Interaction of Polyurethane Model Compounds with Metal Oxides

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ABSTRACT: The chemical interaction of ester and urethane compounds as models for polyurethanes with chromium dioxides and aluminum oxides was investigated. The pigment was coated by suspending it in a solution of the model compound and evaporating the solvent. The amount of the compound remaining after contact with a pigment was determined by gas chromatography. The ester and urethane compounds can be extracted from the pigments in yields of 95–100% with dioxane. They decompose in contact with the pigments by a hydrolytic process. The oxidative potential of the unstabilized chromium dioxide causes an oxidation of the products of hydrolysis. The rate of decomposition is influenced by the temperature, by the water content in the system, by a structural modification of the model compound, and by surface modification of the pigment. The kinetics of decomposition follows a pseudo-first-order process in systems with a water surplus. In the presence of acidic aluminum oxide, adipic acid-di-n-butylester (ADnBE) will decompose faster than will phenylcarbamide acid-n-butylester (PCnBE), whereas the rate of decomposition in contact with basic aluminum oxide is much faster and without any difference between the ester and urethane compound. The surface modification of the pigment has the best effect on the reduction of the decomposition rate as shown with the stabilized chromium dioxide. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2449–2455, 1997

Key words: polyurethane model compounds; mono layers; specific interaction at oxide surfaces; catalyzed hydrolysis

INTRODUCTION

Knowledge of the interaction between polymers and inorganic materials has great importance for the development of composites with high durability. Pigmented coatings are a composite and work as does a filled polymer. They are subject to the regularities of composite materials.[1] Their properties are dependent on the properties and the interactions of the components. The higher the pigment content, the more effective will be interfacial aspects. Depending on the type and the s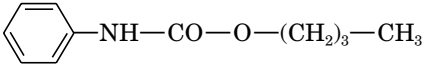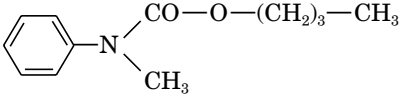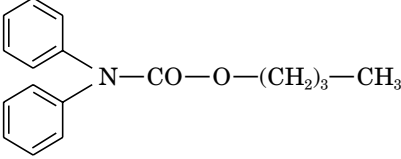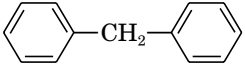urface properties of the pigments, the interactions can be both physical and chemical in nature. Elementary analysis reveals that organic compounds will be oxidized at a highly heated CuO surface. Friedrich et al.[2] observed a redox reaction at 250°C in a composite consisting of polyphenylchinoxaline and CuO, causing an oxidation of the aromatic compound under the formation of copper. This interfacial process influences the soldering stability during the finishing stages of circuitboard manufacture. These changes of the chemical and physical structure in the interfacial region can occur at room and slightly elevated temperatures even if more active pigments are chemically incorporated into the polymer matrix.

As shown by Essig et al.,[3] Auweter et al.,[4] and Bradshaw et al.,[5,6] chromium dioxide is a material

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Table I   Used Model Compounds for Polyurethanes

Structure	Name
H_9C_4—O—OC—$(CH_2)_4$—CO—O—C_4H_9	Adipic acid di-*n*-butylester (ADnBE)
⬡—NH—CO—O—$(CH_2)_3$—CH_3	Phenylcarbamide acid *n*-butylester (PCnBE)
⬡—N(—CO—O—$(CH_2)_3$—CH_3)(CH_3)	*N*-Methyl-*N*-phenylcarbamid acid *n*-butylester (MPCnBE)
(⬡)(⬡)N—CO—O—$(CH_2)_3$—CH_3	*N*,*N*-Diphenylcarbamide acid *n*-butylester (DPCnBE)
⬡—CH_2—⬡	Diphenylmethane (DPM)

used as a magnetic pigment in recording materials, which is able to show interactions with organic compounds. Aluminum oxide shows a similar behavior. It is used in chromatography for substance separation and for binding dyes to wool fibers. Further, aluminum oxide exists at the surface of Al–sheets and influences the adhesion strength of Al–polymer composites.[7,8]

The aim of this investigation was to develop a method for studying the chemical processes in an adsorption layer of an organic compound at an inorganic surface; these processes specifically allow the investigation of the chemical interaction of characteristic structural units of polyurethanes with highly dispersed inorganic materials. A better understanding of the processes at the interfaces will provide new insights for increasing the longtime stability of composite materials.

