Table III
Molecular Weight and Concentration Dependences of ψ_{12}^0, τ_0, and J_e

$CM < 1.35 \times 10^5$	$CM \geq 1.35 \times 10^5$
$\psi_{12}^0 \propto \eta^{02}M/CRT$	η^{02}/C^2RT
$\tau_0 \propto \eta^0 M/CRT$	η^0/C^2RT
$J_e \propto M/CRT$	$1/C^2RT$

concentrated solutions (*i.e.*, in $C \geq C_c^J$), as can be seen in Figure 8.

At moderately high shear rates, the region of $J_s \propto 1/C^2$ still remains, but deviation from the universal line is observed at higher concentrations. In that region, J_s is proportional to C^{-n} $(0 < n < 2)$ and depends on molecular weight. This deviation from the universal line of $J_s \propto 1/C^2$ is due to the change in the effective entanglement density, which would occur from the highly entangling chains first. That is, the change in the effective entanglement density due to high shear rate was given by Graessley as[36]

$$E = E_0 g(\theta)$$

where $\theta = (1/2)\dot{\gamma}\tau = (1/2)\dot{\gamma}(\eta/\eta^0)\tau_0$ and E_0 is the value of E at zero shear rate. The function $g(\theta)$, which gives the rate of change in E with $\dot{\gamma}$, was calculated by Graessley. Therefore J_s is given by

$$J_s(\dot{\gamma}) \propto (1/\nu)E_0RTg(\theta) \qquad (7)$$

Although the absolute values of θ cannot be estimated in the range of $J_s \propto 1/C^2$ and, hence, quantitative comparison between eq 7 and experiments is not possible, the qualitative features of the shear rate dependence of J_s in Figure 8 can well be explained by eq 7.

In the region of $J_e \propto C^{-1}$, it was reported that the superposition of η and J_s with respect to molecular weight, polymer concentration, and temperature can be carried out by applying the theory of Rouse,[34] Bueche,[37] and Zimm.[38] Superposition of the present data is shown in Figure 10A, in which the shift factor τ_0 $(12/\pi^2)(\eta^0 M/CRT)$ is used. Concerning the superposition of η and J_s in the region of $J_e \propto C^{-2}$, it can be speculated from the above discussion that the superposition would be successful if we use the shift factor $\tau_0' = K\eta^0/C^2RT$ where K is a constant. The superposition results are shown in Figure 10B, where $K = 10^6$ cgs is arbitrarily used. Our shift factors for concentrated and dilute solutions agree with the values of Graessley and Segal[26] who reported this superposition first.

As a summary, the polymer concentration and molecular weight dependences of J_e, τ_0, and ψ_{12}^0 $(= \lim(\dot{\gamma}\rightarrow 0)\ (P_{11} - P_{22})/\dot{\gamma}^2)$ are shown in Table III. Except for the numerical factors, we believe that these relationships agree with most experimental results reported previously. However, it is to be noted that these relationships hold only for monodisperse polymers. From the table, moreover, it can be pointed out that J_e is proportional to τ_0/η^0 over the whole concentration range. Since τ_0 can be speculated from the shear rate dependence of η, it may be possible to speculate relative values of J_e from the data on shear rate dependence of η alone.

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(36) W. W. Graessley, *J. Chem. Phys.*, **43**, 2696 (1965); **47**, 1942 (1967).

(37) F. Bueche, *ibid.*, **22**, 1570 (1954).

(38) B. Zimm, *ibid.*, **24**, 269 (1956).

Structure of Silane Adhesion Promoter Films on Glass and Metal Surfaces

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Received July 7, 1972

ABSTRACT: The films of vinyl-, γ-chloropropyl, *p*-chlorophenylethyl-, and γ-aminopropyltrialkoxysilane deposited on glass and metal surfaces from polar and nonpolar solvents were examined using contact angle measurements, internal reflection infrared spectroscopy, ellipsometry, and scanning electron microscopy. These studies showed the films to be polysiloxane coatings, part of which could be easily rinsed from the surface by organic solvents or water. Contact angle determinations on the remaining, strongly held material indicate it to be an open polymeric structure since it was easily penetrated by the wetting liquids. Ellipsometric measurements showed the films from nonpolar solvents to be relatively thick (>1000 Å) and resistant to desorption. The films from polar solvents were generally less than 100 Å thick and easily disrupted by polar liquids. However, the scanning electron microscopy study revealed that over the continuous films measured ellipsometrically there were discrete, widely separate patches of deposit. The significance of these findings to the use of trialkoxysilanes as adhesion promoters is discussed.

The adhesion of polymers to glass and metals can be significantly improved by applying certain trialkoxysilanes to the adherend surface.[1,2] These "silanes" are especially effective in improving the resistance of the bond to attack by moisture. In order to explain their adhesion-promoting effect, it has been suggested that these agents form a chemical link between the adhesive and adherend.[1,3] Other workers hold to the view that the silane affects the mechanical properties of the adhesive near the interface.[2,4,5] At present no theory provides a complete explanation of the adhesion-promoting action. One is inclined to believe that both mechanical and chemical effects are involved.

The work reported here was designed to determine the structure of the films of various silane adhesion promoters on glass and metal surfaces deposited by evaporation from polar and nonpolar solvents. It is hoped that this informa-

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(1) S. Sterman and J. G. Marsden, *Ind. Eng. Chem.*, **58**, 33 (1966).

(2) E. P. Plueddemann, *J. Adhesion*, **2**, 184 (1970).

(3) R. Wong in "Fundamental Aspects of Fiber Reinforced Plastic Composites," R. T. Schwartz and H. S. Schwartz, Ed., Interscience, New York, N. Y., 1968, p 237.

