

## UV CURABLE AQUEOUS DISPERSIONS FOR WOOD COATINGS

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### Abstract

In this paper the characterisation of aqueous dispersions of UV curable resins is described. Two types of dispersions were used: dispersions that are tacky after water evaporation and tack - free before cure dispersions. The physical and rheological properties of these products have been determined and the performance of these dispersions in various formulations, especially for wood applications has been studied. With these dispersions, it is possible to produce coatings having a good cure speed, good surface hardness and good solvent -, chemical - and water resistance.

### Introduction

Due to environmental and legislation constraints the coating industry is moving through a major evolution. Low solids, solvent containing paints are decreasing in importance. As a result of this increasing pressure to reduce VOC's, UV curable coatings are experiencing an important growth in the marketplace. In some application fields like for instance the wood coating industry, coating techniques are used requiring low viscosity. This is rather difficult to obtain with 100% systems. Waterbased UV curable coatings offer an interesting solution for this problem. The advantages of UV curable waterbased systems for many industrial applications have been discussed previously in the literature (1-4).

Recent improvements in dispersion technology such as the surfactant selection, the optimization of various parameters in the dispersion process and the enhancement of dispersion stability have made it possible to disperse a wide variety of radiation curable oligomers in water. These oligomers include epoxy-, urethane- and polyester acrylates. In this paper, properties of dispersion based formulations, before and after cure will be discussed.

One of the limiting factors for the use of radiation curable waterbased systems was the poor performance. This poor performance is mainly due to the use of water as a solvent. Wetting, levelling and coalescence problems are observed, due to the high surface tension of water and its poor solvency. Much work has been done to overcome these problems and very encouraging results were obtained. In this paper, the performance of some of these dispersions will be presented. Products were applied on wood, glass or metal depending on the properties evaluated. Comparisons were made with corresponding undispersed resins. Two types of dispersions will be presented. The first category gives tacky films after the evaporation of the water. The second gives tack - free films after water evaporation but before the UV cure. This type of dispersion can be handled and sanded before the UV curing step. Tack - free before cure systems are interesting because they are less sensitive to dust collection and because they allow

the repair of coating imperfections before the UV curing step. This leads to reduced waste in the production process.

### **Experimental section**

The first type of dispersions were obtained by dispersing oligomers (urethane acrylates, epoxy acrylates, and polyester acrylates) in deionized water using appropriate surfactants. The solids content of these dispersions is in general 60 - 65%.

The second type of dispersions was obtained after chemical modification of the resins. The solids content of these dispersions is approximately 40%.

The viscosity of the dispersions were measured at 25°C using a Brookfield Synchro-Lectric or Haake viscometer. The particle size and the particle size distribution were measured using either light scattering or microscopic techniques.

Coatings were applied on the different substrates by manual draw down or by spray coating, using a HVLP spray gun (nozzle 1.6 mm). Coating thickness was approximately 150 μ, wet, for the manual draw downs and 180μ, wet, for the spray coatings. Water was evaporated before cure. More details will be given in the following section. Samples were cured using one or two 120 watt/cm mercury vapour electrodeless lamps or two focused 80 watt/cm lamps. Depending on the type of property evaluated, the coatings were applied on glass, Parker Bonderite 40 steel or wood (maple, oak or beech).

The properties of these films were then tested according to ASTM (5) or DIN methods, including: adhesion (ASTM 3359-90), adhesion-crosshatch (ASTM K- 3359-83), hardness (ASTM D 3363-74), flexibility (ASTM D 522-88 and ASTM D 2794-90), gloss at 60° inclination (ASTM D 523-90) and chemical resistance according to DIN 68 861. In addition to this other tests were performed including reactivity (dry surface), solvent and water resistance using the double rub method and Persoz hardness (type 299 - NFT 30-016).

### **Results and discussion**

A wide variety of oligomers have been successfully dispersed in water. These include epoxy acrylates, urethane acrylates and polyester acrylates of varying functionality. Some of these systems were first modified chemically to obtain tack - free before cure materials. Depending on the type of product, the viscosity at room temperature varies from 60 mPas to greater than 10 Pas. Typical characteristics for these two types of dispersions are summarised in **Table 1**.

