

How to formulate UV-curing coatings

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Introduction

This paper is meant to be a practical guide for formulating UV- and EB-curing systems. As the vast majority of the commercially available UV- and EB-systems is based on free radical curing systems, emphasis will be on this technology. Within these free radical curing systems, coatings based on unsaturated polyesters in styrene are very limited in applications (mainly wood coatings) and also in geographical area where they are produced and used (mainly Italy and Spain/Portugal). By far the most UV-curing-coatings, for a variety of substrates ranging from paper and wood to plastics and glass - is based on acrylate chemistry. The wide formulating latitude of this chemistry mainly causes this: the formulator has a choice among more than fifty different reactive diluents (monomers, oligoether-acrylates etc.) and a wide range of oligomers. Because of this wide range of formulating raw materials, it is not always easy to select the raw materials that will give the desired performance properties. This paper will help you selecting the right oligomers and monomers/reactive diluents. This will be done in three steps:

1. general guidelines oligomers and monomers
2. short description of various monomers
3. starting point formulations that are illustrative for the principles given in the first two parts.

At the end a few words will be said about formulating UV-systems using a different chemistry: cationic curing.

Acrylate Chemistry

General Guidelines

Oligomers

Oligomers are raw materials that can be compared with the 'resin' in a classical coating. Choice of the oligomer is critical: very often, the oligomer is an or even the most important component in the formulation by weight. Because of this, its choice has a major impact on the final performance of the system. Examples of performance characteristics are:

- reactivity
- gloss
- adhesion
- chemical resistance
- scratch resistance
- abrasion resistance
- non yellowing

Often a combination of these properties is desired. In addition to this, cost is also an important selection criterium.

One of the difficulties for the formulator is the fact that the exact chemical composition of oligomers is not revealed by the raw material suppliers for reasons of confidentiality. Despite this, selection can be made on the basis of several criteria:

- the chemical family of the oligomer

- the functionality
- the molecular weight

The chemical family is normally more or less precisely indicated by the supplier. The same applies to functionality. Molecular weight is more difficult: this can be deducted more or less by looking at properties like viscosity, flexibility etc indicated at the technical datasheet.

In acrylate chemistry, there are several families of oligomers. Each of these has its own advantages and disadvantages. The main oligomer families are:

- epoxy acrylates
- urethane acrylates
- polyester acrylates
- polyether acrylates
- amine modified polyether acrylates
- acrylic acrylates
- miscellaneous acrylate oligomers

Epoxy acrylate oligomers

The name of this family of oligomers may lead to confusion: in most cases, epoxy acrylates do not have any free epoxy groups left. The name epoxy acrylates is derived from the base resin for their synthesis: an epoxy resin. Within the epoxy acrylate oligomers, there are essentially five sub groups

- aromatic difunctional epoxy acrylates
- acrylated oil epoxy acrylates
- novolac epoxy acrylates
- aliphatic epoxy acrylates
- miscellaneous epoxy acrylates

Aromatic difunctional epoxy acrylates. The most important member of this sub group are the bisphenol A epoxy acrylates. This type of oligomers has a very low molecular weight, which gives them several attractive properties: high reactivity, high gloss, low irritation. The cost of these products is low. This makes this type of oligomers suitable for a wide variety of applications, ranging from overprint varnishes for paper and board to wood coatings for furniture and parquet flooring, but also high tech applications like compact disk coatings and optical fiber coatings.

Aromatic difunctional epoxy acrylates have three main drawbacks: their high viscosity, their limited flexibility and the fact that they do yellow to some extent. Because of this, they are less suitable for application on flexible substrates; low viscosity application techniques like spray-, dip-, curtain coating, and applications with high requirements in terms of colour stability over a longer period of time (white and light coloured substrates that have to last long).

Acrylated oil epoxy acrylates, in Europe essentially epoxidised soyabean oil acrylate. This oligomer has a good pigment wetting properties and is flexible in combination with a relatively low viscosity and low cost. Main disadvantage is its slow cure speed. This type of oligomers is mainly used in pigmented systems or to reduce cost.

Epoxy novolac acrylates are really specialty products, mainly used in the electronic industry for printed circuit boards (solder resist) because of their high reactivity, excellent heat resistance. Disadvantages are: high viscosity, lack of flexibility and relatively high costs.

Aliphatic epoxy acrylates are also specialty products. There are various types available to the formulator, varying in functionality, molecular weight and chemical backbone. Properties like flexibility (good for difunctional, poor for trifunctional or higher), reactivity (good for difunctional, excellent for trifunctional) and viscosity (very low for difunctional, medium for trifunctional) and adhesion (good to excellent for difunctional) depend on the functionality. Some difunctional aliphatic epoxy acrylates have the interesting property to be compatible with water, enabling to formulate water dilutable systems with these.

