

# Degradation of zinc oxide thin films in aqueous environment:

## Part II – Coated Films

### Degradation von dünnen Zinkoxidfilmen in wässriger Umgebung: Teil II – Beschichtete Filme

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In Part I of this research, the degradation mechanism of two different bare ZnO thin films was assessed. Degradation of the electrical properties of ZnO as well as changes in morphology were observed for both films. In the current paper, the degradation of zinc oxide thin films coated with protective acrylic paint is addressed during exposure to (i) an aqueous 3.5% NaCl solution at 85 °C and (ii) a standard damp heat test at 85% R.H. and 85 °C. Electrical and electrochemical techniques were employed to monitor zinc oxide degradation during exposure to the test environments. Electrochemical Impedance Spectroscopy was employed to investigate the delamination phenomena at the ZnO/coating interface and a simple equivalent circuit was developed to quantitatively measure the delamination ratio. The effect of different silane based adhesion promoters (glycidil-oxypropyl-trimethoxy-silane and aminopropyl-trimethoxy-silane) was also investigated.

Im Teil I dieser Untersuchung wurden die Degradationsmechanismen von zwei verschiedenen unbedeckten Zinkoxidschichten beurteilt. Sowohl eine Verschlechterung der elektrischen Eigenschaften als auch eine Veränderung der Morphologie wurden beobachtet. In der vorliegenden Veröffentlichung wird die Degradation von ZnO-Filmen behandelt, die mit einer Schutzschicht aus einem Acryllack versehen waren und einer wässrigen 3,5% NaCl-Lösung bei 85 °C einerseits und einem Feuchte-Wärme-Test (85 °C, 85% rel. Feuchte) ausgesetzt wurden. Elektrische und elektrochemische Verfahren wurden angewandt, um die Veränderungen der ZnO-Schicht während der Exposition aufzuzeichnen. Mit Electrochemischer Impedanzspektroskopie wurden die Delaminationserscheinungen an der ZnO/Lack Grenzfläche untersucht und ein einfaches Ersatzschaltbild wurde entworfen, um die Delaminationsgeschwindigkeit quantitativ beschreiben zu können. Der Einfluss verschiedener Silanhaftvermittler (Glycidil-Oxypropyl-Trimethoxy-Silan und Aminopropyl-Trimethoxy-Silan) wurde ebenfalls ermittelt.

## 1 Introduction

As reported in Part I of this work [1], due to the interaction between water and zinc oxide crystals, rapid degradation can result when bare ZnO thin films are exposed to aggressive aqueous environments. The current paper addresses the effectiveness of transparent organic coatings as a means of reducing the degradation rate of zinc oxide in such environments. Organic coatings isolate the substrate from direct contact with the environment and reactants (oxygen, water and electrolyte) then arrive at the interface by permeating through the organic coating. Degradation is, thus, related to the rate of arrival of reactants diffusing through the organic layer to the interface as well as to adhesion at the polymer/substrate interface. In the case of low barrier coatings the diffusion rate of water and

oxygen is 10 to 100 times higher than the rate of consumption at the corroding surface. Therefore electrochemical reactions are the limiting steps for the corrosion mechanism (reaction controlled corrosion) [2, 3]. In the case of high barrier coatings, however, it has been demonstrated that the diffusion of water and oxygen through the polymer is the limiting step of the corrosion mechanism (diffusion controlled corrosion) [2, 3]. During the exposure to wet environment, however, high barrier coatings can lose their barrier action due to the formation of aging-induced pores in the polymer [2]. In this case a diffusion controlled corrosion shifts to a reaction controlled corrosion during the time of exposure. On the opposite some high barrier coatings were found to maintain their barrier actions for prolonged time of exposure to a wet environment. Even significant corrosion can be detected at the polymer /substrate interface (reference). In this latter case the interfacial adhesion between the polymer and the metal plays a main role in the corrosion process (delamination controlled corrosion) [4].

In order to reduce the rate of corrosion in a delamination controlled phenomenon, the adhesive bonds between the coating and the substrate can be enhanced by the addition of silane coupling agents to the coating formulation. Silanes are silicon-organic molecules with a central Si atom covalently bonded to one organic group and to three hydroxyl groups.

