

## **Novel Reactive Pigment Dispersants**

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### **1. INTRODUCTION**

Ultraviolet cured coatings offer distinct advantages over conventional liquid coatings. The advantages of low or zero volatile organic content VOC coatings in an environmentally-minded industry are obvious. UV coatings also allow quick drying time due to the diffusion-limited rates of reaction for radiation induced crosslinking chemistries. These high speeds enable high production rates. Also the wide variety of monomer and oligomer choices offers immense formulation latitude and final coating properties.

Radiation cured coatings have been widely used in graphic arts applications for many years and are showing good growth in both traditional ink sectors, using flexographic and offset processes, and more recently also in newer digital inks (*Ref – Radcure Coatings and Inks – ‘Cost & Performance ‘ Conference Proceedings ,Manchester 20-21 June 2006 ,Paper 1 ,Dr Helma Jotischky,PRA*). Similarly use in coatings applications is perhaps more slowly, led by furniture /wood coatings, but with many applications showing growth. Projections show Asia catching NAFTA and Europe in market share over the next few years, although applications in each region may differ.

In the newer ink applications, the industry trend is to achieve low end use viscosities while still increasing pigmentation levels or utilizing smaller particle size pigments. This has led to increasing performance requirements for the additives in the formulation, particularly dispersants. The use of dispersants in UV ink formulations has been covered in detail previously (*ref RadTech Europe 2003,Conference Proceedings, p521, M Sudder*) and will be briefly summarized here. The emerging requirements of low application viscosity with small particle size pigments will likely require higher dosages of additives with possibly more diluent to provide stable inks.

### **2. Dispersant Design**

Effective pigment dispersants for use in UV systems generally have segmented structures to provide both anchoring to the pigment surface and formation of a steric barrier around the pigment particle. Examples of polymer architectures which may be used are: a single chain with a terminal anchoring functionality or preferably, AB or ABA block copolymers and comb structures. The effectiveness of each has been reported previously (*Ref: The Role of Hyperdispersants in Universal Pigment Dispersions for UV Coatings.,Conference Proceedings. M Sudder, Noveon* ). Dispersants are designed to be effective with different pigment surface chemistries and also show good compatibility in the binder resin of choice. However, in certain situations the compatibility may be less than desired and may lead to the additive being excluded from the resin matrix on

cure. This can potentially lead to a reduction in physical properties of the cured film. If the dispersant itself contained reactive double bonds that can copolymerize during the curing process, the dispersant will become part of the crosslinked matrix.

We are developing a range of novel comb architecture reactive dispersants for use in radiation cured systems. The dispersants may be prepared in solvent, but our focus has been to generate 100% active materials which are preferable to avoid the introduction of solvents into coatings. The dispersants are viscous liquids that are mobile at room temperature and pour readily when warm (50°C) as illustrated in figure 1.0.

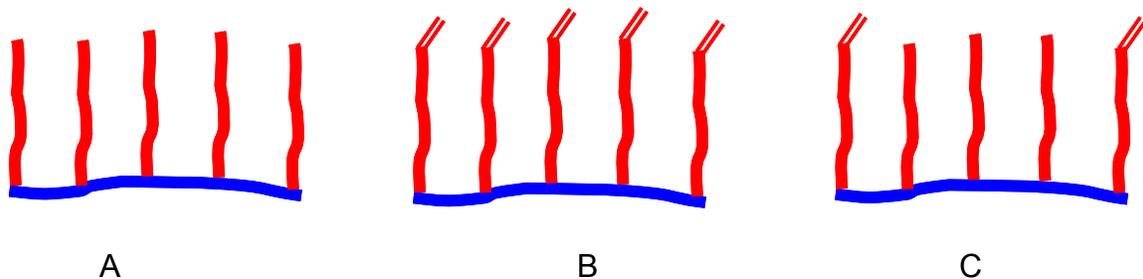


*Figure 1.0 Reactive dispersant poured from glass jar at room temperature (LHS) and at 50°C (RHS)*

The reactive dispersants are also soluble in a wide range of monomers and oligomers.

### **3. Synthesis and Structure**

The comb architecture reactive dispersants may schematically be represented as in Figure 2.0



*Figure 2. comb architecture polymer dispersants A= non-reactive dispersant, B & C reactive dispersants.*

The design of dispersant can be varied, for example: with changes to molecular weight and polarity of the steric stabilising chains, i.e. the teeth of the comb. Acidic or basic functionality can also be incorporated into the polymer backbone to increase the affinity of the dispersant towards different surfaces.