Miscellaneous epoxy acrylates. This group comprises essentially specialty oligomers with fatty acid modification, which give good pigment wetting properties and therefore are used in printing inks and pigmented coatings. Because of their higher molecular weight and lower functionality (part of the acrylate groups has been replaced by fatty acid) these oligomers are not quite as reactive as e.g. bisphenol A epoxy acrylates.

Urethane Acrylates (1)

The chemistry of urethane acrylates is very versatile and therefore there are many different types available to the formulator. Essentially, there are four parameters that can be varied synthesizing urethane acrylates:

- functionality
- type of isocyanate
- type of polyol modifier
- molecular weight

Functionality for urethane acrylates varies in practice between one and six. Generally speaking: the lower the functionality, the lower the reactivity, the better the flexibility and the lower the viscosity. Functionality two and three are good compromises for general-purpose oligomers. Monofunctional urethane acrylates are specialty product, which are used to improve adhesion to difficult substrates and to improve flexibility. These products are very low in viscosity. High functionality urethane acrylates (functionality 4 or higher) are specialty products that are used to improve reactivity, scratch resistance, chemical resistance etc. Because they tend to be very high in viscosity, these products are typically used at low levels in the formulation: typically below say 15%.

Type of isocyanate. Essentially, four types of isocyanates are used for urethane acrylate synthesis: monoisocyanates, aliphatic diisocyanates, aromatic diisocyanates and polymeric isocyanates.

Monoisocyanates are used for monofunctional urethane acrylates only, and this type of oligomer is described above.

Diisocyanates are by far the most widely used in urethane acrylate synthesis. We can divide them in aliphatic and aromatic diisocyanates.

Aromatic diisocyanates are used for the manufacture of the so-called aromatic urethane acrylates. The incorporation of an aromatic diisocyanate makes the urethane acrylate harder, gives it a better scratch resistance. Aromatic urethane acrylates are also significantly lower cost than aliphatic urethane acrylate. This makes them interesting for those applications, where the performance of a urethane acrylate is needed (e.g. a good flexibility or abrasion resistance) but the formulation has to be relatively low cost. The major drawback of aromatic urethane

acrylates is that they tend to yellow and therefore they are less appropriate for long lasting applications on white or light coloured substrates.

Aliphatic diisocyanates are used in aliphatic urethane acrylates. Aliphatic urethane acrylates are slightly more flexible than aromatic urethane acrylates with the same functionality, a similar polyol modifier and at similar molecular weight. The main advantage of aliphatic urethane acrylates is the fact that they are virtually non-yellowing and therefore can be used for long lasting applications, on white or light coloured substrates. If the polyol modifier is well adapted as well, it is possible to formulate systems with good weathering resistance with aliphatic urethane acrylates. Examples of uses of aliphatic urethane acrylates are for topcoates for parquet flooring, on plastic substrates, for optical fibers, for screen inks for flexible packaging etc. Polymeric isocyanates are used less for urethane acrylates than diisocyanates. They are essentially used for higher functionality (3 and higher) urethane acrylates.

The polyol modifier is the backbone of the urethane acrylate (if one is used). Polyol modifiers vary in chemical type (essentially either polyether or polyester), functionality (typically ranging from two to four) and molecular weight. Polyether urethane acrylates are typically more flexible than polyester urethane acrylates and often lower cost. In addition, a polyether urethane acrylate will have a slightly lower viscosity than a polyester urethane acrylate with the same functionality and approximately the same molecular weight.

The big advantage of polyester urethane acrylates (if the isocyanate is aliphatic) is that they have excellent non-yellowing properties and even very good weathering resistance properties. The functionality of the polyol modifier determines very often the functionality of the urethane acrylate. See under functionality for the influence of this parameter on the properties.

The molecular weight of the polyol modifier has a big influence on properties like reactivity, viscosity and flexibility. Generally speaking, the higher the molecular weight of the polyol modifier, the higher the flexibility, the lower the reactivity and the lower the viscosity of the urethane acrylate.

The molecular weight. For di- and trifunctional urethane acrylates, the polyol modifier used mostly determines this property. See above for the influence on properties. For higher functionality urethane acrylates this is not always the case and therefore the general guidelines for property/molecular weight correlation may be different.

Polyester Acrylates

Like for urethane acrylates, the chemistry of polyester acrylates is a versatile one. Because of this, a variety of polyester acrylates is available to the formulator, varying in functionality, chemical backbone and molecular weight.

The influence of the functionality on properties like reactivity, viscosity and flexibility is the same as for urethane acrylates: the higher the functionality, the higher the reactivity, the higher the viscosity and the lower the flexibility.

