

Silsesquioxane Sol-Gel Materials as Overcoats for Organic Photoreceptors

*D. S. Weiss, W. T. Ferrar, and R. Cowdery-Corvan
Office Imaging Division, Eastman Kodak Company,
Rochester, New York*

Abstract

Organic photoreceptors may be overcoated for many reasons among which are the desire to impart wear and scratch resistance, to protect the surface from corona generated chemicals, and to improve the efficiency of electrophotographic process steps, such as toner transfer and cleaning. In this paper we will discuss the use of silsesquioxanes prepared by the sol-gel process as photoreceptor overcoats. Included in our discussion will be the chemistry and procedures involved in overcoat fabrication, the physical and electrophotographic characterization of overcoated photoreceptors, and the effects of chemical structural variations on these characteristics.

Introduction

A typical organic photoreceptor is comprised of one or more doped polymer film layers on an aluminum drum or a flexible polymeric web (3–7 mil) with a conductive metal coating (Al, Cr, Ti, or Ni are common).¹ A two-layer architecture is used when a negative surface potential is desired. The charge generation layer (CGL) is adjacent to the conductive material and is generally a dispersion of light absorbing pigment particles in a polymeric binder (0.2–5 μm). On top of this is the charge transport layer (CTL) which comprises a solution of arylamine hole transport molecules (40–60 wt%) in a polymeric binder (15–30 μm). Both the CGL and CTL are prepared by solvent coating technologies such as dip or ring coating for drums and hopper coating for webs. For positive charging applications the positions of the CTL and CGL may be reversed. In the electrophotographic process the photoreceptor is subjected to a variety of physical and chemical abuses, which may determine its productive lifetime. The photoreceptor surface is relatively soft so that cleaning, whether by blade or brush, leads to surface scratching and abrasive wear. Unintended physical contacts of the surface with hard objects, for example during photoreceptor installation or with carrier-toner agglomerates or with objects which have fallen into the machine from the outside (paper clips and staples), may all result in catastrophic surface scratches requiring immediate photoreceptor replacement. The photoreceptor surface is also relatively permeable and its components reactive towards the ozone and nitrogen oxides generated by

corona chargers. Thus, after extended exposures to these agents the electrophotographic characteristics may degrade to the point where image defects become objectionable and the photoreceptor must be replaced. Because of these factors the lifetime limit of organic photoreceptors is on the order of hundreds of thousands of imaging cycles as contrasted with millions of imaging cycles obtained with the much harder amorphous silicon and arsenic triselenide photoreceptors. Thus, there have been extensive efforts over the years to make organic photoreceptors less susceptible to these undesirable effects. One approach has been to overcoat the photoreceptor surface with a tough, chemically impervious and inert, material. Many protective overcoats have been developed but relatively few have actually been commercialized. Some examples are, electrically insulating overcoats from organic or silicon-based² polymers, conducting overcoats from organic polymers doped with charge transport materials or semiconductive particles, very thin overcoats of refractory materials such as diamond-like carbon (Diamond 4 from HDS Inc.) or aluminum nitride,³ and insulating overcoats of inorganic glassy materials (Ultrasield from Optical Technologies Corp.⁴). In this paper we will discuss examples of the latter in which the overcoat is a silsesquioxane organosilicone polymer prepared by the sol-gel process. After discussion of the chemistry and method of preparation we will show how these materials can be used as photoreceptor overcoats.

Desirable Overcoat Characteristics

The physical, optical, and electrical characteristics of photoreceptor overcoats must satisfy the requirements of the electrophotographic process for which they are intended. The overcoat material must be coatable to form a uniform film without imperfections and the coating must be tough and hard to retard wear and scratches, yet not be so brittle that cracking occurs. Cracking is a particularly challenging requirement for web photoreceptors, which are continually flexed as the web cycles over small diameter rollers. The surface characteristics must be such that toner deposition, transfer, and cleaning (blade or brush) are satisfactory. Whereas many overcoat materials are chemically much different than the polyesters and polycarbonates used as photoreceptor binders, undesirable incompatibilities may occur with surface contacting process elements. The surface must also be highly insulating to avoid unwanted spreading

