotted against the surface tensions of the wetting liquids. A straight line is obtained, and the intercept of this line with cos θ = 1 is the critical surface tension value for the adsorbed film. The somewhat unusual nature of the films investigated in this study led to the critical surface tension being designated as γ_c* rather than the conventional symbol γ_c, because of the limited significance of the critical surface-tension values obtained here. These limitations are due partly to the wide range in polarity of the test liquids used. The choice of these liquids was necessary in order to cover with a single set of test liquids the range of critical surface tensions presented by the adsorbed films studied. The preferred test liquids would be the n-alkanes since many of the literature values of γ_c were determined using this homologous series, but, unfortunately, the n-alkanes do not cover the range of surface tension needed. In one instance, where a comparison between the n-alkanes and the miscellaneous liquids was possible (Fig. 1), it was found that the miscellaneous group gave an estimate of 21 dynes/cm compared with a value of 26 dynes/cm from the n-alkanes. For surfaces of higher γ_c* the discrepancy between the two series is probably smaller because the extrapolation to cos θ = 1 is shorter.

The wetting liquids used to determine γ_c* were hexadecane (γ_{LV} = 27.6 dynes/cm), bicyclohexyl (γ_{LV} = 33.0 dynes/cm), α-methylnaphthalene (γ_{LV} = 38.5 dynes/cm), α-chloronaphthalene (γ_{LV} = 42.9 dynes/cm), methylene iodide (γ_{LV} = 50.8 dynes/cm), and water (γ_{LV} = 72.8 dynes/cm). All contact-angle measurements were made at about 45% RH and 25°C using the sessile drop-buildup method. Surface tensions were measured at 25°C using the duNouy ring method with the usual corrections. Unless otherwise noted in the text, the contact angles were reproducible to ±2° and the critical surface tensions to ±0.5 dyne/cm.

The effect of prolonged contact with water on each film was determined by allowing water to fall dropwise onto the film-covered substrate for a specified length of time. The effect of this treatment was judged by determining the water contact angle and critical surface tension for the area of the test surface struck by the water drops and comparing these values with the values for the original film. The drops fell from a height of 30 cm at a rate of 2 drops/second. The test plates were held in a Büchner funnel at an angle of about 20° to the horizontal. Under these conditions the drops flash-spread over about one-half the area of the specimen surface, and each drop ran off the plate into the funnel before the next drop struck. For simplicity this test is referred to as the "water-desorption test" even though changes other than physical desorption were involved.

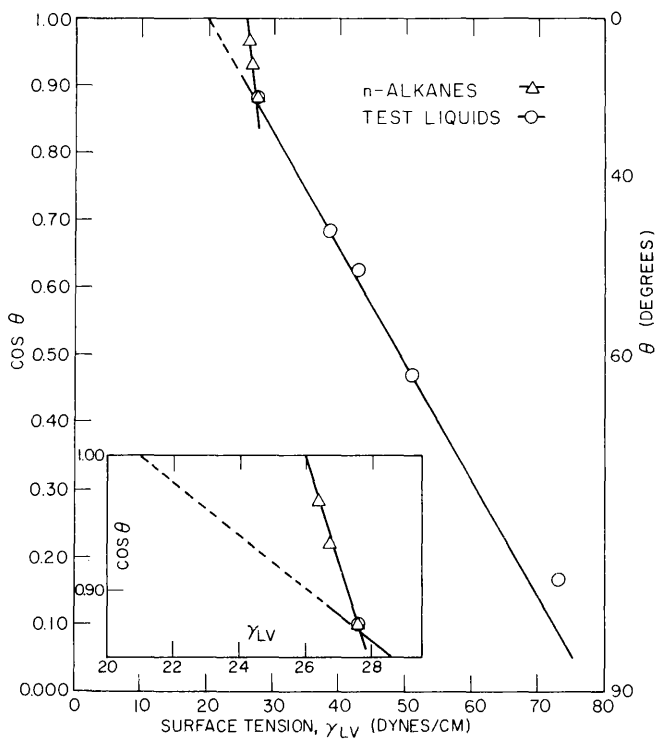


Fig. 1 - Comparison of cos θ-vs-γ_{LV} plots for the n-alkanes and the test liquids of this study on a triethoxysilane film. The film was obtained from a 5% solution of VTES in α-chloronaphthalene after a 20-hr adsorption time.

RESULTS

Ethyltriethoxysilane (ETES)

The critical surface tensions of the ETES films obtained on silica by retraction from 1% solutions in α-chloronaphthalene are plotted in Fig. 2a. The adsorption time (the abscissa) is the time the silica substrate was allowed to remain in contact with the adsorbate solution. Adsorption times longer than 20 hr did not produce any further decrease in γ_c*, and solutions containing 0.1% and 5% ETES gave values within 1 dyne/cm of those in Fig. 2a. Attempts to obtain ETES films from solution in isopropylbicyclohexyl were unsuccessful — the solutions did not retract from the test surfaces even after a 20-hr adsorption time. Isopropylbicyclohexyl has a surface tension of 34.4 dynes/cm, so if the ETES adsorbed to form films having γ_c* values of 33-35 dynes/cm, as it had from α-chloronaphthalene, then the bicyclohexyl solution would not be expected to retract.

The contact angles exhibited by water on the ETES films were anomalous, because in plots of cos θ vs γ_{LV} they frequently did not fit the straight line relationship exhibited by the data for the organic liquids. An example of the failure of the water contact angle to correlate with the organic-liquid data is given in Fig. 3. For long adsorption times of 10-20 hr, the deviation of the water-data points from the straight line decreased, but the anomaly did not disappear even after 170 hr. In addition, the water contact angles were difficult to reproduce. The values changed measurably after the drop was on the surface only a few seconds, and it was rarely possible for a water drop to slide freely over the

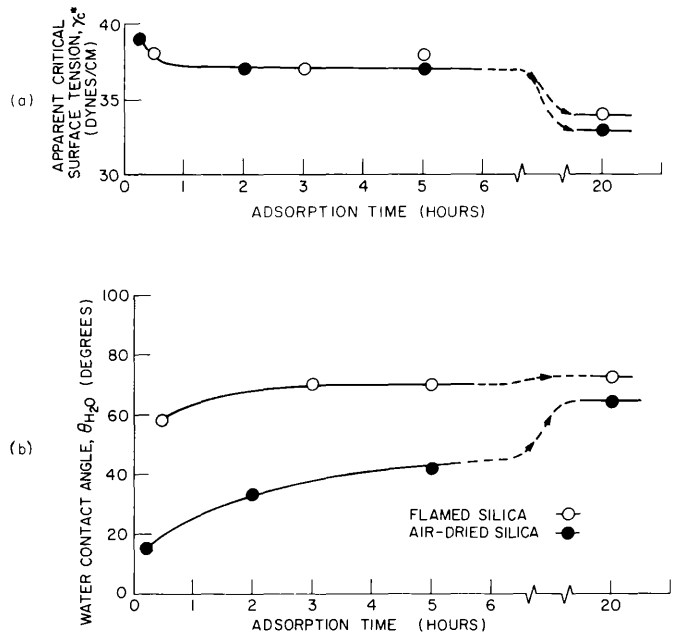


Fig. 2 - The change in apparent critical surface tension (a) and water contact angle (b) with adsorption time for ETES films on air-dried silica and flamed silica (1% ETES in α-chloronaphthalene)