The chemical backbone (which are the monomer building blocks used) has a big influence on properties like reactivity, flexibility, colour stability, viscosity, hardness etc. As no information is given to the formulator regarding this property, it is rather difficult to make use of it in formulating. An exception are the fatty acid modified polyesters that have excellent pigment wetting properties and which therefore are widely used for printing inks and pigmented coatings. The influence of molecular weight in polyester acrylates is often different from that in urethane

acrylates: typically the higher the molecular weight, the higher the viscosity. Like with urethane acrylates, typically the reactivity of higher molecular weight polyester acrylates is lower and their flexibility is higher.

Polyester acrylates are often made in a solvent process, which means that the solvent has to be stripped off. This sometimes leads to higher coloured products. Another drawback of some types of polyester acrylates is their irritancy. This is particularly true for low molecular weight, highly reactive products.

Generally speaking, polyester acrylates may offer to the formulator performance properties between those of urethane acrylates and epoxy acrylates.

Polyether Acrylates

There are rather few polyether acrylates available to the formulator. These products typically are low to very low in viscosity (can be as low as a medium viscosity monomer!) and they often have very high flexibility. An interesting property of some of these oligomers is that they are compatible with water and therefore can be used in formulating water thinnable systems. Drawbacks are poor water resistance and poor chemical resistance. To overcome these, polyether acrylates are mostly used in combination with other types of oligomers or specialty monomers.

Amine modified Polyether Acrylates

This is a rather new family of oligomers. They vary in functionality, chemical backbone, type and degree of amine modification and molecular weight. These variations make that these products range from very low viscosity (as low as a medium viscosity monomer) to medium viscosity. They all have in common that they have high reactivity and typically low irritancy. Amine modified polyether acrylates are typically used with very little monomer or reactive diluent (because of their intrinsically low viscosity) and without free amines or acrylated amine synergist. Although the water resistance and chemical resistance of amine modified polyether acrylates is much better than of polyether acrylates; they still lack the flexibility and toughness of urethane acrylates. Main usages are in wood coatings (furniture) and paper coatings.

Acrylic Acrylates

Like urethane acrylates, the chemistry of acrylic acrylates is very versatile. Variations are possible in functionality, chemical backbone (monomers used) and molecular weight. Today, rather few acrylic acrylates are available to the formulator, often used because of their good adhesion to difficult substrates.

Miscellaneous oligomers

These comprise adhesion promoters, melamine acrylates, silicone acrylates etc. Typically, these are specialty products.

General Guidelines

Monomers (Reactive Diluents Or MFAs) (2)

Monomers are used as reactive diluents in formulations. For this, often low cost, multipurpose products are used. However, because sometimes quite high levels of monomers are used in the

formulation, especially in low viscosity applications, the influence of the monomer on the performance properties of the system can be significant. Especially for those cases, the choice of monomer becomes critical. In addition to being reactive diluents, monomers are also used to achieve a variety of desired properties: improve adhesion, reactivity, chemical resistance, scratch resistance etc. Some monomers are not used as reactive diluents at all, but only to achieve a desired effect, like the reactivity boosters.

Many monomers are available to the formulator; even so many that it is sometimes difficult to select them. Because of this, it is important to keep some general guidelines in mind. Generally speaking, there are four parameters that can vary in monomer chemistry:

- functionality
- type of chemical backbone
- chemical structure
- molecular weight

Functionality. The rule of thumb here is: the higher the functionality, the higher the reactivity. This is easy to understand: the higher the functionality, the higher the number of acrylate double bonds that is available for crosslinking.

The lower the functionality, the lower the viscosity. Therefore, monofunctional monomers are excellent reactive diluents, difunctional monomers are good reactive diluents, trifunctional monomers are fair reactive diluents and multifunctional monomers are poor reactive diluents: they are used to achieve special effects.

The lower the functionality, the polymerisation shrinkage. Because of this, low functionality monomers are often used to improve adhesion to difficult substrates (plastics, metals).

Type of chemical backbone:

Essentially, there are three types:

- hydrocarbones
- ethers
- others

Hydrocarbon type monomers typically have low surface tensions; this is particularly true for the mono- and difunctional types. Low surface tension is important for substrate wetting, which in turn is required for good adhesion. Hydrocarbon type monomers typically have good flexibility (especially for mono- and difunctional types). In addition, they have very low yellowing and good weathering resistance properties. As they are hydrophobic in nature, hydrocarbon type monomers have excellent water resistance properties.

Ether type monomers have a higher polarity than hydrocarbons. Because of this, they are often better reactive diluents, especially for urethane acrylates, polyether- and polyester acrylates. The alpha hydrogens on the carbon adjacent to the etheroxygen atom are abstractable in free radical reactions. Because of this, ether type monomers are more reactive than hydrocarbons, but they are poorer in non-yellowing and weathering resistance properties, as this hydrogen abstraction is a first step in film degradation processes.

In *alkoxylated* monomers (oligoether acrylates), which have been developed because of their low irritancy, a hydrocarbon backbone is combined with either an ethoxy- or a propoxy group.

