APPLICATIONS OF ORMOCERS

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1. INTRODUCTION

Inorganic-organic composites of the ormocer type have now been known for more than 15 years. They are based on sol-gel techniques for synthesizing the inorganic part and organic groupings are used for modifying the inorganic backbone by special organo-functional groups or by reactive groupings, leading to an additional organic polymeric type of network [1 - 6]. While in these papers the molecular type of composite is emphasized, more recently systems have been described with well-defined inorganic phases in the nano range [7 - 9]. Inorganic-organic composites with inorganic phases in the nano range are of interest since in opposition to the molecular type of composite, inorganic solid-state properties can be generated, but if the particle size is kept below the Rayleigh scattering limits, these composites are highly transparent and can be used for optical purposes. In addition to this, solid state properties based on the small size, e.g. quantum size effects, can be introduced into these composites, too.

For obtaining a high optical transparency, it is indispensable to avoid agglomeration of nano-sized particles. For this reason, the surface reactivity of these particles has to be controlled. The control of surface reactivity can be obtained by a variety of means. As shown elsewhere [10, 11], colloidal systems like boehmite can be reacted with acids or ß-diketones [12], and stable surface compounds can be obtained. These particles, depending on the type of surface modification, can show a reduced agglomeration behavior or may have special reactivities if the surface modification with bifunctional molecules is used [13, 14]. In these examples, the surface modification has been used for in-situ grown particles, e.g. methacrylic acid for zirconia, ether alcohols for alumina or amines for titanium nitride or metal colloids. In fig. 1 an overview over possibilies of surface modification of colloidal particles is given.

