

Enhancement of the pigment dispersion in UV/EB inks through an optimisation of the oligomer properties.

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Abstract.

The use of UV and EB is now well established within the printing technologies. The constant growth of penetration of UV/EB inks on the market clearly demonstrate the advantages when compared to conventional printing technologies.

Pigment dispersion in the formulation of an ink is still a challenge where space for improvement really exists.

This paper will present an overview of the several parameters that influence the pigment dispersion, followed by an evaluation of different acrylated oligomers with different pigments. Finally, interpretation of the relationship between the pigment wetting and the oligomer physical properties will be discussed. As a conclusion the paper will demonstrate that selective choice of the oligomer will enable the formulator to optimise the properties of the dispersion.

UV technology is continually evolving. The UV market hasn't stopped growing from the early 60s up to now and since 2000, volumes keep increasing and have almost doubled to reach approximately 80.000 t in 2007. UV technology is now widely used in a variety of applications covering industrial-, wood coatings as well as printing inks and varnishes which represents almost 20% of the volumes. Within the graphic arts industry, the printing inks takes up 40% of the market when UV inkjet is just starting to expand.

Contrary to most coatings (usually transparent), printing inks of all types always contain a pigment, providing the coating its own identity. To ensure the stability, performance of the ink and ease the dispersion process, optimum wetting properties need to be achieved. This depends not only on the resins' nature but also on the pigments' structure and surface treatment which may vary from one pigment to another. The pigment dispersion is where the challenge lies for resin manufacturers, especially with the development of low viscosity systems like ink jet where phenomena such as settling are most likely to occur.

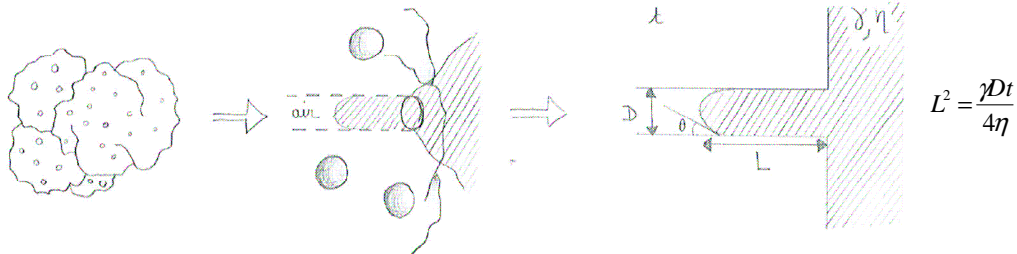
Pigment dispersion, the theories behind

Pigment dispersion directly refers to the dispersion of a solid into a liquid phase. The quality of the dispersion is a combination of several factors answering the following questions which we will then be reviewed in details :

- How well the liquid penetrate and coat the aggregates of solid ?
→ Related to the physical characteristics of the materials.
- How well the solid is dispersed into the liquid ?
→ Related to the process characteristics.
→ Related to the chemical nature of the binder
- How well the dispersion is stabilised?
→ Related to the chemical nature of the binder.

1/ Wetting properties – Flow characteristics.

In the ink system, the solid to disperse is a pigment which, in its powder form, is made of aggregates of pigment particles. Thus these aggregates have a porous structure where the binder can penetrate or flow. The Washburn equation highlights the parameters which influence the flow of the liquid in a defined porous solid.



This shows that for a given solid where the diameter of the pores is D , the penetration of the binder will depend on its surface tension γ and viscosity η . The lower the viscosity and the higher the surface tension the easier the wetting.

2/ Dispersing the solid.

Assuming that our solid is well wet by the binder, it has now to be properly dispersed. This phase consists in breaking the aggregates down into smaller particles. The lower the particle size the lower the impact of the gravity and thus the tendency to settle decreases.

With respect to breaking down the aggregates, two criteria have to be fulfilled :

- A particle has to collide with another one to be dispersed.
- The collision force has to be superior to cohesion forces inside the aggregates.

The first statement refers to the collision probability, P_t , which is linked to the aggregates size or concentration and the dispersion time. The second statement refers to the attractive forces which maintain the particles into the aggregate form and the energy supplied by the milling system, in other words the probability to break down aggregates, P_e . The resulting probability of dispersion P is :

$$P = P_t \times P_e$$

Because both conditions are independent, increasing the milling time will not help compensate a lack of energy input. Thus, the choice of the milling equipment can also impact the quality of the dispersion.

