Silica Sol/Gel Based Nano Structured Hard Coats for Organic Photoconductors

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Abstract

Objective of the present investigation was the development of a scratch resistant and anti-abrasion layer for organic photo-conductors which does not influence the electrophotographic properties like charge transporting properties and print quality A new class of hybrid polymers based on classical sol/gel materials has been developed.This two component material with covalently bonded functionalized silica nano particles in an epoxy matrix made of poly-functional epoxy components produces closed networks and exhibits excellent durability against liquid toner materials.By employing this material as a top coat on OPC drums, hardness and scratch resistance can be improved without having significant impact on printing properties such as the replication of single dots in high resolution digital printing.

Introduction

The worldwide demand of laser printers is expected to increase steadily over the next years.
The market is driven by high growth rates for color laser printers (12.3%) and laser based multifunctional printers (37.5%) [1].
At the "low cost" market there is a trend to higher printing speed and lower OPC drum diameters. This leads to a need for higher scratch and wear resistance of the drum surface.
At the high end market the driving factors are the lifetime of the expensive drums or belts and in the case of liquid toner development the protection against the solvent influence.
Although the lifetime of OPC drums has been impressively increased in the past, in high volume printing applications there is still a need for further improvement.

Figure1 displays the general structure of an organic photoconductor drum with photoactive layers: The substrate which is in many applications an aluminium tube is coated with a blocking layer (BL) inhibiting the charge injection from the substrate, a charge generation layer (CGL) and a charge transport layer (CTL). The CTL which is the outermost layer is subjected to extensive wear in the electrophotographic process. The first way to improve the durability of an organic photoconductor is to modify the polymer matrix of the CTL to increase the wear and scratch resistance.

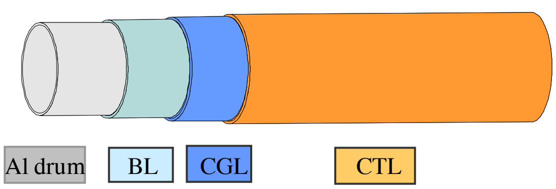


Figure1: *Stucture of an organic photoconductor drum consisting of an aluminum core, a blocking layer (BL), a charge generation layer (CGL), and a charge transport layer (CTL)*

To enhance the anti-adhesive and abrasion-resistant properties of the photoconductive layer it has been proposed to use a mixture of unmodified polysiloxane together with a methacryl modified polysiloxane, a vinyl modified polysiloxane or an alkyl modified polysiloxane [2].The advantage of this approach is to avoid anadditionalproductionstep. But there is strong influence on other layer parameters like optical sensitivity, charge retention, dark decay etc.The second alternative to upgrade the surface properties of OPC is to supply an additional hard coat as an overcoat layer (OCL). The correspondent photoconductor structure is drafted in Figure.2:

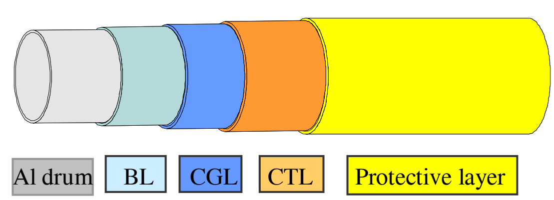


Fig.ure 2: *Structure of an organic photoconductor drum with overcoat layer (OCL)*

With such an additional layer it is possible to optimize the anti-abrasion properties separately and independently from the CTL. The disadvantages may be the blurring of charges at the drum surface and as a result a lower image quality. And there is an additional production step necessary with consequentially higher production costs. This must be compensated by substantially longer lifetime and better performance of printer or copier drums.Several approaches were found in the literature:

Polymeric systems like specific acrylates forming clear and transparent protective plastic films for organic photoreceptor overcoats can be used as such or together with an additional polysiloxane coating to receive additional wear and scratch resistance [3].

Another protective overcoat layer comprises a cross-linked composite polysiloxane-silica generated from the reaction of silyl-functionalized hydroxyalkyl polymers containing hole transporting moieties with an organosilane in the presence of silica particles [4].