**Table 1 : Typical properties of dispersions**

	<b>Type 1</b>	<b>Type 2</b>
<b>Appearance</b>	Milky white liquid	Milky colloidal dispersion
<b>Solids (in v%)</b>	60-65	40
<b>Av. Particle size (μm)</b>	0,4-1,0	0,1-0,14
<b>pH</b>	6,8-7,5	7,7
<b>Viscosity Brookfield(mPa.s - 25°C)</b>	1.200-10.000	70

Type 1 refers to the different families of acrylated oligomers in dispersion. Type 2 are tack - free before cure systems. One of the typical characteristics of dispersions is the

particle size. Particle size depends on a number of parameters including the chemical and the physical properties of the oligomers. Typical particle size distribution curves for type 1 and type 2 dispersions are shown in Fig 1 and Fig 2 respectively.

Fig.1  
Intensity Distribution      Type 1  
Size Distribution(s)

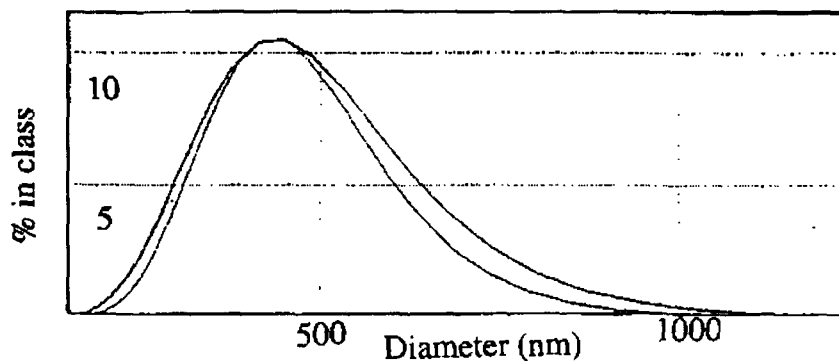
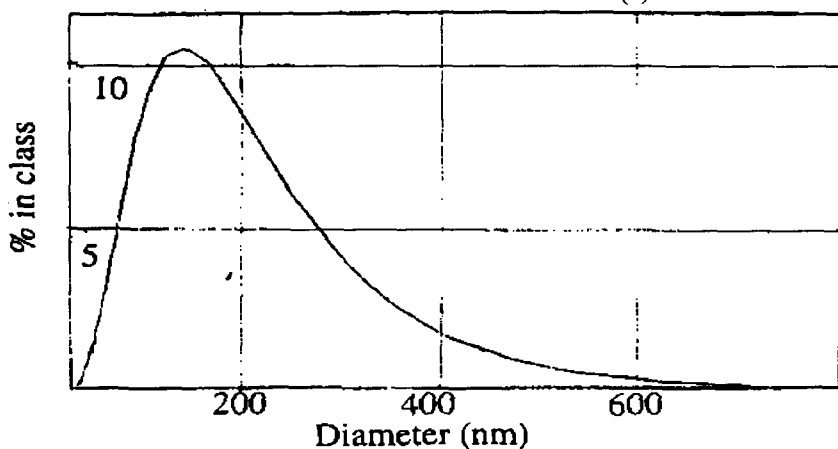


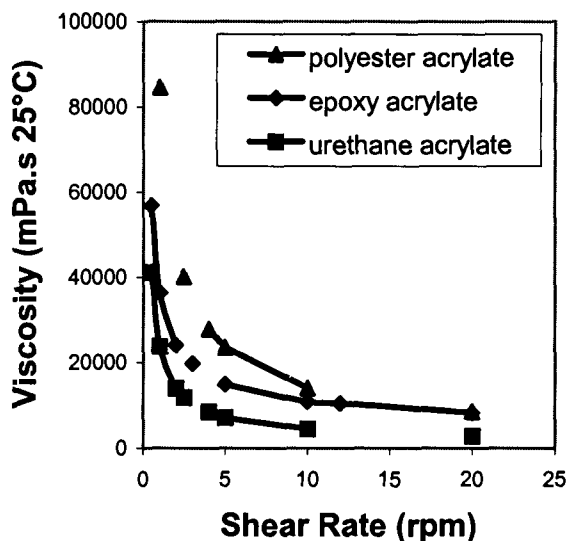
Fig.2  
Intensity Distribution      Type 2  
Size Distribution(s)



