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HYDROTHERMAL STABILITY OF γ -AMINOPROPYLTRIETHOXYSILANE
COUPLING AGENT ON GROUND SILICON POWDER AND E-GLASS FIBERS

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ABSTRACT

Diffuse reflectance Fourier transform infrared spectroscopy (Drift) was used to study the hydrothermal stability of silane coupling agents on the surface of E-glass fibers and ground silicon powder. The coupling agent studied was γ -aminopropyltriethoxysilane (γ -APS). The concepts of chemisorbed and physisorbed silane coupling agent were explored using the Drift infrared technique. The ground silicon powder was used to model the E-glass fiber/coupling agent system. Using the silicon powder, the structure of the siloxane (Si-O-Si) region of the infrared spectrum (1150 to 1000/cm⁻¹) could be investigated. Water was used to remove the physisorbed coupling agent from the substrate. The amount of chemisorbed silane was found to vary slightly as a function of the coupling agent concentration, heat treatment, pH of the coupling agent on the substrate, and the temperature of the water used to remove the physisorbed coupling agent. Spectroscopic evidence was found for chemical bonding of the chemisorbed silane coupling agents to the surface of the substrate used.



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INTRODUCTION

Organofunctional coupling agents are known to improve the mechanical properties [1-3] of composite materials. Much work has been done in an attempt to understand the mechanism by which silane coupling agents function in composite materials. Attainment of hydrothermal stability of fiber reinforced polymer composites has long been sought, as it is one of the major reasons cited for failure of the mechanical and physical properties of composites. In general, it is believed the water attacks the reinforced composite at the glass/coupling agent interface by hydrolyzing the silane coupling agent bonds. However, the mechanism for this proposed hydrolytic degradation is not known because it has been impossible to detect the structural changes which occur on the glass surface. An overview of the past relevant work can be found in the work by Ishida et al. [4] which is summarized below.

Schrader et al. [5] and Johannson et al. [6] were the first to propose the concepts of chemisorbed and physisorbed silane coupling agents on a glass surface. Based on a desorption curve Schrader [7] was able to quantify the amount of coupling agent removed by a water wash using a radioisotope labeled γ -APS. The physisorbed silane coupling agent was defined as the multiple layers of coupling agent which are not interacting with the glass surface and were easily removed by solvent washing. Two layers of chemisorbed silane were defined. One was removed by boiling water, the other was found to be a monolayer or less and was not removed by exposure to hot water. These results suggest that structural differences must exist between the physisorbed and chemisorbed silane coupling agent.

agent to the surface of the mineral fillers at submonolayer quantities of γ -MPS. They were also able to monitor the structural changes in the Si-O-Si region of the spectrum using these systems.

EXPERIMENTAL

The coupling agent used in this study, γ -aminopropyltriethoxysilane (γ -APS), was purchased from Petrarch Systems, Inc. The γ -APS was used as received without further purification.

The silicon plates (49.5 by 6.5 mm) used in this study were purchased from Wilks Infrared Accessories Inc. These silicon plates were ground into a fine powder using a Wig-L-Bug for two minutes. The silicon powder was oxidized by heating at 200°C for one hour in an air oven. Using sieves, the range of particle sizes produced were determined to be between 74 μm and 200 μm .

The γ -APS coupling agent was hydrolyzed in deionized distilled water for 30 minutes. The concentration range of 0.005% to 5% by weight of coupling agent solution was studied. Silicon powder (0.55 grams) was added to a test tube. Five milliliters of hydrolyzed coupling agent was then added and mixed with a stirring rod. The coupling agent was allowed to interact with the silicon powder for 3 minutes. After 3 minutes, the mixture was centrifuged for one minute and decanted. The treated silicon powder was allowed to air dry until analysed.

The FTS-20E Digilab FT-IR Spectrophotometer purged with nitrogen gas was employed to collect the infrared spectra using a narrow band pass mercury cadmium telluride (MCT) detector. A Digilab diffuse reflectance cell (Digilab DRA-100) with 2 hemispherical mirrors collected the diffuse reflectance spectra. The silicon

Belton et al. [8] studied the hydrothermal stability of γ -APS on silicon wafers using Auger Spectroscopy and Ellipsometry. They found that the γ -APS was etched from the surface very rapidly by a NaOH solution. The rate varied inversely with the concentration. This result was attributed to an increase in the crosslink density nearer to the surface. Belton also proposed that the amine groups may be interacting with the surface. Little FT-IR work has been done in this area although, because the specific absorptivity is very low for γ -APS. Ishida et al. [4] are one of few who have studied the hydrothermal stability of γ -MPS. They propose a three layer model for the deposited silane coupling agent similar to that described above by Schrader et al. [7].