This often gives a bit of 'the best of both worlds' properties. Ethoxylated monomers have higher polarity than hydrocarbons, and therefore are better reactive diluents. In addition to this, by ethoxylation abstractable alpha-hydrogens are introduced, leading to higher reactivity despite the higher molecular weight (see below). Propoxylated monomers have low surface tensions in combination with lower viscosity than the corresponding hydrocarbon monomer, leading to good substrate wetting and therefore better adhesion to difficult substrates.

In terms of **chemical structure**, there are three types possible: cyclic, branched and linear. The main effect of the chemical structure is on the glass transition temperature (T_g) of the homopolymer: cyclic monomers have much higher T_g than linear or branched monomers.

Molecular weight is an important property of monomers. Generally speaking the lower the molecular weight, the lower the viscosity, the higher the reactivity and the higher the glass transition temperature. Of course, in changing chemical back-bone or functionality the molecular weight changes at the same time and the overall effect on the properties of the monomer is a balance of the various trends. An example has been given already above when the ethoxylated monomers were discussed.

Short Discription Of Monomers

The monomers described are listed in increasing functionality, are grouped by chemical type and within each chemical type are listed in decreasing molecular weight. Consequently, generally viscosity increases and flexibility decreases going from the top to the bottom.

- 2-(2-Ethoxyethoxy) ethyl acrylate is one of the lowest viscosity monomers. Of the monofunctional monomers, it has the highest reactivity. Good adhesion to plastics.
- Ethoxylated nonyl phenol acrylate reactive surfactant.
- Lauryl acrylate is a low polarity, hydrophobic monomer. Highly flexible.
- Tridecyl acrylate highly hydrophobic, lowest surface tension of all monomers, which makes it suitable to overcome foaming problems (1-3 %).
- Isodecyl acrylate: similar to tridecyl acrylate, slightly more reactive.
- 2-Phenoxyethyl acrylate: excellent reactive diluent, good adhesion.
- Tetrahydrofurfuryl acrylate: because it swells plastics, it greatly improves adhesion to plastic substrates.
- Isobornyl acrylate: combines high T_g with low viscosity and flexibility. Problem: odour.
- Polyethyleneglycol 600 diacrylate highly flexible and water dilutable.
- Polyethyleneglycol 400 diacrylate highly flexible and water dilutable although less than polyethylene glycol 600 diacrylate
- Ethoxylated neopentyl glycol diacrylate low shrinkage, low irritancy, highly flexible
- Propoxylated neopentyl glycol diacrylate low shrinkage, low irritancy, very low surface tension.
- Tetraethylene glycol diacrylate high reactivity, low viscosity. Disadvantage: high irritancy.
- Tripropylene glycole diacrylate general purpose reactive diluent
- Dipropylene glycol diacrylate high reactivity, low viscosity. Disadvantage: high irritancy.
- 1,6-Hexanediol diacrylate excellent adhesion, high reactivity, good flexibility. Disadvantage: high irritancy/skin sensitizer.
- Ethoxylated bisphenol A diacrylate low viscosity 'oligomer'. Low irritancy, good hardness
- Ethoxylated trimethylolpropane triacrylate lowest viscosity of all trifunctional acrylates. High reactivity and low irritancy.
- Highly propoxylated glyceryl triacrylate low surface tension, low irritancy.
- Propoxylated glyceryl triacrylate high reactivity, good water balance properties. Well suited for offset printing.

- Trimethylolpropane triacrylate high reactivity, excellent adhesion. Disadvantage: irritancy/skin sensitizer.
- Pentaerythritol triacrylate high reactivity, excellent scratch resistance. Disadvantage: irritancy/skin sensitizer.
- Tris(2-hydroxyethyl)isocyanurate Triacrylate high reactivity, excellent scratch resistance, especially for use on plastic substrates without losing adhesion.
- Ethoxylated pentaerythritol tetraacrylate low viscosity, high reactivity, low irritancy
- Ditrimehylolpropane tetraacrylate
- reactivity booster. Low irritancy.
- Pentaerythritol tetraacrylate highly reactive, excellent scratch resistance.
- Disadvantage: high irritancy, skin sensitizer.
- Dipentaerythritol pentaacrylate reactivity booster, most reactive product. Low irritancy. Excellent scratch- and chemical resistance.