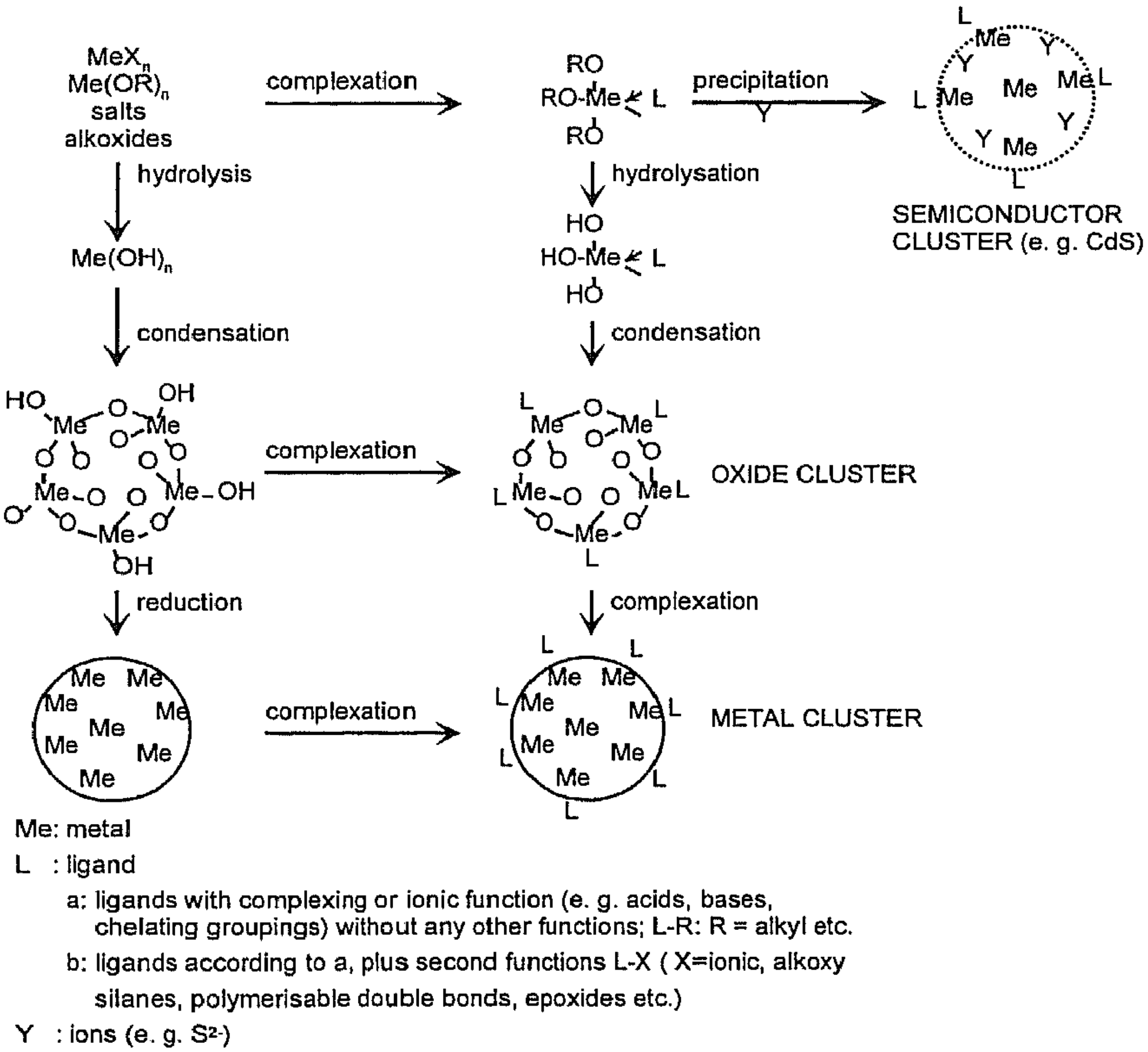

Fig. 1: Synthesis schematics for the preparation and surface modification of ceramic, semiconductor and metal colloids [after 15 - 18].

The surface modification of small colloids provides several aspects. First, the particle growth can be controlled due to the decrease of the surface free energy by selective interaction with the modifying agents. Second, the agglomeration (condensation of hydroxides, hydrogen bonds, van der Waal's forces) can be controlled by the control of surface reacitvity. Third, special reactivities can be generated, as shown in fig. 1, by using second functions like polymerizable or hydrolyzable and polycondensable groupings (e.g. siloxane groupings). In addition to this, special functions based on additional organic groupings can be introduced, like hydrophilicity or hydrophobicity.

In order to obtain composites, the particles have to be introduced into a matrix, or the matrix has to be generated simultaneously, or the particles have to be generated in a liquid or solid already synthesized matrix. In fig. 2 a survey about the possibilities of developing optically transparent composites is shown.

