A 100% solids UV LED curable coating

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Abstract

A 100% solids UV LED curable coating and the machine for its application/cure has been developed. The machine is equipped with a 395 nm UV LED. The coating is suitable for different flooring applications: VCT, hard wood, laminate, marble, terrazzo, concrete. Some of the applications such as hard wood, concrete and terrazzo floors require a 100% solids UV LED curable primer that has been developed as well. The resulting coating is scratch and impact resistant.

Introduction

The industry started implementing UV (Ultra Violet) cure since the 1960s. Energy cure of (meth)acrylated resins is already a well established process that is still gaining further acceptance. The UV curable coatings offer high productivity, low energy consumption if compared to thermally cured ones. A wide variety of commercially available (meth)acrylates allows to achieve desirable properties throughout the spectrum of possible coating properties: from hard and scratch resistant coatings through soft and robust ones.

For slightly more than a decade a new emerging sector of UV cure started forming: UV LED (Light Emitting Diode) cure. This became possible with the recent developments in LED industry allowing production of powerful UV LEDs.

As with UV technology at the beginning years of its acceptance, UV LED found its industrial implementation in graphics and UV printing industries first. The power and efficiency of UV LEDs that are commercially available is increasing constantly making it a valuable cure source for other UV coatings as well as UV adhesives.

The advantages of UV LED technology over well established UV Mercury technology are lower operating temperature, long lifetime, low maintenance. UV LED is an ozone-free and mercury-free environmentally friendly technology. In addition, UV LEDs are very compact. Low operating temperature and low emitted heat allows curing a UV coating on very thermally sensitive substrates. The small compact size of the UV LED machine permits an easy transfer of this technology to field applied coatings.

UV cure is already being implemented in field applied wood, concrete and VCT (vinyl composition tile) floor coatings. Fast return to service, the UV coating is fully cured immediately after the irradiation, of UV curable coatings is a huge advantage of these coating over conventional technology that requires several days for the coated floor to fully return to service.

Traditional medium pressure mercury lamps emit a wide spectrum of radiation with a significant portion of it in the ultra violet region: UVC, UVB, and UVA. This spectral breadth allows a wide variety of photoinitiators to choose from. On the other hand, lots of hard stray UV light from the UV mercury machines that are used to cure coatings in the field today requires strict safety measures to be executed for the people that are in a vicinity of the UV cure machine. It is different for UV LEDs. The stray light that can be reduced to a minimum by bringing the LED head very close to the substrate surface has a wavelength of 495 nm that is essentially free of hard UV, no ozone is produced by the operating UV LEDs. This makes this technology suitable for the field application and the cure of the coating when the public is present. Therefore, a business owner does not have to close the whole facility to coat the floor just a part of it. This means that the job of coating the floor does not have to be done during off hours. It is very useful for the warehouses or stores that are open 24 hours a day.

UV LEDs that are available today have a narrow (almost monochromatic) emission bands in UVA region of the spectrum. High energy UV radiation such as UVC is required to effectively cure standard UV coatings in ambient conditions. Ambient conditions here are defined as the presence of oxygen at concentrations that are equal or above 20% by volume which can be translated into 18 kPa oxygen partial pressure. In these conditions, most of the existing UV curable coatings will not be sufficiently cured under UV LED light even if the UVA absorbing initiators are applied. The surface of the coating does not completely cure i.e. remains tacky after UV exposure due to oxygen inhibition. The practice to apply a nitrogen blanket in order to properly cure UV coating compositions is customary even when Mercury vapor UV lamps are utilized. This is true especially if high scratch or abrasion resistance is required. There are several antioxidants that can offset oxygen presence in the formulation to be cured. Examples of these include thiols, phosphites, amines and borates. In this work, additives that prevent oxygen inhibition such as multifunctional thiols have been successfully applied to overcome this problem.

Environmental protection agency (EPA) VOC regulations are getting stricter each year especially for indoor coatings/finishes. Therefore, the need exists for a 100% solids or water based coating that can be cured in ambient conditions with UV LED light.

It is an object of this presentation to describe an EPA compliant UV LED curable coating formulations. All the described coatings have low viscosity and are efficiently curable with UV LED light in ambient conditions. The performance (scratch, abrasion, impact resistance) of the cured coatings compares to the performance of the conventionally cured UV coatings and in some cases exceeds it.