of the latent image charge⁵ as might occur from the accumulation of surface salts with liquid development,⁶ or corona generated chemicals.^{7,8} The bulk conductivity must also be very low to prevent latent image spreading. However, an overcoat with high bulk resistivity will also have a long time constant for dark discharge of the surface potential leading to an undesirable build up of a residual potential during cycling. Thus, the surface and bulk conductivity characteristics must be finely tuned and insensitive to the environment. The overcoat may also be required to protect the underlying photoreceptor from the chemical effects of corona generated nitrogen oxides⁹ and/or ozone,¹⁰ so it must not permit penetration of these chemicals.

The overcoat must also adhere strongly to the underlying photoreceptor. This is often accomplished with a thin intermediate adhesive layer. Optically, the overcoat should not absorb light from the exposing source, but it may be desirable that it absorbs other wavelengths (often ultraviolet) which could cause photofatigue.¹¹

Thus, a photoreceptor overcoat must increase the process life of the photoreceptor, while not having any detrimental interactions with the various electrophotographic subsystems.

Silsesquioxane Polymers

The name silsesquioxane refers to silicon-based polymers where the monomer unit has the structure $R-SiO_{3/2}$. The monomer structure may also be pictured as $R-Si(-O\sim)_3$ where the oxygens are bonded to the silicons of other monomer units to produce a highly crosslinked polymeric structure. The extent of crosslinking in each monomer unit is defined in terms of "Tx" where "x" is how many of the three $-OH$ units have been converted into $-O-Si-$.¹² This monomer unit structure differs from that of other common silicon based polymers such as silica $Si(O\sim)_2$, and polysiloxanes $R_2-Si(O\sim)_2$. The physical characteristics of polysilsesquioxanes are a combination of those of silica glass and organic polymers and as such are ideally suited for use as protective overcoats for photoreceptors.

Polysilsesquioxanes can be prepared by the sol-gel process¹³ in which highly crosslinked silicon glasses are produced at relatively low temperatures. In this process the precursor monomer, $R-Si(OH)_3$, is allowed to partially polymerize to produce a colloidal suspension or sol, which can be stored for subsequent use. In practice the monomer is typically produced in-situ by the hydrolysis of an alkyltrialkoxysilane, $R-Si(OR')_3$. When desired, the sol is further reacted to cause the silicon to undergo extensive crosslinking—the gel phase of the reaction. Gelation typically involves thermal curing. Silsesquioxane polymers prepared in this manner are sometimes called sol-gels.

The use of the sol-gel process to prepare hard thin polymeric overcoats in a low temperature process, stems from two key US patents: 3,986,997 (1976) H. A. Clark to Dow Corning Corp. and 4,277,287 (1978) R. B. Frye to the General Electric Corp. Principal applications are as abrasion resistant overcoats for plastic such as sunglass lenses.

The physical, chemical, and electrical characteristics of silsesquioxane polymers may be controlled in many ways. Some of these are: variation of the chemical structure of the R group, the incorporation of copolymers or polymer blends, the addition of filler particles which may or may not crosslink into the backbone, the addition of salts, variation of the cure conditions and catalyst to influence the extent of crosslinking, and by the overcoat thickness.