EXPERIMENTAL

Materials

The organic materials which were used as model compounds for polyurethanes are summarized in Table I. ADnBE and DPM were purchased from Aldrich Chemical Corp. PCnBE was synthesized by the reaction of phenylisocyanate with *n*-butanol in the absence of water traces and oxygen. MPCnBE and DPCnBE were obtained from *N*-methylaniline (respectively, diphenylamine and chloroformic acid *n*-butylester). The compounds

had a purity of about 98.6–98.8% by gas chromatography.

Inorganic materials include highly dispersed chromium dioxide provided by BASF Aktiengesellschaft, Ludwigshafen, and aluminum oxide for chromatography purchased from Aldrich Chemical Corp. Data on the metal oxides are summarized in Table II. The possibilities of interaction for aluminum oxide are shown in Scheme 1. It must be taken into account that in the case of chromium dioxide an oxidizing action will be possible, but with the basic aluminum oxide, this action will not occur. It is presumed that this fact will influence the interaction with the model compounds.

Sample Preparation and Method

Ten grams of the pigment were poured into a reaction flask. To coat the pigment, a solution of the model compound in dioxane or methylene chloride was added. The suspension was mixed for 10 min at room temperature under rotation in a rotary evaporator. Then, the solvent was removed by rotary evaporation at 35°C under reduced pressure (15–20 mbar) within 20 min. The amount of the model compound in the dry coated pigment was 0.15–0.4 mmol/g pigment, resulting in a mono- to five-molecular layer at the surface of the pigment.

One gram of the coated pigment was placed in a glass test tube (length 10 cm, diameter 1 cm) fitted out with a 14.5 normal-cut and closed with a glass

Table II Characterization of the Metal Oxides

| Type	Spec. Surface (m^2/g)	Water Content (Wt %)	pH
Unstabilized chromium dioxide (BASF Aktiengesellschaft)	27	0.60	3.0[a]
Stabilized chromium dioxide (BASF Aktiengesellschaft)	26	0.50	6.2[a]
Aluminum oxide for chromatography Type 5016 A (Aldrich)	150	0.60	9.5 ± 0.3
Aluminum oxide for chromatography Type 04 C (Aldrich)	150	0.79	4.5 ± 0.3

[a] pH value of a water suspension consisting of 10 g CrO_2 in 100 ml destillated water after stirring 10 min.

plug. The closed test tubes were stored in a heat cabinet at 80–100°C for varying lengths of time. The sample was then cooled to room temperature. Dioxane was added and the resulting slurry was placed into an ultrasonic bath for 3 min. During this process, 95–100% of the unchanged model compound can be desorbed. The concentration of the model compound in the solution was measured by gas chromatography under the following conditions: Chromatograph Varian Star 3400, 2 m packed column (ID 2 mm), 5 wt % QF1 at Chromosorb W/AW/DMCS, 1.8 L/h nitrogen as the carrier gas, 5 min 110°C, and then with 40°C/min 220°C, 1.5-dibromopentane as the internal standard.
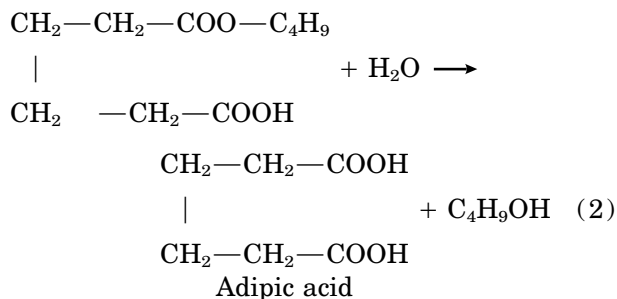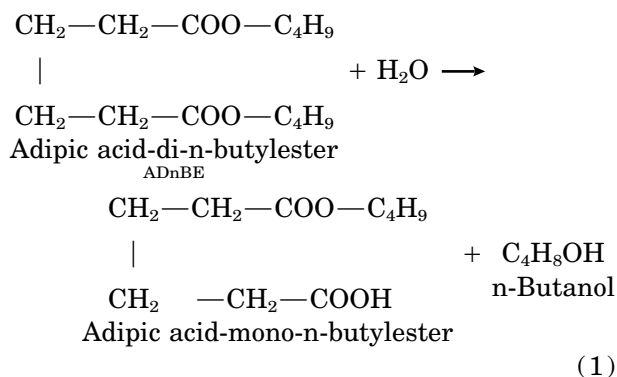
RESULTS AND DISCUSSION