(4) P. W. Erickson, *J. Adhesion*, **2**, 131 (1970).

(5) A. S. Kenyon, *J. Colloid Interfac. Sci.*, **27**, 761 (1968).

TABLE I
WETTABILITY OF THE $ClCH_2CH_2CH_2Si(OCH_3)_3$ FILMS

Wetting liquid	Surface tension, dyn/cm	Cyclohexane				2-Propanol–water			
		Steel		Pyrex		Steel		Pyrex	
		$\theta_{adv}{}^a$	$\theta_{rec}{}^a$	$\theta_{adv}{}^a$	$\theta_{rec}{}^a$	$\theta_{adv}{}^a$	$\theta_{rec}{}^a$	$\theta_{adv}{}^a$	$\theta_{rec}{}^a$
Water	72.8	80	0	80	26	51	0	65	0
Formamide	58.2	64	0	62	0	27	0	48	0
Thiodiglycol	54.0	49	0	44	0	15	0	27	0
Methylene iodide	50.8	37	21	37	21	24	0	31	0
α-Chloronaphthalene	42.9	11	0	14	0	Spreads		Spreads	

[a] Degrees.

tion will aid in understanding the mechanism by which these agents act.

TABLE II
WETTABILITY OF THE $p\text{-}ClC_6H_4CH_2CH_2Si(OCH_3)_3$ FILMS

Wetting liquid	Surface tension, dyn/cm	Methyl ethyl ketone[a]		2-Propanol–water[a]	
		$\theta_{adv}{}^b$	$\theta_{rec}{}^b$	$\theta_{adv}{}^b$	$\theta_{rec}{}^b$
Water	72.8	75	0	80	65
Formamide	58.2	45	0	67	46
Thiodiglycol	54.0	40	0	50	0
Methylene iodide	50.8	37	32	35	31
α-Chloronaphthalene	42.9	10	0	8	0

[a] Steel plates. [b] Degrees.

TABLE III
WETTABILITY OF THE $CH_2{=}CHSi(OCH_2CH_3)_3$ FILMS

Wetting liquid	Surface tension, dyn/cm	Cyclohexane[a]		Methyl ethyl ketone[a]		2-Propanol[a]	
		$\theta_{adv}{}^b$	$\theta_{rec}{}^b$	$\theta_{adv}{}^b$	$\theta_{rec}{}^b$	$\theta_{adv}{}^b$	$\theta_{rec}{}^b$
Water	72.8	86	40	34	0	43	37
Formamide	58.2	78	0	<5	0	27	0
Thiodiglycol	54.0	72	40	24	0	32	0
Methylene iodide	50.8	54	50	40	34	38	31
α-Chloronaphthalene	42.9	38	20	25	10	20	0
Bicyclohexyl	33.0	15	~5	10	0		

[a] Steel plates. [b] Degrees.

Experimental Section

Materials. The trialkoxysilanes studied were vinyltriethoxysilane, $CH_2{=}CHSi(OCH_2CH_3)_3$, γ-chloropropyltrimethoxysilane, $ClCH_2CH_2CH_2Si(OCH_3)_3$, *p*-chlorophenylethyltrimethoxysilane, $p\text{-}ClC_6H_4CH_2CH_2Si(OCH_3)_3$, and γ-aminopropyltriethoxysilane, $NH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$. The vinyl-, chloropropyl-, and aminopropylsilanes were obtained from Union Carbide Corp., Silicones Division. The chlorophenylethylsilane was synthesized at this laboratory by O'Rear.[6] These compounds were purified by distillation except for the aminopropylsilane. The distillation conditions and the physical properties of the purified silanes were reported earlier.[7,8] The aminopropylsilane was obtained directly from production and stored over molecular sieve. It was not redistilled before use since the manipulations involved would expose the material to water and produce as much hydrolysis product as distillation would remove.

The Pyrex substrates were 1 in. × 2 in. plates, 0.1875 in. thick. They were cleaned by soaking in hot nitric–sulfuric acid, thoroughly rinsing with distilled water, and air-drying at 25°. The stainless steel (Type 309) was in the form of 1 in. × 2 in. plates, 0.25 in. thick. Also, plates of germanium and KRS-5 (thallium chloride–bromide salt mixture) were used in the internal reflection spectroscopy study. These were 50 × 20 mm plates, 2 mm thick with the 20-mm edges beveled to 45°. The steel, germanium, and KRS-5 plates were cleaned by polishing with an alumina powder–water slurry followed by a final polishing with water alone to remove loose alumina particles. The plates were then rinsed with distilled water and air-dried at 25°.

The solvents used to apply the silanes were cyclohexane, methyl ethyl ketone, 2-propanol, and distilled water or a mixture of 2-propanol and water at a 1:1 volume ratio. The organic solvents were reagent grade chemicals and the cyclohexane and methyl ethyl ketone were percolated through Florisil before use.

Methods. The silanes were applied to the cleaned substrates from 1.0 or 0.1% solution. Glacial acetic acid was added to the solutions (0.05 vol %) except in the case of aminopropylsilane, for which no hydrolysis catalysis was needed. The substrate plates were allowed to contact the solution for at least an hour and in most cases overnight (~20 hr), after which the plates were removed and the solvent was allowed to evaporate.