Ricoh preferred an additionally reinforced CTL with a specific alumina particle filler, which meets such requirements: Rigidity, abrasion-resistance, transparency to image-recording light and no effects on charging and photo-decay characteristics of organic photoreceptor [5,6].

Overcoat layers are also described in the patents of Xerox as insulating or silica doped second CTL polymer layer [7] and of Canon as siloxane binder resin [8].

We have used a different approach by applying the currently very successfully used technology of organic/anorganic hybrid systems to electrophotographic photoconductors.

Sol/Gel Hard Coat

Subject of the present investigation was the development of a scratch resistant and anti-abrasion layer which does not influence the charge transporting properties.

Other important requirements are transparency, resistance against solvents admitting the use of fluid toner materials, easy to clean properties without adhesion of toner particles and high oxidation resistance especially against ozone emerging with charging.

New systems of hybrid polymers based on classical sol/gel materials should avoid this influence on electrical charge.

The sol/gel process in general terms proceeds along the following reaction scheme:

After hydrolysis and condensation of an organic silane with functional substituents a sol with particles of less than 10 nm is obtained (Figure 3).

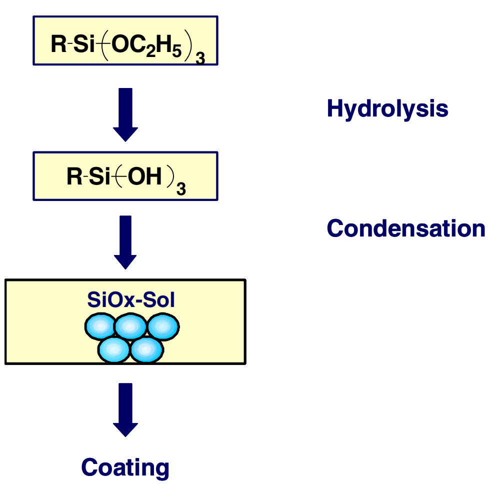


Figure 3: *Reaction scheme of sol/gel process*

After coating and drying this sol formulation a cross-linked layer is formed.

These one component silica nano materials have mostly too strong an influence on the charge transporting properties and therefore negative impact on the image quality.

Most sol/gel materials are either one component hybrid systems with oxygen bridges and particle sizes in 10 nanometer scale or blends of common polymers with more than 20 nm silica particles.

Sensient's material comes from the combination of polymer and sol/gel expertise forming an unique protective layer.

Functionalized silica particles together with poly-functional epoxy components as

two component material produce closed networks under convenient drying conditions and good durability against liquid toner materials. The generic reaction scheme to hybrid sol/gel silica nano materials is shown in Figure 4:

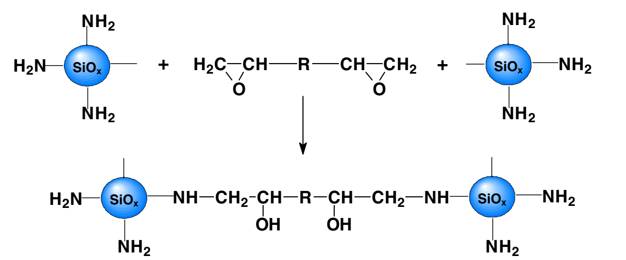


Figure4: *Generic reaction scheme of two component hybrid sol/gel system*

As a result of coating and cross-linking a hybrid polymer is generated with covalently bonded silica nano particles in an epoxy matrix.

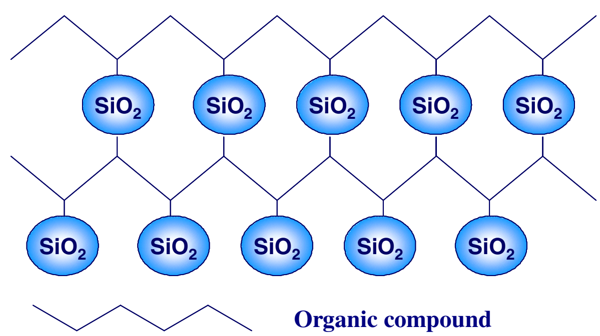


Figure5*: Generic structure of the cross-linked hybrid material*

The epoxies can be monomer or polymer compounds with at least two epoxy groups to get sufficient networking.

