

# Ionic Conduction in Sol-Gel Overcoats for Organic Photoreceptors

W. T. Ferrar

NexPress Solutions LLC, Rochester, New York

D. S. Weiss,<sup>▲</sup> J. R. Cowdery, and L. G. Parton

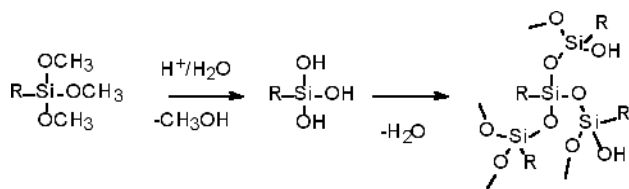
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Silsesquioxanes are a class of silicone polymers that are useful as abrasion resistant overcoats for organic photoreceptors. We have manipulated the electrical properties of this sol-gel matrix by incorporating a solid electrolyte. Solid electrolytes, also referred to as solid ionic conductors, are materials in which electrical conductivity is provided by the motion of ions. We chose (3-glycidoxypropyl)trimethoxysilane (GPS) as the most suitable commercially available monomer to form the polymer matrix for lithium iodide migration. This epoxy silane contains two ether oxygen atoms for coordination to low lattice energy salts. A good correlation was observed between the level of GPS and the electrical properties of the coating, with increasing concentration of GPS in the silsesquioxane resulting in decreased resistivity. The silsesquioxane is a hard material and the resistivity remained relatively high, between  $10^{10}$ – $10^{13}$  ohm-cm. However, this is a desirable resistivity for maintaining image quality with an overcoated photoreceptor.

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## Introduction

Silsesquioxanes are a class of silicone polymers that are useful as abrasion resistant overcoats for organic polymers.<sup>1</sup> In general, these overcoats are between 1.0 and 10 microns thick and are coated from aqueous alcohols. They are usually prepared by the hydrolysis and condensation of methyltrimethoxysilane (Scheme 1, R =  $-\text{CH}_3$ ) to form solgels.<sup>2</sup> Previous workers have modified the silsesquioxanes by adding charge carriers such as ammonium salts. These modified materials are useful as abrasion resistant overcoats for organic photoreceptors.<sup>3,4</sup>



We have previously reported improvements in silsesquioxane overcoats for organic photoreceptors. Propyltrimethoxysilane was introduced to make a more flexible sol-gel, and glycidoxypropyl substituted silane was used to complex with lithium iodide to lower the resistivity.<sup>5</sup> Aminosilanes were used as catalysts to cure the silsesquioxane. Characterizations included cross-

linking, hardness, brittleness, scratch resistance, surface conductivity, bulk conductivity, and chemical permeability.

Here we discuss two series of silsesquioxanes where increasing levels of (3-glycidoxypropyl)trimethoxysilane (GPS) were added to reduce the resistivity. The effect of a resistive sol-gel when used as a photoreceptor overcoat is that a residual potential is observed on corona charging followed by light exposure. We have used the magnitude of the residual potential as a means of monitoring the sol-gel resistivity. One series was made from 85-90 wt % methyltrimethoxysilane (MTMS) and was coated on a negatively charging film. The other series had 60 wt % propyltrimethoxysilane (PrTMS) and was overcoated on a positively charging film.

## Background

Early patents, primarily from Schank at Xerox, describe the application of crosslinked siloxanol and colloidal silica to form silsesquioxane overcoated photoreceptors.<sup>6</sup> These abrasion resistant layers had been developed by Dow Corning and General Electric to protect polyester and polycarbonate lenses from scratching.<sup>7</sup> Subsequent work at Xerox showed that ammonium salts bound to the silsesquioxane matrix provided a means to control the conductivity of the overcoat.<sup>8</sup> This was followed by the introduction of substituted silanes bearing electronegative moieties as conductive substituents.<sup>9</sup> The increased conductivity allowed the use of thicker silsesquioxane layers without the build up of residual charge on the photoreceptor in the electrophotographic process.

We found it difficult to adjust the charge in a silsesquioxane matrix by adding ammonium salts because they also act as catalysts for the condensation of

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<sup>▲</sup> IS&T Member

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silanols. The addition of ammonium salts not only increased the conductivity of the overcoat, but also increased the cure of the material. There is a strong relationship between the material properties of the silsesquioxane layer such as brittleness and the amount of cure. Therefore, we sought to develop a silsesquioxane where the conductivity and the cure could be controlled independently. This was accomplished with a silsesquioxane where the conductivity is based on solid electrolyte chemistry.