Contact angle measurements were made by the sessile drop method. The procedures and the wetting liquids used are described in ref 7. Both advancing and receding angles were measured. The sessile drops were advanced by adding liquid held on a flamed platinum wire. The receding angles were determined by removing liquid with thin-walled glass capillary tubes. The ellipsometry work was done with an O. C. Rudolph and Sons (Caldwell, N. J.) Model 436-200E ellipsometer, and a discussion of this technique has been given previously.[8] The infrared spectra of the silane films were determined by attenuated total reflection spectroscopy (atr) using a Perkin-Elmer Model 457 spectrometer (Perkin Elmer Corp., Norwalk, Conn.) with a Wilks atr sample holder, Model 9000 (Wilks Scientific Corp., Norwalk, Conn.). Some work was done with the Wilks Model 8 internal reflection spectrometer. The scanning electron microscopy (sem) was done with a Cambridge Mark I microscope.

Results

Contact Angles. It was not possible to obtain stable or reproducible contact angles on the initially deposited films. This was probably due to the wetting liquids dissolving weakly held solute from the film. Previous experience had shown this weakly held material could be removed by rinsing the initial film in a stream of acetone for a few seconds.[7,8] This procedure was adopted here, and the advancing and receding contact angles for the acetone rinsed films are given in Tables I–IV. Plots of cos θ *vs.* surface tension for the advancing angles are presented in Figures 1 and 2.

The most significant feature of the tabulated data is the very large contact angle hysteresis. In many cases the receding angle was zero even when the advancing angle was as

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(6) J. G. O'Rear, P. J. Sniegoski, and F. L. James, *Advan. Chem. Ser.*, **No. 87,** 10 (1968).

(7) W. D. Bascom, *ibid.*, **No. 87,** 38 (1969).

(8) W. D. Bacom, *J. Colloid Interfac. Sci.*, **27,** 789 (1968).

Table IV
Wettability of the $NH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$ Films

Wetting liquid	Surface tension, dyn/cm	Cyclohexane[a]		Water[a]	
		θ_{adv}[b]	θ_{rec}[b]	θ_{adv}[b]	θ_{rec}[b]
Water	72.8	53	0	38	0
Formamide	58.2	20	0	10	0
Thiodiglycol	54.0	36	0	10	0
Methylene iodide	50.8	39	30	28	19
α-Bromonaphthalene	44.6	26	14	14	14

[a] Pyrex plates. [b] Degrees.

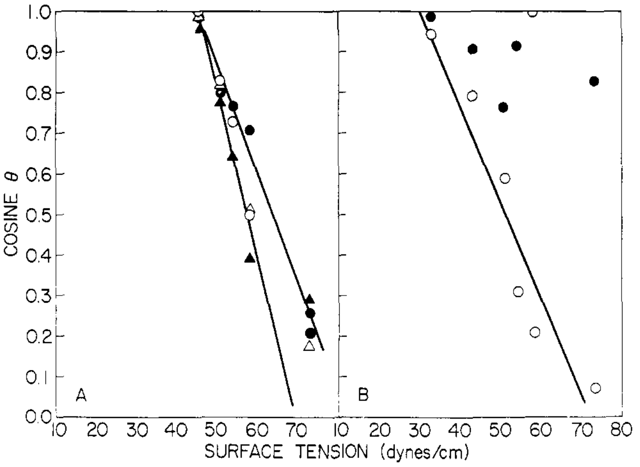

Figure 1. Critical surface tension plots for γ-chloropropyltrimethoxysilane (A) and vinyltriethoxysilane (B) films deposited from cyclohexane (○), 2-propanol (▲), methyl ethyl ketone (●), and 2-propanol–water (△) onto stainless steel.

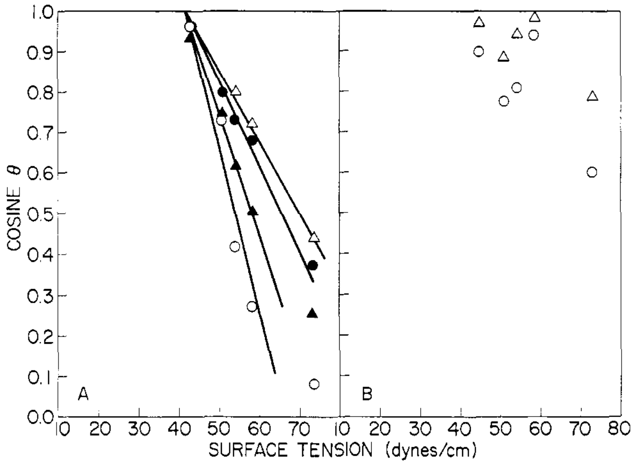

Figure 2. Critical surface tension plots for chlorophenylethyltrimethoxysilane (A) and α-aminopropyltriethoxysilane (B) deposited from cyclohexane (○), methyl ethyl ketone (●), 2-propanol (▲), and water (△) onto stainless steel.

large as 80° (Table I). Only in the case of methylene iodide were the receding angles comparable to the advancing angles. There were no significant differences between the films formed on Pyrex and those on the steel. Consequently, the data for the chlorophenylethyl-, vinyl-, and aminopropylsilane films are given for only one substrate.

The time allowed for substrate–solution contact had a marked effect on the contact angle values. Invariably, the angles increased with time but reached constant values within 3-4 hr. The data in Tables I–IV and Figures 1 and 2 were obtained by leaving the substrate in the solution overnight (~20 hr), which was more than adequate contact time.