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The organic group is highly reactive and forms stable covalent bonds with the organic matrix, while the hydroxyl groups form a triple ionic bond with the inorganic phase. While the ionic bonds are not themselves stable the probability of simultaneously breaking all three approaches zero, ensuring the probabilistic stability of the bond [5]. In this way, silanes act as a bridge between the organic and inorganic phase. A recent investigation on the effect of alkyloxysilanes indicated enhanced wet adhesion for acrylate-urethane coatings on a glass substrate [6].

## 2 Materials and methods

Thin films of ZnO were deposited on glass substrates in a pattern of narrow stripes. On each sample one stripe was left bare and one stripe was coated with the polymer of interest.

A 2 component commercial grade acrylic resin containing isocyanate crosslinker was used. After the coating was deposited with a Gardner knife, it was cured in an oven for 1 h at 120 °C. In order to analyze increased adhesion between the organic matrix and the zinc oxide during exposure to a humid environment, Glycidil-oxypyril-trimethoxysilane (Glymo) and aminopropyl-trimethoxysilane (Ammo) were added to different batches of varnish. In all cases, the adhesion promoter was added at a level of 1.5% by weight.

EIS measurements, in the frequency range 0.02–10<sup>5</sup> Hz, were performed on bare and coated samples exposed to an aqueous aerated 3.5% NaCl solution at 85 °C. All experiments were carried out in a dark chamber to avoid interference between measurements and photoelectrochemical effects. Generally, a Solartron 1260 frequency response analyzer (FRA) was used in combination with a Solartron 1286 potentiostat; however, for high impedance coated samples, the Solartron dielectric interface 1296 was employed. DC resistivity of both coated and uncoated samples was monitored by a PC-driven Keithley multimeter during exposure in a humidity chamber (Weiss-Gerätetechnik Kälte-Wärme Prüfschrank Mod. 305SB) at 85% R.H. and 85 °C.

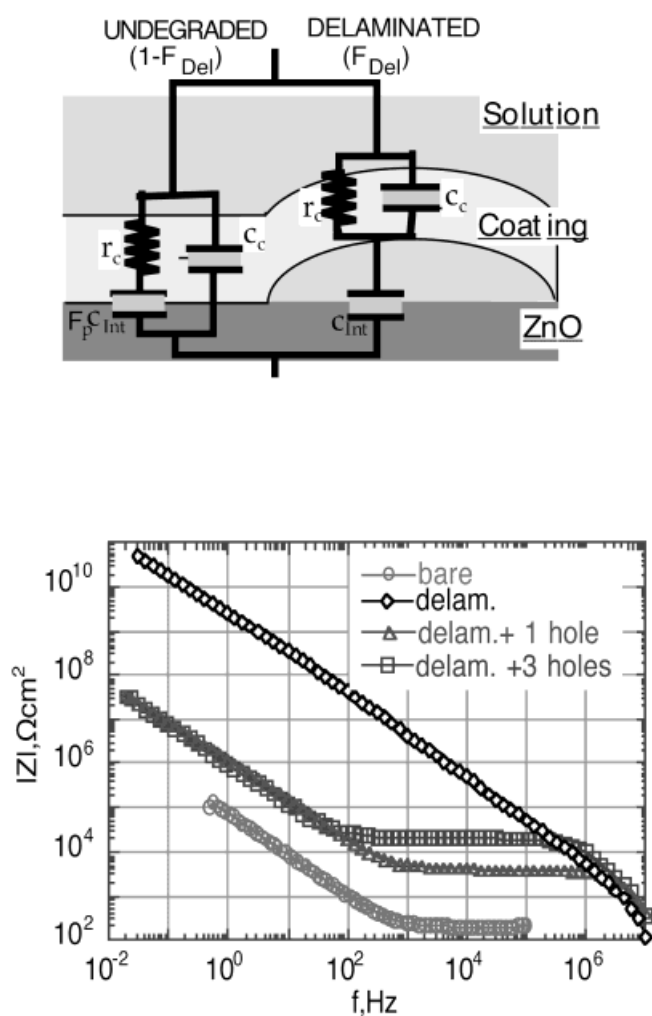
## 3 Results and discussion

### 3.1 Equivalent circuit

The degradation of coated ZnO thin films is characterized by several simultaneous phenomena occurring both in the coating and at the substrate/coating interface. According to common model adopted in the literature, the coating itself is composed of both the homogeneous organic matrix (exhibiting capacitive behavior) and ionically conducting paths exhibiting resistive behavior [7–9]. The number of ionically conducting paths determines the insulating properties of the coating.