Illustrative Starting Point Formulations

In this part, we will look at how the raw materials described in the first two parts are used by looking at some starting point formulations. We will briefly explain why the acrylate oligomers and monomers that are used in these formulations were selected.

a) Low irritancy non-penetrating overprint varnish for paper

CN104180 (1)	Bisphenol A epoxy acrylate, 80 % in NPGPODA	44.0%
SR9003 (1)	Propoxylated neopentyl glycol diacrylate	30.9%
SR355 (1)	Ditrimehylolpropane tetraacrylate	3.2%
CN385 (1)	Benzophenone	6.0%
CN386 (1)	Acrylated amine synergist	9.9%
Irgacure 184 (2)	Photoinitiator	2.0%
Bentone 27 (3)	Thixotropic additive	0.4%
ZnO (4)	Transparent zinc oxide	3.6%
Viscosity at 25 °C	420 mPa.s.	
Thickness:	6 μ	
Cure-speed (1 lamp, 120 W/cm):	50 m/mn	
Gloss 60 °:	77 %	

Overprint varnishes (OPV) are one of the main usages for UV in the graphic arts. In this application, full advantage is taken from some of the features of UV-curing:

- high gloss
- fast cure speed
- no solvent emission

Typically, this kind of varnishes is applied by roller coating and therefore are low viscosity. One of the problems sometimes encountered is the use of highly porous and therefore absorbant paper. This leads to absorption of the low viscosity varnish into the paper resulting in low gloss. Using special additives can solve this: the bentone gives the varnish some degree of thixotropy, which reduces the absorption into the paper. The transparent zinc oxide has a particle size that matches the size of the pores of the paper. This further reduces the absorption. Transparent zinc oxide has little effect on the gloss and the transparency of the coating. As for the acrylates used

in this formulation: skin- and eye irritation is often a problem, as industrial hygiene from the printers is not always as it should be and often the workers do not use the protective gloves, they should use when working with UV-varnishes. Although this is undesirable and the varnish manufacturer should stress the use of protective gloves on the work floor, also low irritancy raw can be used. The oligomer used here is a bisphenol A diacrylate oligomer, diluted in propoxylated neopentyl glycol diacrylate. This oligomer is used as is has excellent reactivity and high gloss and has low skin and eye irritancy. The propoxylated neopentyl glycol diacrylate is used as a reactive diluent as it has low skin- and eye irritancy, good diluting properties, low skin- and eye irritation and excellent substrate wetting because of its low surface tension.

Ditrimethylolpropane tetraacrylate is used to improve cure speed. This product, too, has low skin- and eye irritation.

Benzophenone is used as the surface curing photoinitiator. Benzophenone has to be used in combination with an amine to overcome oxygen inhibition, which would lead to a sticky surface, even when fully cured. CN386 is an acrylated amine synergist, which avoids problems often encountered when using free amines in overprint varnishes on top of printing inks: pigment bleaching and blooming. Irgacure 184 is used to ensure proper through cure.

b) Basecoat for melamine paper

CN704 (1)	Acrylated polyester adhesion promoter	49.9%
CN131 (1)	Low viscosity aromatic monoacrylate oligomer	9.6%
SR9003 (1)	Propoxylated neopentyl glycol diacrylate	32.6%
SR9051 (1)	Acidic triacrylate adhesion promoter	4.0%
Irgacure 184 (2)	Photoinitiator	3.9%

Viscosity at 25 °C	1530 mPa.s.
Thickness of the film:	12 μ
Cure-speed (1 lamp, 120 W/cm):	11.5 m/mn
Adhesion test	
cross hatch:	0 (laboratory standard based on Iso 2409)
tape used:	TESA 4108 (adhesive strength: 200 cN/cm)

Melamine paper, widely used for furniture applications, is a very difficult substrate to get good adhesion to with a UV-coating (3). There are two reasons for this:

- the low surface tension of the substrate
- the shrinkage of the UV-coating during polymerisation

The formulation above works because the selection of acrylates addresses these two problems. CN704 is an acrylated adhesion promoter for non-porous substrates, which improves adhesion because it greatly reduces polymerisation shrinkage of the coating. To achieve this effect, the amount of this product in the formulation has to be high: reduction of shrinkage only works if the main components by percentage in the formulation are low shrinkage. CN131, a monofunctional epoxy acrylate, has also low shrinkage, but it improves the cure speed of the formulation, as it is faster curing than CN704. The propoxylated neopentyl glycol diacrylate is used while it low shrinkage. It further improves adhesion, as it improves wetting of the substrate, a vital element to get good adhesion to a substrate. The acidic adhesion promoter is used to further improve adhesion to this very difficult substrate.

c) Scratch resistant topcoat for wood

CN550 ⁽¹⁾	Amine modified polyether acrylate oligomer	53,2%
CN501 ⁽¹⁾	Amine modified polyether acrylate oligomer	22.8%
CN976 ⁽¹⁾	Aromatic urethane diacrylate	20%
CN385 ⁽¹⁾	Benzophenone	2.0%
Irgacure 184 ⁽²⁾	Photoinitiator	2%
Viscosity at 25 °C		2000 mPa.s.
Thickness:		12 μ
Cure speed (1 lamp, 120 W/cm):		8 m/mn
Persoz hardness (100 μ, steel Q panel):		70 s
Reverse impact resistance (24 μ, steel Q panel):		> 100 cm
Pencil hardness (100 μ, glass panel):		1H-2H