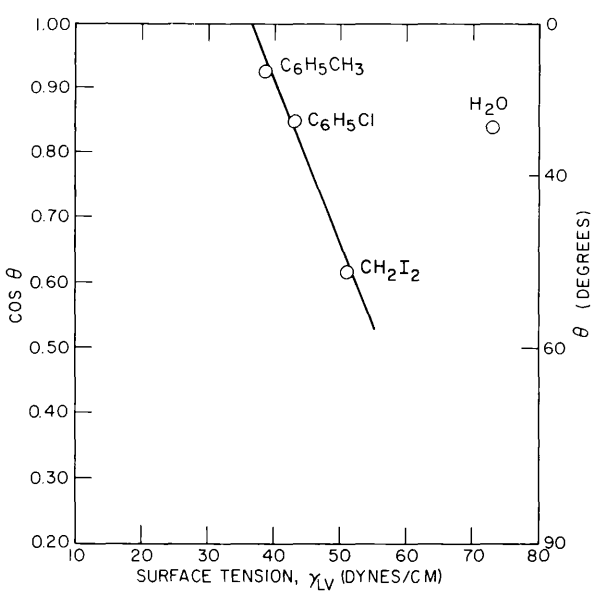


Fig. 3 - The failure of θ_{H_2O} to correlate with the organic-liquid wetting data in γ_{LV}-vs-cos θ plots (ETES on air-dried silica after 2 hr from 1% solution in α-chloronaphthalene)

surface when the test plate was tilted. This behavior was in distinct contrast to the behavior of the organic liquids for which the contact angles were generally reproducible and stable and the drops were easily mobile over the surfaces.

In view of the singular behavior of water on these ETES films, the general practice in this investigation was to determine the value of γ_c* using only the organic liquids and to plot the water contact angles separately as a function of adsorption time. In Fig. 2b the water-contact-angle data are presented for the films formed on silica by ETES from a 1% solution in α-chloronaphthalene. The angles for the films on flamed silica were consistently higher than the corresponding angles for films on air-dried silica, although after 20-hr adsorption time they approached the same value.

ETES films could not be obtained on α-alumina substrates by retraction. Retraction did not occur from solutions of the triethoxysilane even up to concentrations of 5% and adsorption times of many days. This situation occurred when using both air-dried and flamed alumina with α-chloronaphthalene or isopropylbicyclohexyl as the solvent.

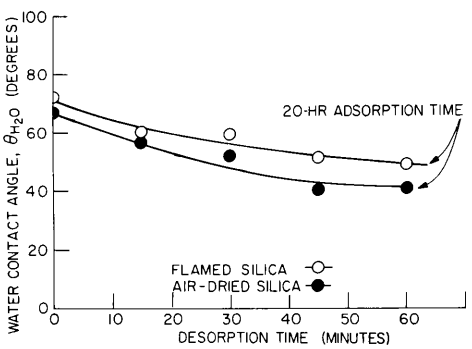


Fig. 4 - The change in θ_{H_2O} in water-desorption test for ETES films on silica (1% ETES in α-chloronaphthalene)

The water-desorption test of the ETES films on silica showed a continuous decrease in the water contact angle θ_{H_2O} for desorption times up to 60 min (Fig. 4). A simultaneous decrease occurred in the organic-liquid contact angles — and thus an increase in γ_c* — but these changes were less pronounced than the changes in θ_{H_2O}. Note in Fig. 4 the decrease in θ_{H_2O} for the films on flamed silica was less than for the films on air-dried silica.

Vinyltriethoxysilane (VTES)

The vinyltriethoxysilane films obtained on silica were more oleophobic (lower γ_c* values) and more hydrophobic (higher θ_{H_2O} values) than the films formed from corresponding ETES solutions. In Fig. 5 the wetting data are presented as a function of adsorption time for the VTES films from α-chloronaphthalene solutions on flamed silica. The most interesting feature of these data was the pronounced concentration effect. For each concentration there was a different limiting value of γ_c* and θ_{H_2O}; the higher concentration solutions had lower γ_c* and higher θ_{H_2O} limits than the dilute solutions. In addition the rate of film formation indicated by the decrease in γ_c* was greater the higher the concentration.

The results obtained for VTES on air-dried silica are presented in Fig. 6. They indicate a concentration effect, although the behavior is more complex than the behavior of the films on flamed silica. For the more concentrated solutions γ_c* passes through a minimum with increasing contact time. The minimum was reached most quickly in the most concentrated solutions. Subsequent to the minimum the increase in γ_c* was complete within a 20-hr adsorption time. However, for a given concentration the final γ_c* attained was seldom the same from one experiment to the next. For instance, γ_c* values from 28 to 32 dynes/cm were observed after a 20-hr adsorption time for the 1% solution.

The water-contact-angle data for VTES on air-dried silica (Fig. 6b) indicate a gradual increase in θ_{H_2O} with time. The rate of increase and the ultimate value of θ_{H_2O} after a 20-hr adsorption time were both greater at the higher concentrations.

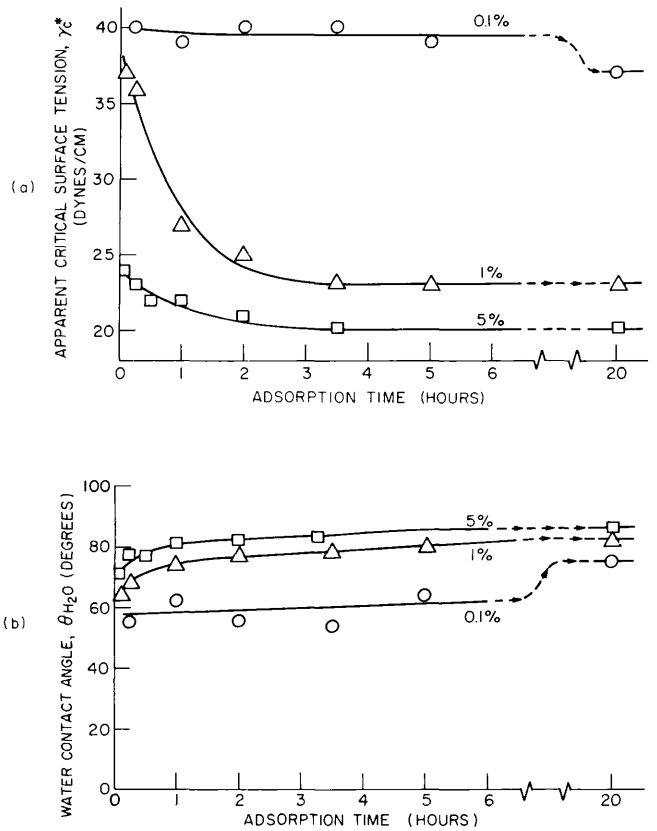


Fig. 5 - Effect of adsorbate concentration on the change in apparent critical surface tension (a) and water contact angle (b) with adsorption time for VTES films formed on flamed silica

