

Advances in waterborne UV coatings

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Introduction

Aqueous radiation curing systems have been presented and discussed with increased frequency for the past 20 years. However, only recently has there been market acceptance for such systems, both industrial coating applications, e.g. UV coatings for parquet primers¹, and graphic arts applications. The aqueous radiation curable systems described here are water-soluble, water-reducible², water-dispersible³, latex-based⁴ and hybrids of all previously mentioned types, the majority of which are capable of free radical polymerisation, although cationic polymerisation has also been reported⁵. In view of the wide range of different chemical approaches employed, the main characteristics, the advantages and disadvantages, are also expected to vary widely. Nevertheless, they all aim to develop:

- VOC free systems with extremely low viscosity (e.g. for sprayable applications or jettable systems).
- Easy-to-obtain surface effects (e.g. matt effect) or incorporating various fillers for improving coating performance, enhancing the scope of possibilities for the formulator.
- Eliminate or reduce the need for irritant acrylate monomers (e.g. HDDA, TPGDA)

Compared with UV polyurethane dispersion and UV latex, the following advantages of externally emulsified acrylate oligomers can be mentioned:

- Direct conversion of current solvent-based UV systems to waterborne UV to meet VOC regulations
- New opportunities for hybrid systems (e.g. acrylic/UV acrylate, alkyd/UV acrylate, PUDs/UV acrylate)
- Greater availability of raw materials and a high degree of freedom for the formulator compared with UV PUDs and UV latex
- One disadvantage of the emulsions compared with UV PUDs is the non tack-free film after water flash-off

This paper presents a new method for making externally emulsified acrylate oligomers for UV/EB curing using an amphiphilic dendritic polymer. Thanks to its non-ionic polymeric structure and large hydrophobic/lipophilic balance, the dendritic emulsifier is believed to be a versatile emulsifier for a number of binder systems, including radiation curable acrylate oligomers, as well as contributing to the coating properties, unlike conventional emulsifiers which are often considered as detrimental to the coating performance.

Amphiphilic dendritic polymer

The amphiphilic polymer, BOLTORN[®] W3000, is a non-ionic dendritic self-emulsifying polymer. It consists of a dendritic, globular structure, with the chain ends terminated by a combination of hydrophobic chains (long unsaturated fatty acid allowing air drying oxidation process) and hydrophilic chains (polyethylene glycol chains). The amphiphilic nature of this dendritic polymer confers both dispersing and stabilizing properties. This behaviour is used to disperse conventional binders such as alkyd resins (initially prepared for solvent-borne systems) in water, and it has been successfully applied to radiation curing oligomers such as epoxy, polyester and urethane acrylate oligomers as described in this paper. A core/shell particle type of emulsion is obtained, the core being the binder that controls the coating properties and the shell being the amphiphilic dendritic polymer which performs as a stabilizer/emulsification agent allowing surfactant-free or almost surfactant-free waterborne systems.

In Figure 1, a schematic image of the amphiphilic dendritic polymer is shown.

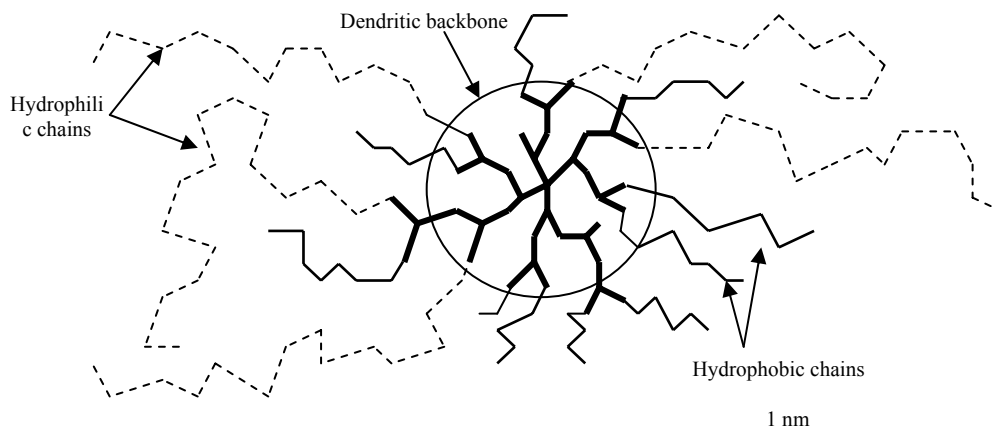


Figure 1. Illustration of the amphiphilic dendritic polymer.

The characteristics of the amphiphilic dendritic emulsifier are given in Table 1.

Table 1. Characteristics of the dendritic emulsifier.

PROPERTIES	ACID NUMBER (mg KOH/g)	VISCOSITY (Pas, 35°C, 30 ^{s-1})	OIL LENGTH (%, CALCULATED AS TRIGLYCERIDE)
Dendritic emulsifier	10 (max)	2 000	45

Experimental

Emulsification

The emulsions were prepared using the emulsification inversion point method. In the emulsification inversion point (EIP) method, water is added to the acrylate resin containing the emulsifier⁶. A water in oil emulsion (W/O) is formed initially. The addition of water will cause the viscosity of the mixture to increase sharply until it reaches its maximum value. At this given water concentration, the W/O emulsion inverts spontaneously (the emulsion inversion point) and forms an oil-in-water emulsion (O/W). The viscosity of the emulsion will decrease further with the further addition of water.

