Acrylic polymer dispersions give novel approach to waterborne coatings.
Dirk Mestach, Derrick R. Twene.

Waterborne UV-curing binders based on acrylic polymer dispersions have been developed. These binders do not contain any low molecular weight monomers and therefore are considered to be non-irritant. These acrylic dispersions can be formulated in a way that is quite similar to other waterborne one component coatings. All of the conventional additives such as dispersants, wetting agents, coalescing solvents and matting agents can be used without problems. When applied to a substrate the coatings will dry to give a tack-free surface. Full curing takes place when UV-radiation is applied to the coated surface. The resulting cross-linked polymeric coating will have excellent mechanical and chemical resistance properties.

Coating compositions that cross-link under the influence of actinic radiation have been known for quite some time. In industrial practice the actinic radiation used is mainly ultra-violet (UV) or electron-beam (EB) radiation. Both free-radical and cationic mechanisms are being used. However in a large number of industrial coating applications the curing mechanism is a free-radical one. In the coating the acryloyl functional binder is mixed with a compound that generates radicals when exposed to UV-radiation - a photo-initiator. Examples of such photo-initiators are bisacrylphosphate-oxide and a-hydroxy ketones. The radicals generated upon exposure to UV-light will start a free-radical polymerisation reaction, polymerising the acryloyl-groups. As a result a polymeric crosslinked network is being formed. The principle of the cross-linking reaction is given (Figure 1).

The current situation
The polymers that are currently used in UV-curing systems are often based on low molecular weight polyester, polyepoxide or polyurethane backbones. These oligomers are modified with acryloyl-groups in order to render them UV-curable. Extensive cleaning of the functionalised oligomer is required in order to remove trace amounts of the acrylic acid or other compounds used to introduce the acryloyl functionality. After the acryloylation modification the viscosity of the oligomer usually increases considerably. In order to reduce the viscosity sufficiently to allow the coatings to be applied on a surface, the known compositions always contain either low molecular weight, acryloyl functional diluents such as 1,4-butanediol diacrylate, diethylene glycol diacrylate or trimethylolpropane triacrylate. These diluents are known to be irritating or toxic [1,2,3]. Upon UV-curing, these diluents are at least partially removed from the polymer network. These systems therefore are theoretically "100 % solids" systems. 100 % solids systems are quite often applied by techniques such as knife or roller coating, limiting the application to flat substrates. When three-dimensional substrates need to be coated, an organic solvent such as butyl acetate is often added to the UV-coating, rendering it sprayable. Needless to say, the VOC emissions from these sprayable UV-curing coatings are comparable to that of conventionally curing solvent-borne coatings.

Waterborne UV-curing binders
In order to retain the low or non-VOC profile of UV-curing coatings, a clear need exists for low-viscosity waterborne UV-curing binders. One approach used in industry is to blend UV-reactive diluents such as trimethylolpropane triacrylate with conventional aqueous polymer dispersions prior to application to give a waterborne UV-curable composition. However upon UV-cure it will be only the acryloyl functional components that forms a polymer network. The acrylic polymer will not cross-link and this has a pronounced effect on the chemical and mechanical resistance properties. Furthermore the diluents may present safety, health and environmental problems.

Attaching UV-reactive groups to waterborne polymers is desirable

What is desirable to covalently attach the UV-reactive acryloyl groups to the waterborne polymer. In this way these groups are bound to a high molecular weight polymer and as a consequence there is no danger of irritation or skin sensitisation effects. A synthesis route that is quite commonly used nowadays is to end-cap a polyurethane dispersion with acryloyl-groups. The synthesis of these products is quite similar to that of conventional polyurethane dispersions except that the isocyanate functional urethane pre-polymer is reacted with an hydroxyl-functional monomer such as hydroxyethyl acrylate prior to emulsification in water instead of being chain extended with a diamine. In order to be able to emulsify the acryloyl functional urethane, a solvent has to be used to reduce the viscosity. Acetone or N-methyl pyrroolidone (NMP) are commonly used for this purpose. Acetone can be stripped from the emulsion by means of vacuum distillation whereas NMP remains present in the product. Because of the relatively low molecular weight of these acryloyl functional polyurethane dispersions, a lot of cross-links have to be formed before the coating becomes tack-free and builds-up chemical resistance properties. Therefore recently UV-curing polyurethane dispersions have come onto the market where acryloyl functional diols are used in the synthesis of the pre-polymer [4].

Acryloyl diol-based binders enable coating to be handled before curing
These binders overcome the problems associated with earlier UV-curing polyure-thanes and exhibit a very good performance comparable with the conventional 100 % solids systems. Besides the fact that the formulation of waterborne UV-curing systems is comparable to that of conventional waterborne binders, especially when it comes to matting and rheology control, the fact that the coating physically dries before the UV-curing takes place is the main advantage. This means that coated articles can be handled (e.g. sanded) prior to the full UV cure.