The flow properties of the dispersions are important for the final coating quality. As was shown in Table 1, the viscosity of the dispersions can vary over a wide range. The experimental investigations indicate that viscosity is closely related to the particle size and the particle size distribution of the dispersions. For a same percentage of water in the dispersion, the viscosity will be higher when the average particle size is lower. The viscosity of the dispersion will also increase with increasing volume content of the dispersed phase (= oligomer). The dispersions of type 1 have a pseudoplastic rheological behaviour. The dispersion viscosity decreases with increasing shear rate, but returns to its original value immediately after removal of shear. This pseudoplastic rheological behaviour is illustrated in Fig 3 for three types of dispersions: dispersion of urethane acrylate oligomer (curve 1), dispersion of epoxy acrylate oligomer (curve 2), and dispersion of polyester acrylate oligomer (curve3).

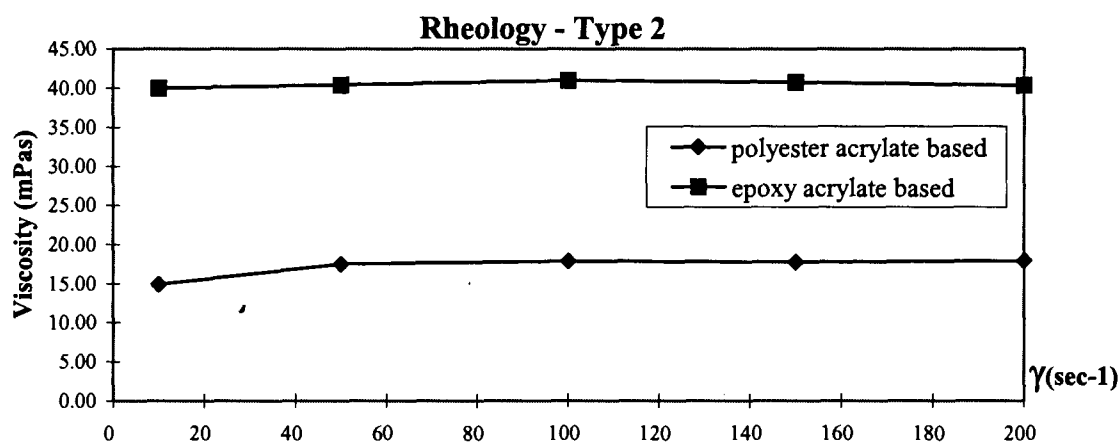
Fig. 3

## Rheological Behaviour of UV-Curable Aqueous Dispersions - Type 1



The dispersions of type 2 exhibit a newtonian behaviour. This is shown in Fig 4.

Fig. 4

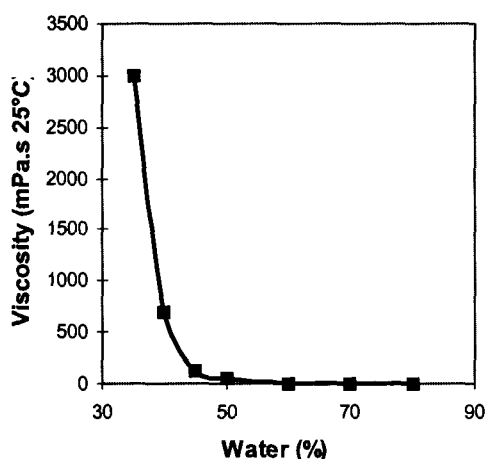


Dispersions are often used to overcome application viscosity problems, for instance for spray applications. The type 2 dispersions are already low in viscosity. The dispersions of type 1 often have rather high starting viscosity's. The viscosity can, however, be adjusted to a wide range by dilution with water. This offers the possibility to combine high oligomer molecular weight with low formulation viscosity. In 100% radiation curable formulations this is sometimes more difficult to achieve as the monomers used for reducing the viscosity are incorporated in the cured coating and therefore modify the coating properties.