#### 4. Dispersion Performance.

The new reactive dispersants must fulfil their primary role as effective pigment dispersants.

To investigate the effectiveness of the reactive dispersants a black pigment (Regal 400R) was milled with no dispersant, a commercially available polyester type conventional dispersant, and two reactive dispersants, one with an acid anchor and another with a basic anchor group.

A millbase was formulated with 30.0% black pigment (Regal 400R ex Cabot) in ethoxylated tripropylene glycol diacrylate (ex Sartomer, Grade SR454) and dipropylene glycol diacrylate (ex Sartomer Grade 508) with dispersant present at 33.3% AOWP (additive on weight pigment) in a glass jar containing 3 mm diameter glass beads. Milling was for a period of 1 hour in a Scandex disperser model 200-K. The rheology flow curves of the millbases generated as measured on a Bohlin V88 rheometer are shown in figure 3.0. Both types of reactive dispersants can be seen to provide effective viscosity reduction in the millbase. The dispersion in the absence of any added dispersant was highly flocculated.

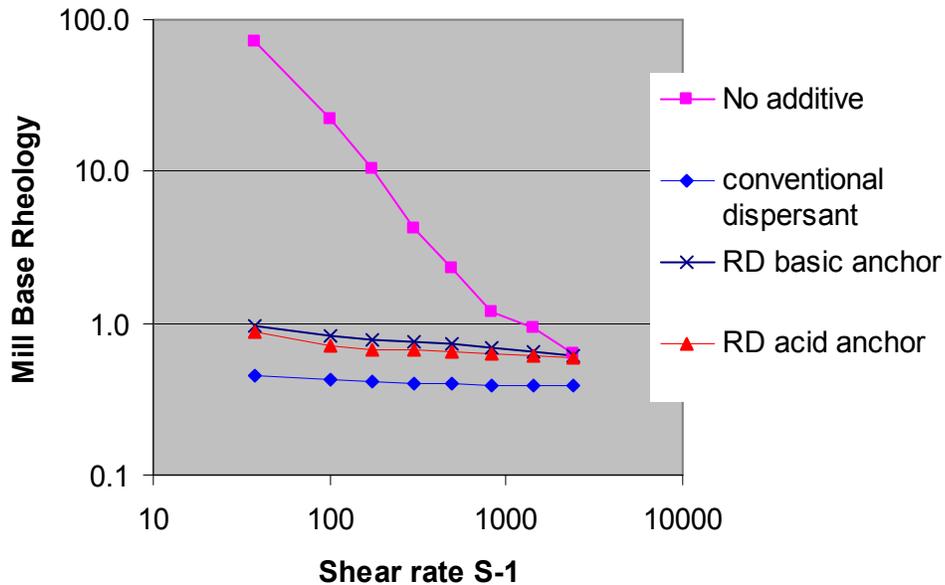
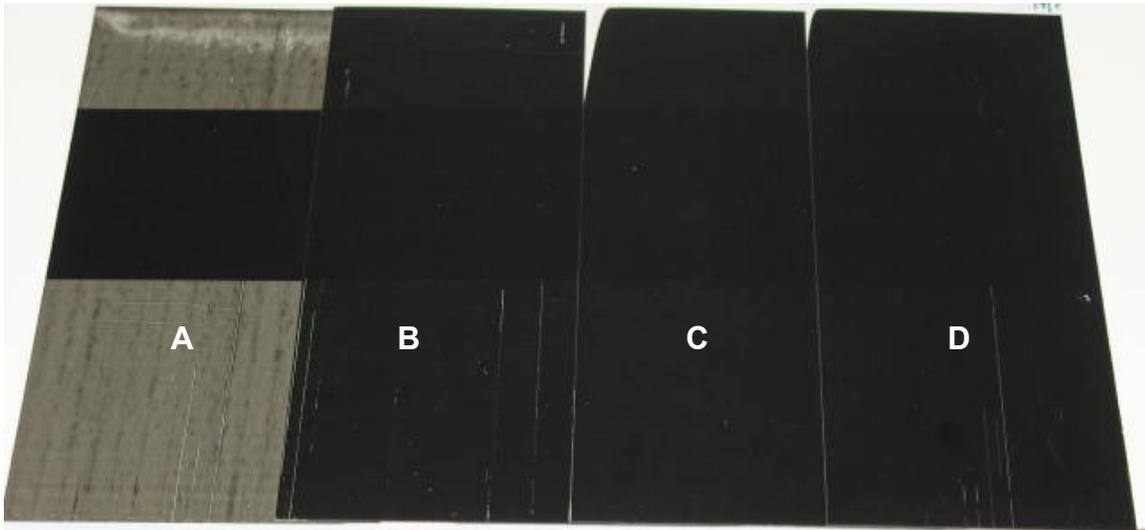