For the acrylic-coated ZnO samples assessed during this study, interfacial behavior was characterized by progressive delamination at localized sites and experimental observations indicate that degradation progressed by rapid coating delamination. The rate of delamination is, therefore, considered to be a critical controlling factor in the rate of degradation for these systems.

In order to describe the impedance behavior of coated ZnO during delamination, a simple equivalent network was developed. As indicated schematically in Fig. 1(a), the network is composed of two parallel equivalent circuits depicting dela-



**Fig. 1.** Equivalent circuit (a) and impedance spectra (b) of an acrylic coating on ZnO thin film exposed to 3.5% NaCl aqueous solution, in presence of delaminated area

**Abb. 1.** Ersatzschaltkreis (a) und Impedanzspektren (b) einer Acrylbeschichtung auf einer ZnO Dünnschicht nach Beanspruchung durch wässrige 3,5% NaCl- Lösung, bei Vorhandensein einer delaminierten Teilfläche

minated and non-delaminated regions. Assuming unitary exposed area, the following five parameters are important to the mathematical description of a partially delaminated coating: (i) the coating resistance,  $r_c$ ; (ii) the coating capacitance,  $c_c$ ; (iii) the ZnO/electrolyte interface capacitance,  $c_{int}$ ; (iv) the fraction of delaminated area  $F_{del}$ ; and (v) the ratio between the area of conductive paths and the exposed area,  $F_p$ . At non-delaminated sites the coating capacitance,  $(1-F_{del})c_c$ , is connected in parallel to the resistance of the ionically conductive paths,  $(1-F_{del})r_c$ , which in turn is in series to the ZnO/electrolyte capacitance at the bottom of these conductive paths,  $(1-F_{del})F_p c_{int}$ . At delaminated sites, the coating capacitance,  $F_{del}c_c$ , and the resistance  $F_{del}r_c$ , are connected again in parallel. In the later case, however, both are connected in series to the ZnO/electrolyte capacitance at delaminated sites,  $F_{del}c_{int}$ . The impedance of: (i) external electrolyte, (ii) undercoating electrolyte at delaminated sites and (iii) the resistance of the ZnO stripes was neglected due to their low values.

According to the equivalent circuit adopted in this investigation, the impedance spectra exhibit capacitive behavior at low frequency, and the real part of complex capacitance  $c'_{lf}$  is given by:

$$c'_{lf} = [c_{int}F_{del} + (c_{int}F_p + c_c)(1 - F_{del})] \quad (1)$$

Equation (1) can be useful to describe the behavior of coatings weakly bonded to the substrate and with a low density of pores ( $c_{int}F_p \ll c_c$ ). For this hypothesis, equation (1) becomes:

$$c'_{lf} = [c_{int}F_{del} + c_c(1 - F_{del})] \quad (2)$$

At an early stage of exposure  $F_{del}$  is close to zero then  $c'_{lf}$  is a measure of  $c_c$ . In turn, at later stages  $F_{del}$  increases and  $c_c$  shifts from its starting value toward  $F_{del}c_{int}$ . Thus, the variation of  $c'_{lf}$  with time of exposure provides data on the delaminated area, as reported in the following equation:

$$F_{del} = (c'_{lf} - c_c)/(c_{int} + c_c) \approx (c'_{lf} - c_c)/c_{int} \quad (3)$$

$c'_{lf}$  and  $c_c$  can be obtained from the low and high frequency part of the spectrum of the coated sample, respectively, while  $c_{int}$  can be obtained from the low frequency part of the EIS spectrum of the bare sample. However, in the case  $c'_{lf}$  can be experimentally measured, the value of  $F_{del}$  is not affected by the value of  $r_c$ . These theoretical results are not restricted by any hypothesis on  $r_c$ , however, in the experimental practice the following condition must be met to observe  $c'_{lf}$  in the investigated frequency range:

$$r_c \ll 1/(2\pi f_{min}F_{del}c_{int}) \quad (4)$$

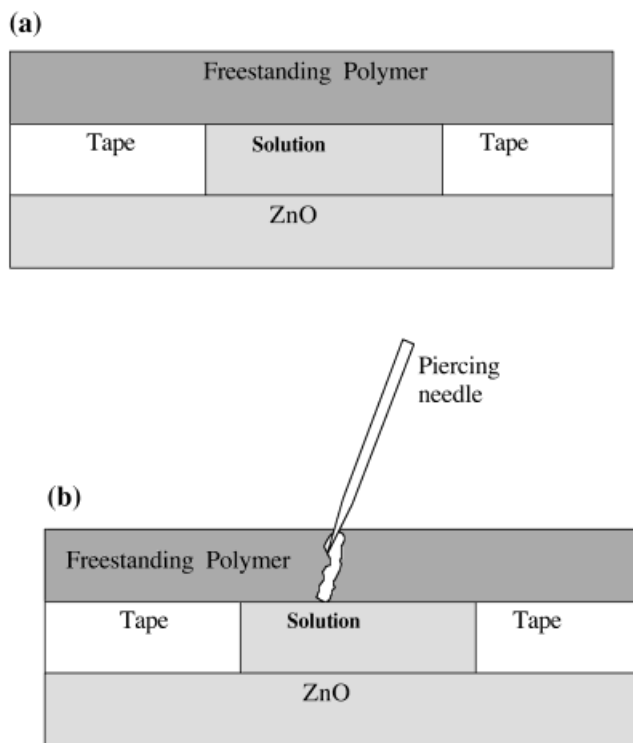
where  $f_{min}$  is the lowest investigated frequency.

### 3.2 Artificial delamination of coated ZnO

In order to experimentally verify the mathematical results, impedance measurements were performed on: (i) bare ZnO, (ii) a coated ZnO sample with an artificially delaminated area (see Fig. 2(a), and (iii) a coated ZnO sample with an artificially delaminated area, which had been pierced (see Fig. 2(b)). The spectra for each of these conditions is reported in Fig. 1(b). The specific interface capacitance  $c_{int}$ , measured from the low frequency (lf) part of impedance spectrum of the bare sample, was equal to  $1.92 \times 10^{-6}$  F/cm<sup>2</sup>. The bare sample was then covered with a 5  $\mu$ m pressure sensitive double sided tape from which a section had been removed. This formed a bare region on the sample surface into which a drop of electrolyte was placed. A freestanding cured acrylic film was then attached to the surface of the sample, thus, forming an artificially delaminated region. The total exposed area of the sample was 200 mm<sup>2</sup> and the area of the artificially delaminated region was 16 mm<sup>2</sup> providing a coating/ZnO system with known fraction of delaminated area being  $F_{del} = 0.08$ .

Despite the presence of an artificially delaminated area, the EIS data for this system exhibits fully capacitive behavior over the entire range of frequencies explored. The value of the capacitance was determined to be  $4 \times 10^{-11}$  F/cm<sup>2</sup>. This result is in agreement with the theoretical case of  $r_c$  not meeting the condition stated in equation (4).

In order to investigate the theoretical situation corresponding to a low  $r_c$ , the artificially delaminated area was pierced