Kegel LLC is a company that develops products, procedures, and systems to enhance the sport of bowling. The presented coating research was performed to create a coating for a synthetic bowling lane. Bowling lanes are subjected to a very high scratch, abrasion and impact forces. A conventional bowling ball that weighs 8-16 pounds is thrown down the lane more than a hundred times during a day, thousands times per year. Current bowling balls are made of the materials that are very aggressive towards the lane surface. US Bowling congress(USBC) requires wooden lane to be resurfaced once a year to meet flatness of the lane requirements. Currently most of the bowling lanes are made with high pressure decorative laminates (HDPL). Melamine-formaldehyde and phenol-formaldehyde resins are the main constituents of HDPL. Melamine-formaldehyde resin as one of the hardest plastic materials is usually utilized for the surface protective layer of HDPL. HDPL lanes get worn out after several years of use. These lanes are not usually resurfaced, they get changed which is expensive. A very hard and scratch/impact resistant coating can prolong a life of a worn HDPL lane. The focus of this presentation is such a coating.

Although the presented coating was designed as a synthetic bowling lane finish in mind, the coating was successfully transferred to many other substrates that need a scratch, abrasion and impact resistant clear or pigmented coat. Such substrates include but not limited to concrete, wood, vinyl tile, terrazzo, marble. Some of the applications including hard wood, concrete and terrazzo floors require a 100% solids UV LED curable primer that has been developed as well. The coating is free of oxygen scavengers such as amines and thiols, stable in the absence of light, low viscosity. The resulting coating is very robust, scratch and impact resistant. The coating is low smell and VOC-free.

Experimental

Components of the coating composition were mixed in ambient conditions with light exposure kept to a minimum. Plastic (polyethylene) containers were used for mixing with a laboratory mixer equipped with a stainless steel blade. Nanoparticle dispersions in acrylic monomers were received as samples from Nanophase Technologies (Romeoville, IL, a part of Evonik Tego Chemie GmbH (Essen, Germany)), Nissan Chemical America Corporation (Houston, TX), other monomers were received as samples from either Sartomer USA, LLC (Exton, PA) or Cytec Industries (Woodland Park, NJ), multifunctional thiols (Thiocure) were samples from Evans Chemetics Inc. (Waterloo, NY), photoinitiators were samples from BASF.

Three different coatings were tested for LED cure:

FC001-epoxy novolak acrylate based coating containing VOC-exempt solvent, reactive acrylate diluents and less than 5% nanoparticles,

FC002-a 100% solids mixture of acrylate monomers containing less than 20% nanoparticles,

FC003—a 100% solids nanocomposite (high concentration of nanoparticles, >20%) in low viscosity acrylate monomers.

Once mixed coatings were applied with a wire rod of different sizes to a PET film to test abrasion resistance (Δ Haze), scratch and onto a sample of synthetic bowling lane for adhesion and impact resistance tests. Other substrates such as vinyl tile, primed concrete, marble and wood have been tested as well.

The coatings were cured with a UV LED light source: 4 W/cm2 395 nm air cooled RX Firefly light source from Phoseon Technology (Hillsboro, OR). All coatings were cured at the speed of 10 fpm at the distance from the LED surface of 5 mm.

Scratch was tested with a 000 steel wool, 20 rubs no weight applied (0= best; 5=worst). Abrasion (∆Haze) was tested with a TABER® Rotary Platform Abrasion Tester. The coating was subjected to a 100 cycles with 500 g load and CS-10F wheels. Haze of the coating was determined before and after the abrasion and the change in haze (∆Haze) was recorded. A bigger number means more scratches, less abrasion resistance.

Abrasion (weight loss) was tested with a TABER® Rotary Platform Abrasion Tester. The coating was subjected to 1000 cycles with 1000g load and CS-17 wheels. The weight loss after these cycles is recorded. Bigger weight loss means less abrasion resistant coating.

Coefficient of friction was tested according the test specified for synthetic bowling lane surface in USBC manual: The force needed to slide a sled with a total weight of 14 pounds across a coated surface at a speed of about 0.5 feet per second is measured. The resulting force is then divided by 14 lb weight to calculate the kinetic coefficient of friction.

