

Chapter 30

Non-Hydrolyzed Resins for Organic-Inorganic Hybrid Coatings: Functional Coating Films by Moisture Curing

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ABSTRACT

This chapter focuses on resins based on non-hydrolyzed, monomeric and polymeric alkoxysilanes. As alternative to classical sol-gel processing, the resins are applied to a surface without a preceding hydrolysis step. Only after application, hydrolysis and condensation of the alkoxysilyl groups occur by means of atmospheric moisture to result cross-linked organic-inorganic hybrid coatings. While the use of non-hydrolyzed silanes is well established, for example by applying polyethyl silicate as binder for zinc-rich anti-corrosive primers, this chapter describes the chemical structures of various novel organic-inorganic hybrid precursors that have significantly extended the area of application to adhesives and scratch-resistant, repellent, or anti-fouling coatings. At present, individual resins are produced and applied at industrial scale in the fields of protective coatings and automotive topcoats.

INTRODUCTION

As an alternative to classical sol-gel processing, organic-inorganic hybrid coatings can be prepared from alkoxysilyl-functional resins that hydrolyze and condense first after application to a surface, generally by means of atmospheric moisture. A complete coating composition usually comprises various components such as resins, pigments, fillers, solvents and diverse additives. The present chapter focuses specifically on the chemistry of the resins as the main component. A compilation of various chemical building blocks is provided and possible applications are highlighted to make knowledge available, but especially to inspire other researchers in the field of functional coatings.

DOI: 10.4018/978-1-5225-1798-6.ch030

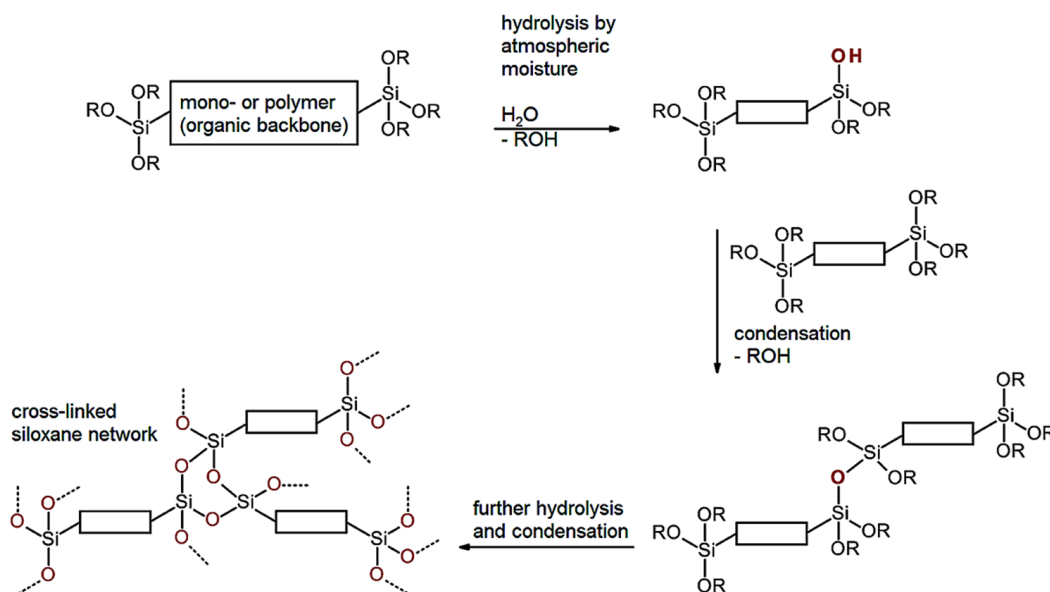
The present materials represent a sub-group of the field of organic-inorganic hybrid materials. The term “non-hydrolyzed” indicates that monomeric or polymeric alkoxy-silanes are applied to a surface without a hydrolysis step prior to application, which distinguishes them from other silane-derived materials. Only after application, atmospheric moisture diffuses into the coating to provide the water necessary for hydrolysis and condensation. Subsequently, a cross-linked network forms as shown in Figure 1.

In a sol-gel process, for comparison, silanes, metal alkoxides or salts are in a first step hydrolyzed and partly condensed by addition of water to form a colloidal solution, a sol. To prepare coatings, the sol is in a second step applied to a surface and forms a gel and possibly subsequently a densified film.

Coatings prepared from non-hydrolyzed silanes have been in focus of both academic research and industrial development. Following early, pioneering work, moisture curing of silanes has seen a significant increase in research and development activities in the past decade and is quite active at present. The number of US-patents filed for epoxy-siloxane hybrid coatings per year as shown in Figure 2 (Witucki, 2013) is a good example for the described development. The results of these activities are novel coatings and, after intense optimization work, commercial products produced in industrial scale, such as, for example, scratch-resistant automotive top coats that do not compromise flexibility or protective coatings. Applications as adhesion primer or repellent coating are as well considered.

The cured films differ from solely organic coatings by including a cross-linked siloxane network. Various investigations report individual inorganic siloxane domains in an organic matrix (Groenewolt et al., 2008; Metal finishing, 2012; Rekondo, Fernández-Berridi, & Irusta, 2006; Sangermano, Vitale & Dietliker, 2014), but two interpenetrating networks or organic domains in an inorganic network are possible as well. Such material can also be prepared by sol-gel processing. However, the application of non-hydrolyzed resins gives the researcher novel opportunities. On the one hand, there are no restrictions to apply large polymeric backbones that are immiscible with water or that would gel too fast in a sol-gel process. This expands the applicability of hybrid coatings to fields that were previously dominated by

Figure 1. Curing by hydrolysis and condensation in an applied coating film



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