Fig 5 shows the dilution effect of water on the dispersion of an epoxy acrylate. The viscosity at room temperature drops from 3000 mPas to 3mPas when the water content is increases from 35% to 80%.

Fig. 5

### Dilution Curve for the Aqueous Dispersion of an Epoxy Acrylate Oligomer



Stability is another important property of dispersions. Not only the stability of the formulation can be a problem when undispersed products are added to the system (e.g. photoinitiators), but also phase separation can occur at room temperature or at elevated temperatures. Most of the dispersions pass the Heat Stability test at 60°C for 7 days without phase separation or particle size changes. Many of these dispersions also pass 1-3 Freeze/Thaw test cycles without phase separation or particle size changes. Film properties have been investigated for films based on the different types of dispersions.

**Table 2** shows a comparison between the properties of epoxy acrylate dispersion of type 1 and the corresponding undispersed epoxy acrylate, neat and with a 45% monomer dilution ( to obtain the same viscosity as the dispersed epoxy acrylate ).

PROPERTY	Dispersion (in 35% water)	Oligomer (in 45% TPGDA)	Oligomer (neat)
Viscosity (cP, 25°C)	4120	4270	> 1.000.000
Cure Speed (m/min)	60	30	30
# Lamps (H lamp, 120W/cm)	1	2	2
Adhesion (%)	100	66	61
Pencil Hardness	9H+	9H+	4H
Conical Bend (cm of crack)	0	0	0
Reverse Impact (in lb.)	6	2	0
MEK Double Rubs	200+	200+	200+
Water Double Rubs	200+	200+	200+
Gloss** (60°)	100	104	107

\* Formulation: 100 p Acrylate + 4 p Darocur 1173 (based on solids)

\*\* Average of 3 readings

Some of the properties are the same for the dispersed epoxy acrylate compared to the undispersed product. The viscosity of the dispersed product can be further adjusted with deionized water, without affecting the final properties of the system. Surprisingly enough, the films made from the aqueous dispersions have faster cure speeds than the films made from the undispersed oligomers. As shown in **Table 2**, the film based on the dispersion has a cure speed of 60 m/min with one H lamp. In contrast, the non-aqueous based film has a cure speed of only 30 m/min with two H lamps. It is believed

that a vapour layer is formed on the surface of the film during the drying process. This (residual) water vapour layer then acts as an oxygen barrier, reducing the effects of oxygen inhibition of cure. A simple experiment has proved this assumption. No differences in cure speed are seen if the aqueous dispersed films are dried, then allowed to sit at room temperature for 30 minutes before curing to allow the water layer to dissipate. A further confirmation was the analysis of the level of unreacted double bonds in both types of cured films. The level was lower when the films are cured under "wet" conditions. The films made from the dispersions have a higher pencil hardness than the films made from the neat resins. This improved hardness could also be due to better surface cure from the mitigation of oxygen inhibition.

The results of the reverse impact tests indicate that the films based on the dispersions have better flexibility than the films made from undispersed oligomers. One possible explanation for this difference could be the flexibilizing effect of the surfactant and residual water in the films based on the dispersed resin. The increase in adhesion could also be due to the presence of surfactant, reducing the crosslink density and therefore reducing the shrinkage upon cure. Solvent and water resistance are good, despite the presence of surfactant.

The systems described until now are based on very simple formulations. As it is the case with conventional 100% UV curable systems, formulation latitude is needed to adjust formulations to specific application and coating requirements. A typical application technique used in wood is spray. The viscosity of the dispersions can be adjusted to the appropriate spray application viscosity by dilution with deionized water. Examples of formulation possibilities are demonstrated in Table 3. Table 4 gives the application and curing conditions of the formulations. Tables 5, 6 and 7 show the coating performance of the cured films.