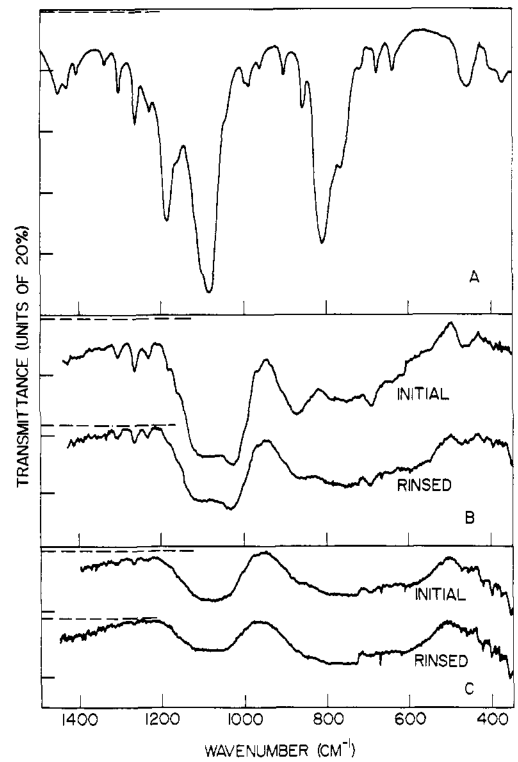

Figure 3. Infrared spectra of γ-chloropropyltrimethoxysilane monomer (A, transmission) and films on KRS-5 deposited from cyclohexane (B, atr) and 2-propanol–water (C, atr).

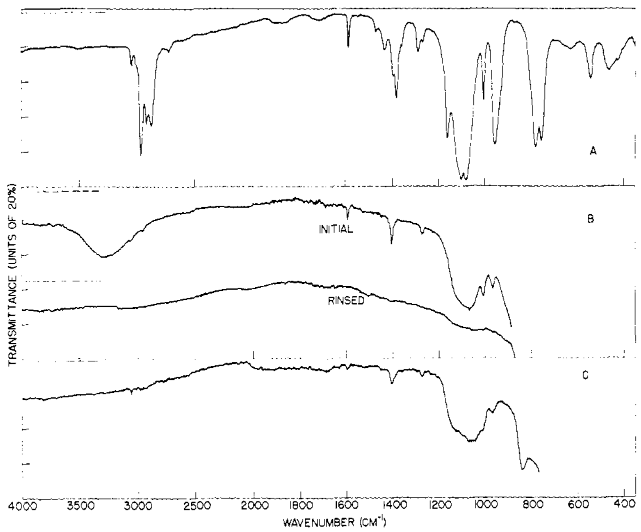

Figure 4. Infrared spectra of vinyltriethoxysilane monomer (A, transmission) and films on germanium deposited from 2-propanol–water (B, atr) and cyclohexane (C, atr). Spectrum C is for the rinsed film.

Infrared Spectroscopy Study. The atr spectra of the silane films deposited directly on KRS-5 or germanium plates are given in Figures 3–8 along with the transmission spectra of the alkoxysilane liquids. The 100% transmission at 4000 cm^{-1} is marked by a dashed line for each spectrum. The spectra of the uncoated plates were essentially featureless except for a gradual decrease in transmission at the lower frequencies. The results for the chloropropylsilane films in

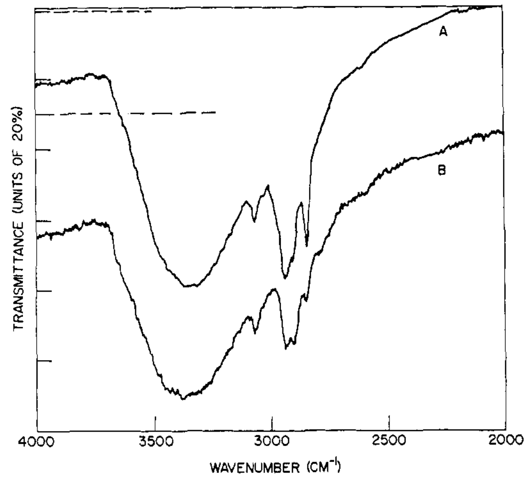

Figure 5. Infrared spectra (atr) of the *p*-chlorophenylethyl film on KRS-5 deposited from cyclohexane: (A) initial film, (B) rinsed film.

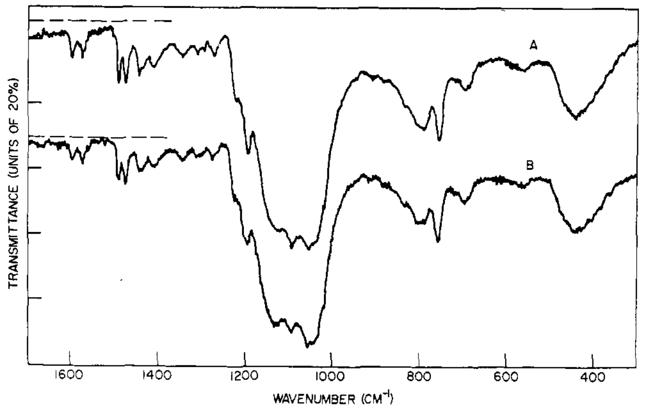

Figure 6. Infrared spectra (atr) of the *p*-chlorophenylethyltrimethoxysilane film on KRS-5 deposited from cyclohexane: (A) initial film, (B) rinsed film.

Figure 3 illustrate three major features found to be characteristic of all the silane spectra. First, the Si–O stretching vibration band at 1090 cm^{-1} was sharp in the spectrum of the silane liquid (Figure 3A) but considerably broadened in the film spectra (Figure 3B and 3C). Secondly, the films from cyclohexane invariably gave more intense spectra than did the films from the other three solvents; *e.g.*, compare 3B and 3C. The third point is that the acetone rinse usually reduced the band intensities, as is evident in Figure 3B and even more so in Figure 4B for the vinylsilane. Note, however, in Figure 3C, that the acetone rinse did not always reduce spectral intensity.