Coating Technology

In order to form the coating formulation the sol/gel materials have to be dissolved in suitable solvents. Then the solution is applied to the OPC drum by ring coating . After drying at temperatures of 80 to 120°C for typically 30 minutes an overcoat layer of 1 to 2 µm is achieved.

Because CTL materials can be dissolved fairly easily restrictions exist to the type of solvent for the hard coat formulation. Using the wrong solvent polymer cracking or total dissolution of the CTL or crystallization of the charge transport material can occur.

Therefore only alcohols as isopropanol or methoxypropanol are suitable. This excludes the usage of aromatic epoxies in the sol/gel formulation because these are only soluble in ketones.

Since the condensation reaction starts as soon as the components of the epoxy system are mixed, the viscosity of the coating solution starts rising, which at a certain point in time leads to processing issues and therefore to a limited pot life of the coating sol.

Selected epoxy systems however have a pot life of about 50 hours. After this time the viscosity of the formulation increases and the solution might become too viscous to be applicable.

Electrophotographic Properties

In order to not impair the electrophotographic properties of the photoconductor drum it is necessary to adjust the charge transport properties of the overcoat layer very carefully. Otherwise a big negative impact on the residual potential can occur. Besides the chemical structure of the constituents of the coating formulation the epoxy to sol ratio in the OCL has a significant influence on the residual potential of the overcoated OPC. By adjusting the epoxy to sol ratio it is possible to control the increase of the residual potential (see Figure 6). It is even possible to find epoxy to sol ratios showing no increase of residual potential.

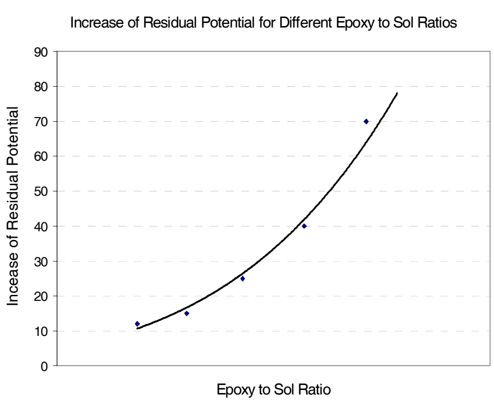
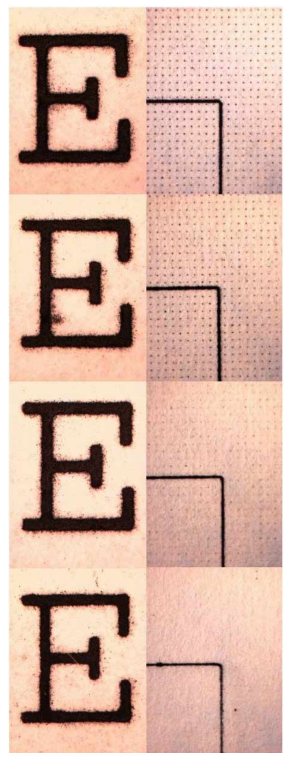


Figure6: *Dependence of residual potential on the epoxy to sol ratio*

On the other hand, if the resistivity of the coating is too low, lateral conductivity at the photoconductor surface leads to blurring of the latent image between exposure and development of the electrophotographic process. Especially single dot print patterns used to print half tone pictures in modern digital print systems cannot be reproduced anymore (Figure 7). This problem has been observed especially when aliphatic epoxies are used in the sol/gel formulation.

With cycloaliphatic poly-functional epoxies this problem cannot only be solved but moreover it is possible to adjust the surface conductivity and thereby the reproducibility of single dots by adjusting the ratio of the epoxy to sol.