Interaction of ADnBE with Unstabilized Chromium Dioxide

The decrease of ADnBE concentration in the coated pigment during storage at 80°C is shown in Figure 1. The decomposition is caused in a first step by hydrolysis. The *n*-butanol thus formed is oxidized in a second step to butyric acid. As shown
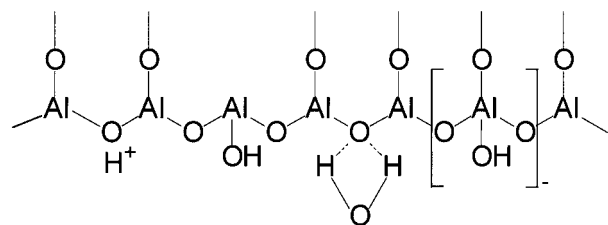
Scheme 1 Functional groups at the surface of aluminum oxides.

in Figure 1, curves (a) and (b), the content of the model compound in the initial coated pigment was measured as 0.35 mmol/g pigment. The area of an ADnBE molecule was estimated to be $434 \cdot 10^3$ m^2/mol by the Hyper Chem Program. The amount of 0.35 mmol/g chromium dioxide corresponds to a five-molecular layer at the surface of the pigment. The water content of the chromium dioxide dried for 1 h at 100°C and analyzed by Karl-Fischer titration was 0.2%. That means that 1 g of the coated pigment had a water content of 0.11 mmol, and with regard to the following chemical equations:

$$CH_2—CH_2—COO—C_4H_9$$
$$|$$
$$CH_2—CH_2—COO—C_4H_9$$
Adipic acid-di-n-butylester
ADnBE

$+ H_2O \longrightarrow$

$$CH_2—CH_2—COO—C_4H_9$$
$$|$$
$$CH_2 \quad —CH_2—COOH$$
Adipic acid-mono-n-butylester

$+ C_4H_8OH$
n-Butanol

$$(1)$$

$$CH_2—CH_2—COO—C_4H_9$$
$$|$$
$$CH_2 \quad —CH_2—COOH$$

$+ H_2O \longrightarrow$

$$CH_2—CH_2—COOH$$
$$|$$
$$CH_2—CH_2—COOH$$
Adipic acid

$+ C_4H_9OH \quad (2)$
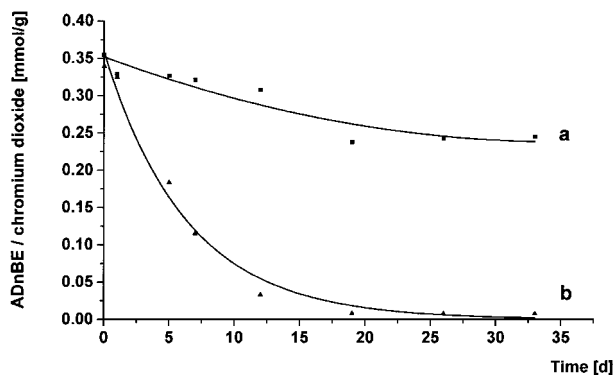
0.11 mmol water can hydrolyze 0.11 mmol of

Figure 1 Kinetics of decomposition of adipic-di-*n*-butylester in presence of unstabilized chromium dioxide at 80°C: (a) without addition of water to the test tube; (b) with addition of 12 mol water/mol ADnBE.

ADnBE by forming the monoester and this explains the results shown by curve (a) in Figure 1. The observed decrease of about 0.1 mmol of ADnBE, about 30% of the initial quantity of ADnBE during the storage, and the cessitation of further decomposition after this time can be explained by the lack of water in the system.