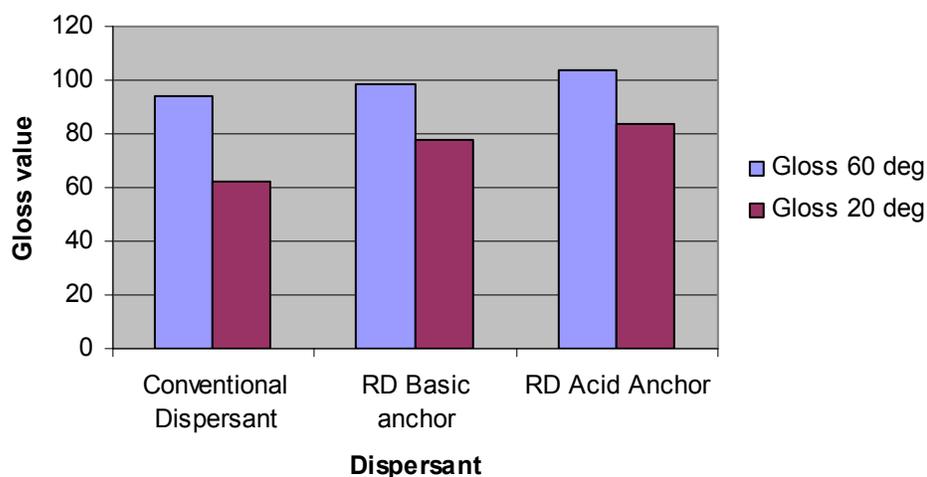
Figure 3.0 Rheology flow curve of 30wt% dispersion of Regal 400R pigment

These millbases were let down into a UV binder system based on dipropylene glycol diacrylate (Actilane 422 ex Akzo Nobel) and polyester-acrylate (Actilane 505 ex Akzo Nobel) containing a photoinitiator blend. The UV ink was drawn down onto black and white card with a number 0 K-Bar and cured in a Fusion DRSE 120 UV system under a D lamp.



*Figure 4.0 shows a photograph of the cured drawdowns. A = no dispersant, B= conventional dispersant, C= basic functional reactive dispersant and D= acid functional reactive dispersant.*

The tinctorial properties of the cured films containing the reactive dispersant were at least as good as that from the conventional dispersant as illustrated in the photograph in figure 4.0. From figure 5.0 the measured gloss value can be seen to be increased for the reactive dispersant relative to the conventional.



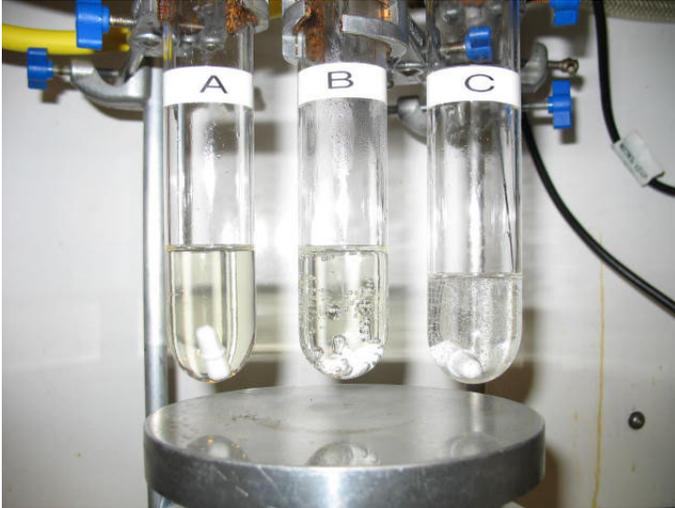
*Figure 5.0 Gloss measurement of Regal 400R based cured inks.*

### **5. How reactive are the dispersants?**

To illustrate the reactivity of the dispersants, the dispersants were thermally cured using a model system based on the solution polymerisation of butyl acrylate (BA) in the presence of 2,2'-Azobis(2-methylpropionitrile) (AIBN) initiator.

The experiment was based on 5 wt% reactive dispersant and 1 wt% AIBN in BA monomer. The monomer was diluted with an equivalent mass of butyl acetate as solvent and heated to 70 °C.