The θ_{H_2O} values for the VTES films were anomalously low on air-dried silica, as had been found for the ETES films. The anomaly persisted even when the adsorption time was extended to many days. On flamed silica, however, the anomaly was small or did not appear at all with films obtained from the 1% and 5% solutions after 2-hr or more adsorption time.

The VTES films on flamed silica proved to be more resistant to change in the water-desorption test than the VTES films on air-dried silica. This difference is illustrated by the data in Fig. 7. On air-dried surfaces after a 1-hr adsorption time, the VTES produced a film that initially had a low water contact angle, and it was not significantly altered in the desorption experiment. By allowing 20 hr contact with the solution a more hydrophobic film was obtained, but it was quickly "desorbed" to a condition equivalent to that for only a 1-hr adsorption time. In contrast, the film adsorbed on flamed silica after a 20-hr adsorption time showed only a slight tendency to lose its hydrophobic character.

VTES films could be obtained on α-alumina by retraction from VTES-(α)-chloronaphthalene solutions. This observation contrasts with the failure of ETES solution to retract from α-alumina. However, neither the organic liquid or water would give stable contact angles on the films formed by VTES.

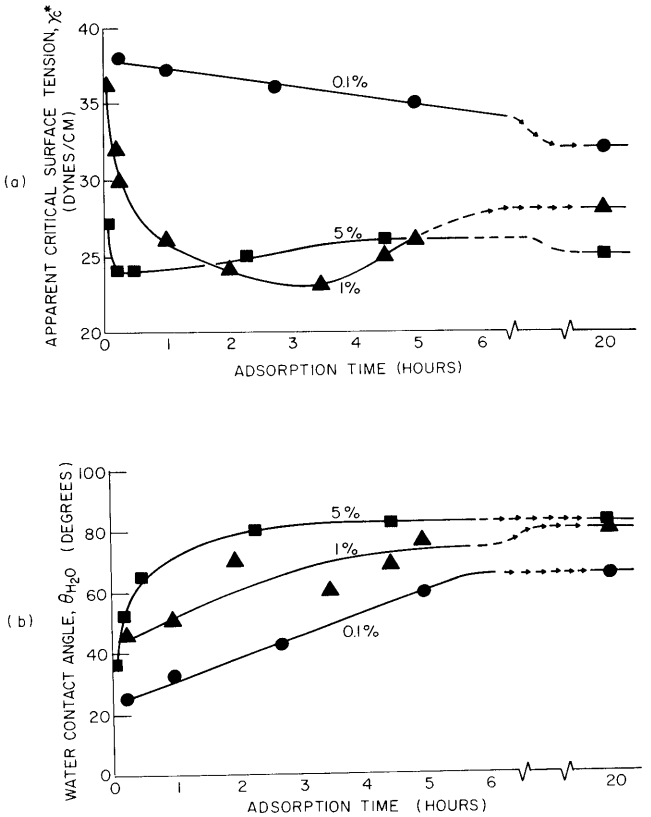


Fig. 6 - Effect of adsorbate concentration on the change in apparent critical surface tension (a) and water contact angle (b) with adsorption time for VTES films formed on air-dried silica

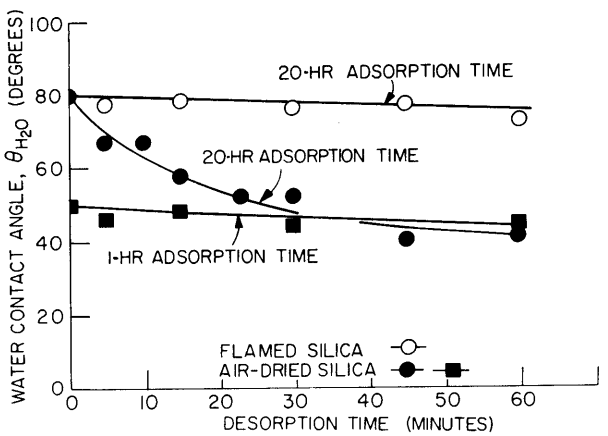


Fig. 7 - The change in θ_{H_2O} in the water-desorption test for VTES films on silica (1% VTES in α-chloronaphthalene)

Acid-Base-Catalyzed Adsorption

It was found that the addition of low-molecular-weight organic acids and bases to the adsorbate solutions produced ETES and VTES films that were much more hydrophobic and resistant to the water-desorption test than the films formed by the triethoxysilanes alone. Tables 1 and 2 list the values of γ_c* and θ_{H_2O} for the films produced in the presence of various acids and bases. Also included are the data for the films formed by ETES and VTES alone. In all cases the adsorption time was 20-24 hr, the solvent was α-chloronaphthalene, and the triethoxysilane concentration was 1-wt-%. The adsorption process was apparently complete within 20 hr since the same γ_c* and θ_{H_2O} values were obtained after 48 hr and 72 hr. Note that without ETES or VTES present, solutions of these acids and bases in α-chloronaphthalene did not retract from the silica test plates.

Before reaching the values listed in Tables 1 and 2, γ_c* usually went through a minimum between the first and third hours. Two examples of this minimum are shown in Fig. 8a. For these same films θ_{H_2O} increased continuously as indicated in Fig. 8b. The water contact angle θ_{H_2O} increased rapidly during the first 3 hr of adsorption and then more slowly to the final value at 20 hr. These changes in γ_c* and θ_{H_2O} with adsorption time are typical of all the films formed by the trialkoxysilanes in the presence of an acid or base.