To prepare an emulsion using the dendritic emulsifier and the EIP method, the procedure described below could be used:

1. Mix the dendritic emulsifier thoroughly together with the acrylate resin(s) and the other possible binder, photo initiator, optional co-solvent/coalescing agent and the possible thickener at 50 -60 °C to obtain a homogeneous blend.
2. Optionally neutralize to pH 6 to 8 with an aqueous base (aqueous solution of N,N-dimethyl ethanolamine or tri-ethyl amine)
3. Add optionally a surfactant to the mixture (1 to 4 wt % on solid).
4. Add the optional drier salts to the solution (about 0.05 - 0.1% metal on solids).
5. Mix the ingredients well for at least 15 min.
6. Slowly add heated deionised water to the resin mixture while stirring, preferably heated to the same temperature as the blend, over a period of 20 min – 2 h until to the final desired solid content of 40 to 50 wt % is reached. Remove the heat source, and cool the emulsion slowly while stirring.

Emulsions

Several emulsions were prepared using the procedure described in the emulsification section; the compositions are listed in Table 2.

Formulations 1-6 were all emulsions of different acrylate oligomers. To compare the impact of a small addition of another acrylate, the di-functional Polyol R2490 (alkoxylated neopentyl glycol) acrylate was added in formulations 2, 4 and 6 in order to increase the hardness and chemical resistance of the coatings.

The white, milky low-VOC emulsions were applied to both glass and aluminium plates as 100 µm thick coatings. Before UV curing, the water and co-solvent were flashed-off at 80 °C for 5 min, and then cured directly afterwards with 2 passes at 10 m/min beneath an H-bulb of 160 W/cm (Fusion F600). Clear coatings with a thickness of approximately 40 µm were obtained by this means. The hardness was evaluated using a pendulum hardness tester, the flexibility with an Erichsen testing equipment and the chemical resistance with ethanol double rubs. The maximum UV curing speed was defined as the maximum speed at one pass beneath an H-bulb of 160 W/cm in order to achieve a tack free surface.

Table 2. Emulsion compositions.

	Form. 1	Form. 2	Form. 3	Form. 4	Form. 5	Form. 6
Dendritic emulsifier	5,60	5,60	3,85	3,85	3,85	3,85
Disponil SUS IC 875					0,35	0,35
Cirrasol 292X3	0,70	0,70	0,70	0,70		
EB 851 (polyester tri-acrylate)	33,40	33,40				
EB 657 (polyester tetra-acrylate)			34,20	34,20		
EB 265 (urethane tri-acrylate)					35,00	35,00
Polyol R2490 acrylate		2,00		2,00		2,00
Acrysol RM8W	0,70	0,70	0,20	0,20		
Acrysol R2020	0,70	0,70	1,90	1,90	1,90	1,90
DPnB	9,40	9,40	9,40	9,40	9,40	9,40
DMAE	< 0,1	< 0,1				
Deionized water	47,90	45,90	48,15	46,15	47,90	45,90
Irgacure 500	1,55	1,55	1,55	1,55	1,55	1,55
Additol VXW 6240	0,05	0,05	0,05	0,05	0,05	0,05
Total	100,00	100,00	100,00	100,00	100,00	100,00

Disponil SUS IC 875 available from Cognis

Cirrasol 292X3 available from Uniqema

EB 851, EB 657 and EB 265, Additol VXW 6240 available from Cytec Surface Specialties, BE

Acrysol RM8W and Acrysol R2020 available from Rohm and Haas

Dowanol DPnB available from Dow

DMAE: N,N di-methyl ethanol amine

Irgacure 500 available from Ciba Specialty Chemicals, CH

Polyol R2490 and Dendritic emulsifier available from Perstorp Specialty Chemicals AB

Table 3. Properties of emulsions.

	Form. 1	Form. 2	Form. 3	Form. 4	Form. 5	Form. 6
Viscosity (25 °C, plate & plate 100s ⁻¹) mPas	379	385	70	73	130	140
Mean diameter (µm)	2,91	-	0,45	-	0,47	-
Solid content % w/w	43	45	42	44	43	45
pH	6	6	3,5	3,5	4,5	4,5

The viscosity of the emulsions could be lowered easily by further dilution due to their rather high solid content. Very good stability of the emulsions can be expected with a small mean particle size, as in formulation 3 and 5.

Results

The coatings of the emulsions described in Table 2 were all evaluated in respect of properties such as pendulum hardness, flexibility, chemical resistance and maximum reactivity. The properties of the coatings are described in Table 4.

Table 4. Properties of coatings and waterborne coatings after 24 h.

	Form. 1	Form. 2	Form. 3	Form. 4	Form. 5	Form. 6
Maximum UV curing speed. m/min (after water flash off, 5 min 80 °C, in air, H-bulb, 160 W/cm)	5	15	20	30	10	20
40 µm +/- 5 µm dry on glass and aluminum, 5 min 80 °C and 2 pass at 10 m/min (~500 mJ/cm ²)						
Hardness (K.s.)	63	71	30	32	26	33
Erichsen flex. (mm)	1,7	1,7	4,6	4,5	5,8	5,7
# Ethanol dbl rubs	> 200	> 200	130	> 200	120	> 200

The improvement in the coatings from the Polyol R2490 acrylate could clearly be seen when looking at the chemical resistance together with an increased hardness, while retaining flexibility. The maximum UV curing speed was also increased with this small addition. The dendritic emulsifier offers good possibilities for using different acrylate oligomers and, as a result, different coating properties can be tailored depending on the choice of oligomers and compositions used.

Conclusions

- The amphiphilic cross-linkable dendritic emulsifying polymer is an effective emulsifier for acrylate oligomers, which can be used to develop aqueous UV systems.
- Ease of converting and use existing acrylate oligomers and low-irritant monomers into waterborne equivalents with low or no VOC.
- Hardness and chemical resistance of the formulated coatings can be increased easily by a small addition of a low-skin or non-irritant monomer.

References

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