Silsesquioxane Overcoated Photoreceptors

Examples of silsesquioxane overcoated photoreceptors are mostly found in the patent literature. In an early Xerox patent¹⁴ Schank reported the use of Dow Corning Vestar Q9-6503 and General Electric SHP-1000 and 1010 in the fabrication of silsesquioxane overcoats of crosslinked siloxanol and colloidal silica. An acrylic polymer, General Electric SHP-200 was used to form an adhesive interlayer and ammonia gas was used as the condensation catalyst. Overcoat thicknesses less than 0.5 μm were difficult to apply and those $>5 \mu m$ had a tendency to crack and were difficult to cure. A follow-up patent¹⁵ suggested the incorporation of a small proportion (2–10%) of quaternary ammonium salts, $(RO)_3-Si-(CH_2)_3-NR_4^+ Cl^-$ monomer unit, to act as a catalyst and to increase the overcoat conductivity to allow for increased overcoat thickness. The preferred major component was $(RO)_3-Si-CH_3$ for maximum hardness and it was suggested that resins added as plasticizers and lubricants were beneficial. Further refinements¹⁶ were to incorporate monomer units where the $-Si-$ alkyl substituent contained an electron acceptor moiety such as nitrile or chlorine. In the absence of ammonia, typical curing conditions were 100–140°C. In another patent assigned to the Japan Atomic Energy Research Institute, Shindengen Electric Manufacturing Co., and Yamanashi Electronics Co.¹⁷ improvements were made to reduce the humidity sensitivity of the conductivity. The key feature was to incorporate component alkyltrialkoxysilane monomers such that neither acid or catalyst salts were necessary to effect crosslinking. A typical formulation consisted of adding water to a mixture of methyltrimethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and γ -aminopropyltri-ethoxysilane to effect the hydrolysis. A coating solution was made by the addition of excess ethanol. The solution was coated onto an organic photoreceptor and cured at 80°C for 1 hour.

In this report we describe the preparation and characterization of overcoated photoreceptors and show how chemical composition and physical structure affect their properties.

Results and Discussion

We have investigated Ultrashield (Optical Technologies Corp.) as well as our own formulation overcoats on Kodak photoreceptors. In the latter, the factors that were controlled were composition, cure conditions, and thickness. Many overcoat characteristics were measured as a function of these factors. Some of the measured characteristics and the methodologies are the following:

Crosslinking	^{29}Si NMR: T^2 (-60 ppm)/ T^3 (-70 ppm)
Hardness	nanindentation
Brittleness	ANSI wedge brittleness test
Scratch resistance	diamond stylus scratch with AFM imaging
Surface conductivity	electrostatic image spreading (RH dependence)
Bulk conductivity	electrophotographic residual potential (RH dependence)
Chemical permeability	corona gas exposure and electrical-only electrophotographic cycling (RH dependence)

Some representative compositional elements that we have investigated and the overcoat characteristics that are expected to be most affected are the following:

methyltrimethoxysilane	hardness and scratch resistance
propyltrimethoxysilane	“organic” character-plasticity
3-aminopropyltrimethoxysilane	extent of cure and bulk conductivity
3-glycidoxypropyltrimethoxysilane	crosslinking and bulk conductivity
lithium iodide	bulk conductivity

Other compositional elements such as lubricants, plasticizers, crosslinking agents, and organic or inorganic fillers also affect the overcoat characteristics.

A typical formulation procedure is as follows.¹⁸ Glacial acetic is added dropwise to the stirred mixture of substituted trialkoxysilanes (molar ratio of about 0.5). Hydrolysis is accomplished by the addition of water (approximately a twofold molar excess relative to the trialkoxysilanes). After stirring overnight the clear solution is diluted to approximately 20% solids with ethanol and the stirring continued for 1 week to accomplish partial crosslinking and sol formation. Just prior to coating other addenda such as fillers (if involved in crosslinking these can be added to the mixture prior to hydrolysis), lubricants, plasticizers, and/or salts are added.

The photoreceptor to be overcoated is typically previously overcoated with a thin (0.1–0.5 μm) primer layer, such as poly(methacrylate-co-methylmethacrylate-co-methacrylic acid). Web coating is typically carried out at 10 ft/min with ramped heating (approximately 90°C). Post-coating curing was typically at approximately 80°C for 24 hours. Overcoats are prepared in the range of 1–5 μm thickness and the resulting photoreceptor package evaluated as described above.