**Fig. 2.** Schematic of artificially delaminated high barrier coating: (a) before and (b) after the piercing

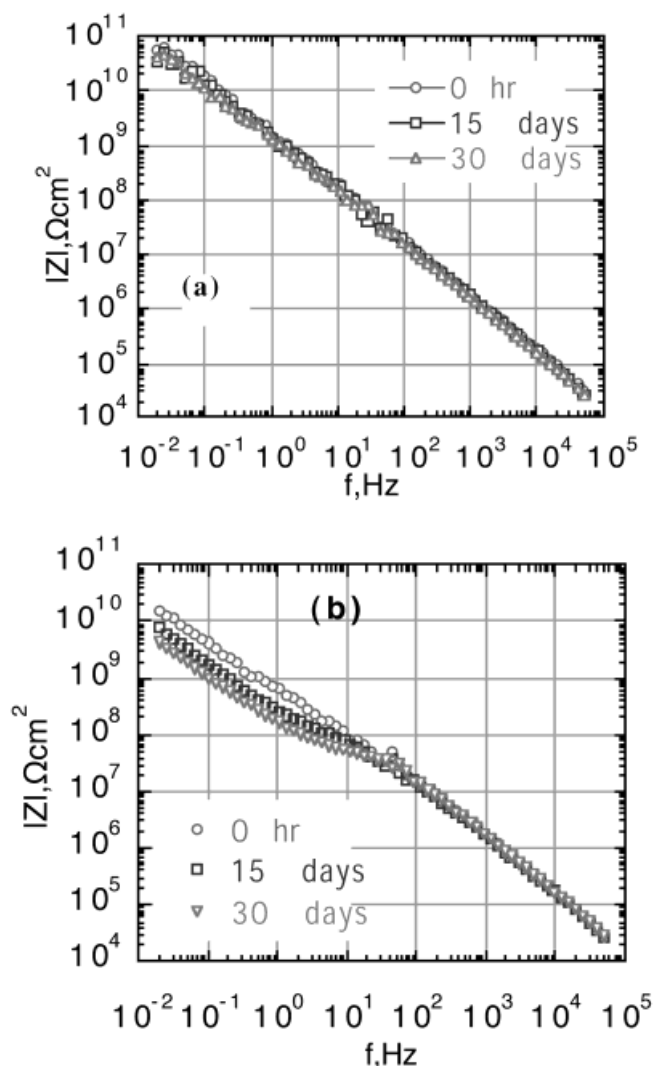
**Abb. 2.** Schema einer künstlich delaminierten Barrierebeschichtung: (a) vor und (b) nach der Durchlöcherung

with a needle to create a small hole. The resultant spectrum is presented in Fig. 3(b). From the Lf and Hf regions  $c'_{lf} = 1.48 \times 10^{-7}$  and  $c_c = 4 \times 10^{-11}$  F/cm<sup>2</sup> were obtained. On the basis of these values and that of the capacitance of the bare sample reported above, a fraction of delaminated area equal to  $F_{del} = 0.077$  was calculated by equation (3). This result is in a good agreement with the known  $F_{del}$  value. The coating resistance,  $r_c$ , determined from the impedance data was  $2.02 \times 10^4 \Omega\text{cm}^2$ . Finally, the sample was pierced with two additional holes and the relative data are reported in Fig. 3(b). The value of  $r_c$  decreased due to the additional conductive paths, while the values of  $c'_{lf}$  and  $c_c$  remain unchanged. These results suggests that equation (3) can be used to evaluate the delaminated area in the frequency range  $10^{-2}$ – $10^6$  Hz for low to medium resistance coatings. Use of equation (3) is not recommended for evaluating delaminated area for very high resistance coatings unless a wider range of frequency is also explored.

### 3.3 Degradation of coated ZnO

In order to assess the relative improvement in the adhesion characteristics of acrylic coatings applied to ZnO thin films, samples produced with the addition of either (i) 1.5% by weight Glymo or (ii) 1.5% by weight Ammo were evaluated. In both cases, samples were exposed to aqueous aerated 3.5% NaCl at 85 °C for extended times.

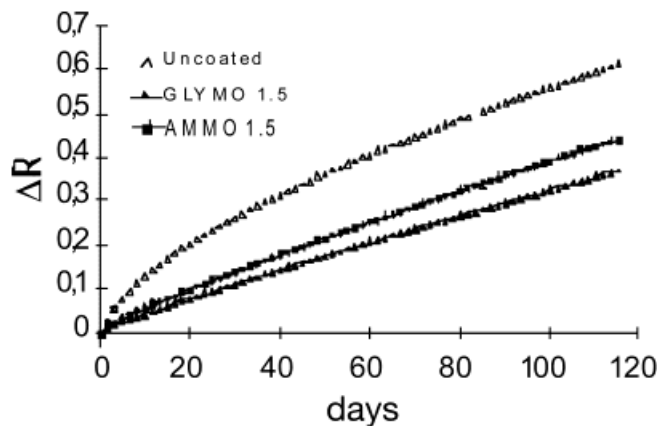
The development of impedance spectra with exposure time for the sample containing Glymo are reported in Fig. 3(a). Even after 30 days of exposure, no distinction can be made



**Fig. 3.** Impedance spectra of ZnO coated with acrylic varnish containing a) 1.5% by weight glycidil-ossiproyl-trimethoxy silane and b) 1.5% by weight of amminepropyl-trimethoxysilane