An addition of water to the coated pigment in the test tube increases the rate of ADnBE decomposition and the total amount of the hydrolyzed ADnBE [curve (b) in Fig. 1]. After about 20 days, all the ADnBE is decomposed. Theoretically, about 0.7 mmol of water is needed for the whole decomposition, if the initial quantity of ADnBE was 0.35 mmol. A 12-fold amount of water was used. The water content in the system is in such a surplus that the following equation for a pseudo-first-order process can be used for calculation of the rate constant:

$$-\ln C_{\mathrm{ADnBE}} = k \cdot t \qquad (3)$$

where k is the pseudo first-order rate constant of ADnBE decomposition, and t, the reaction time of ADnBE with chromium dioxide at 80 or 100°C. The existence of only one rate constant for the whole reaction process at 80°C ($k = 2.35 \cdot 10^{-6}$ s^{-1}) is a further confirmation that hydrolysis is the main process in this decomposition.

The rate of decomposition can be influenced by the water content in the system and the temperature during storage (see below). The oxidative action of the unstabilized chromium dioxide can be observed distinctly by interaction with diphenylmethane, which is a suitable model compound for the MDI (4,4'-diphenylmethane diisocyanate), mostly used in polyurethanes. The oxidation of
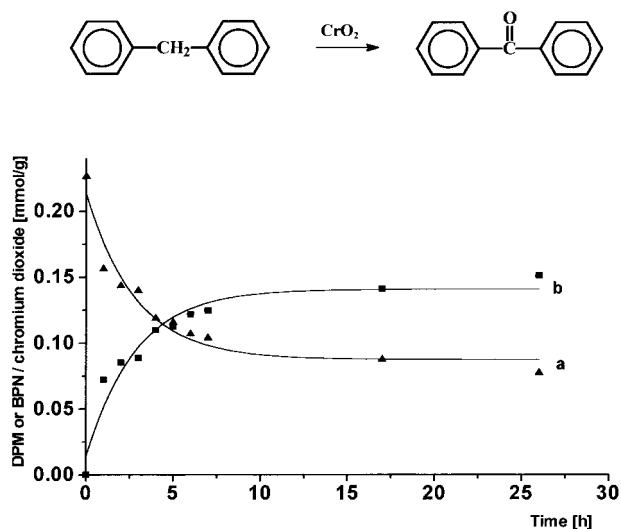

Figure 2 Oxidation action of unstabilized chromium dioxide by interaction with diphenylmethane: (a) decrease of diphenylmethane (DPM); (b) increase of benzophenone (BPN).

DPM results in the formation of benzophenone as shown in Figure 2. These observations are in agreement with previous results described by Bradshaw and Falcone.[9]

Interactions of Different Urethanes with Unstabilized Chromium Dioxide

In contact with unstabilized chromium dioxide, the concentration of the PCnBE decreases very rapidly at 100°C as shown in Figure 3. Compared to ADnBE (Fig. 1), the decomposition of the PCnBE stops nearly at the same concentration of the model compound as 0.02 mmol/g chromium dioxide. The decomposition mechanism seems to be hydrolytic as well. It is presumed that the
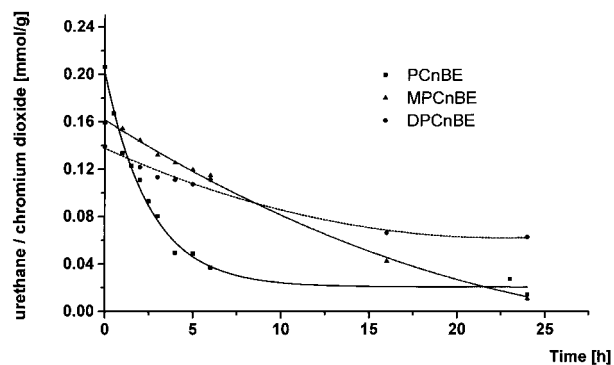

Figure 3 Kinetics of decomposition of urethanes in presence of unstabilized chromium dioxide at 100°C and addition of 12 mol water/mol urethane.
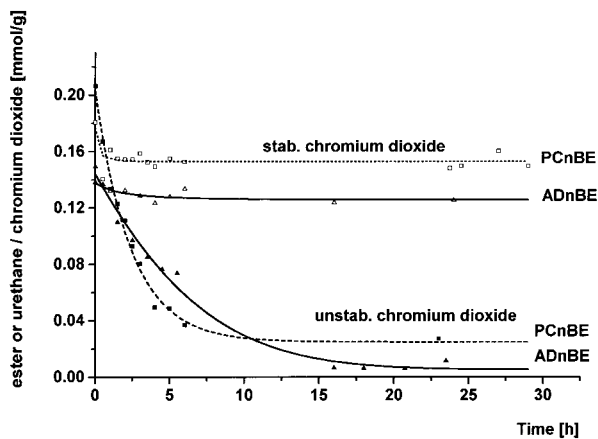
Figure 4 Influence of the chromium dioxide type on the decomposition rate of model compounds at 100°C and addition of 12 mol water/mol model compound.