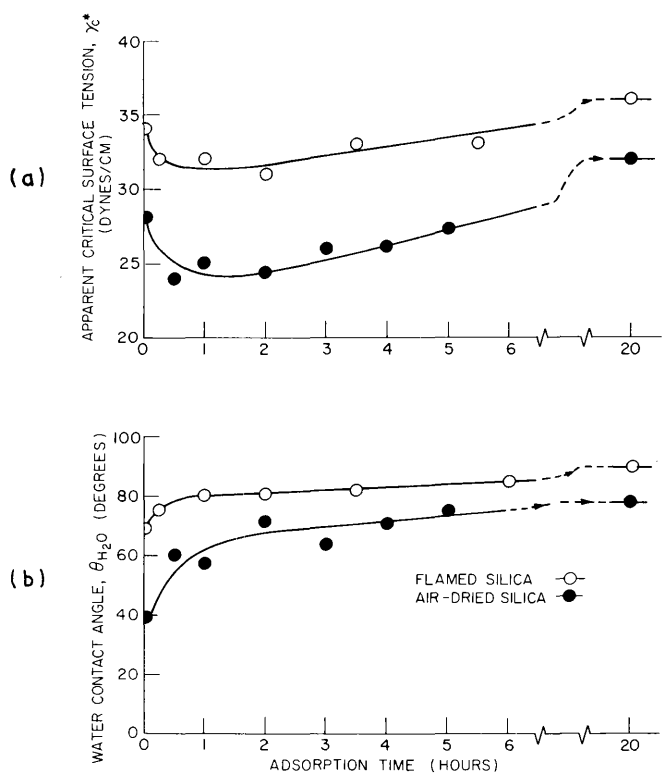


Fig. 8 - Adsorption of ETES in the presence of acetic acid. The change in apparent critical surface tension (a) and water contact angle (b) with adsorption time for films on flamed silica and air-dried silica (1% ETES and 0.03% acid in α-chloronaphthalene).

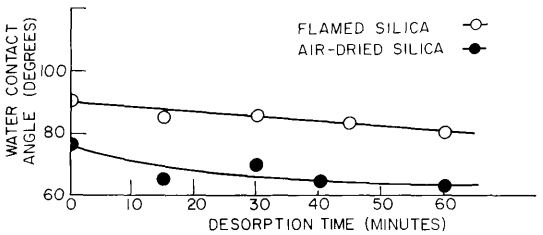


Fig. 9 - The change in θ_{H_2O} in the water-desorption test using acetic acid catalyst for ETES films formed on flamed and air-dried silica (20-hr adsorption time, 1% ETES, and 0.03% acetic acid in α-chloronaphthalene)

The resistance of these films to alteration in the water-desorption test is also indicated in Tables 1 and 2 and further illustrated by the data in Fig. 9. For the most part, the films produced in the presence of acids and bases were highly resistant to change in the water-desorption test — even the film formed on α-alumina (Table 1). Some exceptions to this water stability were the ETES and VTES films formed on air-dried silica using the organic acids (Tables 1 and 2), and the ETES film produced using pyridine as the catalyst.

A curious relationship between γ_c* and θ_{H_2O} is discernible from the data in Tables 1 and 2. Those films that were least wet by water (high θ_{H_2O} values), were also the most wettable by the organic liquids (high γ_c* values).

Certain features of the adsorption from solutions containing n-propylamine were unusual and deserve special comment. For the solutions at ETES-amine mole ratios of 4, retraction was unusually slow, requiring as long as 10 min to clear the entire surface. Retraction was clearly occurring since the retreating edge of the liquid film made a distinct angle of contact with the solid surface. Oftentimes retraction was incomplete so that regions of adsorbate solution were left on the surface. All other ETES solutions containing added acid or base — including the ETES-(n-)propylamine solution at a mole ratio of 10 — retracted in a few seconds to leave the entire surface clear. All of the VTES solutions retracted readily except the VTES-(n-)propylamine solution, which failed to retract from any part of the surface. When the silica plates were taken from this solution and subjected to the water-desorption test, the thin layer of adsorbate solution was quickly displaced by the water. This water treatment left the surface dry and free of visible film; γ_c* and θ_{H_2O} determinations were made on these "washed" surfaces (Table 2).

A finely divided precipitate was noticed in the ETES-(n-)propylamine (mole ratio = 4) solution when the solution had aged for at least 48 hr. At 48 hr adsorption-time retraction usually failed to occur at all, even though it had been at least partially complete at 24 hr, as indicated in the previous paragraph. (The solution age corresponded to the adsorption time plus 10 to 15 min.) A similar phenomenon was encountered during the n-propylamine-catalyzed adsorption of VTES. A precipitate developed in the VTES-(n-)propylamine solutions within the first few hours after preparation. Presumably these precipitates were particles of high-molecular-weight polyethyl (or vinyl-)siloxane.

To determine the effect of polysiloxane molecules in the adsorbate solution on film properties, a solution was prepared containing polymerized ETES as well as the ETES monomer. This solution was made by shaking intermittently for 4 weeks a 1% solution of ETES in α-chloronaphthalene with aqueous 0.1N HCl solution until a faint precipitate appeared in the aqueous phase. The two phases were separated, and the organic phase was washed with water to remove acid. This solution, which undoubtedly contained polyethylsiloxane fragments as well as the ETES monomer, was used to generate films on air-dried silica. The changes in γ_c* and θ_{H_2O} with adsorption time are indicated in Figs. 10a and 10b. The γ_c* values were low even after a 20-hr adsorption time, and the limiting value of θ_{H_2O} was approached rapidly. In the water-desorption test these films proved to be very stable (Fig. 10c). Retraction was quite rapid from these solutions, and no precipitate appeared in the solution during the adsorption experiments. However, after the solution stood for many days, a finely divided precipitate appeared.

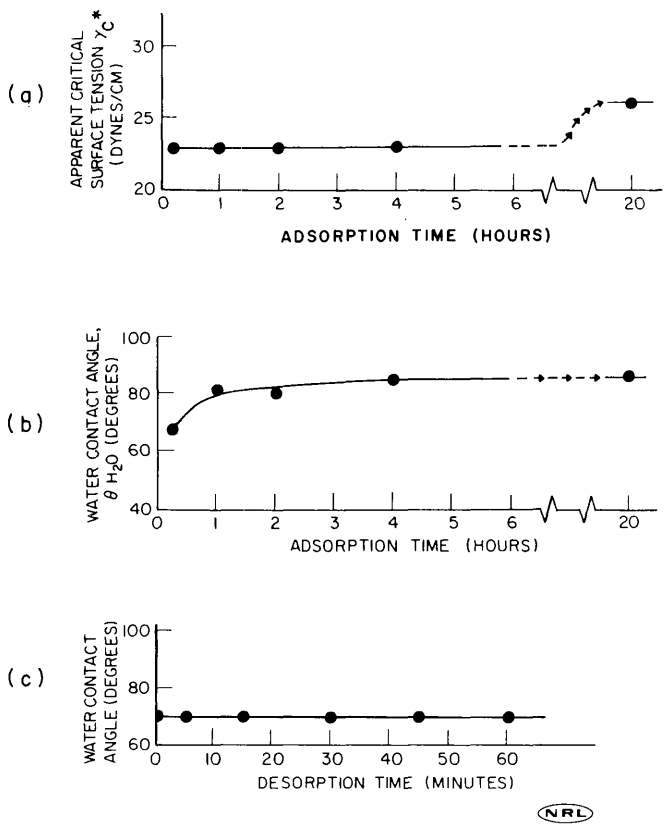


Fig. 10 - The properties of films generated by an ETES polymer-monomer solution on air-dried silica; (a) the change in γ_c* with adsorption time, (b) change in θ_{H_2O} with adsorption time, and (c) the change in θ_{H_2O} in the water-desorption test (20-hr adsorption time)

DISCUSSION

Some insight into the chemical constitution of the adsorbed trialkoxysilane films can be derived from their wettability characteristics. However, caution must be exercised in making these interpretations. Due to the complexity of the adsorption process, a number of configurations are possible for the adsorbed molecules in these films. Some of these configurations may not be distinguishable from wettability data alone. In the discussion that follows, a general model is proposed for the structure of all the films reported, and postulates are offered as to how various factors might influence the detailed configuration of the model. Using the proposed model and these postulates, an attempt is made to explain at least some of the observed wettability data.