UV-coatings are widely used on wooden substrates, essentially for furniture and parquet flooring. In this application, cure speeds are not quite as high as in the graphic arts industry. The main advantages of UV in these applications are:

- no solvent emission
- immediate cure which enables immediate stacking or sanding
- low temperature cure
- high gloss
- high chemical resistance
- high abrasion resistance

The example above is a starting point formulation for a scratch- and abrasion resistant topcoat for wood, either furniture or parquet. For furniture, the scratch resistance is important. For wood parquet, both scratch- and abrasion resistance are important.

In this formulation, the scratch resistance is achieved by using two amine modified polyether acrylate oligomers, that give excellent surface cure and hardness. CN550 is the base oligomer; CN501 is used to reduce the viscosity to (roller) application viscosity, without losing the surface hardness. The aromatic urethane acrylate is a high molecular weight polyether type urethane acrylate. Because of this, it is a soft product that brings flexibility. Good abrasion resistance is a property that can be achieved by using soft, flexible oligomers (4). This is why the aromatic urethane acrylate is used in this formulation.

As two amine modified polyether acrylates are used in this formulation, the amine value is high enough not to have to use any free amine or acrylated amine synergist in this formulation in combination with the benzophenone to obtain good surface cure. Irgacure 184 is used in this formulation. Probably, Irgacure 651 (benzoyldimethylketal), a lower cost photoinitiator would give similar performance at lower cost.

d) Low gloss topcoat for wood (vacuum applied)

CN502 (1)	Amine modified polyether acrylate	61%
SR9003 (1)	Propoxylated neopentyl glycol diacrylate	20%
CN385 (1)	Benzophenone	3%
Irgacure 184 ⁽²⁾	Photoinitiator	1%
Orgasol 3501EXD NAT1 ⁽⁵⁾	Matting agent	15%

Viscosity at 25 °C (Din 4 Cup):	47 s
Thickness of the film:	12 μ
Cure-speed (1 lamp, 120 W/cm):	10 m/mn
Gloss 60 °:	25% (measured on black cardboard)

The difficulties to overcome in this formulation for wood furniture are:

- very low viscosity
- low gloss

The main oligomer used here is an amine modified polyether acrylate: the lowest viscosity oligomer available to the formulator. This type of oligomer gives excellent reactivity, especially surface cure. This makes achieving low gloss levels very difficult, as gloss is a result of micro roughness at the surface. This is achieved by the particles of the matting agent that migrate to the surface during cure. This is more difficult if the surface cure is high. Consequently, more matting agent has to be used, which leads to higher viscosity, which is undesired in this formulation. The solution of this problem is the use of a special matting agent, which can be used at higher concentrations, without resulting in a significantly higher viscosity. The propoxylated neopentyl glycol diacrylate is used in this application because it has low surface tension.

e) Low irritancy coating for PVC

CN965 (1)	Aliphatic urethane acrylate	36%
SR355 (1)	Dimethylolpropane tetraacrylate	19%
SR9003 (1)	Propoxylated neopentyl glycol diacrylate	29.9%
SR285 (1)	Tetrahydrofurfuryl acrylate	8%
CN385 (1)	Benzophenone	4%
N-methyldiethanolamine (6)	Coinitiator	2%
Irgacure 184 (2)	Photoinitiator	1%
DC57 (10)	Slip agent	0.1%

Viscosity at 25 °C:	480 mPa.s.
Thickness of the film:	12 μ
Cure speed (1 lamp, 120 W/cm)	20 m/mn
Adhesion test	
cross hatch:	0 (laboratory standard based on ISO 2409)
tape used:	TESA 4108 (adhesive strength: 300 cN/cm)
nail scratch resistance:	good

Adhesion to flexible PVC is typically difficult to achieve because of migration of the plasticizer. Best results are obtained if (3):

- substrate wetting is good
- shrinkage is low
- monomers, that swell the substrate are used.

Low shrinkage is achieved by use of the high molecular weight aliphatic polyester urethane acrylate, which further is non-yellowing, which makes application on light colours and even white PVC possible. Obviously, for a flexible substrate, a flexible coating is needed to avoid cracking. This, again, is obtained by using the aliphatic urethane acrylate. Finally, the aliphatic urethane acrylate is non-irritant.

