

# KEY FACTORS FOR UV CURABLE PIGMENT DISPERSIONS

B. Magny - E. Pezron - Ph. Cicéron - A. Askienazy

Cray Valley, Resin Division, 60550 Verneuil en Halatte, FRANCE

Phone : 3-44556686 Fax : 3-44556693

email : pacgroup.cv@wanadoo.fr



MY0001443

## ABSTRACT

UV oligomers with good pigment dispersion are needed to allow good formulation flexibility and possibility to apply thinner films.

Pigment dispersion mainly depends on three phenomena : the wetting of agglomerates, the breakage of agglomerates by mechanical stress and the stabilization of smaller agglomerates and primary particles against flocculation. It has been shown that oligomers with low viscosity and low surface tension induce a good pigment wetting.

Examples of monomers and oligomers for good pigment dispersion are given.

## 1. INTRODUCTION

At the present time, UV inks offer many advantages compared to conventional solvent based inks. It remains that UV inks have to meet a lot of applicative criteria. Primarily, an ink has to exhibit the right colour strength and the right rheology (good flow for instance). These two parameters are interrelated. Moreover, inks must be solvent/stain resistant, and have good printability... The objective of this study is to better understand pigment dispersion through a UV vehicle in order to better control the rheology of the ink and its colour strength. Due to the fact that UV inks for lithography, flexography and screen process are similar in composition, we try to define guidelines for ink formulation.

Advantages of an optimized pigment dispersion are the possibility to have a greater flexibility of formulation or to apply thinner films with the same colour strength.

In this study, we will present the main parameters that influence pigment dispersion, some guidelines to obtain a good pigment dispersion and finally how rheology measurements can help to better understand flow/colour strength behaviours of inks and concentrates.

## 2. EXPERIMENTAL

Raw materials are as follows : Red Magenta PR 57.1 and Yellow PY 74.

Oligomer and monomer viscosities were measured by a Brookfield viscometer. Pigment dispersion viscosity was measured with a controlled stress apparatus (Rheometrics SR 200) through viscoelastic measurements.

Surface tensions have been measured by the Du Nouy Ring Method with a Sigma KSV tensiometer at 25°C.

### 3. PIGMENT DISPERSION PRINCIPLES

The primary objective of pigment grinding is to incorporate pigment particles into a liquid vehicle in order to obtain a fine particle dispersion. Quality of ink is directly linked to pigment dispersion status. The most important property of an ink is its colour strength. Colour strength increases when particle size decreases, due to the fact that colour intensity is correlated to the light absorbed by the pigment particles. However by increasing pigment dispersion, ink viscosity increases which leads to poor flow.

Dispersion processes may be divided in three independent steps (1-2)

- the wetting of agglomerates
- the breakage of agglomerates by mechanical stresses
- the stabilization of smaller aggregates and primary particles against flocculation.

#### • Wetting of agglomerates

In the dry state, powders usually contain aggregates of primary particles. The liquid has first to wet these aggregates and must also displace (if possible) air from the internal surfaces between the particles in the clusters. The penetration of liquids into the dry pigment is essentially described by the Washburn equation (3) :

$$v_p \propto \left[ \tau \frac{\gamma \cos \theta}{\eta} \right]^{1/2} [\text{time}]^{1/2} \quad [1]$$

- $v_p$  rate of penetration of liquids into pores of agglomerates
- $\tau$  average radius of pores
- $\gamma$  surface tension of liquid
- $\eta$  viscosity of liquid
- $\theta$  contact angle of liquid on pigment

From this equation, it is clear that viscosity and surface tension of oligomers and monomers will have a great role in the first step of pigment dispersion. Toussaint & al have shown that these two parameters are very important for dispersion in « high solids » resins (4).

#### • Mechanical breakage of agglomerates

Winkler (1-2,5) has proposed the « hammer/nut » model to explain the influence of mechanical breakage on agglomerates. In order for the nut (agglomerate) to be cracked (dispersed), it must

- 1) be hit
- and
- 2) be hit hard enough

By using this analogy, the toughness of the nutshell is similar to the strength of the agglomerates.