It will assist the discussion to first summarize the principle experimental findings. (a) It required up to 20 hr for the ETES and VTES films on silica to reach stable values of γ_c*. In some cases γ_c* passed through a minimum before reaching a stable value (Figs. 6 and 8). (b) After a 20-hr adsorption time, the VTES films formed on silica without added acid or base had lower γ_c* values and higher θ_{H_2O} values than the corresponding ETES films (compare Figs. 5 and 6 with Fig. 2). (c) In the presence of an organic acid or base the wettabilities of the films produced by ETES and VTES were quite similar. Some of the films formed in the presence of an acid or base were notably hydrophobic

(high θ_{H_2O}) but also oleophilic (high γ_c). (d) On α-alumina, ETES films could not be obtained by retraction, and the VTES films were unstable toward all the wetting liquids. However, when adsorbed in the presence of n-propylamine, the films produced by ETES on α-alumina had wettability characteristics nearly identical with those of films formed on silica from the same solution (5). After prolonged contact with water, the VTES films on flamed silica showed little change in θ_{H_2O}. On the other hand, the VTES on air-dried silica and the ETES films on either air-dried or flamed silica showed a marked decrease in θ_{H_2O}. When formed in the presence of added acid or base, the VTES and ETES films were usually resistant toward contact with water — even the ETES film on α-alumina.

Some of these results suggest that one or more chemical reactions were involved in the adsorption of ETES and VTES. For example, the times required for film formation to become complete were longer than are usually associated with physical adsorption. Also, the differences between the films formed on α-alumina and those formed on silica suggest a specificity toward the silica substrate — at least in the absence of added acid or base. Finally, the results obtained by adding acids and bases to the adsorbate solution suggest that they have a catalytic effect on film formation.

Two reactions of the adsorbate molecules are probably involved in the adsorption process on silica. The first reaction is between the adsorbate molecules and the surface silanols (~ Si—OH);

$$\sim\mathrm{Si{-}OH} + \mathrm{C_2H_5OSi(OC_2H_5)_2{-}CH{=}CH_2} \rightleftharpoons \sim\mathrm{Si{-}O{-}Si(OC_2H_5)_2{-}CH{=}CH_2} + \mathrm{C_2H_5OH}. \tag{1}$$

Various studies indicate that certain alkoxysilanes react with surface silanol groups (4,5), but nothing has been reported for ETES and VTES specifically. The second type reaction is between two adsorbate molecules to form a siloxane polymer linkage

$$\mathrm{CH_2{=}CH{-}Si(OC_2H_5)_2{-}OC_2H_5} + \mathrm{HOH} \xrightleftharpoons{\mathrm{H^+(OH^-)}} \mathrm{CH_2{=}CH{-}Si(OC_2H_5)_2{-}OH} + \mathrm{C_2H_5OH} \tag{2a}$$

$$\mathrm{CH_2{=}CH{-}Si(OC_2H_5)_2{-}OH} + \mathrm{C_2H_5O{-}Si(OC_2H_5)_2{-}CH{=}CH_2} \rightleftharpoons \mathrm{CH_2{=}CH{-}Si(OC_2H_5)_2{-}O{-}Si(OC_2H_5)_2{-}CH{=}CH_2} + \mathrm{C_2H_5OH}. \tag{2b}$$

There is a substantial body of literature on the hydrolysis of alkoxysilanes (7), including a study of ETES (8). Note that all three reactions, 1, 2a, and 2b, are probably subject to acid-base catalysis, but only for reactions of type 2a has catalysis been demonstrated (7,8).

The films generated in these experiments are best visualized as polysiloxane networks having at least an occasional chemical attachment to the surface. This model implies that reactions 1, 2a, and 2b all contribute to the adsorption process. However, there will be differences in the extent of polymer formation and the extent of surface attachments depending upon which triethoxysilane is involved and the conditions under which it is adsorbed. The water required for the polymerization reaction was probably available on all the surfaces studied — even on the flamed silica, which was cooled in air

containing 400 ppm of water. This water content is believed sufficient to promote the reforming of most surface silanols groups lost by flaming and to allow the adsorption of at least a partial monolayer of molecular water.

The surface attachments to silica are probably through siloxane linkages (i.e., reaction 1). The question of the attachments to α-alumina is discussed below.

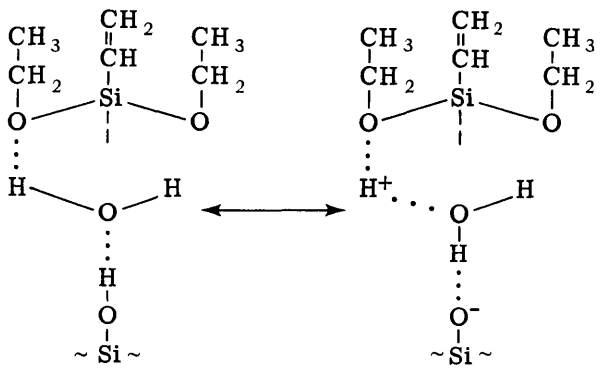
For any particular trialkoxysilane film the detailed configuration, and therefore the wettability, will depend on a number of factors which affect either the extent of polymerization, the extent of surface attachments, or both. To explain the experimental results, it is necessary to postulate that the following five factors are important in the adsorption process on silica:

1. The number of specific siloxane attachments made to the surface will depend in part on the reactivity of the alkoxysilane and in part on the acidity of the individual surface silanol groups. It is assumed that there is a high, but undetermined, density of silanol groups on both air-dried and flamed surfaces. In general, the sites on any given surface will vary widely in chemical activity. This dependence of the extent of surface attachments on adsorbate and adsorbent reactivity reflects the fact that when an alkoxysilane molecule approaches a surface silanol, the reaction rate must be fast enough for bond formation to occur during the time the adsorbate molecule is physically held at the surface site.