The Drift technique as demonstrated by Maulhart [9] in a study of γ -MPS on glass fibers and Ishida et al. [10] in a study of γ -MPS on particulate fillers seems ideally suited to study such surface reactions because it will yield the desired molecular structure information. The basic principle behind the Drift technique is that light incident upon a solid or powdered surface will be diffusely scattered in all directions. The scattered light is collected with the proper optical set up and directed to the IR detector for analysis. The general theory which describes the diffuse reflectance process for powdered samples was developed by Kubelka and Munk (K-M theory) [11,12] and updated by Fuller et al. [13]. This theory relates the sample concentration to the scattered radiation intensity. Recently Ishida et al. [10] used the Drift technique to study γ -MPS on a number of filler surfaces. They were able to detect hydrogen bonding of the carbonyl groups of the coupling

powder was analysed neat. KBr powder was used as the reference material so that the K-M reflectance plot could be produced. All spectra were recorded in the single beam mode. Two hundred scans of the sample and reference were taken. All spectra were recorded in the K-M mode with double precision at a resolution of 2 cm^{-1} . The frequency was calibrated to an accuracy of better than 0.01 cm^{-1} with an internal helium-neon laser. All subtractions were made using a linear least squares program which yields a scaling coefficient. This coefficient was used to perform the actual subtractions.

For the pH study, after the γ -APS was added to the distilled water, the coupling agent solution was adjusted to the desired pH by adding HCl or NaOH solutions. The total hydrolysis time was 30 minutes.

For the heating studies, all samples were heated in an air convection oven. Distilled deionized water was used to remove the physisorbed silane coupling agent. The water washings were performed by soaking the samples with water in a test tube. After washing, the samples were removed and dried in air.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of oxidized silicon powder and the results of depositing various solution concentrations of γ -APS on silicon powder. The most interesting feature of the oxidized silicon powder is the band at 3744 cm^{-1} which is due to the free Si-OH groups of the surface oxide layers. This free Si-OH band serves as a molecular probe which can be used to monitor when more than an effective monolayer coverage by the coupling agent of the oxidized silicon has occurred. It is known that the amount of coupling agent

adsorbed on a substrate is dependent upon the treating solution concentration [14]. The remainder of the Drift spectra in Figure 1 are not subtracted to show that the amount of γ -APS deposited on the silicon powder depends on the solution concentration. At very low concentrations (0.1% and below) less than a monolayer of γ -APS is deposited as evidenced by the presence of the band at 3744 cm^{-1} . However, above 1.0% solution concentration more than a monolayer of γ -APS is deposited. The bands at 3600 to 2800 cm^{-1} are due to the CH, NH_2 , and intermolecularly hydrogen bonded Si-O groups and the bands from 1640 to 1300 cm^{-1} are characteristic of γ -APS [15,16]. Therefore at solution concentrations of about 0.2% and below submonolayer coverage is achieved. At higher concentrations multilayers formed. Presently submonolayers of γ -APS on E-glass fibers can be studied only from 3800 to 1500 cm^{-1} . But with the oxidized silicon powder and Drift, one has sufficient surface sensitivity to study submonolayer amounts of γ -APS from 3800 to 700 cm^{-1} on powdered samples.

The silicon powder was not diluted with KBr for the Drift experiment. Figure 2 shows the calibration curve for γ -APS deposited on silicon powder. The normalized area of the CH stretching region is plotted against the solution concentration of γ -APS. The fit is good and follows the expected behavior [17]. That is, the curve does not pass through zero because the γ -APS molecules are separated in solution at low concentrations and are not adsorbed onto the substrate at the same rate as when more concentrated solutions are used and the γ -APS molecules are in the form of small oligomers. It is very impor-

tant to note that most of this study is done on the adsorption of γ -APS oligomers from solution onto a substrate. The results of Figure 2 indicate that the use of neat powdered samples follow the K-M theory in a linear manner. A very similar plot was obtained for the E-glass fiber system with slightly more scatter in the data. The results indicate that about 3 times as much γ -APS was deposited on E-glass fibers at each concentration compared to the silicon powder indicating differences in surface area and topology.