Solid electrolytes have been prepared by modifying GPS with ethylene oxide moieties.<sup>10</sup> The epoxy groups of GPS and ethylene glycol diglycidioxy ether were copolymerized along with 3-(methacryloxypropyl)trimethoxysilane and LiClO<sub>4</sub>. Ionic conduction is facilitated by competitive cation binding with ether oxygens. This results in increased ion diffusion and increased conductivities,  $\sigma$  approaching 10<sup>-5</sup> ohm<sup>-1</sup> cm<sup>-1</sup>. The sol-gel reaction, of hydrolysis and condensation of the alkoxy silane, results in an inorganic-organic copolymer. These ORMOCERs (ORganically MODified CERamics) have been proposed as mini-batteries, rechargeable systems and electrochromic windows. Specialized lithium conductive ORMOSILs (ORganically MODified SILicates) known as AMINOSILs use aminosilanes to form conductive electrodes where the cation is the protonated amino group and the anion moves through the matrix to carry the charge.<sup>11</sup>

We combined alkylsilanes to control the mechanical properties of the coating, glycidoxysilanes to complex low lattice energy salts such as lithium iodide to control conductivity, and aminosilane to control the level of cure of the material. The mechanism for the transport of a salt through a hard, high  $T_g$  matrix of the silsesquioxane is not clear. Solid electrolytes of amorphous polymers are usually based on segmental motion of a flexible matrix. The high field across the photoreceptor may be responsible for the ion migration in the overcoat.

Previous studies used similar sol-gel chemistry to form photoreceptor overcoats, but did not add salt or any other catalyst that could dissociate in the polymer network to carry the charge.<sup>12</sup> The absence of salt minimized image spread at high humidity, but limited the protective layer to less than two microns.

## Experimental

Two series of sol-gels were prepared with varying levels of GPS. Methylsilsesquioxanes had GPS increasing from 10 to 12.5 to 15 wt %, with a corresponding decrease in the MTMS content. Dialkoxysilanes were also added at the same level to each. 3-Aminopropyltrimethoxysilane (APTMS) was added to the "methyl" sol-gels at 4.0 wt % to achieve a consistent cure. Two levels of LiI were examined as the mobile charge carrier at 1.5 and 0.75 wt %. The "propyl" sol-gel consisted of 60 wt % PrTMS, a GPS concentration range of 5 to 10 to 20 wt %, with the balance in methylsilane MTMS. Aminosilane APTMS 4.0 or 7.5 wt %, and 0.75 wt % LiI were then added. Syntheses of the silsesquioxanes were carried out by mixing the alkoxy silanes, followed by the dropwise addition of glacial acetic acid. Water was added dropwise at a level of 2 equivalents per alkoxy silane. The reaction was stirred for two days, and then diluted with an approximate equivalent amount of ethanol. The reactions were stirred for an additional 2 weeks before adding addenda: 1 wt % of low molecular weight poly(dimethylsiloxane) (PDMS) to act as a lubricant, lithium iodide, and 10 wt % of bis(4-

[N-ethyl-N-(2-hydroxyethyl)]anilino)diphenylmethane as an acid scavenger.

The photoreceptor is first overcoated with a thin (0.1-0.5 micron) primer layer, such as poly(methacrylate-co-methylmethacrylate-co-methacrylic acid). Sol-gel web coating was typically carried out at 10 ft/min with ramped heating (90 °C average). Post curing was at approximately 80 °C for 24 h. The thickness of the overcoat ranged between 1-5 microns.

The bulk conductivity of the overcoats was evaluated by measuring the residual potential after photo-discharge of the corona charged photoreceptor using two different techniques. Low intensity continuous exposure (LICE) characterization employs a corona to charge a photoreceptor sample that is then exposed to 1 erg/cm<sup>2</sup>sec of light at the wavelength of interest through a "transparent" electrostatic probe. The surface potential is continuously recorded before, during, and after exposure. The residual voltage was recorded 14 sec after initial exposure of the sample. Measurements at different relative humidities (RH) were carried out after the films were equilibrated for approximately 5 min.