During the dispersion phase, a mechanical force is applied to the dispersion, this is the shear rate, $\dot{\gamma}$. The shear stress, τ , undergone by the aggregates in the binder is directly related to the shear rate of the equipment and the viscosity, η , of the binder.

$$\dot{\gamma} = \frac{\tau}{\eta}$$

This shows that the higher the viscosity of the binder the higher the shear stress and thus the state of dispersion.

In the previous section we saw that the lower the viscosity the better the wetting. Viscosity has clearly to be well balanced to help wetting on one side but also to maximise the dispersion process on another side.

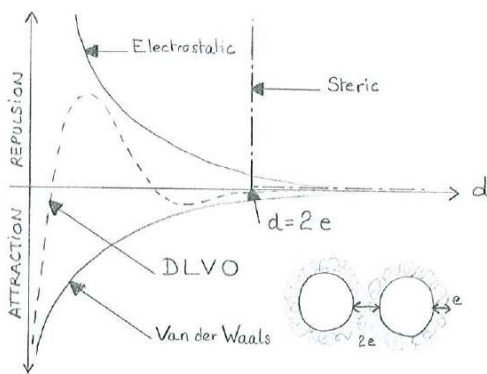
As explained above, in a printing ink the initial state of dispersion strongly influences the stability of the dispersion itself because when it is achieved properly it prevents the settling of pigment particles. It is also worth highlighting that the quality of the dispersion has a direct impact on the colour strength. Fine and properly dispersed individual particles will lead to a better colour development. Finally an optimum dispersion tends to have a Newtonian behaviour, which is a key parameter in many printing processes.

3/ Dispersion and stabilization

Once the aggregates are broken down into smaller primary particles, they have to be stabilized. If not, the primary particles will flocculate leading to a loss of colour strength and a change in rheological behaviour. In the worse case, the “re-formed” aggregates will be subjected to gravity and will settle. Sometime a phase separation will occur if there are poor affinities between the various components of the ink.

The stability of a dispersion depends on the resultant between attraction (eg Van der Waals) and repulsion (eg electrostatic) forces applied to pigment particles. Also, the surface of the pigment particles is often treated to improve the final visual properties of an ink which is an extra difficulty to overcome to get pigment wetting.

Stabilisation can be achieved electrostatically, when then particles are charged, or sterically by an adsorption of a polymer in the binder, or both. The simplification of the Derjaguin – Landau – Verwey - Overbeek Theory (D.L.V.O) combines the Van der Waals attraction and the electrostatic repulsion (taking into account the double layer of counter ions) which give a good picture of how a system can evolve when the distance between two particles decreases.



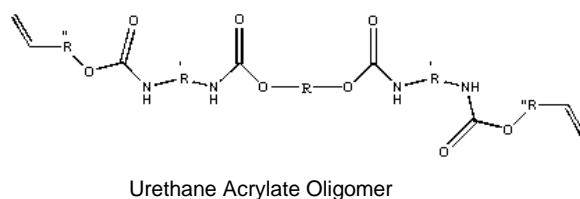
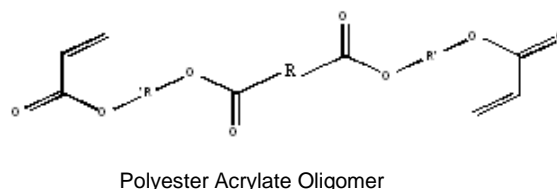
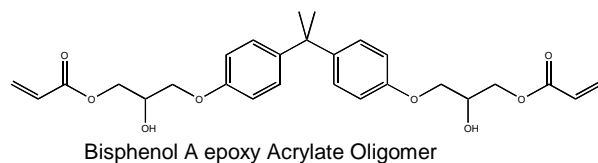
This show that using a polymer with a good affinity with the pigment surface prevents flocculation, that is to say it is important to select the nature/formulation of the liquid binder. Knowing that most pigments are not design for UV or EB applications, it makes it more challenging for photocurable raw material suppliers to build molecules suitable for pigment dispersion.