2. Few of the individual trialkoxysilane molecules will make multiple attachments to the surface. This limitation exists because there is little probability that an adsorbing alkoxysilane molecule will form three or even two attachments to the surface simultaneously. Most molecules will make an initial single attachment and then rotate about this bond until one or both of the remaining ethoxy groups are properly positioned for reaction with surface silanols. Consequently, the formation of multiple attachments is a slow process. It is likely to be outrun by the reaction of the remaining ethoxy groups with other triethoxysilane molecules to form siloxane linkages. Also, when the adsorbate solution is concentrated, the number of trialkoxysilane molecules available at the surface is large, so that most silanols on the silica will have reacted with separate molecules before many multiple attachments can be made. Only for dilute adsorbate solutions is there likely to be an appreciable number of multiply attached triethoxysilane molecules.

3. The number of surface attachments will be limited if the molecules are prevented access to the surface silanols by adsorbed water or any other adsorbate that can H-bond to the silanol group.

4. The surface silanols can still catalyze the polymerization of triethoxysilane molecules even if there is one or more adsorbed layers of water on the surface. Presumably, the triethoxysilane molecule H-bonds to the surface via water molecules after which it requires only an electron shift to make a silanol proton available to the alkoxysilane molecule. This sequence is illustrated by the following structures:



A B

where H-bonds are indicated by dotted lines and the bond from the silicon to the third ethoxy group behind the plane of the paper by a dashed line. Since one molecule of water disappears for each siloxane linkage formed (reaction 2a), some of the surface molecular water is removed as the reaction proceeds. As this occurs, the ~Si—OH sites on the surface will become exposed and accessible for direct reaction.

5. Differences in adsorption behavior on air-dried and flamed silica are attributed to differences in the rate at which water within the silica can diffuse to the surface — the rate being much less for the flamed surfaces. Therefore, any adsorbed molecular water that is removed from the air-dried surfaces as a result of polymer formation (postulate 4) will be quickly replaced by molecular water held in the silica immediately below the surface. On the other hand, the rate of replacement for flamed silica is believed to be much slower. In general, the presence of molecular water in glass and in fused silica is well established (9), and preliminary studies using infrared spectroscopy confirm its presence in the silica plates used here. Flaming would remove a large portion of this interior water from the first one or two microns below the silica surface.

Plausible explanations can be given for the various wettability results in terms of the proposed model. In doing so certain interpretations are made of the wettability parameters γ_c* and θ_{H_2O}. The apparent critical surface tension γ_c* reflects the density of methyl and methylene (and sometimes vinyl) groups in the surface of the adsorbed film, including the ethyl of unhydrolyzed ethoxy groups. The water contact angle θ_{H_2O} will be more sensitive than the organic wetting liquids to any polar groups with which water can H-bond. The contact angle of water will also be affected if the water hydrolyzes ethoxy groups to make the film surface more polar.

In the desorption experiments, changes in film characteristics are assumed to include the displacement of physically adsorbed or entangled molecules, the hydrolysis of ethoxy groups, and possibly the hydrolysis of some ≡Si—O—Si≡ linkages.

Ethyltriethoxysilane - Silica

The properties of the ETES films on silica indicate that this triethoxysilane does not react extensively with the surface silanols, probably because of the low hydrolytic reactivity of this particular alkoxysilane. There is obviously some adsorption of ETES, since retraction does occur from the α-chloronaphthalene solutions at least. However, the poor water stability of the resulting films shows that the adsorbate is not strongly held to the surface (e.g., the disparity between θ_{H_2O} and the organic-liquid wetting data and the marked decrease in θ_{H_2O} during the water-desorption tests). Evidently, the ETES is too poorly reactive to interact with the surface silanols either to form extensive surface attachments or an adsorbed polysiloxane network (postulates 1 and 4). Consistent with this interpretation is the fact that in low-polarity solvents the hydrolysis of ETES requires catalysis by strong acids or bases (8).

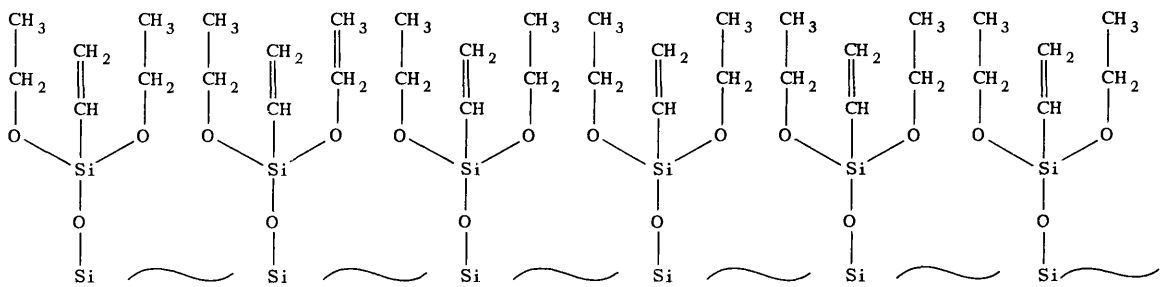
Vinyltriethoxysilane - Silica

The VTES appears to be more reactive than ETES and, therefore, able to interact more extensively with the surface silanols. The coverage by VTES on flamed silica gives a high density of hydrocarbon groups (low γ_c*, Fig. 5a), at least at the high concentrations. These films are stable toward water since the θ_{H_2O} values are consistent with the organic-liquid wetting data, and the films resist water desorption (Fig. 7).

In an exploratory study the VTES was found to be slightly more hydrolytically reactive than the ethyl compound. Also, a higher hydrolytic sensitivity for VTES than for ETES can be justified on theoretical grounds. If p_π-d_π bonding can occur between the

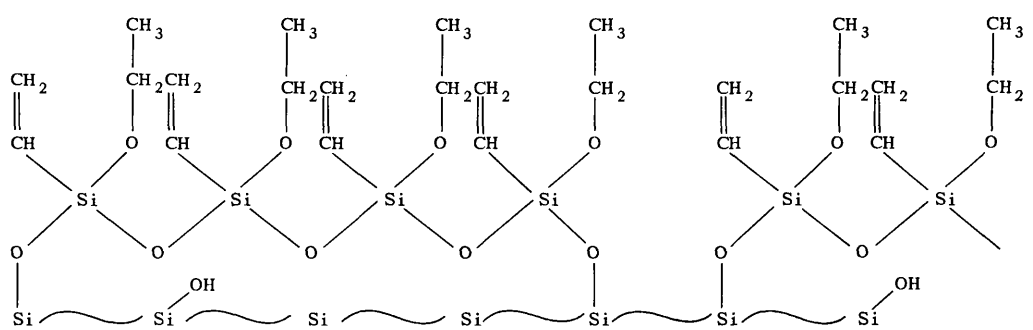
silicon atom and the vinyl group (10,11), then structures such as $CH_2^+-CH=Si_2^--(OC_2H_5)_3$ may be important in the hydrolysis reaction mechanism. The increased electron density on the silica would serve to weaken the ≡Si—O— bond. Similar ionic structures cannot be written for ETES.