Ditrimethylolpropane tetraacrylate is used to improve reactivity and chemical resistance. It has low irritancy. Propoxylated neopentyl glycol diacrylate is because it has low surface tension, resulting in good substrate wetting, a vital requirement for good adhesion. Tetrahydrofurfuryl acrylate is a monomer that slightly attacks the PVC, resulting in the formation of an interpenetrating polymer network (IPN) at the surface of the substrate, greatly improving the adhesion. As this formulation is non-yellowing as far as the acrylates is concerned, as little benzophenone as possible is used to bring sufficient surface cure as this photoinitiator increases yellowing. Irgacure 184 is a non-yellowing photoinitiator.

f) Coating for white polyurethane coated polycarbonate

CN965 (1)	Aliphatic urethane diacrylate	10%
SR368 (1)	Tris (2-hydroxyethyl) isocyanurate triacrylate	27%
SR295 (1)	Pentaerythritol tetraacrylate	19%
SR238 (1)	1,6 hexanediol diacrylate	23%
SR285 (1)	Tetrahydrofurfuryl acrylate	14%
Darocur 1173 (2)	Photoinitiator	4%
Irgacure 184 (2)	Photoinitiator	1%
Byk 306 (7)	Surfactant	2%

Viscosity DIN CUP 4 at 25°C:	25 s
Thickness of the film:	16 m/mn
Adhesion test	
cross hatch:	0 (laboratory standard based on ISO 2409)
tape used:	TESA 4108 (adhesive strength: 300 cN/cm)
Impact resistance (t = 30°C/1 kg/Height = 40 cm):	good

UV-coatings are also used as topcoats for motorcycle helmets. In addition to the obvious advantages as no solvent emission
fast cure speed
UV-coatings also bring additional technical advantages like
excellent scratch resistance
excellent chemical resistance
These coatings are typically spray-applied. The main difficulties to overcome are:
adhesion
low viscosity
non yellowing
impact resistance

As we have seen before, this has to be achieved by combining several approaches (3):

- good substrate wetting through low surface tension
- low shrinkage
- swelling monomers

Low shrinkage and low yellowing is obtained by using a high molecular weight aliphatic polyester urethane acrylates oligomer. 1,6-Hexanediol diacrylate and tetrahydrofurfuryl acrylate are both swelling monomers that attack the polyurethane coating to give excellent adhesion. Pentaerythritol tetraacrylate gives excellent scratch resistance and high reactivity. High

reactivity and low viscosity without losing the adhesion characteristics are achieved by using THEIC triacrylate, which further improves scratch resistance. Two non-yellowing photoinitiators are used. Combination of photoinitiators often improves adhesion, as it modifies the ration of surface to through cure and therefore the 'curl' of the formulation.

g) Coating for impact resistant polystyrene

SR454 (1)	Ethoxylated trimethylol propane triacrylate	85.5%
SR238 (1)	1,6 hexanediol diacrylate	9.5%
CN385 (1)	Benzophenone	3%
N methyl diethanolamine (6)	Coinitiator	2%
Darocur 1173 (2)	Photoinitiator	1%

Viscosity at 25°C:	80 mPa.s.
Thickness of the film:	24 μ
Cure speed (1 lamp, 120 W/cm):	8 m/mn
Adhesion test	
cross hatch:	0 (laboratory standard based on ISO 2409)
tape used:	TESA 4108 (adhesive strength: 300 cN/cm)
nail scratch resistance:	good

Polystyrene is another difficult substrate for UV-coatings to adhere to (3). Adhesion in this formulation is achieved by the use of two swelling acrylates: an oligoether acrylate ethoxylated trimethylolpropane triacrylate and 1,6-hexanediol diacrylate. Because of this, adhesion is excellent, even at this very low viscosity.

h) Coating for polyolefine

CN704 (1)	Acrylated polyester adhesion promoter	39.9%
CN965 (1)	Aliphatic urethane diacrylate	15%
SR9003 (1)	Propoxylated neopentyl glycol diacrylate	31%
CN386 (1)	Acrylated amine synergist	9%
CN385 (1)	Benzophenone	4%
Irgacure 184 (2)	Photoinitiator	1%
Fluorad FC430 (8)	Surfactant	0.1%

Viscosity at 25°C:	1800 mPa.s.
Thickness:	6 μ
Cure-speed (1 lamp, 120 W/cm):	8 m/mn/L

Polyolefines (polyethylene and polypropylene) are the most difficult plastic substrates for UV- (and other) coatings to get adhesion to (3), as they have very low surface tensions and are completely inert, which makes it impossible to find acrylates, which will attack these substrates, forming an IPN. Therefore, polyolefines (typically used for flexible packaging) are typically corona- or flame-treated before coating. Even then, it is extremely difficult to achieve good adhesion. The only parameters that can be used are:

- substrate wetting by lowering the surface tension
- low polymerisation shrinkage

Low shrinkage applies to all components in this formulation. Propoxylated neopentyl glycol diacrylate is used as a reactive diluent with very low surface tension.