Unfortunately UV-curing polyurethane dispersions tend to be rather expensive as a result of the raw materials used (diisocyanates, hydroxyl-functional monomers) and the multi-step production process used in their production.

Acrylic UV-curing dispersions by emulsion polymerisation
The emulsion polymerisation technique has been known for quite some time as the most economical way to produce waterborne binders. The polymers are formed directly in an aqueous medium without the need for organic solvents. The great challenge however is to synthesise an UV-curing acrylic polymer dispersion by means of emulsion polymerisation. The acryloyl groups needed for the UV-curing will also react with the radical initiators used in
the process. The only way to achieve this is to attach the acryloyl groups to the polymer dispersion in a post-modification step.

A polymer-stabilized dispersion has been used as the basis for the development of the UV-curing acrylic dispersion. These polymer stabilized dispersions are synthesized using a proprietary process. In the first step an acid functional oligomeric acrylic polymer is made by means of emulsion polymerisation. After this first stage polymerisation a base such as ammonia is added to the polymer dispersion to solubilise it. Depending on the acid value of the oligomer anything from a completely clear to a turbid colloidal solution might be obtained. The effect of acid value on the appearance of the solubilised oligomer is illustrated (Figure 2).

Even though the solution may appear to be completely clear, micellar aggregates with mean particle sizes of about 100 nanometers still exist as can be proven by means of photon correlation spectroscopy.

Polymer can contain other functional groups

Butterfly carboxylic acid functionality in the oligomeric acrylic polymer can contain additional functional groups. These groups can be incorporated in order to be used in the acrylic modification step. Optionally these groups can be used in an additional crosslinking reaction. Carbonyl-groups in the acrylic oligomer can, for example, be used in combination with a polyhydroxide to obtain a dual-cure system.

Just as with surfactant based micelles, the oligomeric micelles can be swollen with a mixture of hydrophobic acrylic monomers that can be polymerized in a second stage polymerization. The final morphology of the acrylic polymer particle will be "core-shell"-like where the second stage polymer forms the core and the first stage acrylic oligomer forms a stabilizing shell (Figure 3).

Using ultra-centrifugation and gel-permeation chromatography it was proven that about 50 % of the stabilizing oligomer becomes covalently grafted onto the second stage polymer [5].

The next step in the production process is the post modification. To this end an acryloyl functional molecule is added to the polymer dispersion. This molecule has a second functional group that is reactive towards functional groups in the oligomeric stabilizer, which may be the acid groups, but also the other functionalities present in the oligomer. The coupling of the acryloyl compound is carried out in the presence of a catalyst in order to ensure complete conversion.

Synthesis of the acrylic oligomer

An acrylic oligomer was synthesised by polymerising a mixture of butylacrylate, styrene and methacrylic acid using sodium dodecyl sulphate as surfactant and potassium sulphate as initiator. A chain-transfer agent was used to control the molecular weight.

To the oligomer dispersion, ammonia was added until a pH value of 8 was reached. A clear solution of the oligomer was obtained. In the second stage of the polymerisation a mixture of styrene and butylacrylate was polymerised in the presence of the oligomer solution. The resulting dispersion was than modified by the addition of glycidylmethacrylate (GMA) using a proprietary catalyst. The oxirane group of the GMA reacts with part of the carboxylic acid functionality of the oligomeric stabilizer, introducing the acryloyl functionality. The properties of the acryloyl functional acrylic dispersion thus obtained are: solids content 40 %, pH 6.5 and particle size 300 nm. The amount of double bonds in the modified product is about 1 Meq/gram.

Investigating the dispersion when formulated into a varnish

The UV-curing dispersion described above was formulated into a clear varnish. The formulation is given (Table 1). This formulation will be referred to as UV-ACR.

As a reference a commercially available UV-curing varnish based on a acryloyl functional polyurethane dispersion was used (UV-PUD).

The varnishes were applied using a wire coater either onto glass or onto wooden panels with a beech veneer. The water was flashed off for 10 minutes at ambient temperature (23 °C). The UV-curing was carried out by passing the coated panels under a Hg/Ga lamp (three passes at 15 m / minute). Although the UV-PUD formulation could be handled after flash-off of the water, it retained a certain degree of tackiness. The coating could not be sanded. The UV-ACR formulation was completely tack-free after flash off and could be sanded. After the UV-cure cycle the tackiness of the UV-PUD formulation had disappeared (Table 2).

Coatings from new dispersion are harder

The Koenig hardness of the coatings before and after UV-cure was determined according to DIN53 157 at 23 °C. The effect of layer-thickness was also investigated by applying wet layers with thicknesses of 100 and 200 micron. For both thicknesses, both after flash off and after UV-curing, the Koenig hardness was better for the varnishes made from the new dispersion (Figure 4).