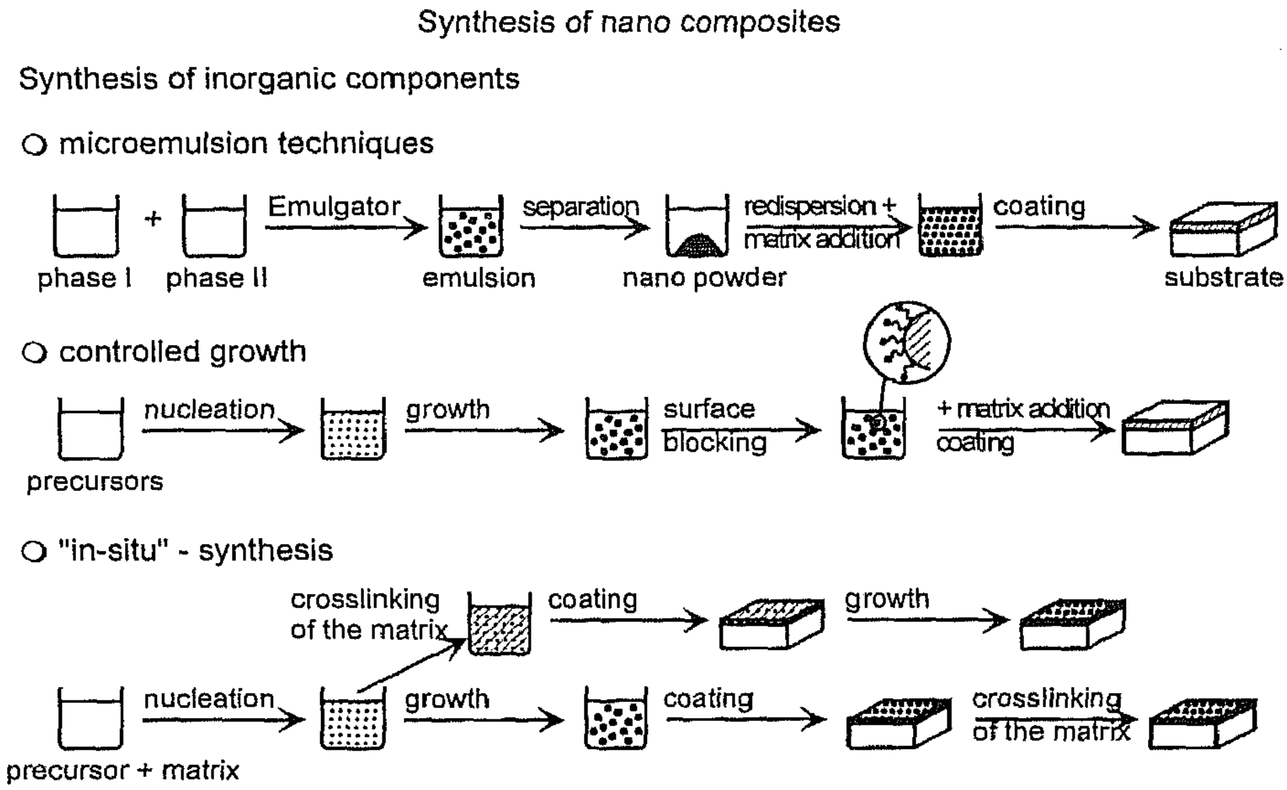

Fig. 2: Schematic overview over a variety of different possibilities for fabricating optical composites.

The concept of formation of a nanocomposite type of inorganic-organic materials provides a variety of different possibilities. In the following a series of material developments will be shown using the described principles.

2. MATERIAL DEVELOPMENT

2.1 Coatings for Optics

As described in detail elsewhere [19, 9], photopolymerizable systems have been prepared on the basis of methacryloxy containing silanes, zirconia and methacrylic acid. These systems show high optical transparency (less than 1 dB/cm in planar waveguides), interesting surface hardness (less than 2 % haze by standardized taber abrader test [DIN 52347]) and can be photopolymerized due to the methacryloxy groupings. As shown elsewhere [20], polymerization can be carried out efficiently by using photoinitiators and UV light. This has been used to fabricate planar waveguide and micro-optic systems like lens arrays, gratings and fresnel lenses. The photopolymerization has been used for holographic pattern fabrication by laser-two-wave mixing and subsequent development to surface patterns or to burried patterns by post bake. The systematics of the process is shown in fig. 3.

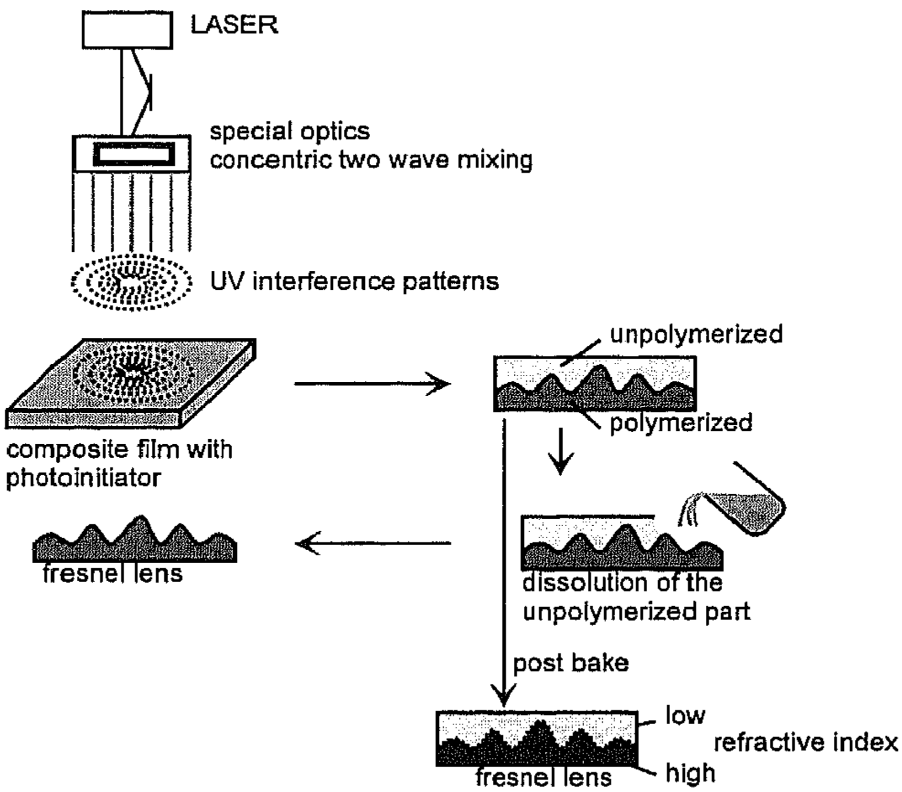

Fig. 3: Systematics of the holographic process for producing gratings or micro-lenses.