Two different configurations are proposed for the adsorbed molecules in the VTES films on flamed silica. Both models attempt to account for the surprisingly low critical surface tensions exhibited by the films from 1% and 5% solutions. An apparent critical surface tension of 21 dynes/cm – or 26 dynes/cm as determined using n-alkanes (Fig. 1) – is usually associated with closely spaced hydrocarbon groups. Examination of molecular models indicates that to obtain such close spacing there must be an average of at least one unreacted ethoxy group remaining on each adsorbed triethoxysilane. One configuration that satisfies this requirement has each adsorbed molecule singly attached to the surface:



C

Alternately, the film could consist of short vinylsiloxane polymer segments bridging from one point of surface attachments to another, i.e.,



D

As suggested earlier, the water necessary for polymerization was probably available even on the flamed silica. The molecular models suggest that to obtain a close spacing of hydrocarbon groups in a film of polyvinyl siloxane the polymer segments must be held against the surface as in structure D. If the polymer units were attached to the surface but allowed to extend in a random fashion into the adsorbate solution, a larger proportion of polar groups would be accessible to a contacting liquid.

The contention that polymer adsorption can result in oleophobic (low γ_c*) and water stable films is given support by the results using the ETES polymer-monomer solution (Fig. 10). In this case, preformed polymer was present in the solution along with the monomer ETES, and the resulting films had a wettability not unlike the wettability of the films formed by the 1% and 5% VTES solutions on flamed silica. The water stability of

the ETES or VTES films can be best explained by assuming a film structure that is predominately polymer units, each having a number of surface attachments. Desorption then requires the simultaneous breaking of many bonds, which is a statistically unlikely event.

At least three explanations are possible for the relatively high γ_c* values of the films from the 0.1% VTES solutions. (a) As suggested by postulate 2, the VTES molecules may form multiple attachments to the surface. If so, the number of unreacted ethoxy groups in the adsorbed film will be less than in the films formed at the higher concentration, where only singly attached molecules (structure C) or polymer molecules (structure D) are expected. (b) The high γ_c* values may merely indicate sparse coverage of the surface. If a significant part of the adsorbate at the higher concentrations is physically held, then at the lower concentration the surface density of these weakly held molecules will be lower. (c) At the low solution concentration, the rate of reactions 1, 2a, and 2b may be too slow to give full surface coverage within the adsorption times allowed, which was about 3 days. Enough information is not available to differentiate between these three rather speculative explanations.

VTES films on air-dried silica differed in both wettability and water stability from the VTES films on flamed silica (Figs. 5, 6, and 7). These differences are attributed to a greater rate of water diffusion to the surface from the bulk silica during the course of the adsorption process on air-dried silica than occurs in the case of flamed silica (postulate 3). The continued supply of water to the surface of air-dried silica is believed to significantly reduce the formation of siloxane surface attachments which would explain the poor water resistance of these films.

The minimum in γ_c* observed after a few hours adsorption time for VTES on air-dried silica (Fig. 6a) probably corresponded to an initial surface coverage by small polymer molecules and unreacted VTES molecules H-bonded to the surface. At these early stages of adsorption the θ_{H_2O} values were highly unstable, indicating easy disruption of the film. Subsequent reaction of the adsorbate molecules to form further polymer linkages and possibly surface attachments would explain the increase in water stability after 20 hr. A gradual loss of ethoxy groups from the film will accompany these processes and would contribute to the increase in γ_c* at the later adsorption times (Fig. 6a).

The Effect of Acid and Base Catalysts

The addition of organic acids and bases to the adsorbate solution is believed to promote considerably more polymer formation, and possibly more surface attachments, in the films formed by ETES and VTES than when either triethoxysilane is adsorbed without added catalyst. In fact, from the triethoxysilane-catalyst solutions the adsorption process is likely to continue beyond the initial surface coverage by "monolayer" films, such as structure C or D. Any unreacted ethoxy groups in the initially adsorbed film are highly susceptible to hydrolysis because of the ready availability of catalyst in the overlying solution. The water necessary for hydrolysis is available from the silica substrate or from the adsorbate solution into which trace amounts may have been introduced inadvertently during preparation. Therefore, polymer buildup on the surface will continue until one of the reactants becomes depleted or until steric factors limit further polymerization. The net effect of these processes is reflected in the observed change in γ_c* with adsorption time (Fig. 8). The minimum in γ_c* at 1 to 3 hr of adsorption time reflects the high density of unreacted ethoxy groups in the initial film. The subsequent increase in γ_c* corresponds to the loss of the ethoxy groups as this initial film becomes more crosslinked, and a gradual buildup of randomly oriented polymer segments occurs.

The films generated by the triethoxysilane-(n-)propylamine solutions (at adsorbate/amine mole ratios of 4 or greater) differed in a number of ways from the films formed from any of the other adsorbate solutions. Some of the unusual phenomena noted in

connection with these n-propylamine-catalyzed systems were that: (a) the films were strongly hydrophobic (high θ_{H_2O}) but at the same time were surprisingly oleophilic (high γ_c*), (b) retraction from these solutions was slow and oftentimes incomplete, and (c) retraction failed to occur at all when a finely divided precipitate was formed in some of these adsorbate solutions. In connection with the γ_c*'s of these films, it should be noted that in the cos θ-vs-γ_{LV} plots the wetting data did not give as exact a linear relationship as was obtained for the other films of this study. Instead, the wetting data showed a marked scatter through which a best fit straight line was drawn. Because of this scatter, there is an uncertainty of ±5 dynes/cm in the γ_c* values for the n-propylamine-catalyzed films in Tables 1 and 2.

It is believed that the above phenomena result because adsorption in this case resulted in polymer films which formed so rapidly that monomer, polymer fragments, amine catalyst, and solvent molecules were physically trapped in the adsorbed layer. An important consequence of this adsorption process is that the films can be penetrated by the organic test liquids. The visible precipitates observed in the triethoxysilane-(n-) propylamine solutions are presumed to be particles of high-molecular-weight polysiloxane. This suggests that the rate of polymer formation is greater in these amine-catalyzed solutions than in the other adsorbate-catalyzed solutions. Undoubtedly, much smaller polysiloxane units were present in the adsorbate solution before the particle became visible. Thus, the buildup of the adsorbed film may include small, preformed polymer aggregates, as well as the triethoxysilane monomer. In fact, if adsorption proceeds rapidly enough, molecules of solvent, catalyst, and unreacted triethoxysilane monomer and polymer are likely to be trapped in the adsorbed network without actually being chemically linked to it.