In comparing the spectrum of the vinylsilane liquid with the film spectra (Figure 4), the C–H stretching vibration region between 2500 and 3000 cm^{-1} has been included, and it is interesting that there was a much greater loss in intensity for these bands (and the C–H bending vibration bands at 1390 and 1295 cm^{-1}) than for the vinyl bands at 1600 cm^{-1} (C═C stretch) and 1405 cm^{-1} (C—H bend of the ═CH_2 group). Another point of interest in Figure 4B is the broad band at about 3300 cm^{-1} presumably due to the O–H stretching vibration of H-bonded hydroxyls. A broad band at 3400 cm^{-1} was also evident in the spectra of the chlorophenylethylsilane from cyclohexane (Figure 5).

The chlorophenylethylsilane films deposited from methyl ethyl ketone (Figure 7) and from 2-propanol were unusual in that the initial deposit underwent a spontaneous change that reduced the overall band intensity and broadened the Si–O stretch band at 1090 cm^{-1}. These spectral changes were complete within 4 hr. At the end of this time the plate was rinsed with acetone, and the resulting spectrum showed only two weak broad bands at 1000–1100 and at 700–900 cm^{-1}.

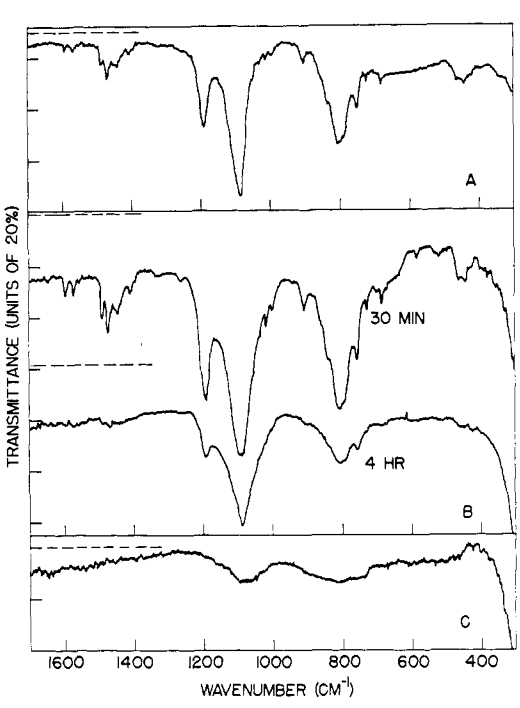

Figure 7. Infrared spectra of the chlorophenylethyltrimethoxysilane monomer (A, transmission) and films on KRS-5 deposited from methyl ethyl ketone; B, unrinsed; C, rinsed.

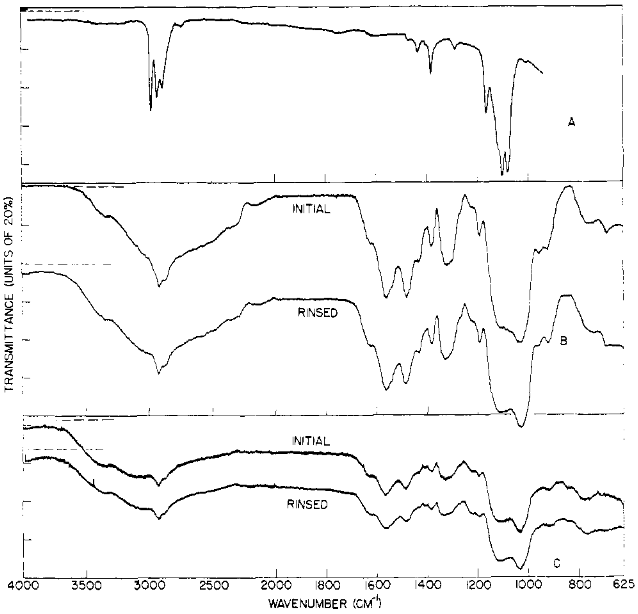

Figure 8. Infrared spectra of γ-aminopropyltriethoxysilane monomer (A, transmission; 5% in tetrachloroethylene) and films on germanium from cyclohexane (B, atr) and water (C, atr).

The transmission spectrum of the aminopropylsilane liquid was obtained from a 5 vol % solution in tetrachloroethylene (Figure 8A). Note that at this dilution none of the N–H stretching or bending vibration bands appeared in the 1300–1600-cm^{-1} region. However, the atr spectra of the films did exhibit the N–H (and C–H) bending bands as well as the siloxane band (1000–1200 cm^{-1}). The band for the N–H

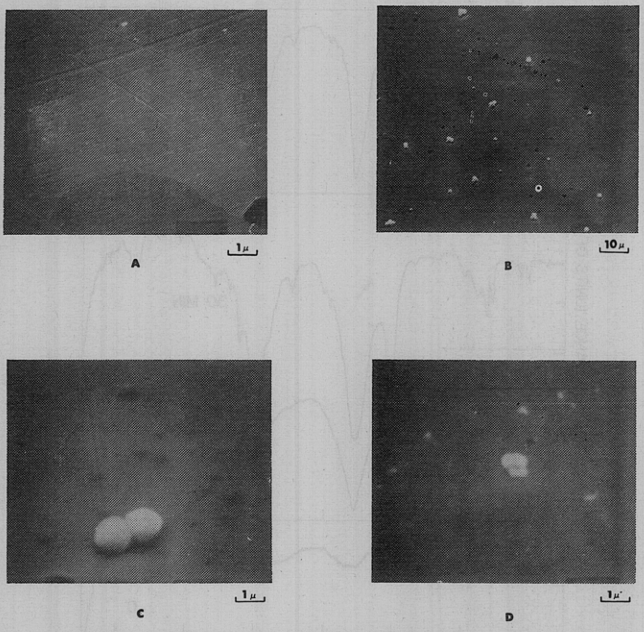

Figure 9. Scanning electron photomicrographs of γ-chloropropyltrimethoxysilane deposits on stainless steel: uncoated steel (A), deposit from cyclohexane (B, C), and deposit from 2-propanol–water mixture (D).