The probability for an agglomerate to be dispersed in a dispersing medium has been shown to be the product of two probabilities :

$$P = P_t \times P_e \quad [2]$$

$P_t$  : the probability for an agglomerate to be hit

$P_e$  : the probability for an agglomerate to be hit hard enough

The partial probability  $P_t$  for an agglomerate to be hit is :

$$P_t = 1 - \exp\left(-\frac{k \cdot V_{\text{eff}} \cdot t}{V_T}\right) \quad [3]$$

$k \cdot V_{\text{eff}}$  = effective volume per time unit

$V_T$  = total volume of mill base in the milling chamber

$t$  = time

The partial probability  $P_e$  for the agglomerates to be hit hard enough is

$$P_e = 1 - \exp\left(-\frac{a \cdot E}{V_T \cdot \sigma}\right) \quad [4]$$

$a$  = mediation constant

$\sigma$  = agglomerate strength

$E/V_T$  = energy density

These equations highlight the fact that a lack of energy density during a dispersion can not be substituted by longer dispersion time and vice versa. Coming from these probabilities, the achieved degree of dispersion corresponds to an agglomerate size which is determined by the difference between energy density (maximum stress) and agglomerate strength.

In order to improve the final state of dispersion, it must be given the most severe mechanical stress to the agglomerate in order to increase energy density factor.

Stress is directly related to the viscosity of dispersion and shear rate. Shear rate values greatly depend on the grinding equipment (6). For instance, with an impeller, shear rate is between

100 s<sup>-1</sup> and 300 s<sup>-1</sup>, as compared with a three roll mill with a shear rate of 20 000 s<sup>-1</sup> to 80 000 s<sup>-1</sup>. It is easy to understand that better dispersion will be obtained with a three roll mill apparatus.

- **Stabilization of smaller aggregates and primary particles against flocculation**

The third step is to maintain the dispersed state since the particles have a natural tendency to reaggregate. For a UV vehicle, stabilization is mainly due to steric stabilization. The conformation of the adsorbed oligomer on the pigment particle is the main parameter that influences flocculation.

#### 4. PIGMENT DISPERSION WITH UV VEHICLES

As presented just above, wetting is the first condition for a good dispersion. In this section, we do not discuss the effect of mechanical breakage that mostly depends on the grinding apparatus used.

Most organic pigments have low surface tension. In order to wet the pigment surface, oligomers and monomers used in an ink formulation must have a low surface tension. As described by the Washburn equation [1], penetration of the UV resin in the dry pigment is more favorable in case of low viscosity.

To highlight the effect of resin viscosity and surface tension, pigment concentrates have been prepared with the Yellow PY 74 pigment by a impeller grinding apparatus. Viscosities of the pigment dispersion have been measured at various shear rates (see figure 1). This allows determination of pseudo plastic behaviour of the concentrate. The dispersion viscosity is directly related to the pigment dispersion state :

$$\eta_{\text{dispersion}} = \eta_o \left[ \frac{1}{1 - \frac{\phi_{\text{eff}}}{\phi_m}} \right]^2 \quad [5]$$

$\eta_o$  : resin viscosity

$\phi_m$  : maximum particle volume fraction

$\phi_{\text{eff}}$  : effective volume fraction (depends on number of primary and aggregates particles)

As presented in Table 1, monomer surface tension has a great influence on pigment dispersion rheology : a decrease in surface tension leads to a better wetting of pigment particles by monomer and then to a better dispersion state. Propoxylated neopentyl glycol diacrylate (SR 9003) leads to better dispersion state than tripropylene glycol diacrylate (SR 306). The effect of the initial monomer viscosity has a great influence on pigment dispersion rheology as shown on Table 2. For instance, tetrahydrofurfurylacrylate (SR 285) exhibits lower dispersion viscosity than trimethylolpropane triacrylate (SR 351). Same characteristics have been

observed for oligomers : increasing initial viscosity of the neat oligomer leads to a higher dispersion viscosity (see figure 2).

With regard to Magenta pigment, its aggregation state in dry powder is too strong to be dispersed just by an impeller apparatus. Trials have been done with monomers but the quality of dispersion is too poor (observed by optical microscopy) to investigate rheological characteristics. This observation is in good correlation with the mechanical breakage model of Winkler (1-2). To obtain pigment dispersion with good colour strength, a three roll mill has been used to prepare dispersion based on Magenta. One of the constraint of using a three roll mill is that the initial viscosity of the vehicle has to have a minimum viscosity value. Therefore, a monomer / oligomer blend has been used for Magenta dispersion.

Pigment concentrates based on Magenta exhibit very high viscosity. Characterization of concentrates based on epoxidized soya bean oil acrylate (CN 111) and bisphenol A epoxy diacrylate (CN 104) through viscoelastic measurements instead of shear viscosity has been done. Values of elastic modulus  $G'$  and loss modulus  $G''$  have been determined in the linear domain of the gel. Examples of graphs are presented in figure 3. Depending on the oligomer used,  $G'$  can be lower or greater than  $G''$ . A concentrate based on CN 104 exhibits a value of  $G'$ , that is greater than the value of  $G''$  : this means that the elastic component of the gel is predominant compared to the viscous component. This could be interpreted by a 3 dimensional structure that corresponds to a flocculated structure. Flocculated systems usually exhibit very poor flow properties.