Test protocol.

1/ Raw materials

The aim of this study is first to determine which building blocks of a molecule impact the pigment wetting. Thus several oligomers structures are tested such as epoxy-, polyester- and urethane acrylates, as well as monomer (see preliminary tests below).

	Type	Specific Building Block
Epoxy Acrylates	EA 0	-
	EA 1	-
	EA 2	A
Epoxy Acrylates (Bisphenol A based)	EA 3	B
	EA 4	-
Epoxy Acrylates (Novolac based)	EA 5	A
	PEA 1	C
Polyester Acrylates (Type 1)	PEA 2	D
	PEA 3	B/E
	PEA 4	-
Polyester Acrylates (Type 2)	PEA 5	F
	UA 1	G
Urethane Acrylates	UA 2	H
	UA 3	I
	Monomers	3EO TMPTA
6EO TMPTA		
3PO TMPTA		
GPTA		



2/ Testing method

In the following paper, simplified pigment pastes have been prepared for screening purpose. The general composition is as follow :

Pigment	20%
Oligomer	60%
Monomer	20%

To compare monomers, PEA2 is used as a standard. To compared oligomers, GPTA is used as a standard.

Each paste is pre-dispersed and then grinded on a triple roll mill from Bühler. The rheology is assessed on a Carrimed rheometer, using the following pocedure :

Spindle : 2cm flat plate
Gap : 200 μ m
Temperature : 25°C
Viscosity is given in Pa.s

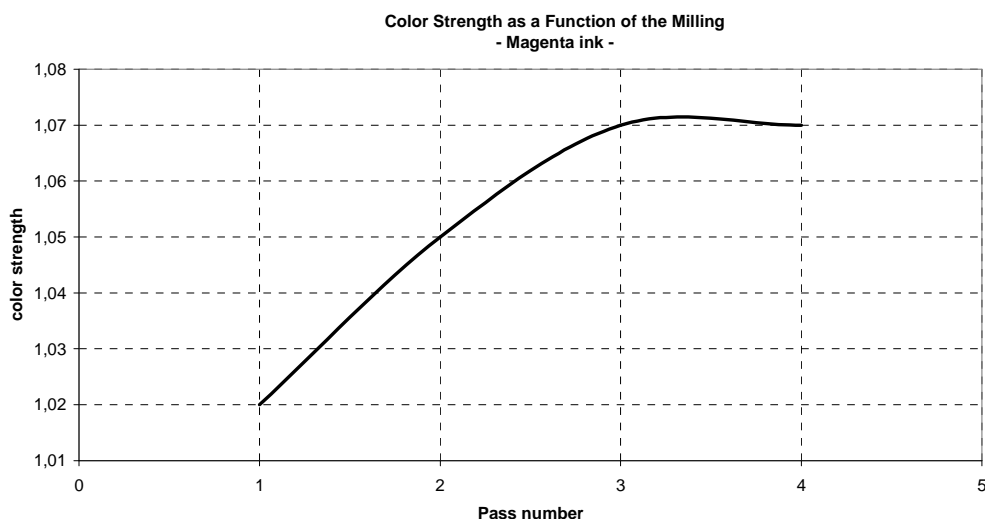
"Pre-shearing"	1s ⁻¹	30s
Low shear	1s ⁻¹	120s
High shear	100s ⁻¹	60s
Low shear	1s ⁻¹	180s

On the black serie, the color strength is measured with a spectrodensitometer 500 series from X-Rite.

Experimentals

1/ Colour strength and milling

It is important to know the number of passes required on the milling equipment to achieve the maximum colour strength. A comparison based on the number of passes made on the mill was realized in Sartomer on fully formulated lithographic inks.