Overcoated films were also evaluated for residual voltage after 2000 electrophotographic cycles at 50°C and 15% RH for the methylsilsesquioxane and 5000 cycles at 25°C and 30% RH for the propylsilsesquioxane. This regeneration sensitometry characterization is an electrical only test carried out on a belt drive apparatus fitted with a DC gridded corona charger, voltmeters, erase lamp, and a 160  $\mu$ sec Xenon flash lamp for exposing the film. Each revolution of the film takes 5 sec.

The conductivities of the overcoats were compared using a lateral image spread technique described previously.<sup>13</sup> The overcoated photoreceptor is corona charged and then exposed through a 2.5 mm slit to produce a "square well" surface potential pattern. The latent image shape is recorded by moving the photoreceptor past a high-resolution surface voltmeter probe. The image shape is measured as a function of time, where a greater change in image shape indicates higher overcoat conductivity.

## Results and Discussion

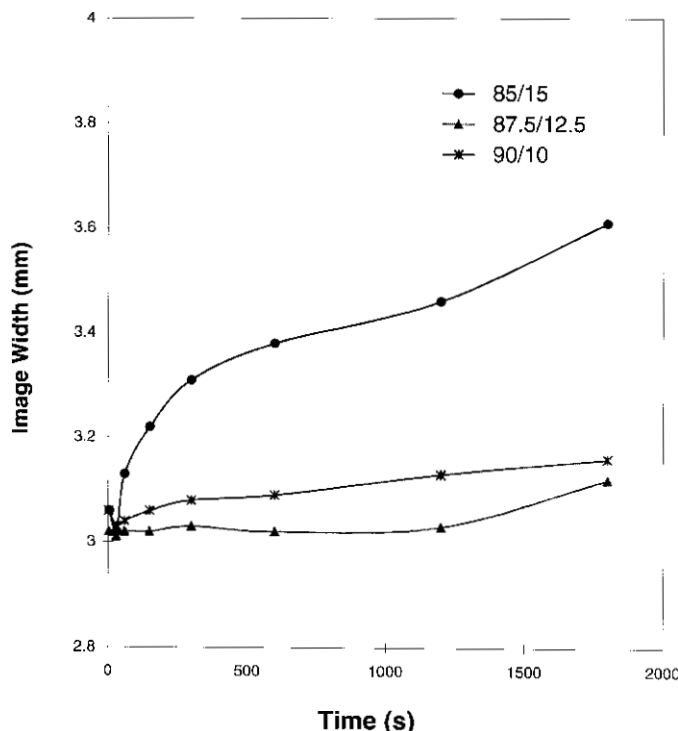
### Methylsilsesquioxanes

Abrasion resistant silsesquioxane overcoats are generally made from methylsilsesquioxanes because they give the highest degree of scratch resistance. We found that incorporating 10 to 15 wt % of GPS and 0.75 to 1.5 wt % of LiI produced a photoreceptor overcoat that was useful in electrophotographic applications. Results from measurements of the residual potential for three silsesquioxane overcoats with increasing GPS content are shown in Table I. The silsesquioxanes were 1 micron thick on a negative charging photoreceptor. Photosensitivity measurements were made at 39% and 5% RH using a low intensity continuous excitation (LICE) lamp exposure. The trends in the data indicate a lower residual voltage with increasing GPS content. A dependence on RH is also evident, indicating water plays a role in the charge migration. The contribution of the aminosilane to the conductivity should be constant in each sample. The lithium iodide content was the same in each sample at 1.5 wt %.

The capability of the abrasion resistant hard coats to dissipate charge with cycling was studied by placing the films through 2000 charge, expose, erase cycles. Three sol-gels with the same silane compositions, but with half

**TABLE I. Residual Voltage of Methylsilsesquioxane Overcoated Film (1.5 % LiI)**

| MTMS/GPS  | 39% RH (Vres) | 5% RH (Vres) |
|-----------|---------------|--------------|
| 90/10     | -22           | -28          |
| 87.5/12.5 | -20           | -34          |
| 85/15     | -15           | -22          |

**Figure 1.** Image spread of three methylsilsesquioxanes with varying levels of GPS on negative charging photoreceptors. (Ambient temperature, 51% RH)

the level of conductive salt, were prepared in the same way as those above. As shown in Table II, all of the overcoated films had a higher residual voltage than the film with no overcoat. However, the increase was greater for the overcoats with lower levels of GPS. This trend was observed in separate experiments using front and rear erase, although the effect was exaggerated when the photoreceptor was exposed with the erase lamp from the back of the film.