Table 3-4-5-6-7

<b>Table 3 : Formulations</b>						
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>EA dispersion Type 1</b>	39.20	39.20	39.20	39.20	39.20	39.20
<b>Eb 160</b>	-	5.00	10.00	-	-	-
<b>UA dispersion Type 1</b>	-	-	-	2.80	5.50	11.00
<b>Flatting Agent</b>	2.40	2.40	2.40	2.40	2.40	2.40
<b>Thickening Agent</b>	0.30	0.30	0.30	0.30	0.30	0.30
<b>Photoinitiator</b>	0.70	0.70	0.70	0.70	0.70	0.70
<b>Wetting Agent</b>	0.03	0.03	0.03	0.03	0.03	0.03
<b>Water</b>	57.40	64.00	70.70	60.50	69.70	69.70
<b>TOTAL</b>	<b>100.03</b>	<b>111.63</b>	<b>123.30</b>	<b>105.93</b>	<b>112.63</b>	<b>123.33</b>
Viscosity : approximately 20" DIN 4 mm - 20°C						
Solids : 42-43 %						
Reactivity : 10m/min for 1 lamp of 80W/cm (focussed)						
<b>Table 4 : Application and cure conditions</b>						
<b>Coatings on glass : (hardness)</b>						
Application	: manual draw down					
Film Thickness	: 150µm wet					



standard, low gloss system, based on an epoxy acrylate dispersion. Thickening agents are used to improve the aspect of the film surface when the water evaporates. In these formulations Irgacure 500 (Ciba Geigy) was used as photoinitiator, however, other systems are also possible. Formulations 2 and 3 show the influence of the addition of an undispersed trifunctional oligomer on the coating properties. In formulations 4, 5 and 6, mixtures are made with a type 1 dispersion of a hexafunctional urethane acrylate.

**Table 5** clearly shows the influence of the increase in crosslinking on the properties. Adding 5 or 10% of the hexafunctional urethane acrylate dispersion increases the gloss level, indicating an increased surface cure. Persoz hardness and pencil hardness both increase as a function of the amount of Eb 160 or hexafunctional urethane acrylate added to the formulation. Solvent resistance (**Table 6**) but also water resistance is good for all formulations evaluated. In **Table 7**, the chemical resistance using various types of stains was evaluated. The figures reflect exactly the different categories as described in the DIN 68 861 specification. In practice, a gradual improvement of the chemical resistance is observed with increasing crosslinking (addition of Eb 160 or hexafunctional urethane acrylate). For instance for the blue ink resistance, the marks become weaker going from formulation 1 to 6 even if formulations 1 to 5 all have a score of 3 following the DIN 68 861 specification.

Formulations were also made based on the tack - free before cure dispersions of Type 2. Formulating these systems is less obvious because they have to keep the tack free before cure property. This limits for example the amount of low viscosity diluting monomer one can add. A typical formulation and the evaluation of the properties are given in **Table 8**.

<b>Table 8 : Formulations and properties Type 2 dispersion*</b>		
	<b>A</b>	<b>B</b>
<b>Gloss 60° on wood</b>	-	35
<b>Persoz Hardness (seconds)</b>	80	255
<b>Pencil Hardness</b>	3B	6H
<b>Water double rubs</b>		> 100
<b>Acetone double rubs</b>		75
<b>Isopropanol double rubs</b>		75-100
<b>Water</b>		0
<b>10% Ammonia in water</b>		3
<b>Red wine</b>		1
<b>Coffee</b>		1
<b>Acetone</b>		1
<b>Mustard</b>		0
<b>Isopropanol</b>		0
<b>Blue ink</b>		2-3

\*Formulation: 40p Dispersion + 2 p Flatting Agent + 1p Photoinitiator + 60p Water  
Viscosity : 20" DIN 4 mm -20°C (+/- 50 mPa.s)

Curing conditions were the same as described in **Table 4**. A is referring to properties before cure and B are the results after UV cure. As can be seen, this type of tack free before cure dispersion exhibits very interesting characteristics. Hardness and chemical resistance are good. Properties before and after cure were compared to check the influence of the UV exposure. As these systems are tack free after evaporation of the



water, the possibility existed that the UV cure was not efficient due to the lack of mobility in the coating. The increase in hardness (Persoz and pencil) proves that curing occurred on UV exposure. Further prove was obtained from an FTIR and a TMA analysis as shown in Fig 6 and Fig 7.