With the monolayer sensitivity of the Drift technique the spectral differences between "chemisorbed" and "physisorbed" γ -APS silane was studied [18]. To summarize: 1) the Si-O-Si region is different, suggesting that the network structure of the polymer may change as a function of the solution concentration; 2) the effects of the bicarbonate salt are drastically reduced (1650 to 1300 cm^{-1}); 3) the amine deformation bands shifted to higher frequencies which indicates hydrogen bonding of the NH_2 groups which may be due to surface interactions; and 4) the NH_2 stretching bands shift to lower frequencies which indicates hydrogen bonding of the amine groups.

The CH stretching region of the spectrum was used to monitor the amount of γ -APS removed by the water washings. Figure 3 shows the results of exposing various concentrations of γ -APS on silicon powder to water at 70°C for 3 hours. This series of spectra show that all of the multilayers of γ -APS are removed by a warm water wash after 3 hours. Some of the γ -APS was removed from the 0.1% samples also as evidenced by the presence of the Si-OH band at

3744 cm^{-1} . It can also be seen that the amount of γ -APS washed off, depends on the amount deposited. Therefore, these spectra yield a qualitative method to quickly see the effects of the water washings. Figure 4 shows the subtraction spectra of 5% γ -APS exposed to water for 3 hours at 70°C. The bands in the NH deformation region are shifted slightly further upfield compared to the spectrum of 0.1% γ -APS, suggesting hydrogen bonding to the surface. This would explain the reduction in the number of amine groups reacting with CO_2 at low solution concentrations as previously reported by Culler et al. [16].

Table 1 shows results of exposing samples of γ -APS on silicon powder at various concentrations to different water treatments. The values listed are the percent of the γ -APS silane coupling agent retained on the silicon surface, those molecules not removed by the water washings. The difference from this listed value and 100% would be the amount of physisorbed γ -APS, coupling agent removed by the water washings. The general trend for the air dried γ -APS samples is: 1) the percent retention of the chemisorbed γ -APS is much greater at loadings that produce less than a monolayer coverage of the surface; 2) the amount of γ -APS removed from the surface of the oxidized silicon depends on the temperature of the water and the length of time the sample was exposed to the water; and 3) at less than monolayer loadings the amount of γ -APS removed is significantly reduced indicating that these silane molecules are very strongly bound to the surface oxides. Examination of the spectra (Figure 3) indicates

that the coupling agent is removed to less than a monolayer coverage by exposing it to water at 70°C for 3 hours.

In the next experiment, the γ -APS on silicon powder was heated in air for one hour to further condense the Si-OH groups to Si-O-Si linkages. The results are shown in Table 2. The results indicate that at low concentrations (below 1%) more of the coupling agent is converted to chemisorbed silane. Only slight differences are seen at higher loadings. In general, heating appears only to affect the layers which are very close to the surface in terms of hydrothermal stability. Again, the three hours exposure to warm water of heated samples of γ -APS on silicon removed the coupling agent to less than a monolayer coverage regardless of the initial treating concentrations.

It is known that the structure of the adsorbed coupling agent can be changed by changing the pH of the treating solution [15,16]. The results of exposing different pH samples, treated from 2% by weight solution, to water at two temperatures are shown in Table 3. The results indicate that the only hydrothermal stability achieved was at the high pH's of 11.5 and above. The natural pH of γ -APS is 10.6 in distilled deionized water. Because the samples were treated from 2% solutions, multilayers of γ -APS were adsorbed on the silicon substrate at all pH's except those above 12. At the high pH's the Si-OH groups would be in the Si-O^- form which is not a favorable form to bond to the silicon surface or to associate in solution. This provides an explanation for the low absorption of γ -APS at high pH values. Since less than a monolayer was deposited on the silicon

powder, the amount of coupling agent removed by the water washings is significantly less than when multilayers are deposited. These results further emphasize the findings that the maximum hydrothermal stability is achieved when hydrolyzed silane monomers are deposited from solution. When oligomers are deposited, multilayer formation occurs and the hydrothermal stability is greatly reduced. When oligomers are deposited, the availability and reactivity of the Si-OH groups are greatly restricted.

Similar experiments were performed on an E-glass fiber substrate. The results of heating γ -APS on E-glass fibers prior to exposure to 20°C water for 10 hours are shown in Table 4. It is seen that at higher concentrations, above 1.0%, most of the coupling agent is physisorbed. Heating the samples prior to exposing them to water increases the amount of chemisorbed γ -APS on the E-glass fibers also. The most dramatic effects are seen in the low concentration samples where the amount of physisorbed silane initially deposited is less. The results of varying the pH of the treating solution for E-glass fibers are shown in Table 5. These results indicate that little hydrothermal stability is achieved by varying the pH of the treating solution at 2% by weight. This indicates that more γ -APS is deposited at higher pH's on E-glass mats than on oxidized silicon powder since only a slight increase is observed at pH 12 on E-glass mats. It also shows that more coupling agent is removed with warmer water washings compared to room temperature water washings although both appear to be very effective at removing the physisorbed γ -APS.