The experiments above suggested that the bulk conductivity of the overcoats increased along with the GPS content. We were also able to compare the surface conductivity of the three methylsilsesquioxane overcoats with a lateral image spreading techniques described previously.<sup>13</sup> The shape of a square well latent image is determined as a function of time, and a greater change in the latent image correlated to higher conductivity. The plots in Fig. 1 show that the 10 and 12.5 wt % GPS silsesquioxane overcoated photoreceptors exhibited little change in the image over the time of the experiment. This suggests that the surfaces of these two overcoats are similar to that of the photoreceptor with no overcoat, which yields a horizontal line under the same conditions. However the width of the latent image on the photoreceptor that was overcoated with 15 wt % GPS showed a greater increase with time, suggesting a higher degree of lateral image spread due to

**TABLE II. Residual Voltage of Methylsilsesquioxane Overcoated Film by Regeneration Sensitometry (0.75 % LiI)**

| MTMS/GPS    | Residual Voltage (V) |             |
|-------------|----------------------|-------------|
|             | Rear Erase           | Front Erase |
| 90/10       | 182                  | 50          |
| 87.5/12.5   | 175                  | 48          |
| 85/15       | 150                  | 45          |
| No overcoat | 140                  | 20          |

50°C; 15% RH

**TABLE III. Residual Voltage of Propylsilsesquioxane Overcoated Film by LICE (0.75 % LiI)**

| PrTMS/MTMS/GPS | 34% RH (Vres) | 0% RH (Vres) |
|----------------|---------------|--------------|
| 60/35/5        | 53.3          | 63.3         |
| 60/30/10       | 56.7          | 63.3         |
| 60/20/20       | 6.7           | 30.0         |

increased overcoat conductivity. All of the overcoats contained 0.75 wt % lithium iodide.

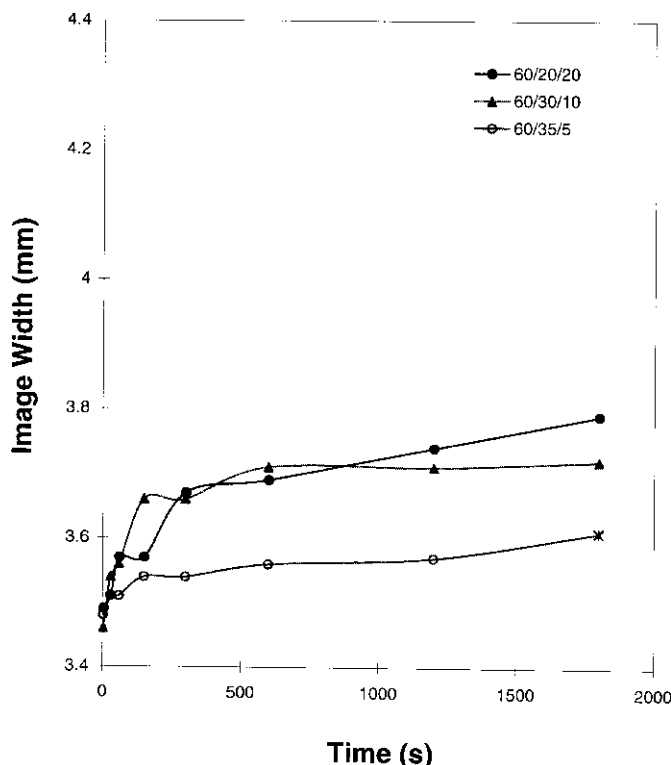
### Propylsilsesquioxanes

A less brittle silsesquioxane overcoat was prepared by formulating a sol-gel with higher organic content. PrTMS was incorporated at 60 wt %, and the balance was made from three variations in the ratio of methyl to glycidoxysilanes (MTMS/GPS). Because these coatings were less brittle and also not as scratch resistant, they were coated at 4 micron thickness. Also, the photo-receptor in this case was positive charging. Residual voltages obtained by single exposures of the charged films are given in Table III. Little difference was seen in the LICE measurements at 5 and 10 wt % GPS, but lower residual voltage was observed at 20 wt %. The resistivity of all three overcoats increases at 0% RH.