OPC without hard coat for reference

hard coat with good single dot reproduction

hard coat with reduced reproduction of single dots

hard coat with inferior reproduction of single dots

Figure 7: *Print samples of different OCL formulations showing variations in single dot reproducion*

Using these cycloaliphatic poly-functional epoxies together with amino functional silica nano particles an excellent hard coat formulation is obtained [9]. In Table 1 the electrophotographic parameters of a photoconductor before and after coating the OCL are compared. The residual potential is slightly increased in order to achieve good single dot reproduction.

Table 1:Comparison of photoconductor with and without OCL

The dark decay is monitored for a time period of 3 sec. Starting at a drum voltage of 600V.

The residual potential is determined at 800nm and a light intensity of 4.5 µJ / cm^2

The sensitivity is measured as the potential drop due to an exposure intensity of 0.12 µJ / cm^2 (800nm wavelength), starting at a charge potential of 600V.

	Layer Thick-ness (µm)	Charge Acceptance (V)	Dark Decay (V)	Resdi-dual Potential (V)	Sensiti-vity (V)
Without OCL		615	10	55	245
With OCL	28,2	613	20	70	235

The effect on the lifetime of the photoconductor drum is displayed in Figure 8. This diagram shows layer thickness measurements performed during a life test in a Hewlett Packard 5Si printer. This printer has been chosen as a convenient test device because of two reasons: first the printing speed is relatively high resulting in short life time test cycles; second the OPC wear in this device is generally quite high which additionally shortens the test procedure.

The OPC drum which has been life tested had got a top coating only on one half of the surface. This area being represented on the right hand side of the diagram shows nearly no reduction in layer thickness after 50,000 prints whereas the uncoated OPC is reduced in layer thickness from 23 µm to 7 µm, roughly.

Summary

With Sensient's hard coat formulations of hybrid polymers based on sol/gel materials the hardness and scratch resistance of organic photoconductor drums can be improved significantly. By properly selecting the type of epoxy component and adjusting the epoxy to sol ratio it is possible to minimize the influence on the electrophotographic properties of the OPC drum providing a long life photoconductor drum suited for high resolution digital printing systems.

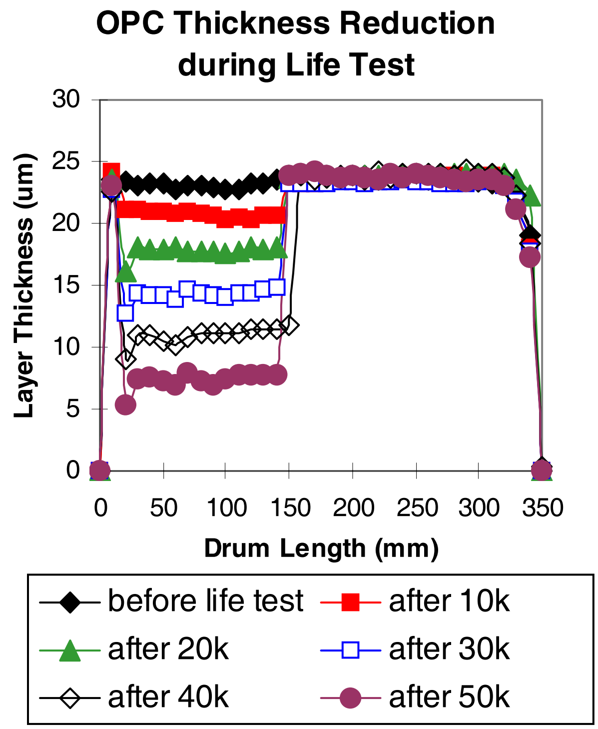


Figure8: *Life test in a Hewlett Packard 5Si printer with an OPC drum being overcoated partly with a silica nano-structured hard coat. Comparison of photoconductor thickness measurements without (left) and with (right) overcoat .*

References

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