It has been shown that by light-induced diffusion, phase separation takes place in the films, according to the intensity fluctuation of the mixed laser beam. The induced gratings can be stabilized by a second polymerization with unmodulated light, leading to so-called burried gratings, as indicated in fig. 3. If UV polymerization can be carried out during embossing, micropatterns can be formed and stabilized very efficiently. A focused laser beam can also be used as light source leading to programmable patterning, e.g. for channel waveguides.

In fig. 4 a survey over the already produced types of micro-optical systems is given.

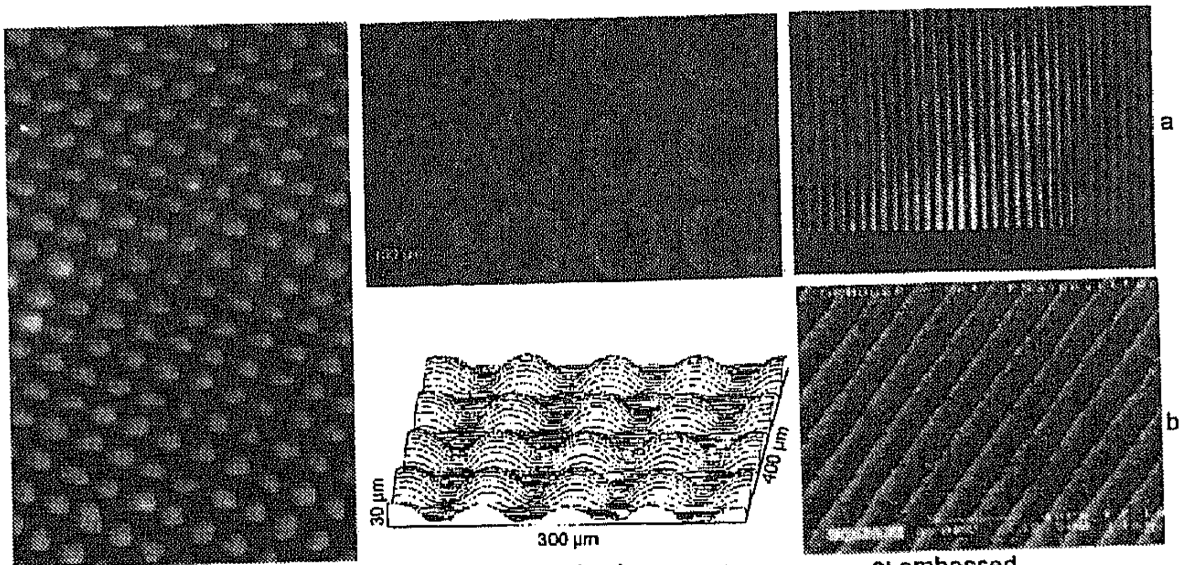

Fig. 4: Examples for micro-optical systems.

2.2 Low Surface Free Energy Systems

If, in addition to the methacryloxy group containing silanes (e.g. methacryloxy propyl triethoxy silane, MPTS), silanes with perfluorinated organic side chains are used, coatings with low surface free energies can be obtained [21, 22]. In these cases, even with rather low contents of fluorinated side chains, it is possible to obtain surface free energies of about 18 mJ/m², which is below the surface free energy of polytetrafluoro ethylene. These systems can be used as transparent, dust-repellent coatings on plastics, metals or glass. They can be cured by thermal initiation or photoinitiation at relatively low temperatures (depending on the desired hardness between 90 and 150 °C). If the zirconia methacrylate system is replaced by tetraethyl orthosilicate and methyl triethoxy silane as precursors, the systems can be fired up to 400 °C without losing its low surface free energy properties. These coatings, applied on glass, withstand 500,000 wiper cycles under wet conditions without remarkable decrease of the surface free energy. The lowest content of fluorinated silane causing sufficient reduction of surface free energies is as low as 1.7 mole% and is due to the fact that the system undergoes a self-alignment during coating. The adhesion of these systems used as coatings on glass, for example, can be promoted by polar groupings of the silanes (e.g.