Gloss was measured by a BYK micro-tri-gloss meter on the coatings of the same thickness applied to a black VCT surface and cured.

Results and Discussion

There are a couple of approaches to get a VOC compliant formulation. One is to go solventless. Another is to use a VOC-exempt solvent such as acetone, methyl acetate (MeAc), p-Chlorobenzotrifluoride (PCBTF). Two new additions to VOC-exempt solvent list are Dimethyl Carbonate (DMC) and Propylene Carbonate (PC). The third approach would be a UV curable aqueous dispersion. In this presentation the focus is on the solvent-borne (VOC-free) and 100 % solids formulations.

Besides being impact, abrasion and scratch resistant, the bowling lane coating has to meet several requirements described in USBC (United States Bowling Congress) bowling lane specifications. The Sward rocker hardness of the coating should be 35 or higher, the coefficient of kinetic friction of the coating should be lower than 0.29. In addition, the coating should maintain its recoatability. Bowling lanes are conditioned (oiled) daily and the coating should not interfere with that. Some of synthetic HDPL lanes are glow in the dark (black light fluorescent), the coating is expected not to block the fluorescence or the excitation light wavelength as well.

In order to meet all the aforementioned requirements nanocomposite formulations were investigated. The additions of nanosilica helps scratch, abrasion resistance dramatically and improves the hardness of the coating to meet exceed the required Sward rocker hardness limit. In order to ensure effective surface cure of the coating with UV LED, multifunctional thiols are usually added.

Two coating formulations have been investigated for UV LED cure. FC001 is a mix of an epoxy novolak acrylate with VOC-exempt solvent and reactive acrylate diluents to reduce the viscosity containing less than 5% nanoparticles. FC002 is a 100% solids mixture of acrylate monomers containing less than 20% nanoparticles.

The influence of the addition of thiol on surface properties and surface cure of the FC001 and FC002 have been studied. In tables 1 and 2 the influence of thiol concentration onto the properties of the coatings is demonstrated.

The results collected in the tables below show that scratch resistance of the coating and therefore surface cure depends significantly on the amount of the added thiol. Solvent-borne formulation requires at least 3.5% of thiol in order to achieve sufficient scratch resistance while solvent-free formulation requires only 1.5%.

Table 1. Solvent base UV LED bowling lane finish

FC001, % Thiol (by w of resins)	Coefficient of Friction	Scratch (5-worst, 0-best, no scratches)	∆Haze (Abrasion)
0	0.36	4	15.1
0.15	0.34	2-3	12.9
0.35	0.33	2-3	14.9
0.6	0.33	3	13.2
1.2	0.28	0.5-1	14.6
2.4	0.29	0.25	12.2
3.5	0.305	0	13.5
5	0.35	0	12.4
10	0.36	0	12.8

Table 2. 100% solids UV LED bowling lane finish.

FC002, % Thiol (by w of resins)	Coefficient of Friction	Scratch	∆Haze (Abrasion)
0	0.38	2	8.0
0.5	0.40	0.5	7.8
1	0.38	0-0.25	8.2
1.5	0.36	0	5.6
2.5	0.35	0	5.9
5	0.39	0	6.0
10	0.40	0	5.9

The impact on abrasion resistance is not as dramatic but the abrasion resistance continually improves with the increase in thiol concentration.

The effect of thiol addition on the coefficient of friction is present as well. The coefficient of friction decreases with the addition of thiol at lower concentrations of thiol until the full cure of the surface of the coating is achieved. After that, the coefficient of friction increases with further increase in thiol concentration.

Besides fighting oxygen inhibition while the coating is cured with UV LEDs thiol makes the formulations unstable for storage since oxygen inhibition of spontaneous polymerization is absent in this case. At concentrations of thiol above 10% the formulations become very unstable, solvent-free formulations gel almost instantly. The shelf life of the solvent borne coating formulation is more than 6 month in a glass container at room temperature, the shelf life of 100% solid formulation depends on its composition but generally is much shorter than that of solvent borne composition.