The results of heating the γ -APS at different temperatures and exposing the sample to water for 3 hours at 70°C are shown in Table 6. The same general trend, that heating increases the amount of γ -APS in the chemisorbed layers is seen. A comparison of the results in Table 4 with Table 6 indicates that approximately the same amount of coupling agent is removed with the two different water washings. Heating the samples to 120°C for 1 hour yields the most hydrothermal stability.

CONCLUSIONS

The Drift technique has sufficient surface sensitivity to study submonolayer quantities of γ -APS adsorbed on silicon powder and E-glass fibers. The silicon powder is a good model for the E-glass fiber system. With the sensitivity of Drift one can study the effects of exposing the coupling agent samples to different water treatments. There is a direct correlation between the solution concentration and multilayer formation which is controlled by the degree of oligomerization of the γ -APS molecules in solution. The results indicate that when multilayers are deposited some of them are easily removed by water (physisorbed), whereas layers near the surface are not (chemisorbed). Heat treatment of the γ -APS/substrate prior to exposure to water increased the percentage of chemisorbed silane. The pH of the silane treating solution imparted better hydrothermal stability only at pH's greater than 11. Water easily removed physisorbed layers, revealing the hydrogen bonded amine groups and the reduced amount of CO₂ reaction near the surface. These results suggest that the chemi-

sorbed γ -APS is bound to the surface through Si-O-Si linkages and that the amine groups are also interacting with the surface. These results support the multiple layer theory for coupling agent adsorption as proposed by Schrader and Ishida.

ACKNOWLEDGEMENTS

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Figure 2) Calibration of Drift technique for γ -APS on silicon powder. The normalized area of the CH stretching region is plotted against the treating solution concentration.

Figure 3) Unsubtracted Drift spectra of γ -APS on silicon powder exposed to water for 3 hours at 70 C as a function of treating solution concentration.

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Table 5) The results of varying the pH of the γ -APS treating solution on the hydrothermal stability of γ -APS on E-glass fibers.

Table 6) The results of varying the heat treatment of γ -APS on the hydrothermal stability of γ -APS on E-glass fibers.