Fig. 6

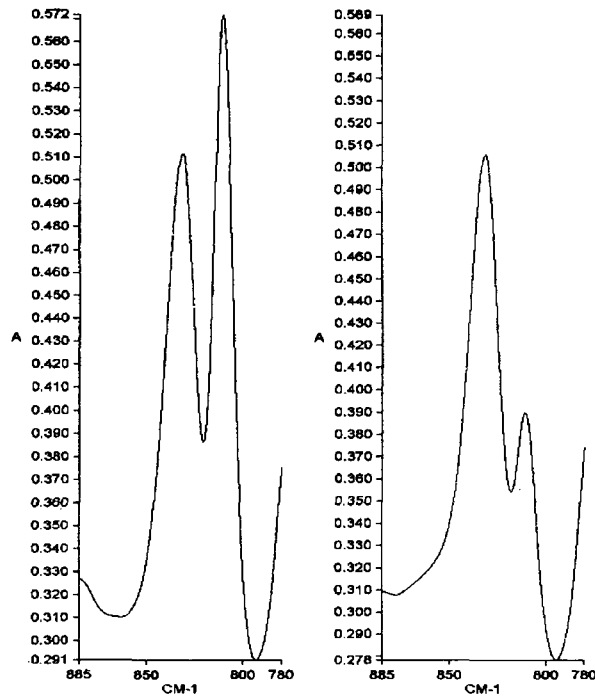
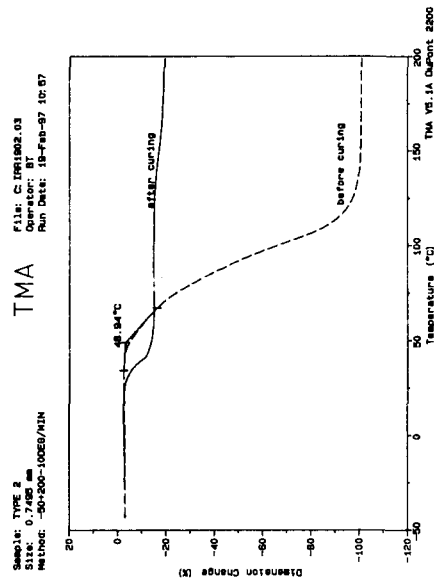


Fig. 7



The FTIR spectrum shows the disappearance of the double bond peak when the sample, after evaporation of the water, is exposed to UV light. The TMA analysis clearly indicates the important decrease in penetration in the substrate after UV cure. These different measurements show that an efficient UV curing occurs even in this low mobility system.

## **Conclusion**

A wide variety of radiation curable oligomers was successfully dispersed in water. The stability (also thermal) of these dispersions pure or in formulations is good. The application viscosity requirements can be adjusted by adding water. The formulation possibilities, especially for wood coatings were demonstrated. The properties of the formulations can be adapted by adding dispersed or undispersed products to the system. Two types of dispersions were investigated. Both have their advantages and their limitations. The tack-free before cure dispersions are less sensitive to dust collection during the application process. On porous substrates, no migration of uncured product, that could be present in the depth of the pores, to the surface will occur. On the other hand, possibilities to adapt the performance properties of the coatings is more limited because the addition of liquid radiation curable products to this type of dispersion will destroy the tack - free before cure property.

The other type of dispersion gives much more formulation flexibility. Various dispersed and undispersed products can be added to modify the properties. After water evaporation these systems will, however, be more sensitive to dust on the surface and uncured material on very porous substrates will eventually migrate to the surface.

It is therefore clear that the final choice between the two systems will depend on the type of application that is envisioned.

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