New dispersion improves crosslinking

The crosslinking density of the cured coatings was estimated by submitting them to 50 methyl ethyl ketone (MEK) double-rubs. After the test the damage to the coating was judged and rated on a scale of 0 (no damage) to 5 (severe damage). Micro-scratch resistance was tested by rubbing the coating with a felt-pad (50 double rubs). The damage to the film (loss of gloss) was also judged. The varnishes made from the new dispersion, UV-ACR, showed considerably less damage under both the micro scratch and MEK resistance tests than the varnishes made from the commercial dispersion UV-PUD (Figure 5).

Chemical resistance is equal for new and commercial systems

Finally the chemical resistance properties according to DIN 68861 were determined and the results for a number of difficult stains are illustrated (Figure 6). From these photographs it becomes clear that the chemical resistance of both the UV-ACR and the UV-PUD formulation are equal.

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References


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Results at a glance
- An acryloyl functional acrylic dispersion has been made and formulated into a varnish. This has been compared to a varnish based on a commercial dispersion.
- Although the commercial formulation could be handled after flash-off of the water, it retained a certain degree of tackiness and the coating could not be sanded until after the UV-cure cycle. The formulation based on the new dispersion was completely tack-free after flash off and could be sanded.
- At thicknesses of 100 and 200 micron, both after flash off and after UV-curing, the Koning hardness was better for the varnish made from the new dispersion.
- The varnish made from the new dispersion showed considerably less damage under both the micro scratch and MEK resistance tests than the varnish made from the commercial dispersion.
- The chemical resistance of the new system is the same as that of the commercial system.

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Figure 1: Principle of UV-curing
Figure 2: Influence of acid value oligomer on degree of solubilisation
**Figure 3: Synthesis of a polymer stabilised acrylic dispersion**

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
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<tbody>
<tr>
<td>Surfactant-free emulsion polymerisation of acid rich monomer mixture</td>
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<tr>
<td>Solubilisation (add base)</td>
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<td>Addition and polymerisation of second stage monomer mixture</td>
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<tr>
<td>Modification of functional groups in polymeric stabiliser with acryloyl groups</td>
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</tbody>
</table>
Figure 4: Koenig hardness build-up as a function of layer thickness for a varnish from the new dispersion (UV-ACR) and one from a commercial dispersion (UV-PUD)
Figure 5: Damage to UV-cured coatings: MEK resistance and micro-scratch resistance for the varnishes from the new and commercially available dispersions.
Figure 6: Chemical resistance properties according to DIN 68861. Left: UV-PUD, right: UV-ACR. Staining agents; artificial sweat (5 h), Iodine (1 h), shoe polish (1 h), Ethanol 98 % (2 m), Coffee (16 h), Black ink (16 h) and red wine (16 h)
### Table 1: Composition of the new UV-curing clear varnish (UV-ACR)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight</th>
<th>Function</th>
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<tbody>
<tr>
<td>UV-curing acrylic dispersion</td>
<td>213.40</td>
<td>Binder</td>
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<tr>
<td>Proxel XL2</td>
<td>0.13</td>
<td>Biocide</td>
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<tr>
<td>Surlynol 104 (50% in DPM)</td>
<td>0.80</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>Dowanol DPM / Dowanol PnB / H2O (25:25:50)</td>
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<td>co-solvent blend</td>
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<tr>
<td>Irgacure 500</td>
<td>2.60</td>
<td>Photo initiator</td>
</tr>
<tr>
<td>Tegoglide 482</td>
<td>0.26</td>
<td>Additive</td>
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<tr>
<td>Demineralised water</td>
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<td>dilution</td>
</tr>
<tr>
<td>Viscoplus 3000</td>
<td>1.40</td>
<td>thickener</td>
</tr>
<tr>
<td>Dehydran 1293</td>
<td>0.50</td>
<td>defoamer</td>
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Table 2: Comparison of the tackiness of formulations based on the new dispersion UV-ACR and a commercially-available dispersion UV-PUD before and after UV-curing

<table>
<thead>
<tr>
<th></th>
<th>UV-ACR</th>
<th>UV-PUD</th>
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<tbody>
<tr>
<td>tackiness</td>
<td>++</td>
<td>−/+</td>
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<tr>
<td>before UV-cure</td>
<td>++</td>
<td>−/+</td>
</tr>
<tr>
<td>sandability</td>
<td>+</td>
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<tr>
<td>before UV-cure</td>
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<td>−</td>
</tr>
<tr>
<td>tackiness</td>
<td>++</td>
<td>++</td>
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<tr>
<td>after UV-cure</td>
<td>++</td>
<td>++</td>
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