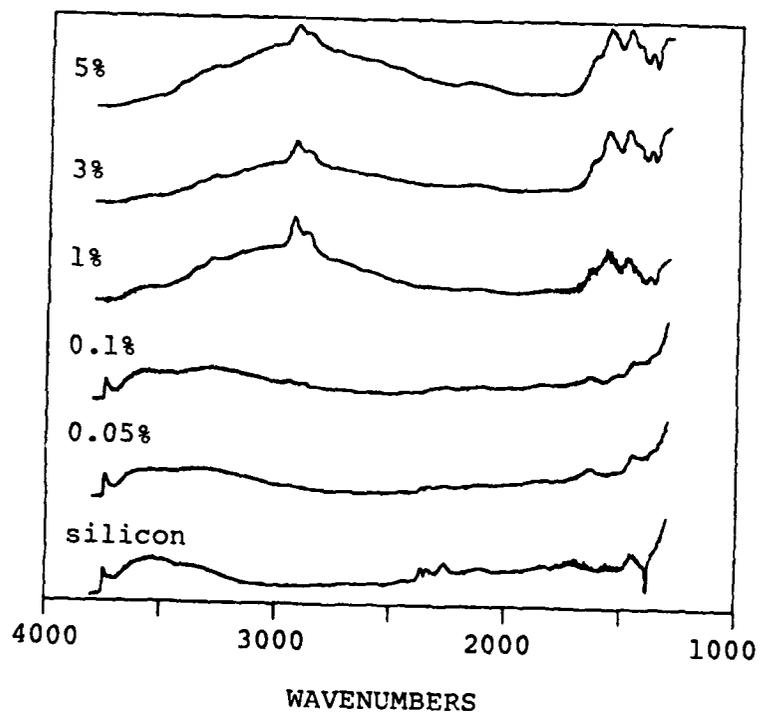


Figure 1

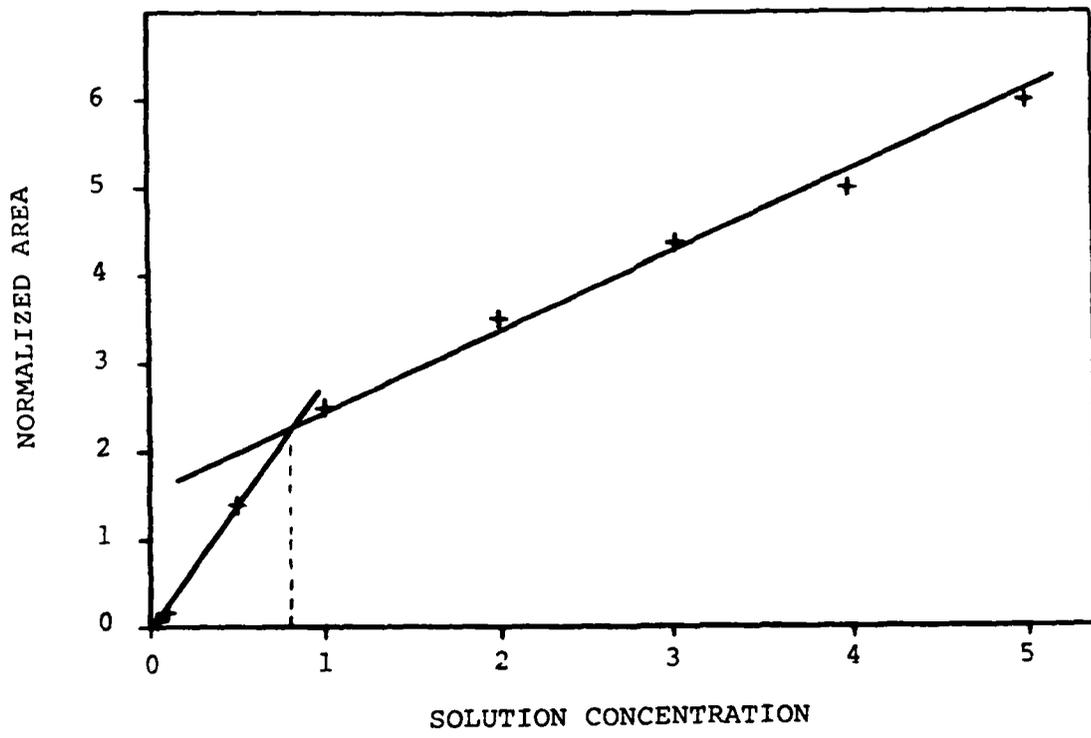


Figure 2

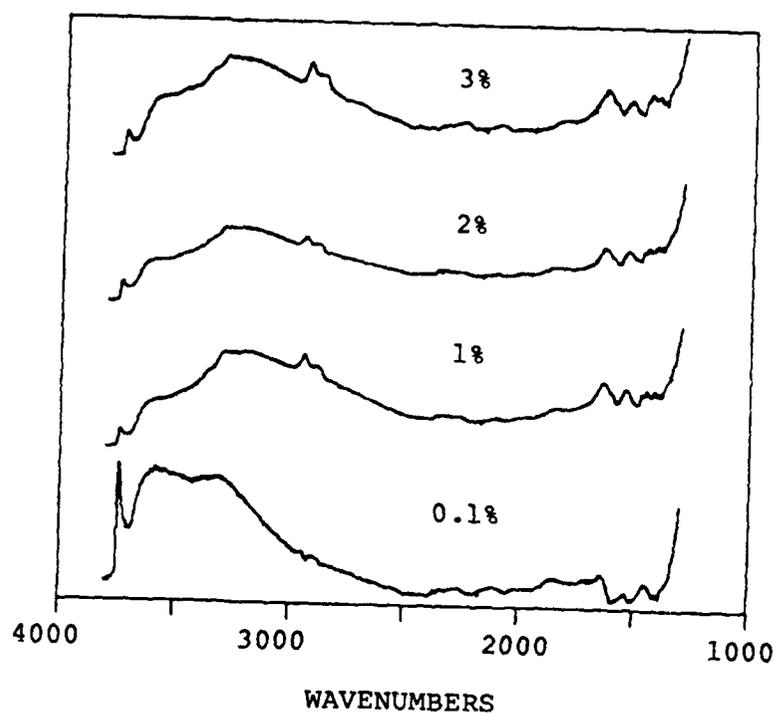


Figure 3

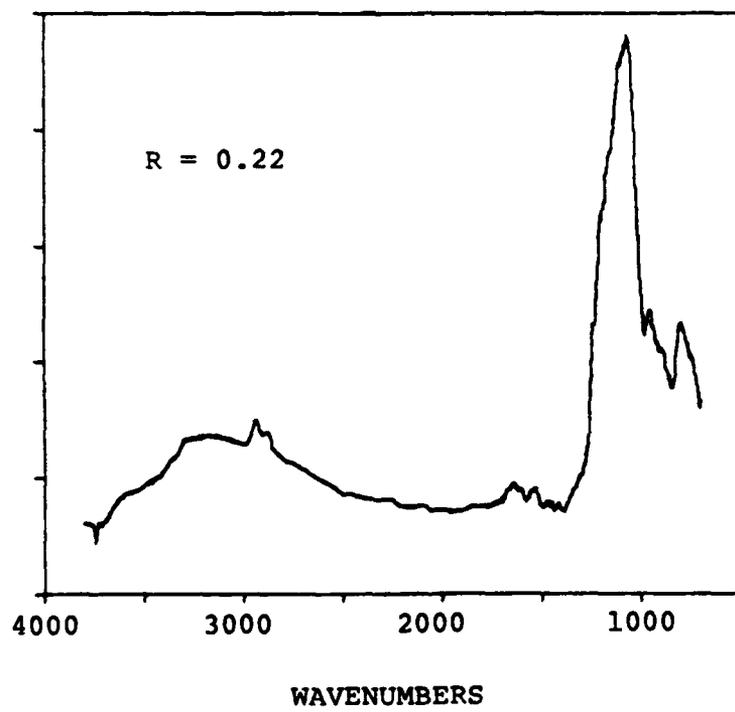


Figure 4

SOLUTION CONCENTRATION	% γ -APS RETAINED WATER WASHED 10 HRS. AT 20 C	% γ -APS RETAINED WATER WASHED 20 HRS. AT 20 C	% γ -APS RETAINED WATER WASHED 3 HRS. AT 70 C
0.005%	90%	81%	75%
0.05%	90%	84%	72%
0.5%	43%	20%	32%
1.0%	38%	35%	25%
4.0%	41%	27%	12%
5.0%	32%	18%	8%

Table 1

SOLUTION CONCENTRATION	% γ -APS RETAINED HEATED 120 C FOR 1 HR. WATER WASHED 3 HRS. AT 70 C	NUMBER OF EQUIVALENT MONOLAYERS
0.005%	90%	0.1
0.05%	90%	0.3
0.1%	54%	0.4
0.5%	40%	0.9
1.0%	26%	0.8
2.0%	10%	0.1
3.0%	14%	1
4.0%	20%	1
5.0%	12%	1

Table 2

PH	2 7-APS RETAINED	2 7-APS RETAINED
	WATER WASHED 23 C FOR 15 HRS.	WATER WASHED 70 C FOR 3 HRS.
1.0	—	82
3.0	72	72
7.0	72	62
8.0	152	82