≡SiOH) and is excellent. ZrO_2 or SiO_2 nanoparticles provide a high abrasion resistance, not affecting transparency. In fig. 5a the self-aligning effect and in fig. 5 b the dust-repellent effect of the coating is shown.

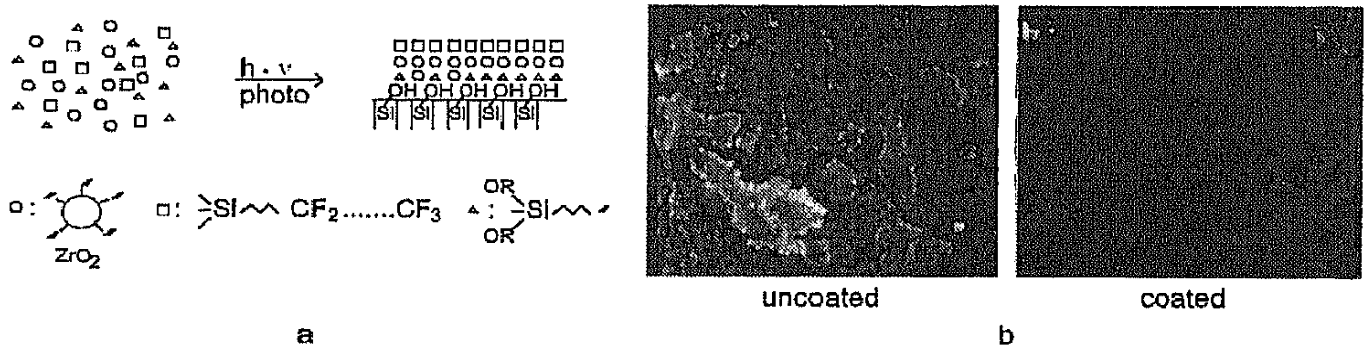

Fig. 5a: Schematics of synthesis and self-alignment of the ZrO_2/MPTS/ methacrylic acid/fluorinated silane system to a gradient coating [after 21];
5b: effect of the coating in a soiling experiment: repeated treatment with a suspension of fused silica/motor oil in water, no cleaning.

In fig. 6 another application of the coating for preventing the carry-over with liquids pumped through thin pipes is shown, which is very important for all type of automated liquid analyses or pipe systems switching between different liquids frequently. In the applied systems no carry-over was observed.

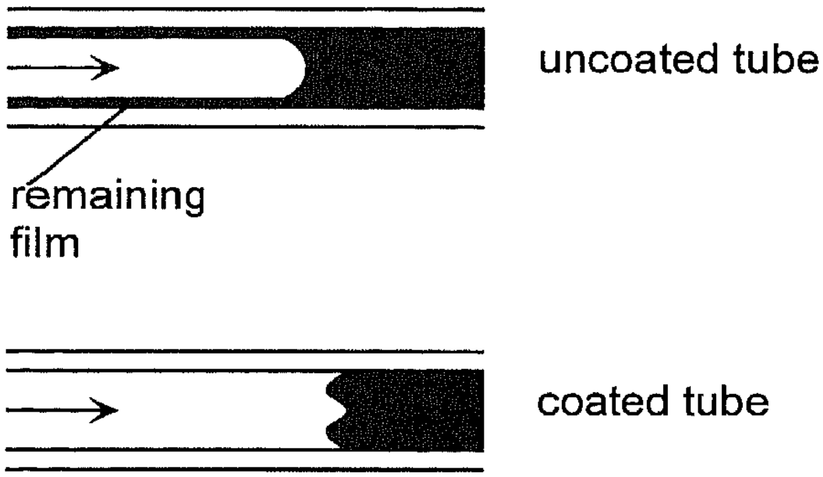

Fig. 6: Schematics of avoiding of carry-over in thin pipes.

Other successful applications with low surface free energy coatings already in industrial use are conveyer belts from stainless steel as substrates for the production of back-side foamed carpets or coated Al bottles for the food industry.