We have found that the following characteristics pertain to the silsesquioxane overcoat performance:

Extensive crosslinking (T^2/T^3 ratio of less than 1) maximizes hardness and scratch resistance and decreases the bulk conductivity and its RH dependence. Brittleness increases with increased crosslinking. The initial extent of crosslinking is related to the overcoat thickness and coating temperature (thicker coatings and higher temperatures increase crosslinking). Increased crosslinking is also related to a high methyl content, the presence of amines, and the

presence of glycidoxy substituents. Post coating cure has a minor effect on the extent of crosslinking, but is necessary for optimum performance.

Increased “organic” content helps to overcome the brittleness associated with a highly cured material having only methyl substituents. Hardness and scratch resistance are degraded with increasing organic content.

The inclusion of a salt (such as LiI at about 0.5–2.0 wt% of the silsesquioxane) in combination with a complexing agent to prevent surface “blooming” increases the bulk conductivity especially at low RH.

Decreasing the overcoat thickness reduces the electrophotographic residual potential.

The full report will give the details of these relationships.¹⁹

References

- Borsenberger, P. M. and Weiss, D. S., *Organic Photoreceptors for Xerography*, Marcel Dekker, Inc., NY, 1998).
- Kochelev, K. K., Zhylina, V. I., Khots, G. E., Kocheleva, O. K., and Sleptsov, V. V., IS&T's NIP12: International Conf. on Digital Printing Technol., 1996, p. 483.
- Miao, X. S., Chan, Y. C., Wong, C. K. H., Webb, D. P., Lam, W. W., Leung, K. M., and Chiu, D. S., *J. Electronic Materials* **26**, 387 (1997).
- Cornelius, L., R&R News, July, 1994, p. 34.
- Weiss, D. S., Cowdery, J. R., Ferrar, W. T., and Young, R. H., *J. Imaging Sci. and Technol.* **40**, 322(1996).
- Chen, I., Mort, J., Machonkin, M. A., and Larson, J. R., *J. Imaging Sci. and Technol.* **40**, 431(1996).
- Yarmchuck, E. J. and Keefe, G. E., *J. Appl. Phys.* **66**, 5435(1989).
- Kobayashi, T., Saito, T., Aratani, S., Suzuki, S., and Iwayanagi, T., *J. Imaging Sci. and Technol.* **39**, 485(1995).
- Weiss, D. S., *J. Imag. Sci.* **34**, 132(1990).
- Takenouchi, S., Hirano, A., Yoshioka, H., Jujimaki, Y., and Moriguchi, H., Proceedings of the Fourth International Congress on Advances in Non-Impact Printing Technologies (A. Jaffee, Ed.), SPSE, Springfield, Va., 1988, p. 22.
- Ref. 1, page 639.
- Glaser, R. H., Wilkes, G. L., and Bronnimann, C. E., *J. Non-Crystalline Solids* **113**, 73(1989).
- Hench, L. L. and West, J. K., *Chem. Rev.* **90**, 33(1990).
- Schank, R. L., U. S. Patent 4,439,509 (1984).
- Schank, R. L., U. S. Patent 4,595,602 (1986).
- Schank, R. L., U. S. Patent 4,923,775 (1990).
- Kumakura, M., Kaetsu, I., Horigome, M., Isomura, T., Yomeyama, T., and Murata, T., U. S. Patent 4,912,000 (1990).
- Ferrar, W. T., Cowdery-Corvan, J. R., Miskinis, E. T., Newell, C., Rimai, D. S., Sorriero, L. J., Sinicropi, J. A., Weiss, D. S., and Zumbulyadis, N., U. S. Patent 5,731,117 (1998).
- Weiss, D. S., Ferrar, W. T., Cowdery-Corvan, J. R., Parton, L., and Miller, G., *J. Imaging Sci. and Technol.* to be submitted.

Biography

David S. Weiss is a Research Associate at Eastman Kodak Company. He received his BS in Chemistry from Lehigh University in 1965 and his Ph.D. in Chemistry from Columbia University in 1969. His interests are in

photoreceptor technology and in the photochemistry and photophysics of photoactive materials. He is an Associate Editor of the Journal of Imaging Science and Technology (since 1988) and is currently Past Chair of the Rochester Section of the American Chemical Society.

email: dweiss@kodak.com