WATER-BASED RADIATION CURABLE OLIGOMERS OPEN NEW HORIZONS FOR HARDCOATS

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Abstract

Water-based radiation curable polymers largely respond to the current environmental concerns and to the quest for high-end coating performances. Radiation Curable coatings are renowned for their hardcoat properties and are consequently extensively used on consumer electronic devices. Due to the high viscosity of the multi-functional urethane acrylates, the coating formulation usually requires a solvent dilution (up to 50%) for spray application. Formulators may use monomers rather than solvent for the dilution but such addition significantly lowers the hardcoat performance. To better meet the increasing environmental awareness and the market demand for high performing hardcoat with low VOC, Cytec has developed a novel proprietary technology that enables formulators to develop a solvent free UV hardcoat for spray application. Using water as the diluent, the unusually high solid content product (65%) provides hardcoat properties that are similar to a 100% UV resin. Performance results and detailed properties of this technology are presented.

I. Introduction

Plastics coatings represent a growth segment of the coating industry and target advanced surface finishes covering aesthetics needs as well as additional protective and functional features [1]. The product applications in this market are endless and typically associated to consumer electronics (like mobile phone, computer, television, compact disk), to industrial plastics (like film, label, box, toy, sport equipment, garden furniture) and to automotive plastics for interior application (like dashboard, trim) or exterior application (like headlight, mirror, bumper, wheel cover).

The radiation curing technology has been used successfully for over 30 years and is especially renowned for superior hardcoat properties. Consequently, suitable radiation curable compositions have been used as hardcoats on plastics for their excellence in scratch & abrasion resistance, stain & chemical resistance, clarity & gloss, adhesion and outdoor weatherability. Due to the high viscosity of the multi-functional acrylates composition, it is usually required to dilute the hardcoat with a solvent (possibly up to 50wt%) allowing a suitable viscosity for spray application. This option constitutes a severe concern for health, environment and occupational safety. As a consequence, the introduction of water-based compositions is the only valuable alternative to meet the market demand for high performing hardcoat with a minimum environmental impact (low VOC) and a low viscosity for applications by spray.

Radiation-curable polyurethane dispersions (UV-PUD's) have been used a lot in the modern industry. They usually consist of anionically-stabilized unsaturated polyurethane colloids in water showing a good colloidal stability [2] and a suitable application rheology [3]. They encompass a very large range of compositions and molecular weights with a linear or branched polymeric architecture. As such, it has been possible to develop clear and pigmented coatings delivering a good balance of chemical & mechanical properties and a good adhesion on various substrates [4]. However, despite the fact that unsaturated polyurethane dispersions present a high functionality suitable for hard coats (expressed as the number of (meth)acrylic unsaturation present on the polymer), it is also the case that the total amount of (meth)acrylic unsaturation (expressed in meq/g) remains limited. This last situation is less favorable for hardcoats requiring a dense crosslinking for superior hardness and resistance.

The optimum chemical nature of radiation curable hardcoats is thus a (meth)acrylated oligomer presenting a high acrylate functionality associated with a low equivalent weight, like is typically the case with urethane acrylates or polyester acrylates. Cytec has developed a novel proprietary technology that enables formulators to propose a solvent-free UV hardcoat for spray application. Using water as the diluent, the unusually high solid content product (65wt%) combined with an excellent colloidal stability (more than 10 days at 60°C) provides hardcoat properties that are similar to a state of the art 100% UV resin.

II. Stabilization of Water-based Radiation Curable System

The stabilization of radiation curable molecules in water is primarily dependent on their physico-chemical nature and principally their molecular weight, whether they are present as liquid-in-liquid (emulsion) or solid-in-liquid (dispersion). Most of these heterogeneous systems are stabilized either by electrostatic or steric repulsion at the interphase of the droplets (in the case of an emulsion) or particles (in the case of a dispersion) preventing their coalescence or flocculation [5]. In the case of *(a) electrostatic stabilization* [6], two particles having charges at the interphase (either anionic or cationic) give a Coulomb repulsion when coming into close contact and allow the system to remain stable. Electrostatic stabilization is understood in terms of an electrical double-layer, constituted from charges at the particle surface and a more diffuse cloud of oppositely charged ions around it. The stabilization increases along with the thickness of the repulsive layers characterized by the Debye length. In the case of *(b) steric stabilization* [7], two particles having their surface covered by adsorbed or grafted amphiphilic polymer chains (usually containing polyethylene oxide) give a steric repulsion when coming into close contact. Due to the oligomeric nature of the target polyacrylate molecules that we want to bring into water for hardcoat compositions, we will essentially consider making and stabilizing emulsions (i.e. liquid-in-liquid compositions).