The slow and incomplete retraction of the solutions containing n-propylamine is attributed in part to the presence of weakly held polysiloxane material on an underlying and more coherent film. The fact that the solution retracted at a low contact angle (about 20° to 30°) cannot completely explain the inordinately slow retraction. It is more likely that a loose, gel-like, polymeric structure impeded and (in some instances) prevented the withdrawal of the retracting liquid. When retraction failed to occur, the residual solution was easily displaced by water. Undoubtedly, this "displacement" is a complex process of desorption, liquid-liquid displacement, and hydrolysis of the polymer film.

The wettability of these films is adequately explained when they are viewed as adsorbed polymer films into which solvent and other molecules are entangled. The high γ_c* values obtained reflect both the random-oriented polymer segments and the inclusion in the film of the relatively-high-surface-tension solvent, i.e., α-chloronaphthalene (γ_{LV} = 42.9 dynes/cm). However, the θ_{H_2O} values for these films are much higher than was to be expected from their γ_c* values. This discrepancy is best illustrated by reference to the work of Shafrin and Zisman (12), who have studied the relation between θ_{H_2O} and γ_c* for over 60 organic polymers and adsorbed organic films. They found that for a given value of γ_c* there is a corresponding upper limit for θ_{H_2O}. On this basis those films in Tables 1 and 2 having a γ_c* value of 38 dynes/cm, for example, should have a θ_{H_2O} value of not over 85°, which is 20° lower than the 105° observed. Other examples of such unusually high water contact angles are underlined in Tables 1 and 2. Note that in all cases these polysiloxane films had been deposited from solutions containing n-propylamine as the catalyst. This apparent discrepancy between observed and predicted water contact angles in no way invalidates the generalizations made by Shafrin and Zisman. The comparison is made to emphasize the unusual oleophilic-hydrophobic character of these films. The explanation of the discrepancy is probably that molecules of the organic test liquids penetrate the polysiloxane layers, thus raising their apparent critical surface tensions. The unusually large deviation of the wetting data from a straight-line relationships also suggests specific interactions between the individual test liquids and these polysiloxane films. Shafrin and Zisman, of course, purposely excluded

from their data any systems in which there were strong, specific interactions between the surface and the wetting liquids.

The adsorbed films encountered in this study were very thin when compared with the much thicker, visible coatings of alkoxysilane used in technical practice. All of the films studied were too thin to show interference tints, thus indicating they are less than 1000Å thick. Even the loosely held, gel-like material formed from some of the solutions containing the n-propylamine catalyst was not thick enough to be visible. Its presence was inferred only because of the unusual impeding effect on the retraction process. On the other hand, the technical finish coatings applied to adherend surfaces by evaporation of aqueous or nonaqueous solution are easily visible and thus many times thicker than the adsorbed films described here.

Adsorption of ETES and VTES on α-Alumina

In the absence of acid or base catalysts, it was not possible to obtain ETES films on α-alumina by retraction, and the VTES films were unstable toward the organic wetting liquids as well as water. This failure of both the ETES and VTES to form strongly held films can be attributed to the weakly basic character of α-alumina surfaces. The isoelectric point of alumina is usually between pH 7.5 and 9.0 (13), which is a rough measure of the base strength of the =Al—OH surface groups. Silica, on the other hand, has its isoelectric point at a pH of 2, signifying a moderately strong acid character for the ≡Si—OH group. In terms of acid-base strength, the α-alumina presents a much less chemically active surface for trialkoxysilane hydrolysis than does silica.

The hydrolytic stability of =Al—O—Si≡ surface attachments is questionable even if such bonds are formed. Experience with organic aluminosiloxane polymers has shown that the =Al—O—Si≡ linkage does not have the stability usually associated with the ≡Si—O—Si≡ group, especially toward water (14).

When n-propylamine was introduced into the ETES adsorbate solution, the resulting films on α-alumina had the same wettability characteristics and water stability as the films obtained from a similar solution on silica. It can be reasonably assumed that the amine base catalyzed the formation of an adsorbed polysiloxane network on the α-alumina. However, it is again questionable whether the water stability of these films can be attributed to the formation of =Al—O—Si≡ surface attachments. The water stability is more likely due to the highly polymeric structure of the film.

Implications for the Use of Trialkoxysilanes as Finishing Agents

The water stability of the adhesive bond between organic resins and inorganic adherends has been reported to be significantly improved by precoating the inorganic surface with certain trialkoxysilane finishing agents. These compounds have proved useful for such adherends as glass (2), aluminum (15), porcelain (16), and natural tooth surfaces (17). The finishing-agent coating may be applied from aqueous or nonaqueous solution or as an additive in the adhesive-resin liquid.

There are three important implications of this investigation for the use of trialkoxysilanes as finishing agents when applied from nonaqueous solutions or when used as resin additives. (a) The trialkoxysilane can serve to chemically scavenge water adsorbed on the adherend surface and trace amounts of water in the liquid resin. (b) The adsorbed-polysiloxane network can serve as a hydrophobic barrier to the entry of bulk water into the interfacial region. It may also hinder readsorption of water, at least in the case of glass, by chemically combining with hydrophilic surface groups. (c) The extent to which

the trialkoxysilane will serve to scavenge water and form an adsorbed, hydrophobic barrier will depend on its hydrolytic reactivity and the conditions under which it is applied, such as the amount and type of acid or base present, the amount of water present, and the acid-base character of the substrate.

The triethoxysilane compounds thus satisfy two requirements indicated by Zisman (18) for useful finishing agents. They are able to displace water from the substrate surface and to prevent its readsorption.

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13. ABSTRACT

Critical surface tensions γ_c and water contact angles θ_{H_2O} have been determined for adsorbed films of ethyltriethoxysilane and vinyltriethoxysilane on silica and α-alumina. The films were formed by retraction from hydrocarbon solution. Studies were also made of film resistance to desorption and alteration when in prolonged contact with water. The vinyltriethoxysilane films were generally more oleophobic (low γ_c values) and more hydrophobic (high θ_{H_2O} values) than the films formed by the ethyl analog. The vinyltriethoxysilane films were also more resistant to disruption and desorption when contacted with water. Neither vinyl- nor ethyltriethoxysilane formed strongly held films on α-alumina. The addition of low-molecular-weight organic acids or bases to the adsorbate solutions resulted in both the ethyl- and vinyltriethoxysilane forming hydrophobic and water resistant films on silica and α-alumina. The results suggest that the adsorption process involves the adsorbate molecules reacting with silanol groups on the silica to form siloxane linkages to the surface and reacting with themselves to form adsorbed siloxane polymer. The properties of the resulting film will depend upon the number of surface attachments and the extent of crosslinking between adsorbate molecules.

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Finishing agents						
Critical surface tensions						
Water contact angles						

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