2.3 Non-Linear Optical Systems

Coatings with χ^3 properties have been developed using the in-situ synthesis of metal colloids, e.g. gold [16]. In these systems, based on the zirconia methacrylate systems as a matrix, soluble ionic gold compounds can be introduced with diamine group containing triethoxy silanes as ligands [23]. The schematics of the synthesis is given in fig. 7.

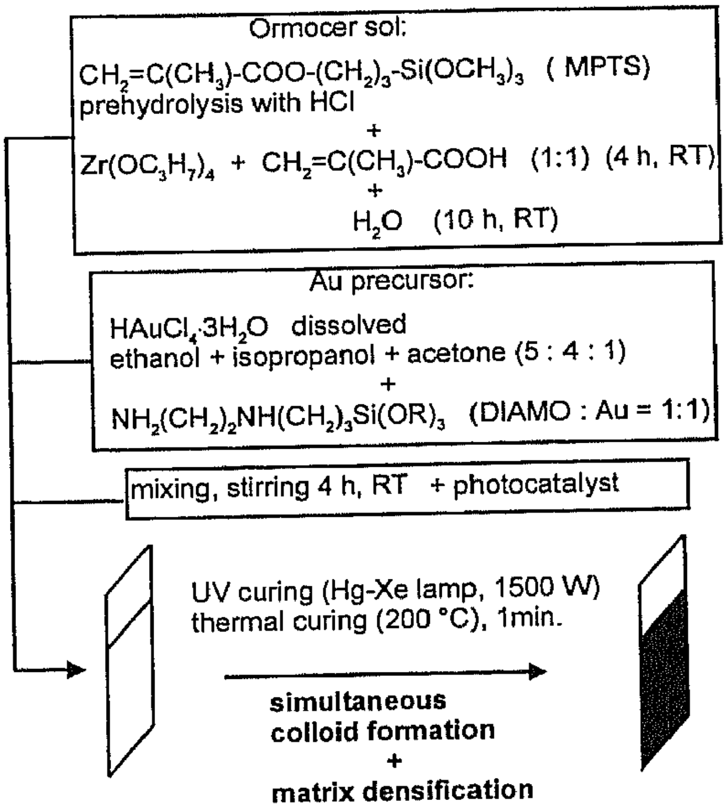

Fig. 7: Schematics of the synthesis of gold-containing films [after 23].

After stabilizing the gold ions in the inorganic-organic composite matrix, a nucleation process can be initiated thermally, leading to a growth of gold colloids in the composite matrix. The growth process depends on the ligands used for the ion stabilization. The gold colloids show high χ^3 values in the case of diamino ligands (with $\chi^3_m = 2.6 \cdot 10^{-6}$) and response time below 7 ps [24]. Other metal colloid containing systems have been prepared with similar routes [25, 26]. Due to the variable matrix system, all types of micropatterning processes can be employed to these systems.

2.4 Hard Coatings

As reported earlier [27, 28], a molecular inorganic-organic composite type of materials had been developed for hard coatings on CR[39] eye glass lenses and used in industrial applications since 1987. It could be shown recently [29] that the scratch resistance can be substantially increased if additionally nanoparticulate systems like boehmite or γ-alumina are added to epoxy silane/$Si(OR)_4$(≡TEOS)-based systems. As shown elsewhere [27 - 29], epoxy based systems lead to higher scratch resistance than systems based on methacrylic groupings containing silanes. In the case of the addition of nano-scale alumina particles to epoxy silane/TEOS based systems, the polymerization of the epoxide to the polyethylene oxide polymer chain is catalyzed by the aluminum oxide, leading to a very special structure with alumina nano-particles embedded in polymer networks and additionally crosslinked to the SiO_2 and the alkoxysilane, as proved by ^{28}Al NMR spectroscopy. These systems can be cured to coatings with extremely high scratch resistance and are used in industry for CR[39] eye glass lenses.

Recent investigations for polycarbonate [30] show that even with 1000 cycles of taber abrader the haze obtained is below 1.5 %. This may lead to new opportunities for polycarbonate applications. The described systems have been used for scratch-resistant coatings for metals, too.