On the other hand, a concentrate based on epoxidized soya bean oil acrylate (CN 111) presents a loss modulus  $G''$  higher than elastic modulus  $G'$ . This concentrate has a more viscous behaviour and it is favorable for a good flow.

## 5. CONCLUSION

This article reviewed the main parameters influencing pigment dispersion : wetting of agglomerates, breakage of agglomerates and stabilization of agglomerates.

Influence of surface tension and viscosity of oligomers and monomers has been shown. In order to reach a good pigment dispersion, monomers and oligomers with low viscosity and low surface tension are required. An example of an epoxidized soya bean oil acrylate (CN 111) as a good candidate for pigment dispersion is given.

## REFERENCES

- (1) Winkler, E. Klinke, L. Dulog, J. Coat. Techn., 1987, 754, 35
- (2) Winkler, L. Dulog, J. Coat. Techn. 1987, 754, 55
- (3) Nelson, « Handbook of powder technology : Dispersing powders in liquids »  
Vol. 7, 1988, Elsevier Science Ed.

(4) Toussaint, I. Szigetvari, Double liaison, 401-404, 1989, 69

(5) Winkler, Forum de la connaissance, Paris , November 1994

(6) T.C. Patton, « Paint flow and pigment dispersion », 1979, J. Wiley & Sons Ed.

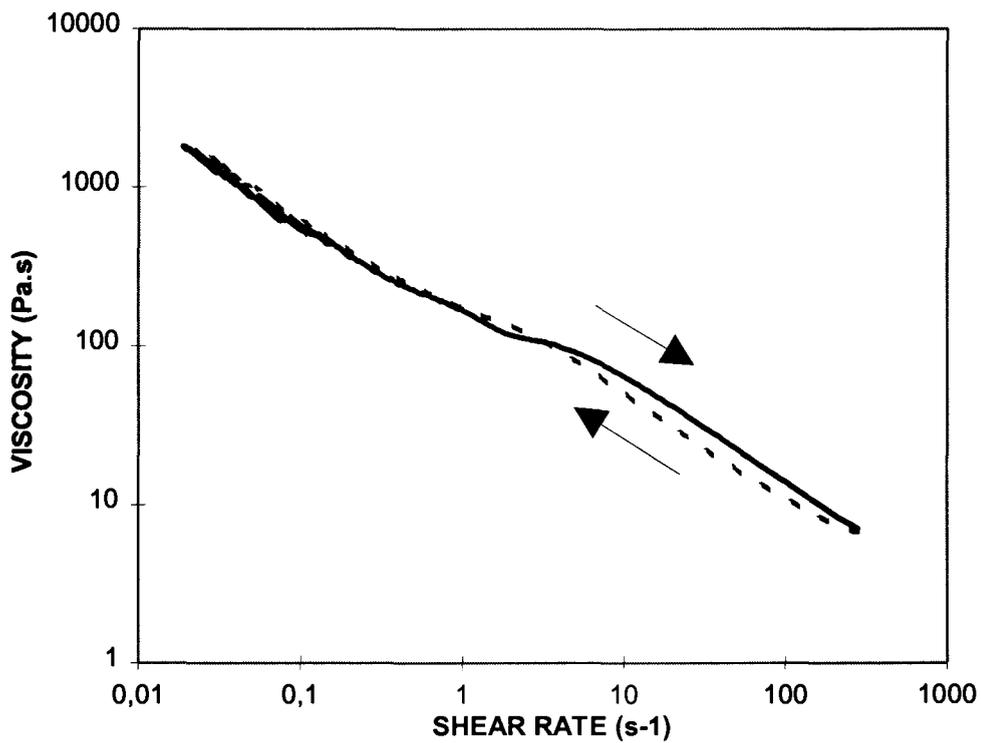


Figure 1 : Evolution of pigment dispersion viscosity with shear rate TMPTA (SR 351), 40% Yellow Pigment