**Abb. 3.** Impedanzspektren von ZnO mit Acryllackbeschichtung mit Zusatz von a) 1,5 Gew.% Glycidil-Oxypropyl-Trimethoxy-Silan und b) 1,5 Gew.% Amminopropyl-Trimethoxy-Silan

between the capacitance measured at low frequency and that measured at high frequency. Thus,  $c_{if}$  is representative of the coating capacitance ( $10^{-10}$  F/cm<sup>2</sup>) and the interfacial capacitance cannot be detected. This behavior could result either from: (i) a delaminated coating/ZnO system with  $r_c$  higher



**Fig. 4.** Relative change of resistivity of bare and coated CVD-ZnO during exposure to damp heat (85 °C, 85% RH)

**Abb. 4.** Relative Änderung des Widerstands von beschichtetem und unbeschichtetem ZnO im Feuchte-Wärme-Test (85 °C, 85% RH)

than  $10^{11}$  Ωcm<sup>2</sup>, or (ii) a non delaminated coating/ZnO system; unfortunately, the EIS data do not permit the distinction to be made. The analogous impedance data for the sample containing Ammo are reported in Fig. 3(b). Unlike the data presented in Fig. 3(a), a second time constant was observed after 15 days. As reported in Table 1, the fraction of delaminated area and interfacial capacitance can be evaluated by equation (3) for exposure times of 15 and 30 days.

The normalized DC resistance  $(R(t) - R_0)/R_0$  as a function of exposure time for both bare and coated ZnO samples exposed to an 85% R.H. environment at 85 °C is presented in Fig. 4. The normalized resistance of both bare and coated ZnO increases with the time of exposure. The rate of increase is, however, higher during the early stages of exposure and tends to develop a linear trend during the latter stages.

Relative to the bare sample, the increase in resistance is less pronounced for coated samples containing either Glymo or Ammo and this disparity increases with time. In agreement with EIS results, samples containing Glymo exhibit superior performance.

#### 4 Summary and conclusions

The degradation of zinc oxide thin films was investigated during exposure (i) to air at 85% R.H. and 85 °C, and (ii) to an aqueous 3.5% NaCl solution at 85 °C. A simple equivalent circuit was developed to describe the effect of progressive delamination on the impedance of coated ZnO, and an equation

**Table 1.** Equivalent components of the coated samples at different time of exposure to 3.5%wt aqueous solution at 85 °C

**Tabelle 1.** Komponenten des Ersatzschaltkreises für die beschichteten Proben nach verschiedener Zeit der Behandlung in 3,5%iger Lösung bei 85 °C

Sample	Time (days).	$r_c$ (Ωcm <sup>2</sup> )	$c_c$ (F/cm <sup>2</sup> )	$c_{if}$ (F/cm <sup>2</sup> )	$F_{del}$
GLYMO	0	-	$9 \times 10^{-11}$	-	-
	40	-	$1.1 \times 10^{-10}$	-	-
AMMO	0	$8.22 \times 10^9$	$9.4 \times 10^{-11}$	-	-
	15	$7.54 \times 10^7$	$1.22 \times 10^{-10}$	$8.64 \times 10^{-10}$	$4. \times 10^{-4}$
	30	$5.49 \times 10^7$	$1.07 \times 10^{-10}$	$1.41 \times 10^{-9}$	$7.3 \times 10^{-4}$

was proposed to evaluate the fraction of delaminated area from the low frequency capacitance.

DC measurements indicated that the electrical resistance of both bare and coated ZnO increases with time of exposure to an 85% R.H. and 85 °C atmosphere. The rate of resistance increase exhibited by coated ZnO is, however, reduced relative to that of bare ZnO.

In order to assess the adhesion characteristics of acrylic coatings applied to ZnO thin films, samples produced with the addition of either (i) 1.5% by weight glycidil-oxypropyl-trimethoxy-silane or (ii) 1.5% by weight aminopropyl-trimethoxy-silane were evaluated. No delamination was observed after 30 days of exposure to NaCl solution in the presence of the former silane, whereas delamination of coated samples after 15 days of exposure was observed when the latter silane was employed. It was therefore concluded that for the conditions tested coatings containing glycidil-oxypropyl-trimethoxy-silane as adhesion promoters exhibited better performance than those containing aminopropyl-trimethoxy-silane.

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