To complete the big picture of stabilization in aqueous systems, the chemical functionality necessary to ensure the droplet or particle stabilization can either be incorporated into the molecules of the dispersed phase (internal stabilization) or be provided by a tensionactive component (external stabilization) although it must be noted that these two cases can coexist. In the case of an external stabilization, the stabilizing tensio-active molecules are always adsorbed on the interphase, so that electrostatic and steric effects prevent other particles from approaching close enough to cause coalescence or flocculation.

The “Hydrophilic-Lipophilic Balance” of the emulsifier (HLB) is commonly used for nonionic emulsifiers and defined as the weight percent of polyethylene oxide in the molecule, divided by 5. Emulsifiers with a high HLB value will be more hydrophilic (water soluble) and emulsifiers with a low HLB value will be more lipophilic (oil soluble). The HLB of an emulsifier can be determined experimentally [8] and matching its HLB value with the requirement of the organic phase brings optimum emulsion stability, since the emulsifier is essentially present at the organic – water interphase. If the HLB value of emulsifier is too low, then the emulsifier will tend to have a higher affinity for the oil and be less efficient at the droplet interphase to provide colloidal stability and vice-versa.

III. Results & discussion

We have developed a structure-property relationship leading to the selection of model compositions. The process parameters have been further studied based on model and we will present some of the most informative results showing the boundaries of the composition and the process capability in regard of the final system characteristics.

a. Product Characteristics:

Table 1. Characteristics of a model system (Product A)

Aspect	white liquid
Solids (%)	65 ± 1.5
Viscosity (mPa.s)	500 ± 200
pH	3 ± 1
Droplet size (nm)	500 ± 200
MFFT (°C)	<0
Stability 60°C (days)	>10

The characteristics of our model system (Product A) are reported in Table 1. The product is characterized by an unusual ratio between high solids and low viscosity, required for further formulation and application by spray; it can be further diluted with water to meet every requirement. The reduced amount of water is beneficial in terms of transportation cost but also for water release and film formation requiring less energy. It does not contain any volatile organic content (VOC). The minimum film formation temperature is below 0°C which is normal for an oligomer system which is not physically drying, meaning that the film obtained after evaporation and prior to cure is tacky. Blending with others water-based UV resins required the pH to be adjusted to higher values by addition of an amine, for instance triethylamine or Advantex®. Finally, the system stability exceeds 10 days at 60°C.

b. Benchmarking:

In order to better appreciate the benefits of our new prototype (Product A) in terms of hardcoat performance, an investigation of the basic coating properties was carried out and involved the benchmarking with a reference water-based UV-PUD (Product B, highly unsaturated polyurethane dispersion in water) and a reference hardcoat (Product C, hexa-functional UV aliphatic urethane acrylate oligomer diluted in a solvent). Table 2 details the formulations which were considered in this study.

Table 2. Coating formulations

Ingredients	Formulation A Based on new product	Formulation B Reference water-based UV-PUD	Formulation C Reference solvent-based oligomer
Product A (65%)	100	-	-
Product B (35%)	-	100	-
Product C (60%)	-	-	60
Dowanol® PM (co-solvent)	-	-	40
Esacure® HB (photo-initiator)	2.8	1.5	2.8
Tego® Twin 4100 (flow/wetting)	0.5	-	-
ADDITOL® VXW 6396 (flow/wetting)	-	0.4	-
UCECOAT® 8460 (1:1) (thickening)	-	1.5	-
MODAFLOW® 9200 (flow/wetting)	-	-	0.25

All three formulations were applied by bar-coater application at lab scale on either glass (coat weight approx. 40 to 50 g/m² dry), on plastic substrates or on Leneta® opacity charts (coat weight approx. 10 g/m² dry). Water and solvent flash-off was 5 min. at 50°C and radiation curing was carried out with two passes at 10 m/min. under a 120 W/cm Hg lamp.

i. Adhesion Performance:

The adhesion was assessed with the cross hatch tape adhesion test and reported using a 0-100% scale. Direct adhesion was obtained on poly(methylmethacrylate) (PMMA), acrylonitrile butadiene styrene (ABS), poly(vinylchloride) (PVC), poly(ethyleneterephtalate) (PET), poly(cyclohexyl dimethylene terephthalate) (PCTg) and isopropanol-cleaned polycarbonate (PC). There is however no direct adhesion on polystyrene (PS), corona-treated polyethylene (PE) and corona-treated polypropylene (PP) so that a primer coat would be required in this particular cases. The same conclusions apply to the solvent-based hardcoat benchmark.

ii. Optical, Mechanical & Chemical Resistance Performance

Table 3 details the gloss, hardness and scratch resistance of all three formulations. The new prototype displays similar and/or higher performance when compared to the reference hard coat products for all of these physical properties.