In Figure 6.0 Schlenk tube A contained a conventional dispersant (non reactive), Schlenk tube B contained a reactive dispersant and Schlenk tube C contained no dispersant only BA and AIBN.



*Figure 6.0 Radical polymerisation of butyl acrylate*

After 30 minutes the contents of Schlenk B gelled and became immobile whereas the contents of Schlenk A and C increased in viscosity, but were still fluid.

This experiment indicated that 5% reactive dispersant was sufficient to generate a crosslinked polymer network under radical polymerisation conditions. This was further demonstrated by carrying out a similar experiment where the reactive dispersant had been used in the milling of a pigment.

A yellow pigment (Novaperm Yellow H2G, ex Clariant) was milled at 20% pigment loading in butyl acetate at 25% AOWP in the presence of a conventional dispersant and a reactive dispersant. The millbases were then milled with glass beads for 16 hrs on a horizontal shaker. Both mill bases produced fluid dispersions. In a control experiment with no dispersant added to the mill base the dispersion was too viscous to flow.

An equivalent mass of butyl acrylate containing 1 wt% AIBN was then added to each millbase and the dispersions were placed in two Schlenk tubes and heated to 70°C. As previously the presence of the reactive dispersant caused the reaction mixture to gel.

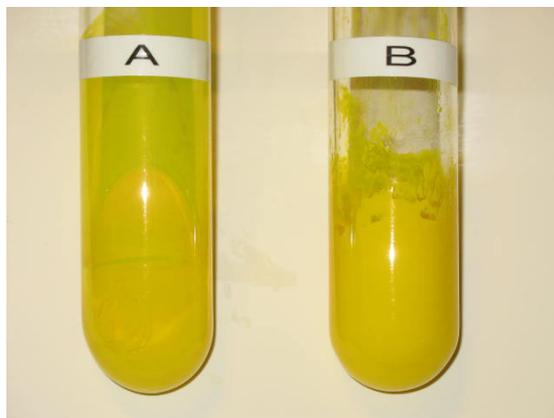


Figure 7.0 Polymerization of butyl acrylate in the presence of a yellow mill base

These experiments have demonstrated the participation of the reactive dispersant in crosslinking with acrylate comonomers. However, the reactive dispersants (100% active) themselves are stable. We have demonstrated no change to the dispersants in the absence of initiator on storage at the elevated temp of 50°C for one month.

## 6. Physical Properties of the Inks/Coatings.

### 6.1 Hardness

The ability to crosslink into the binder system could potentially yield benefits in terms of film hardness and cure speed to achieve a certain level of solvent resistance.

The effect of dispersants was investigated in a hard clearcoat formulation based on the following mixture of monomers and oligomers available from Sartomer:

Sartomer CN704 acrylated polyester adhesion promoter  
Sartomer CN UVE151M aromatic epoxy acrylate  
Sartomer SR833S difunctional acrylate monomer  
Sartomer SR506D, isobornyl acrylate  
Sartomer SR285 tetrahydrofurfuryl acrylate  
Sartomer SR368 tris (2-hydroxy ethyl) isocyanurate triacrylate

A photoinitiator package and the dispersant at a level of 6wt% were added to the formulation. Glass panels were coated using a 24 micron well using a Kcoater. Three individual panels were prepared for each formulation.

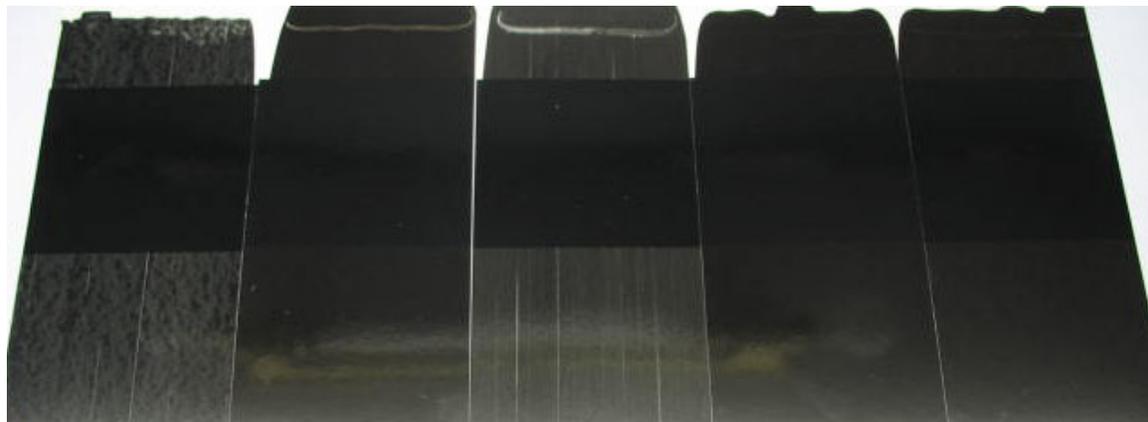
All the panels were cured under the same conditions in the Fusion DRSE 120 UV system under a D lamp. The pendulum hardness of the cured films was determined and is shown in the following table.