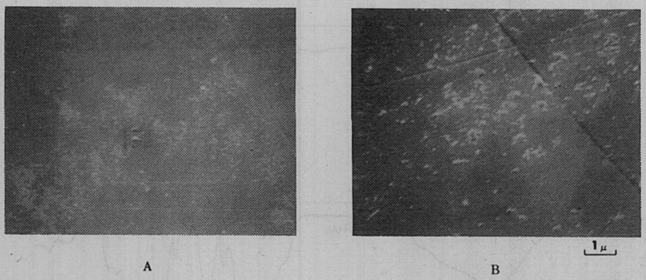

Figure 10: Scanning electron photomicrographs of vinyltriethoxysilane deposits from 2-propanol–water (A) and methyl ethyl ketone (B) on stainless steel.

stretching vibration normally found at 3350 cm^{-1} has been shifted to a broad band at about 3000 cm^{-1}, presumably the result of H bonding of the amine hydrogen. The high frequency shoulder on this 3000-cm^{-1} band is most likely due to H-bonded hydroxyls.

Scanning Electron Microscopy. Films of the chloropropyltrimethoxy- and vinyltriethoxysilane were deposited on stainless steel disks from the various solvents. The film-coated disks were rinsed with acetone and examined using the sem. Discrete patches of deposit were observed, and these patches were usually comprised of spherical particles. In Figure 9 the chloropropylsilane deposits from cyclohexane showed nearly perfect spheres that were more than 1 μ in diameter (Figure 9A–C). When this silane was applied from 2-propanol–water (Figure 9D), a particulate deposit was obtained but the spheres were 0.5 μ in diameter or less. The chloropropylsilane also gave deposits of small (<0.5 μ) spherical particles from methyl ethyl ketone.

The patches of particulate material observed for the vinylsilane films are shown in Figure 10. The particles are much smaller (<0.1 μ) and their shapes more irregular than the chloropropylsilane particles.

Ellipsometry. The thickness (d_f) and refractive index (n_f) of the chloropropylsilane films on steel as determined ellipsometrically are given in Table V. The films from the polar solvents were too thin to allow an unambiguous determination of both thickness and refractive index. This difficulty arises because one of the optical parameters measured is insensitive to changes in d_f and n_f for films less than 100 Å thick. However, it was possible to determine a range in thickness for a given range in refractive index, and these results are presented in Table V for the initial and acetone-rinsed films. The initial films deposited from cyclohexane were so uneven in thickness that it was impossible to make meaningful ellipsometric measurements. However, the acetone-rinsed film had a sufficiently uniform thickness to allow values of both d_f and n_f to be determined.

Table V
The Thickness of $ClCH_2CH_2CH_2Si(OCH_3)_3$ Films on Steel

	Film properties			
	Initial		Rinsed	
Solvent	d_f, Å	n_f	d_f, Å	n_f
	25°			
2-Propanol–water (1:1)	44–24	1.3–1.5	44–24	1.3–1.5
2-Propanol	40–22	1.3–1.5	49–27	1.3–1.5
Methyl ethyl ketone	38–20	1.3–1.5	42–23	1.3–1.5
Cyclohexane			2748	1.42
	60°			
2-Propanol–water (1:1)	48–35	1.3–1.5	24–18	1.3–1.5
Methyl ethyl ketone	64–46	1.3–1.5	50–36	1.3–1.5

The ellipsometry study was not extended to the other silanes, since the most that could be determined was a range of film thicknesses. Furthermore, the instrument available for this study was unable to resolve the patches of deposit (seen in the sem) from the thinner intervening film.

Discussion

The hydrolysis–polymerization of trialkoxysilanes is a complex, intractable process catalyzed by acids and bases and subject to many variables including the chemical composition of the silane, the availability of water, and the type of solvent.[9,10] In homogeneous systems the products are high molecular weight, amorphous polymers that are difficult to characterize. Therefore, it was not surprising to find the silanes forming relatively thick, insoluble films whose structures depended on the choice of silane and also on the solvent from which they were applied. In this work the role of the catalyst was not explored; instead, acetic acid was added to provide sufficient catalyst to overwhelm any minor impurities or the acid–base character of the substrate itself. A study of the catalytic role of the silica surface in alkoxysilane hydrolysis will be reported elsewhere.[11]

The acetic acid was not added to the aminopropylsilane solution, since the strongly basic aminopropyl group makes this silane autocatalytic. As for the water needed for hydrolysis, the principle sources for the nonaqueous solvent systems were the acetic acid (which was not anhydrous) and adsorbed water on the metal or glass surfaces.