2.5 Anticorrosive Systems with Tailored Interfaces

Systematic investigations have been carried out with systems based on epoxy group containing silanes in combination with aluminum alkoxides, additionally modified by tetraethyl orthosilicates. These systems, the synthesis of which is described elsewhere [31] have been tested with respect to their corrosion protection on the metal surfaces. The synthesis process controlled by NMR analysis shows that sols synthesized from alkoxy silanes containing methacryloxy or epoxy groupings can be prepared with sufficient reactive silane or siloxane groups (SiOR and SiOH) to provide chemical bonds between the coating and metal surfaces as far as they are coated by an hydroxide layer (e.g. Al). Corrosion protection was tested using a two weeks salt spraying test which does not show any traces of corrosion and without any decay of adhesion, even if cross-cuts are made before the corrosion test. The effect is attributed to a tailored interface with bonds immobilized by the inorganic-organic backbone. The coatings can be applied in thicknesses up to 20 μm and are still flexible after curing. They can be applied to

Al without any pretreatment except cleaning. In addition to this, organic dyes or inorganic pigments can be introduced to obtain colored coatings. Penetrating water still is able to cleave bonds, but due to the impossibility to remove "the corrosion products", the balance of mass equilibrium still remains on the binding side. The hypothesis is shown schematically in fig. 8.

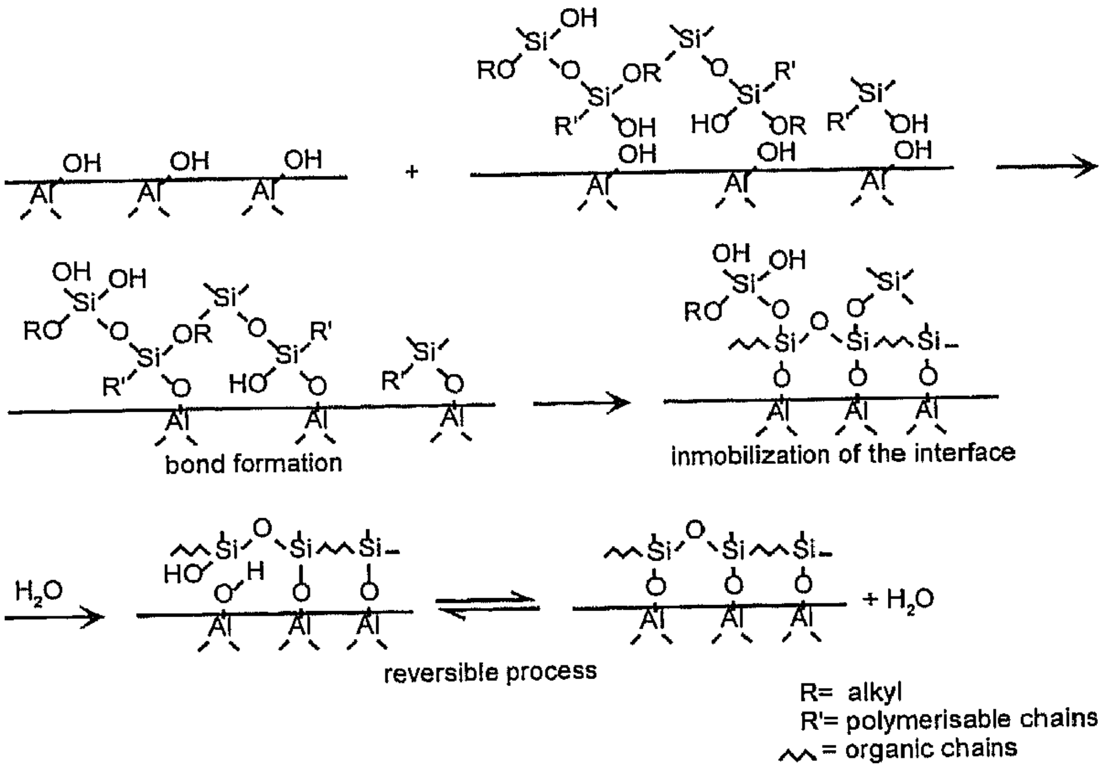

Fig. 8: Schematics of the corrosion protection effect of tailored interfaces.

Similar results have been obtained with iron, zink or magnesium surfaces.

3. CONCLUSION

The investigations carried out show that using basic principles, interesting materials for a variety of applications already used to a great deal in industry have been obtained, ranging from optical high-tech areas down to multifunctional or even passive coatings on a variety of substrates.

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Anlage A

Micro patterning of the nanocomposite system MPTS/Zr/MAS