9.0	142	112
10.0	—	162
11.5	—	602
12.0	592	442
13.0	612	—

Table 3

SOLUTION CONCENTRATION	% γ -APS RETAINED NO HEAT WATER WASHED 20 C FOR 10 HRS.	% γ -APS RETAINED HEATED 80 C FOR 1 HR. WATER WASHED 20 C FOR 10 HRS.	% γ -APS RETAINED HEATED 120 C FOR 1 HR. WATER WASHED 20 C FOR 10 HRS.
0.05%	48%	84%	87%
0.5%	50%	50%	90%
1.0%	2%	4%	12%
4.0%	1%	1%	3%
5.0%	1%	1%	5%

Table 4

PH	% γ -APS RETAINED WATER WASHED 20 C FOR 10 HRS.	% γ -APS RETAINED WATER WASHED 70 C FOR 3 HRS.
3.0	6%	4%
8.0	9%	7%
10.0	6%	3%
12.0	14%	10%

Table 5

SOLUTION CONCENTRATION	S 7-APS RETAINED NO HEAT WATER WASHED 70 C FOR 3 HRS.	S 7-APS RETAINED HEATED 60 C 1HR. WATER WASHED 70 C FOR 3 HRS.	S 7-APS RETAINED HEATED 120 C 1HR. WATER WASHED 70 C FOR 3 HRS.
0.05%	95%	—	95%
0.1%	75%	85%	95%
1.0%	25%	35%	65%
4.0%	25%	25%	65%
5.0%	65%	65%	25%

Table 6

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