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Cure of coatings with ambient Light indoors

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Abstract

The study demonstrates that UV-curable acrylate coatings or patches incorporating colored phosphine oxide initiators can be effectively cured by ambient laboratory light within 5–7 minutes under specified experimental parameters. No further processing is required following the application of these coatings. The paper also provides a brief overview of Type I and Type II photoinitiators.

Keywords: Acrylates; Photoinitiation; Ambient light; Type 1 and 2 Photoinitiators

Introduction

In this brief note we discuss valuable products which polymerize or vitrify, namely coatings, paints, sealants, calks, patches, adhesives, glues. Fortunately, after applications many these products do not require any additional efforts of a chemist or a construction worker: vitrification or cure occurs by "itself" in the ambient atmosphere. In this note, we will use "cure" and "coatings" as shorthand for related products and curing methods. A novice in this field may ask a question: Why does the coating not cure in a commercial container or tube but polymerizes in the air? The simplest for understanding is the case is the latex paint which is an aqueous colloidal solution: water evaporates leading to a finished paint. Many adhesives or glues have solvents which evaporate after application, different physical chemical processes and/or formed polymer have a higher Tg than the application's temperature. Common popular silicone products undergo polymerization in the air. Silicones contain alkoxy silicon groups SiOR that react with air moisture to form silanol SiOH and alcohol ROH. SiOH condenses to form a polymer with a ~~Si-O-Si~~ fragment. (The valency of Si is obviously four.) The impressive cyanoacrylate glue or adhesive (Krazy Glue or Super Glue) cures quickly in the presence of air moisture.

Typical range of absolute humidity of water (g) in the air is 0–30 g/m^3 depending on temperature, the warm air holds more moisture In this context, we are referring to atmospheric pressure. It turns out that only moisture is an important component. What are the other reactive compounds in the ambient air which could initiate cure? Concentration of reactive ozone in the ambient air is 40 -300 mg/m3 depending upon the temperature and pollution of the air. It is negligible concentration. Dioxygen presents in the air with a high concentration of 0.27 kg/m^3. Dioxygen has a few uses in polymerization. Oxidative polymerization of monomers with two or more unsaturated groups has been used to produce hydrophilic polymers [1]. However, the process requires elevated temperatures, passing of the air [1]. That does not correspond to the initial approach "do nothing" for cure after application of coating. Moreover, there are additives to coatings which serve as antioxidants and anti-ozonators which expand life span of coatings. Dioxygen slows down free-radical polymerization [2]. A number of coatings undergo slow cure while stored in their containers, so commercial products are recommended to use within a year or so of manufacture.

Visible light

The previous section reviewed established polymerization methods of products for the reader's convenience. In addition to reagents in the air, ambient visible light (400-800 nm) from fluorescent lamps or sunlight through windows also acts as an indoor "reagent". Typical fluence (irradiance) indoors is I =1-20 W/m2. This light has enough energy to trigger photoinduced reactions. UV-curable coatings are supplied in drums for commercial use or brown Nalgene bottles for research. Both types of containers prevent penetration of UV and visible light. We will consider below only free-radical polymerization (FRP) [3-5]. FRP coatings of (meth)acrylate and others need a photoinitiator (PI) that absorbs visible light [3,4]. Such PI are common commercial phosphine oxides with trade names Irgacure 819, Irgacure TPO, Darocur 4265, and some other PI capable for photodissociation [3,4].

These PI are colored; upon irradiation with visible light, they undergo Norrish splitting I [3]. Such PI is also called Type I PI [3,4]. Absorption spectra of the colored PI are presented [4] and on the Internet. Absorption spectra of phosphine oxides PI extend up to λ 425 nm and of Irgacure 819 up to λ 440 nm. It is improbable that it may be synthesized Type 1 PI with longer photoactive wavebands in visible region. The energy of visible light will not be enough for the weakest bond dissociation. Our initial experiments showed that ambient light can cure acrylate monomers with suitable PI, even in thick layers and with $CaCO_3$ filler, within minutes. The coating or patch was uniformly mixed. The composition and properties of such coatings are presented in Table 1.

Table 1: Composition and Characteristics of Ambient Light Cured Coatings [6].

Formulation	A, wt.%	B, wt.%.
SR506C, f=1	9.2	14.7
Ebecryl 8301R, f=6	17.0	-
Ebecryl 8602, f=9	-	14.7
Irgacure TPO	1.8	-
Irgacure 819	-	1.0
Additol VXW	1.0	1.0
$CaCO_3$	71.0	68.6
pH	8.8	9.2
Viscosity, P.s	30.4	47.5
Cure tme, min	4-5	6-7
Hardness of the cured coatings Shore A, units	86	88-90

Irradiance was I = 4-6 W/m2. Experiments are done at room temperature. Thickness of an uncured product was 3 mm. SR, Ebecryls and Additol – flow control additive - were of Allnex. f stands for acrylate functionality of a monomer/oligomer. Therefore, it has been observed that ambient indoor light can achieve curing within minutes, even when using a light-scattering filler at approximately 70 wt.% concentration. Cure was achievable up to 3 mm, but not beyond, under our conditions. One does not need a conveyor system, light sources. Ambient light curing works well for individual samples when speed isn't important. Experienced experimenters know that fully curing paints, adhesives, and glues takes significant time.

Type 2 PI for Ambient Light

It appears to be unfeasible to obtain a PI composed of common chemical elements that dissociate into reactive radicals upon irradiation with visible light at λ > 440 nm, see above. At the same time there are many colored compounds with an absorption spectrum protruded up till IR region which are photoreactive. These compounds don't split into radicals, but can abstract or sometimes donate a hydrogen atom, generating two radicals. H-abstraction may follow an electron transfer reaction. These are the known Type 2 PI [3,7]. Such PI abstract H-atom from monomer/oligomer upon absorption of light. The formation of two radicals occurs more efficiently in the presence of coinitiator or accelerator of FRP which is a good H-donor. Usually coinitiators are amines, borates or thiols. The radical of a complex PI is often less reaction in the initiation of FRP than a "simple" active radical of coinitiator.

Below are listed some commonly used Type 2 photoinitiators. Camphorquinone (2,3-bornanedione) absorbs visible light to produce radicals from coininiator amine. This process is widely applied in dentistry during the free-radical polymerization of methacrylate fillers. Natural and bio-derived colored compounds are used as PI [8]. Examples are riboflavin, curcumin, flavonoids, see ref. [8]. Oster et al. [9] demonstrated in 1957 that riboflavin can photoinitiate polymerization of acrylamide. Xanthene dyes [10], colored aromatic ketones and quinones as well as cationic dyes are PI. New highly efficient, complex structure Type 2 photo-initiators (PI) have been documented in [11,12]. Stable free radicals are usually colored. Some aroxyl radicals being photoexcited abstract H-atom [13]. Colored Type 2 PI allow deep curing due to long-wavelength absorption [3]. Dyes bleach during photopolymerization but not necessarily completely. The cured product can be colored.

Conclusion

Acrylate coatings have been shown to be cured under ambient room light when colored Type I phosphine oxide PI are present. While the curing process is gradual, typically requiring between 5 and 30 minutes in our different experiments, it eliminates the need for conveyors or dedicated light sources. This method is particularly suitable for do-it-yourself applications. Furthermore, it is hypothesized that with appropriately formulated, highly light-sensitive colored Type I or II PI, curing times may be reduced to as little as one to two minutes. Proper cure of coatings in indoor environments is essential to ensure optimal performance and durability. Factors such as irradiance, temperature, humidity impact the cure, and maintaining steady ambient conditions help achieve a required cure.

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