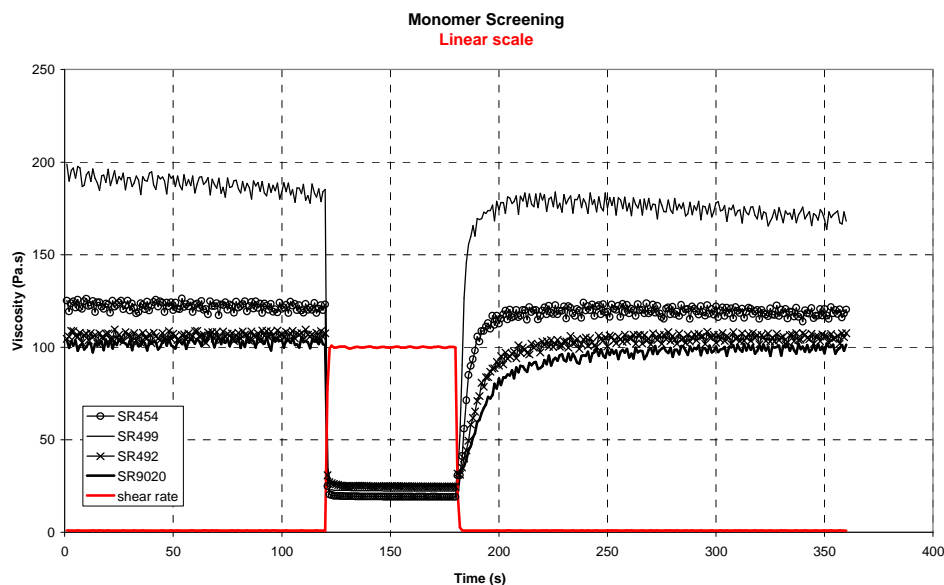
The results displayed on the graph above highlights that 3 passes on the mill are necessary and sufficient to reach a maximum colour strength.

2/ Monomer screening

In a first study four monomers were selected, three of them having the same core structure but different level of alkoxylation. Blends with PEA2 and black pigment were prepared and evaluated.

Monomer		Viscosity (mPa.s @25°C)	Surface Tension (N/m)	Viscosity @ 1s-1	Viscosity @100s-1	Shortness Index*
3EO TMPTA	SR454	60 - 80	36,5	122,2	19,4	6,3
6EO TMPTA	SR499	75 - 100	38,9	188,3	22,7	8,3
3PO TMPTA	SR492	40 - 140	32,8	106,2	25,1	4,2
GPTA	SR9020	80 - 110	33,5	102,4	26	3,9

* Shortness Index = (visco. @1s-1 / Visco. @100s-1). Newtonian fluid have an index of 1.



In this case, because the viscosity of the monomers are alike, we can reasonably assume that the purely mechanical dispersion process is similar in the four blends. Thus wetting properties are related to the affinity existing between the monomer and the pigment. The results disclosed in the table above highlight that pigment wetting depends on the nature of the alkoxylation and precisely that propoxylated groups are more favorable than ethoxylated groups. It seems then that for black pigment, pigment wetting is improved when the hydrophobicity of the binder increases.

3/ Oligomer screening

Such as for the monomer, a screening of various oligomers is critical to understand which building block contribute to improve pigment wetting. All the oligomers mentioned in the raw material section have been screened using standard monomer GPTA with black pigment. The rheological behavior of each blend has been assessed.

	Type	Specific Building Block	Viscosity @ 1s-1	Viscosity @100s-1	Shortness Index*	DO
Epoxy Acrylates	EA 0	-	128,8	11,3	11,4	2,21
	EA 1	-	/	/	/	2,04
Epoxy Acrylates (Bisphenol A based)	EA 2	A	268	30,9	8,7	1,98
	EA 3	B	29	10,6	2,7	2,23
	EA 4	-	63,2	10,2	6,2	1,96
Epoxy Acrylates (Novolac based)	EA 5	A	20,1	16,4	1,2	4,17
	PEA 1	C	21,7	5,3	4,1	2,44
Polyester Acrylates (Type 1)	PEA 2	D	102,4	26	3,9	2,56
	PEA 3	B/E	10,6	9,9	1,1	4,82
	PEA 4	-	103,4	3,3	31,7	2,31
Polyester Acrylates (Type 2)	PEA 5	F	52,9	5,4	9,8	3,13
	UA 1	G	11,8	10,5	1,1	2,47
Urethane Acrylates	UA 2	H	21,9	9,4	2,4	2,41
	UA 3	I	136,2	9,6	14,1	2,47