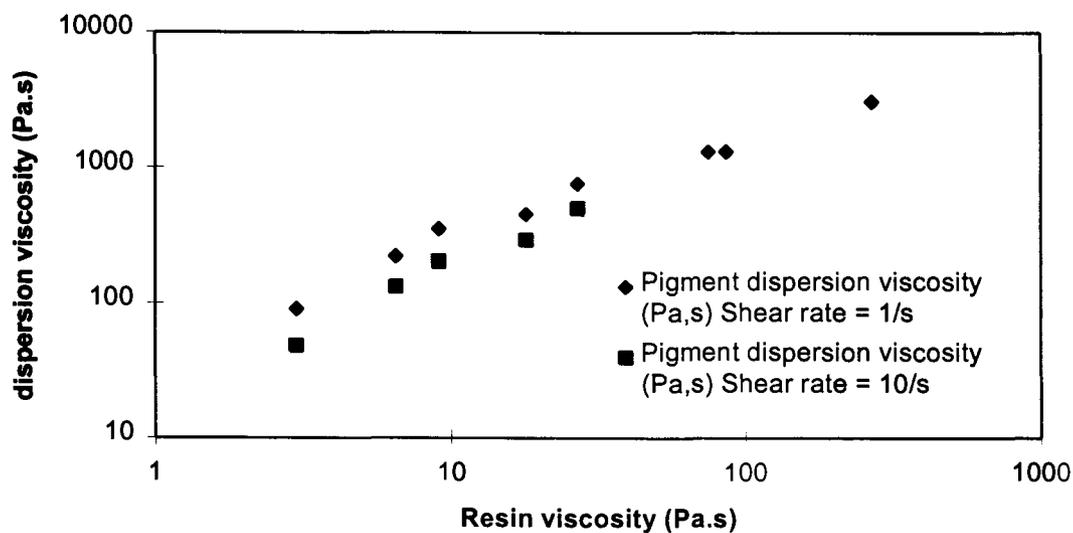


Figure 2 : Evolution of the dispersion viscosity with resin viscosity for oligomer with the same surface tension

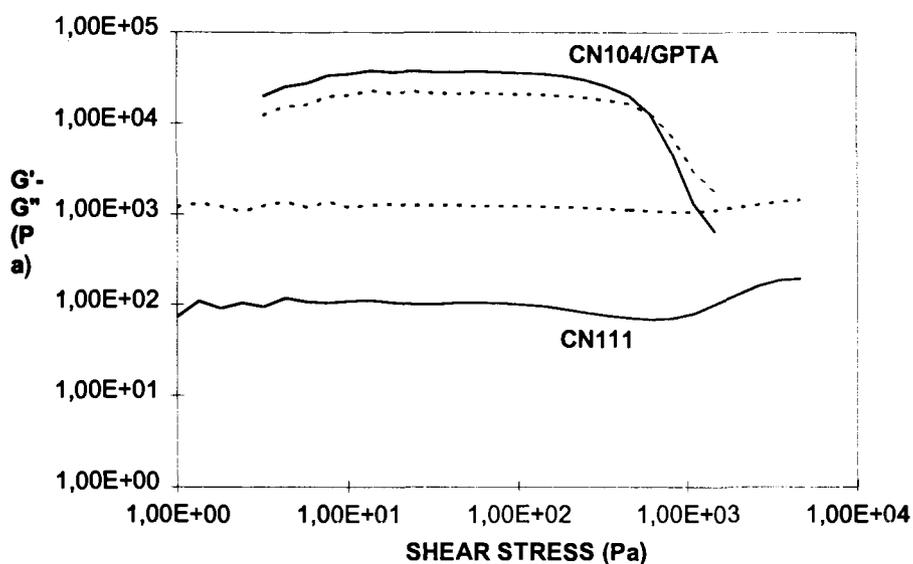


Figure 3 : Schematic viscoelastic properties obtained with Magenta pigment dispersions

*Dashed line : loss modulus (G'')*

Ref.	Monomer name	Monomer viscosity (mPa.s)	Monomer surface tension (mJ/m <sup>2</sup> )	Pigment dispersion viscosity (Pa.s)	
				at 1 s <sup>-1</sup>	at 50 s <sup>-1</sup>
SR 272	Triethylene glycol diacrylate	16	40	119	25
SR 306	Tripropylene glycol diacrylate	14	34	68	14
SR 9003	Propoxylated Neopentyl glycoldiacrylate	15	32	48	10

Table 1 : Influence of surface tension on pigment dispersion

Ref.	Monomer name	Monomer viscosity (mPa.s)	Monomer surface tension (mJ/m <sup>2</sup> )	Pigment dispersion viscosity (Pa.s)	
				at 1 s <sup>-1</sup>	at 50 s <sup>-1</sup>
SR 285	Tetrahydrofurfuryl-acrylate	36	37	68	9
SR 351	Trimethylolpropane triacrylate	96	37	164	22
SR 355	Ditrimethylolpropane tetraacrylate	727	37	313	38

Table 2 : Influence of viscosity on pigment dispersion