PCnBE hydrolizes and forms phenylcarbamide acid and *n*-butanol. The phenylcarbamide acid rapidly decomposes in carbon dioxide and aniline. The latter can either react with a chromium compound under formation of a complex or it can be oxidized. Therefore, it was not possible to find aniline in the hydrolized and oxidized system. Amino compounds can form strong complexes with chromium (III) compounds and CrOOH, which are also present at the surface of chromium dioxide.[10,11]

The second product of the PCnBE hydrolysis, *n*-butanol, may be oxidized to butyric acid, where it forms a salt with the aniline or N-derivates of the aniline. Therefore, the products of hydrolysis and oxidation could not be detected by gas chromatography.

The substitution of the proton at the nitrogen by a methyl or phenyl group decreases the decom-
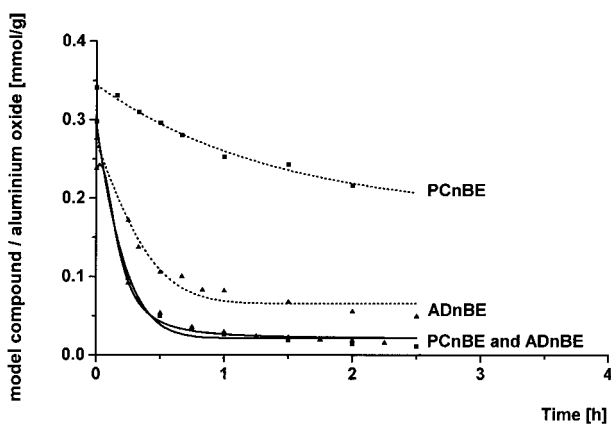

Figure 5 Interaction of ADnBE and PCnBE with different types of aluminum oxide at 100°C: (− − −) acidic aluminum oxide; (———) basic aluminum oxide.
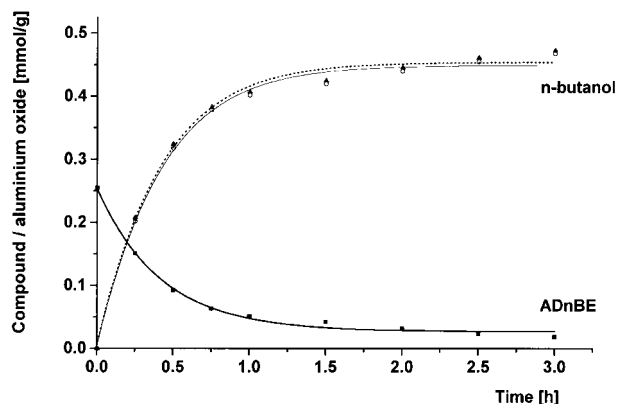

Figure 6 Hydrolysis of ADnBE in presence of aluminum oxide at 100°C: (———) experimental; (− − −) theoretical.

position rate of the urethane model compound. The phenyl group is more effective than is the methyl group at the nitrogen. It seems that the decomposition of the DPCnBE stops, when about half of the model compound is decomposed. These results show that the decomposition process can be influenced by the chemical structure of the model compound.

Interaction of Model Compounds with Surface-modified Chromium Dioxide

To reduce the chemical interaction activities of chromium dioxide, it is necessary to change the chemical composition of the surface by increasing the content of CrOOH. BASF Aktiengesellschaft has produced a stabilized chromium dioxide with a high content of CrOOH at the surface.[3]

This modification greatly influences the decomposition rate of the ester and urethane model compound as shown in Figure 4. Unstabilized chromium dioxide decomposes PCnBE more quickly than does ADnBE (see dashed curve in Fig. 4). The decomposition of PCnBE stops at 85% conversion. This may be explained by the reactions of the resulting hydrolysis products at the pigment surface and their stabilizing action against further decomposition.