Since the addition of thiol as an oxygen scavenger is getting accepted for low energy cure and thiol-ene reactions in general are getting more attention from industry, there were studies on the stabilization of thiol-containing formulations. It has been demonstrated that a stable thiol-(meth)acrylate formulation is possible when a classical radical stabilizer is combined with acidic co-stabilizers. The significantly improved storage stability of thiol-acrylate system has been demonstrated [1].

During the search for another way of overcoming the oxygen inhibition without the oxygen scavengers the effect of the addition of particles to the 100% solids formulation has been studied. The example of the influence of the nanoparticle concentration on the oxygen inhibition of UV LED cured TMPTA is shown in Table 3. The effects of oxygen inhibition is significantly minimized in the presence of about 35% of Nanoparticle and the coating with the thickness of about 30-35 microns can be successfully cured with a UV LED without the oxygen scavenger present.

Table 3. The effect of nanoparticle concentration on oxygen inhibition of UV LED cure of TMPTA, concentration of photoinitiators is 5.5% (w).

Percent of nanoparticles in TMPTA	Scratch	Δ Haze, %
50	0	5
45	0	5.4
40	0	5.3
35	0	5.5
30	0.3	6
25	2	8.2
20	5	11.5
15	>5	12.8

The UV LED storage-stable coating formulation is based on the findings above. FC003—a 100% solids nanocomposite (high concentration of nanoparticles, >20%) in low viscosity acrylate monomers. The properties of all three discussed UV LED formulations were compared to a commercially available UV field applied topcoat formulation in Table 4.

Table 4. UV LED coatings comparison to a commercially available field applied UV top coat.

Coating	Abrasion, Δ Haze	Abrasion, Weight loss	Coefficient of friction	Scratch	Gloss (at 60º)
Uvolve Topcoat (DSM)	25	40	0.166	1-2	85
FC-001 (thiol, no nanoparticles)	25	25	0.236	1-2	85-90
FC-002 (thiol, with nanoparticles)	10	5	0.272	0.5	85
FC-003 (no thiol)	6	2	0.407	0	85

The chemical resistance of FC003 coating was assessed as well. The results are collected in Table 5.

Table 5. Chemical resistance of UV LED 100% solids coating.

Chemical	30 min	1 day	1 month
Nitric acid (70%)	No effect	No effect	Not tested
Sulfuric acid (2.5M)	No effect	No effect	Not tested
Hydrochloric acid (37%)	No effect	No effect	Not tested
Sodium hydroxide (30%)	No effect	No effect	Not tested
Ammonium Hydroxide (30%)	No effect	No effect	Not tested
Ketchup	No effect	No effect	No effect
Red 40 dye in water	No effect	No effect	No effect
Pickle Juice	No effect	No effect	No effect
Mustard	No effect	No effect	No effect
Olive Oil	No effect	No effect	No effect
Cleaners	No effect	No effect	No effect

Since the coating was intended for the bowling lane other specific tests were run on it. For example, a machine shoots a bowling ball to the coated lane twice a minute from ~ 1m height to the same spot. The coating presented can withstand 25000-30000 impacts.

Conclusions

Presented here are a low viscosity 100% solids and a VOC-free UV LED curable nano-composite coatings. It was found that the coating formulations can be cured effectively in ambient conditions without a nitrogen blanket or addition of oxygen scavenger that make the formulation unstable for storage in the dark. The coating is environmentally friendly. Besides being UV LED cured and low viscosity, the coatings have outstanding abrasion, scratch, and impact resistance characteristics. Although the presented coating was designed and tested as a synthetic bowling lane finish in mind, the coating can be applied to many other substrates that need a scratch, abrasion and impact resistant clear or pigmented coat. The coating is suitable for different flooring applications such as: vinyl tile, hard wood, laminate, marble, terrazzo, concrete. Some of the applications such as hard wood, concrete and terrazzo floors require a 100% solids UV LED curable primer that has been acquired as well. The coating is low odor and solvent-free.The UV LED machine for the cure has been developed as well. The machine is equipped with 395 nm UV LEDs and is self-propelled.

References:

“Storage Stable Thiol-Ene Formulations And advances applications thereof” XIAOHUA QIN, PARICHEHR ESFANDIARI, SAMUEL C. LIGON, ALEKSANDR OVSIANIKOV, ROBERT LISKA; RadTech Europe 2013 presentation.