The infrared atr study provides direct evidence that the films are polysiloxane coatings. The broad band between 1000 and 1100 cm^{-1} observed in all of the film spectra is characteristic of high molecular weight polysiloxanes. It is attributed to the Si–O–C and Si–O–Si stretching vibration modes and is observed for both cyclic and linear polysiloxanes

(9) M. M. Sprung and F. O. Guenther, *J. Polym. Sci.*, **28**, 17 (1958).
(10) M. M. Sprung, *Fortschr. Hochpolym. Forsch.*, **2**, 442 (1961).
(11) W. D. Bascom and R. B. Timmons, *J. Phys. Chem.*, **76**, 3192.

and silica itself.[12–14] In the silane spectra the Si–O stretching band at 1100 cm^{-1} was sharp and split into a doublet for the ethoxy compounds, as noted by Conley.[15] The sharp band at 1150–1200 cm^{-1} in the monomer spectra is probably due to the stretching vibration of alkoxy C–O bond, and as expected this band in the film spectra is weak relative to the Si–O stretching band. The Si–C and Si–O bending vibrations give rise to bands between 400 and 600 cm^{-1} which are relatively sharp in the monomer spectra but quite broad in the film spectra.

Further evidence of the hydrolysis–polymerization of the deposited silane is the loss in intensity of the C–H stretching band of the alkoxy groups (3000–2800 cm^{-1}) relative to the bands of the functional groups (*i.e.*, vinyl-, aminopropyl-, chloropropyl-, etc.). For example, in the spectrum of the vinylsilane monomer, the C–H stretching bands were very intense compared to the C=C bands, but the relative intensities were reversed in the film spectra. Also, the N–H bending vibration bands were too weak to be observed in the spectrum of the aminopropylsilane solution but were actually stronger than the C–H stretching bands in the film spectra.

A comparison of the spectra of the initial and rinsed films deposited from the polar solvents indicates a marked reduction in band intensity and thus a removal of material. The reduction in band intensity was much less for the films from cyclohexane. The rinse did not alter the band widths or their relative intensities, which suggests that in terms of molecular structure the material removed did not differ significantly from the residual film. However, it should be noted that for polysiloxanes having more than about ten siloxane linkages, the infrared spectra are not very sensitive to differences in molecular weight or cross-linking. Consequently, the rinse could have removed low molecular weight polymer from a more insoluble high molecular weight polysiloxane network.

Certainly the particles observed on the rinsed films in the sem indicate the formation of a high molecular weight polymer. The shape of these particles implies a uniform, radial growth dictated perhaps by the spherical geometry offering a minimum solid–liquid interfacial energy. Presumably, these spheres formed within the solution and were deposited on the surface as the solvent evaporated.

There is ample reason for believing that, in addition to the particles, the substrates were covered by a thin, uniform polysiloxane film. Such a continuous film would not be resolved in the sem even if the film thickness exceeded the resolution of the microscope (about 50 Å), as is probably the case for the chloropropylsilane from cyclohexane ($d_f \approx 2000$ Å). However, note in Figure 9 that the surface scratches prominent on the uncoated steel (Figure 9A) are barely discernible on the film-covered surface, which suggests that the scratches had been filled by the polychloropropylsiloxane coating. The scratches on these mirror surfaces range between 100 and 1000 Å in width and depth. On the other hand, the vinylsilane film was so thin ($d_f \approx 30$ Å) that it is not surprising that the scratches were not masked by this film (Figure 10). The film thicknesses, d_f, represent average values that include both the particles and the continuous film. The particles cannot account for the observed thickness by themselves. For example, the spheres of polychloropropylsiloxane from cyclohexane (Figure 9) are about 10,000 Å in diameter but cover less than 10% of the surface, and so the intervening, continuous film must be about 2000 Å thick if the average film thickness is nearly 3000 Å (Table V).

The large contact angle hysteresis is best attributed to penetration and in some instances swelling and solution of the film by the wetting liquids. The roughness of the films due to the particulate deposits may have been a contributing factor but probably a minor one. Such a geometric roughness should have affected all the wetting liquids, yet the hysteresis for the methylene iodide was consistently less than for any other liquid.

Contact angle hysteresis due to penetration of the wetting liquids into adsorbed films has been demonstrated by Timmons and Zisman for monolayers of perfluoroheptylheptadecanoic acid on chromium.[16] They found that the hysteresis was related to the molecular volume of the liquid and that the contact angle hysteresis was negligible when the average diameter of the liquid molecules was larger than the average cross-sectional diameter of the intermolecular pores. No such relation was observed here; the liquids having the largest molar volume were thiodiglycol and α-chloronaphthalene (103.4 and 136.3 cm^3/mol, respectively), yet both showed marked hysteresis. It is possible that all the films had pores large enough to admit these molecules, but it is just as possible that the film structure was opened or swelled by the wetting liquids. It is interesting that the receding angle was frequently zero. For this to occur the critical surface tension of the film must increase to a value equal to or greater than the surface tension of the wetting liquids. This could happen if the liquid penetrates and swells the film to the point where the liquid is in effect attempting to recede from itself. The methylene iodide was exceptional in that it did not show as great a hysteresis as the other liquids. A possible explanation is that when these molecules penetrate the film they orient with the iodide atoms toward the substrate so that the methylene groups are exposed to the receding drop. A high density of methylene groups would decrease rather than increase the critical surface tension.

It is somewhat surprising that the advancing angles had such high values if the wetting liquids are penetrating the films as much as the receding angles would suggest. However, Johnson and Dettre[17] have shown that advancing angles are less sensitive to surface heterogeneity than receding angles. Moreover, we find here that despite the hysteresis many of the advancing angle data gave reasonably linear γ_{LV}–cos θ plots. The results for the chloropropyl films and the chlorophenylethyl films are particularly interesting in that the plots of the data for the films from different solvents had different slopes. Possibly, the lower angles (*i.e.*, lower slope) indicate a more open and penetrable structure. However, the films may also differ in molecular constitution owing to differences in the extent of hydrolysis and polymerization. In this instance, the films giving lower angles may have more polar groups such as unhydrolyzed alkoxy or unreacted hydroxyl groups.