However, in the presence of stabilized chromium dioxide, the decomposition rate and the amount of decomposed model compounds are considerably reduced. At the beginning of storage at 100°C in the presence of a 12-fold molar amount of water surplus, only 5–10% of the ester and urethane compound decomposes and then the decomposition process is finished. The model com-
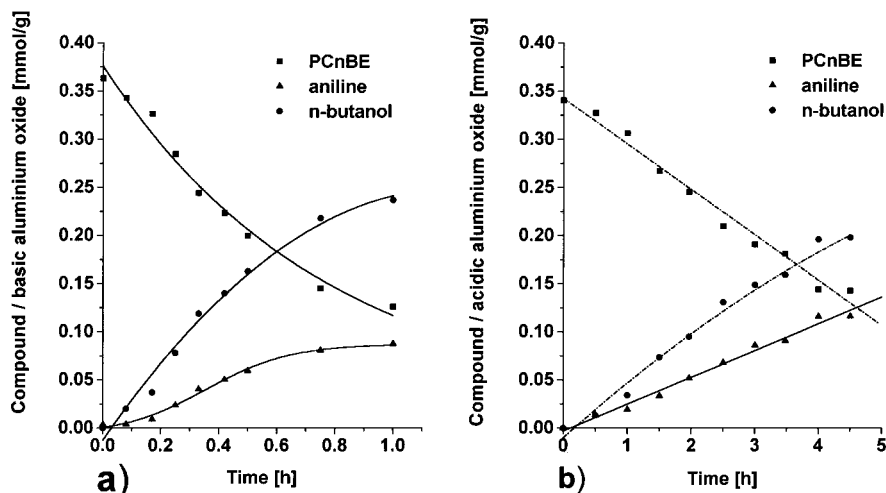
Figure 7 Hydrolysis of PCnBE by interaction with basic and acidic aluminum oxide at 100°C: (a) basic aluminum oxide; (b) acidic aluminum oxide.

pounds show no chemical changes during continued storage.

Interaction of ADnBE or PCnBE with Aluminum Oxide

Aluminum oxide is a pigment which contains Al—OH groups, Lewis centers, and adsorbed water at the surface as shown in Scheme 1. It is supposed that these groups will not have such a strong chemical interaction with the model compounds as will the unstabilized chromium dioxide (Table II). Aluminum oxide cannot oxidize the model compounds and the products formed by the decomposition.

Nevertheless, in the presence of the basic aluminum oxide (Fig. 5), the decomposition rate of both model compounds is higher than in the case of unstabilized chromium dioxide (Fig. 4). Comparing the basic aluminum oxide with the acidic compound, we found the former to be much more effective for the hydrolytic decomposition of ADnBE and PCnBE (Fig. 5). The decomposition occurs by hydrolysis. After interaction of ADnBE with basic aluminum oxide, the n-butanol thus formed was found by gas chromatography in a stoichiometric relation as shown in Figure 6.

A similar behavior was observed in the ADnBE-coated acidic aluminum oxide. In the system with PCnBE, the formation of n-butanol was found with both types of aluminum oxide at the same level and thus agrees with theoretical calculations. The formed phenylcarbamide acid resulting from the hydrolytic process is decomposed to aniline and carbon dioxide. The aniline can be

registered by gas chromatography in the two cases as well but in a lower concentration than n-butanol (Fig. 7). An incomplete decomposition of the formed phenylcarbamide acid or a partial adsorption of the aniline at active centers on the aluminum oxide surface may account for these results.

All these results confirm that the model compounds decompose in contact with the aluminum oxides by hydrolysis. The same decomposition mechanism occurs in the systems with unstabilized chromium dioxide, but the oxidation of the formed hydrolytic products and their binding at the pigment surface prevent their registration by gas chromatography.

CONCLUSIONS

In this article, a method for investigating the chemical interactions of organic model compounds with inorganic powders has been described. The compounds selected contain characteristic structural units of polyurethanes, which are polymeric binders in pigmented coating systems. Decomposition in the presence of chromium dioxide or aluminum oxide occurs by hydrolysis. In the case of unstabilized chromium dioxide, the products of the hydrolysis which may be a part of the initial compound will be oxidized. The rate of the decomposition can be influenced by temperature, water content, structural variation of the model compound, and surface modification of the pigment. Surface modification of the pigment has the most

significance on the reduction of the decomposition rate.

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