As with the methylsilsesquioxane overcoats, these trends in bulk conductivity were also observed by measuring the image spreading. The temporal change in latent image for the propylsilsesquioxanes is shown in Fig. 2. The image width of the propylsilsesquioxane with 5 wt % GPS changes very little with time indicating little overcoat conductivity. The 10 and 20 wt % GPS containing propylsilsesquioxanes have small changes in the image width that are most pronounced at the beginning of the experiment. The conductivity leading to image spread of these two is about the same, even though the 60/20/20 had a lower residual voltage than the 60/30/10 silsesquioxanes.

The 60/35/5 and 60/30/10 samples both had high residual voltages between 53 to 63 V at ambient and low RH. The residual voltage as measured by LICE was similar to those given in Table I when 20 wt % of the glycidoxysilane GPS was incorporated into the overcoat. The mechanical properties were similar for the three propylsilsesquioxanes. Thus, the electrical properties were adjusted by controlling the concentration of the GPS in the formulation, while the concentration of aminosilane APTMS impacted both the conductivity and the cure.

When preparing propylsilsesquioxanes for photoreceptor overcoats, we found that higher levels of the aminosilane content were desirable because these formulations were more difficult to cure than the methylsilsesquioxanes. The level of cure was determined with Solid State <sup>29</sup>Si Nuclear Magnetic Resonance



**Figure 2.** Image spread of three propylsilsesquioxanes with varying levels of GPS on positive charging photoreceptors. (Ambient temperature, 45% RH)

(NMR) spectroscopy, and reported elsewhere.<sup>14</sup> We found the propylsilsesquioxanes discussed above (Table III), that were made with same levels of aminosilane used in the methylsilsesquioxanes, had lower levels of siloxane bond formation and correspondingly poorer physical properties. Thus it was necessary to almost double the aminosilane concentration for the 'propyl' as compared to the 'methyl' sol-gel. The higher concentration of APTMS (7.5 wt %) produced a level of cure in the propylsilsesquioxane that was similar to that observed for the methylsilsesquioxane. Equal extents of siloxane formation as measured by NMR spectroscopy produced propylsilsesquioxanes that had similar abrasion resistance to the methylsilsesquioxanes. This increased quantity of amino substituent also resulted in higher levels of conductivity. In contrast to changing the level of aminosilane, varying amounts of the glycidoxysilane GPS between 0 to 20 wt % had a much smaller effect on the extent of cure and physical properties.

Table IV shows the regeneration residual voltage for the three propylsilsesquioxane films containing 4.0 wt % APTMS, and another 60/20/20 overcoated film containing 7.5 wt % APTMS. The residual voltage was measured after 5000 cycles at 25°C and 30% RH. Consistent with the static analysis by LICE, the photoreceptors with the overcoat that have only 5 and 10 wt % GPS show little discharge, while the 20 wt % GPS results in

**TABLE IV. Residual Voltage of Propylsilsesquioxane Overcoated Film by Regeneration Sensitometry (0.75 % LiI)**

| PrTMS/MTMS/GPS | Wt % APTMS | Residual Voltage (V) |
|----------------|------------|----------------------|
| 60/35/5        | 4.0        | 390                  |
| 60/30/10       | 4.0        | 390                  |
| 60/20/20       | 4.0        | 215                  |
| No overcoat    |            | 20                   |
| 60/20/20*      | 0.75       | 60                   |

\*5% Ludox Colloidal Silica  
25°C; 30% RH

a lower residual voltage. However, all three of these overcoats cause an unacceptable high residual voltage compared to the photoreceptor with no overcoat.

Improved electrical discharge, as well as improve the mechanical performance of the propylsilsesquioxane overcoat, was obtained when aminosilane content was increased to 7.5 wt % APTMS. This is evident in Table IV by the residual voltage of 60 volts obtained for the photoreceptor overcoated with the sol-gel that contained this higher level of aminosilane and 20 wt % GPS. This silsesquioxane overcoat with the lower residual voltage also contained 5 wt % of colloidal silica for improved mechanical properties.<sup>14</sup>

## Conclusions

Ionic conductivity can be introduced into a silsesquioxane abrasion resistant overcoat through the combination of a polar etheric substituent with a low lattice energy salt, such as lithium iodide. These addenda have only a small effect on the level of cure in the overcoat when compared to aminosilanes, that has a large effect on both conductivity and the cure. Thus, it is possible to partially separate the control of the electrical and mechanical properties of a silsesquioxane overcoat to allow for protection of the photoreceptor with minimal degradation of the electrophotographic image. ▲

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