The advancing angles for the vinylsilane films from methyl ethyl ketone (and 2-propanol–water) were very low and did not give linear γ_c plots. Evidently, the acetone rinse depleted these films so much that the surface heterogeneity severely affected the advancing as well as the receding angles. The atr study of these films supports this explanation, since the acetone rinse essentially eliminated the band spectra (Figure 4B).

Low advancing angles were also obtained on the aminopropylsilane films. However, these films were not depleted

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(12) N. Wright and M. J. Hunter, *J. Amer. Chem. Soc.*, **69**, 803 (1947).

(13) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

(14) I. Simon and H. E. McMahon, *J. Chem. Phys.*, **20**, 905 (1952).

(15) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 177.

(16) C. O. Timmons and W. A. Zisman, *J. Colloid Interfac. Sci.*, **22**, 165 (1966).

(17) R. E. Johnson and R. H. Dettre, *J. Phys. Chem.*, **68**, 1744 (1964); **69**, 1507 (1965).

by the rinse judging from the small change in infrared band intensity. However, the amino groups can interact rather strongly with the wetting liquids, especially those capable of hydrogen bonding. Such interaction would lower the contact angles and in a way that would not be a systematic function of the liquid surface tension, thus obviating any linear γ_{LV}–cos θ relationship.

Conclusion

The trialkoxysilane films were found to be essentially polysiloxane coatings, part of which could be rinsed away by acetone, but in all cases there remained a more firmly held polymer network. Among the four silanes examined, the polyvinylsiloxane films were the most severely depleted by this rinse. The residual coating was composed of patches of spherical polymer particles deposited on a thin, uniform polymer film. On a molecular scale this film had an open structure easily penetrated and swelled by water and organic liquids. In applying the silanes from various solvents the only major difference was that the films from cyclohexane were generally thicker than those from the more polar solvents. As far as the substrate was concerned, there were no distinguishable differences between the films formed on steel, glass, or the atr plates.

In technical practice the silane-adhesion promoters are applied to adherend surfaces by evaporation from solutions, as was done here. The solvent is usually water (or alcohol–water mixtures), although nonaqueous solvents have been employed. Presumably, the coating material found here to be easily removed by acetone would dissolve into the adhesive resin and the resin molecules would penetrate the polysiloxane network. It is known that too thick a coating of the silane can be detrimental to the bond strength, so the use of nonpolar solvents does not seem advisable. It is not immediately obvious why the application of thin, penetrable polysiloxane films should give better bond strength than just thoroughly cleaning the adherend surface. It would be incorrect to view the siloxane films as protective barriers, since they are not dense enough to block the diffusion of water molecules. Explanations based on the silanes forming covalent bonds to the adherend are inconsistent with the ability of these finishing agents to improve the wet strength of resin-to-metal adhesion, if we take account of the low water stability of metal–oxygen–silicon bonds.[7]

It is possible that in reacting with water to form the siloxane film the silanes serve as water scavengers. Also, it has been suggested[18] that the functional group of the film (vinyl, aminopropyl, chloropropyl) influences the resin polymerization and thereby the resin structure near the interface. The end result could be an improvement in the mechanical properties and/or the moisture resistance of the resin in the interfacial region.

Acknowledgments. The author wishes to thank Dr. Robert L. Patrick of Alpha Laboratories Inc., Elverson, Pa., for providing the sem results and for many helpful discussions during the course of this work. Appreciation is also extended to Mr. Robert L. Cottington for his help in this study.

(18) Bascom, W. D., *J. Adhesion* **2,** 161 (1970).

Magic-Angle Carbon-13 Nuclear Magnetic Resonance Spectra of Filled Rubber

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Received June 15, 1972

ABSTRACT: Line narrowing by a factor of 3–4 has been achieved in the ^{13}C nmr spectra of a carbon-black-filled, vulcanized *cis*-polyisoprene by 1-kHz sample rotation at the magic angle. The narrowing permits the resolution of a new methylene-carbon line not present in the spectrum of an unfilled, nonvulcanized, otherwise comparable *cis*-polyisoprene.

An analysis of the ^{13}C nmr spectra of carbon-black-filled *cis*-polyisoprene, $+\!CH_2CCH_3{=}CHCH_2\!+_x$, has indicated that the line broadening of the filled polymer relative to the unfilled polymer can be attributed to incomplete motional narrowing of the nmr lines.[2] By this analysis the broadening results from low-frequency motion, described by long correlation times, associated with the residual dipole remaining from an incomplete spatial average. When line broadening is due to dipolar interactions with long correlation times, it is reasonable to expect that line narrowing can be achieved by any of several techniques including multiple-pulse schemes,[3,4] high-speed sample rotation[5] at the "magic angle," or strong decoupling (double resonance) experiments.[6] We have, in fact, achieved substantial line narrowing in the ^{13}C nmr spectra of carbon-black-filled *cis*-polyisoprene by use of magic-angle spinning.

Experiments under magic-angle conditions were performed on a solid, 60-pph HAF carbon-black-filled, sulfur-vulcanized,

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(1) (a) Monsanto Co.; (b) Washington University.

(2) J. Schaefer, *Macromolecules*, **5,** 427 (1972).

(3) (a) See, for example, U. Haeberlen and J. S. Waugh, *Phys. Rev.*, 185, 420 (1969); (b) J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.*, **48,** 662 (1968).

(4) P. Mansfield, *Progr. Nucl. Magn. Resonance Spectrosc.*, **8,** 41 (1971).

(5) E. R. Andrew, *ibid.*, **8,** 1 (1971).

(6) F. Bloch, *Phys. Rev.*, **111,** 841 (1958).