i) Chemical resistant coating for steel

CN704 (1)	Acrylated polyester adhesion promoter	15%
CN132 (1)	Low viscosity aliphatic diacrylate oligomer	30%
CN104 (1)	Bisphenol A epoxy diacrylate oligomer	5%
SR256 (1)	2-(2-Ethoxyethoxy) ethyl acrylate	18.9%
SR454 (1)	Ethoxylated trimethylolpropane triacrylate	16.1%
SR9051 (1)	Adhesion promoting trifunctional acid ester	7%
CN385 (1)	Benzophenone	2.5%
Irgacure 184 (2)	Photoinitiator	5%
Tego Rad 2200 (9)	Slip aid	0.5%

Viscosity at 25°C:	205 mPa.s.
Thickness:	12 μ
Cure-speed (1 lamp, 120 W/cm):	8 m/mn
Solvent resistance (ethanol, MEK, methyl chloride):	50 rubs
Water resistance:	1 hour in boiling water
Flexibility:	ok

Adhesion to metals is also very difficult to achieve with UV-curing coatings (3). The best adhesion is achieved by using acidic adhesion promoters, that attach the metal surface and provide a chemical bond between the metal surface and the coating. Further polymerisation shrinkage has to be limited as much as possible. 2-(2-Ethoxyethylacrylate) is used in this very low viscosity formulation, as it is the highest reactivity and lowest viscosity monofunctional acrylate monomer. Ethoxylated trimethylolpropane triacrylate is used, as it is the lowest viscosity trifunctional acrylate, trifunctional and therefore used to improve the adhesion. The acrylated polyester adhesion promoter reduces shrinkage. The low viscosity aliphatic epoxy acrylate gives improves adhesion and reactivity, but does not increase viscosity.

k) Solvent based formulation for aluminium and steel

SB400 (1)	Carboxyl functional multifunctional methacrylate oligomer, 70 % in methoxy propanol	43.6%
SR399 (1)	Dipentaerythritol pentaacrylate	29.2%
SR9051 (1)	Acidic triacrylate adhesion promoter	4%
CN385 (1)	Benzophenone	4%
Irgacure 184 (2)	Photoinitiator	4%
MEK	Solvent	12.2%
Ethyl acetate	Solvent	3%

Curing conditions:	
Solvent flash off:	5 mn at 70 °C
UV:	8 m/mn, 1 lamp, 120 W/cm
Viscosity at 25 °C:	260 mPa.s.
Thickness of the film:	24 μ
Percentage non-volatile:	71.7%
Adhesion test	

tape used: TESA 4108 (adhesive strength: 200 cN/cm)
nail scratch cross hatch: 0 (laboratory standard based on ISO 2409)
nail scratch resistance: good

This is an example of a solvent containing formulation, which can be spray applied. Adhesion is achieved by combining an acidic adhesion promoter with a carboxylic functionalized oligomer. Dipentaerythritol pentaacrylate is an oligoacrylate with free OH-functionality, which also improves adhesion. This product is essentially used to improve reactivity: it is the fastest curing acrylate available. It further improves scratch resistance.

- (1) CRAY VALLEY
- (2) CIBA
- (3) RHEOX
- (4) BAYER
- (5) ELF ATOCHEM
- (6) BASF
- (7) BYK CHEMIE
- (8) 3 M
- (9) GOLDSCHMIDT
- (10) DOW CORNING

Cationic Chemistry

The products available to the formulator for cationic curing are essentially:
cycloaliphatic epoxies
triarylsulfonium photoinitiators
vinyl ethers
polyols

As the chemistry is completely different to acrylates, different formulating rules apply. One of the most important things to remember is that polyols are used in combinations with cycloaliphatic acrylates to improve reactivity and flexibility. This is because polyols will lead to chain transfer reaction, which will increase the mobility of the polymerising species, resulting in higher cure speeds and reducing the average molecular weight of the polymerised film, resulting in better flexibility. In formulating cationic systems, one has to respect stoichiometric ratios between the cycloaliphatic epoxies and the polyols.

References

- [1] J.A. Arceneaux: J.A., Hall, Z.J. Wang: Structure-Properties Relationships of Urethane Acrylates. Proceedings RadTech North America 1996, p 233
- [2] R.C.W. Zwanenburg: Correlation-Study between Chemical Structure of Monomer and Physical Properties before, during and after Cure. Proceedings RadTech Europe 1989, p 477
- [3] B. Magny, A. Askienazy, E. Pezron: How to Tackle Adherence Problems with UV-Formulations. Proceedings RadTech North America 1996, p 203
- [4] A. Askienazy, B. Magny: Abrasion Resistance of UV-Curable Coatings, Proceedings RadTech North America 1996, p 244.

Recommended further reading

Chemistry & Technology of UV & EB Formulation for Coating, Inks & Paints, Volume 4 Formulation.
P.K.T. Oldring, editor, SITA Technology 1991.