	Koenig hardness (sec.)			
	panel 1	panel 2	panel 3	average
No additive	172	158	165	165
Conventional dispersant	78	81	82	80
Competitor 1	53	58	47	53
Competitor 2	85	77	78	80
Reactive dispersant basic anchor	148	156	157	154
Reactive dispersant acid anchor	154	153	149	152

The reactive dispersants have significantly less impact on the hardness of the coating than the non reactive dispersants.

## 6.2 Solvent Resistance

A black UV flexographic ink formulation was also investigated based on Special Black 250 (available from Degussa) in which the different dispersants were used at the milling stage. The inks were applied on Leneta Black and white card using a 0-K bar. The L, a, b values of the cured coatings were determined. The jetness of the coating obtained with the basic functional reactive dispersant was equally as good as the best conventional dispersants as can be seen from the photograph (figure 8.0) and the graphical representation of the L values in Figure 9.0.



No additive	conventional	competitor 2	RD basic	RD acid
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*Figure 8.0 Photograph of cured Special Black 250 flexographic formulation on Leneta Black and white card*

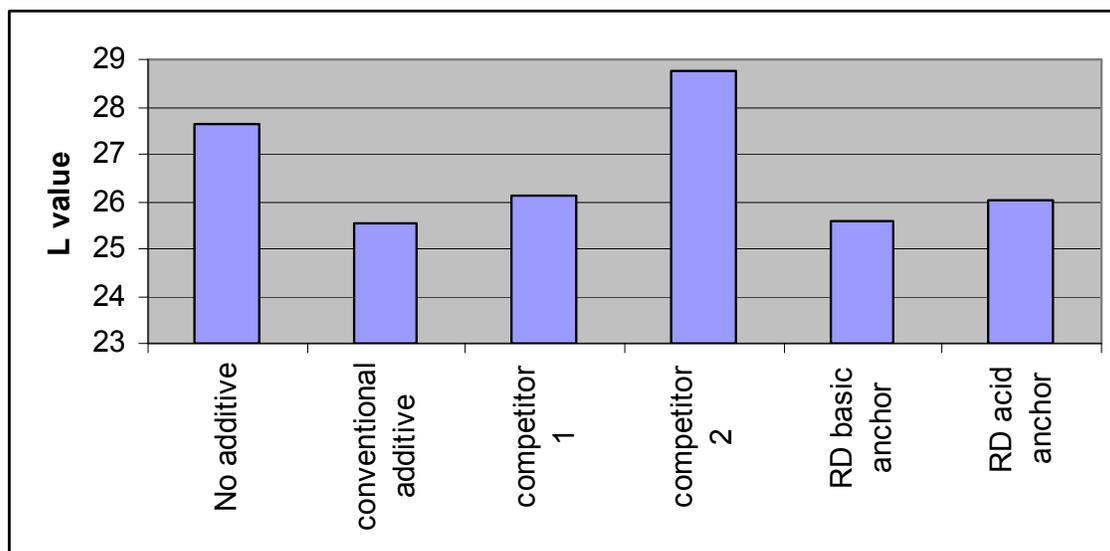


Figure 9.0 Comparison of L values of black flexographic ink formulation

The presence of a dispersant within the cured film may lead to reduced chemical resistance. A simple resistance test was carried out in which a cotton wool swab soaked in methyl ethyl ketone was placed on the cured ink and covered with a watch glass. The appearance of the panel was monitored every 5 mins. The time taken for visible deterioration (eg pitting, blistering) to occur was noted in each case.

Dispersant type	Time to film deterioration / minutes
No additive	>60
Conventional dispersant	25
Competitor 1	30
Competitor 2	25
Reactive dispersant basic anchor	50
Reactive dispersant acid anchor	50

All dispersants have had an adverse effect on the resistance to MEK but the effect is much reduced for the reactive dispersants.

## 7. Conclusion

We have developed a range of novel reactive dispersants and have demonstrated their ability to co-cure in both model and UV ink formulations. Various physical properties of the coatings have been measured and benefits demonstrated.