Table 3. Optical and mechanical performance

Property	Formulation A Based on new product	Formulation B Reference water-based UV-PUD	Formulation C Reference solvent-based oligomer
Gloss 60° (on opacity chart) (%)	94.9	95.1	95.4
Persoz hardness (on glass) (s)	342	356	361
Pencil hardness (on glass)	8H	5H	8-9H
Scratch resistance (on PC sheet)	-	-	-
10 double rubs steel wool	no damage	scratches	no damage
100 double rubs steel wool	no damage	scratches	no damage

Table 4 discloses the stain resistance of coatings evaluated on coated Leneta® opacity charts. The stains are applied under a glass slide for 16 hours, then removed with water and detergent (for tar and black marker, the exposure is 1 hour or 5 minutes respectively, after which the stain is removed with isopropanol). Here again, our new prototype ranks as high as the reference hardcoat benchmarks by exhibiting high (maximum) performance. All the cured coatings show >100 acetone double rubs.

Table 4. Stain resistance (ranking from 1 = severe trace visible to 5 = no trace left)

Stain resistance test	Formulation A Based on new product	Formulation B Reference water-based UV-PUD	Formulation C Reference solvent-based oligomer
#1 black shoe polish	5	5	5
#2 tar	5	5	5
#3 black marker (Artline® 70 N)	5	5	5
#4 blue colorant (BB750 H2O)	5	5	5
#5 sudan red colorant (SR380-WS)	5	5	5
#6 yellow colorant (SG146-WS)	5	5	5
# 7 iso-betadine	4.5	4	5
Average stain resistance	4.9	4.9	5

Table 5 presents the water resistance of the coatings. The basic test protocol [24h; RT] was found to provide optimal results on polycarbonate (PC) and acrylonitrile butadiene styrene (ABS) for the water-based prototype and the solvent-based benchmark. For the water resistance in more severe test protocols like [2h; 80°C] and [72h; 90°C; 95%RH], the two products also perform at an optimum level on acrylonitrile butadiene styrene (ABS) but some weakness on adhesion is recorded on polycarbonate (PC) immediately after the water resistance test.

Table 5. Water resistance as expressed by adhesion before/after exposure
(ranking from 0% = no adhesion to 100% = excellent adhesion)

Water resistance test	Formulation A Based on new product	Formulation B Reference water-based UV-PUD	Formulation C Reference solvent-based oligomer
24h; RT (ABS) (%)	100/100	-	100/100
2h; 80°C (ABS) (%)	100/100	-	100/100
72h; 90°C, 95% RH (ABS) (%)	100/100	-	100/100
24h; RT (PC) (%)	100/100	-	100/100
2h; 80°C (PC) (%)	100/0	-	100/100
72h; 90°C, 95% RH (PC) (%)	100/0	-	100/0

It is worth mentioning that the new prototype was also formulated for spray application. Table 6 discloses the formulation having a solid content of 54 wt% and a viscosity of 16 s. DIN Cup4. It was successfully applied at 50 g/m² coat weight (dry) on pigmented PVC panels, confirming again a high gloss and scratch-resistant coating with 100 % adhesion.

Table 6. Formulation for spray application

Ingredients	Formulation D Based on new product
Product A (65%)	100
Esacure® HB (photo-initiator)	2
Deionized water (dilution)	20
Tegowet® 265 (flow/wetting)	2
ADDITOL® VXW 6386 (defoaming)	0.5

Our water-based polyacrylate composition can also be used as a booster component in the formulation of conventional waterborne polymer dispersions, like energy-curable polyurethane dispersions.

IV. Conclusions

Cytec has developed a novel patented technology that enables formulators to develop a solvent free UV hardcoat for spray application. Using water as the diluent to better meet the increasing environmental awareness, the unusually high solid content product (65%) provides a low application viscosity together with hardcoat properties that are similar to a 100% UV resin in terms of adhesion, chemical and mechanical resistance on plastic substrates. Thanks to its low viscosity, it can be used as main binder in water-based hardcoat formulations for spray or curtain coater. This novel product can be blended with other water-based UV resins (after pH neutralization) to increase solid content and/or hardness property. The innovative possibilities associated with these new multifunctional acrylate system family open new horizons for high performing hardcoat application with low VOC.

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