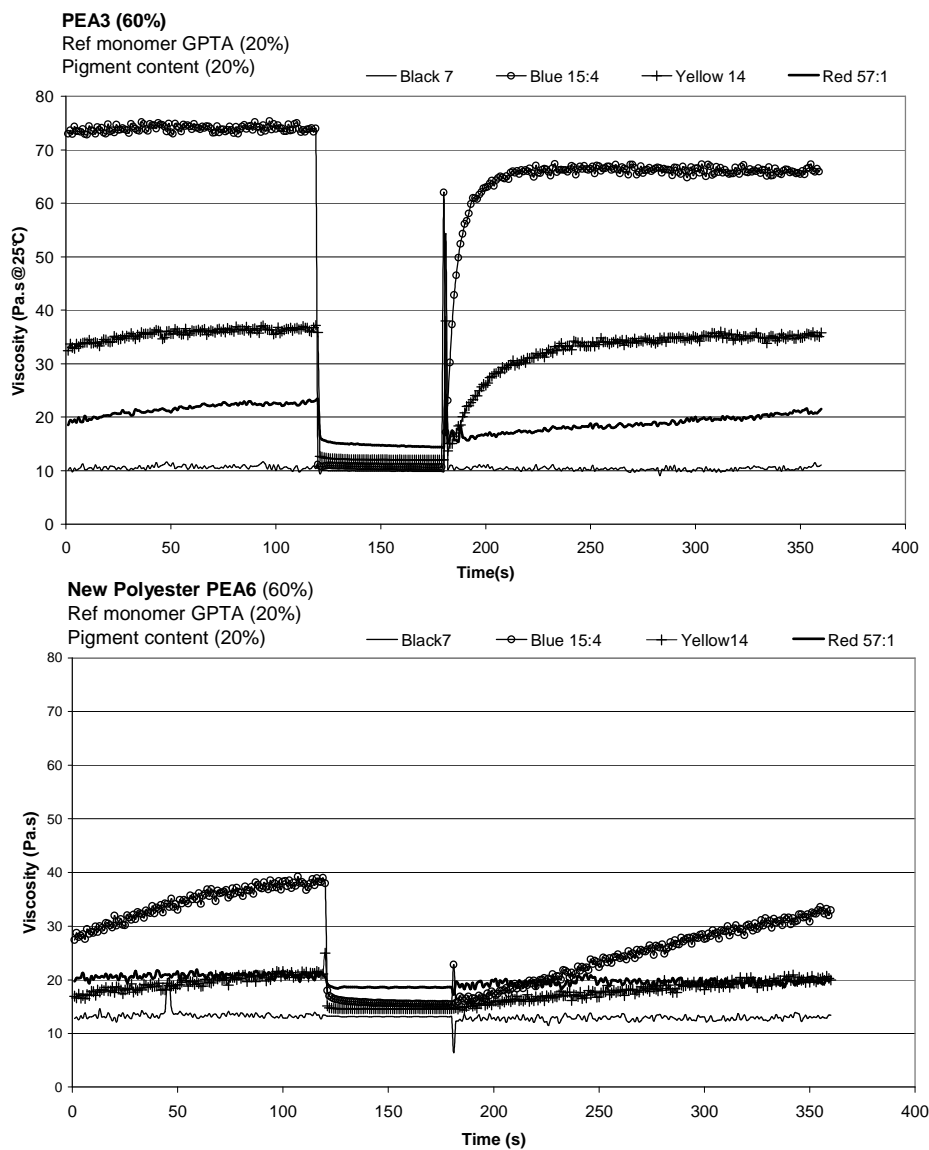
The results presented in the previous chart show that there are structures which when they are modified improve either colour strength or the rheology of the blend, both being related to pigment wetting. In the Bisphenol A based epoxies, building block B show a significant improvement on the rheology. The same contribution is noticeable on the polyester (Type 1) structure in PEA3. UA1, 2 and 3 have the same core structure, which enable to see that building blocks G, H also bring rheology improvements. We also notice that polyester acrylate can potentially offer very high colour strength.

Knowing which building block are to be used, several new structures could be proposed. Because all the building blocks highlighted can obviously not been combined all together we had to pick some of them to build a new molecule.

Taking into account the results from the monomers' and oligomers' screenings, a new polyester has been developed : PEA6.

PEA6 has a polyester type 1 structure, including modification B, H and a new modification to increase hydrophobicity.

This new polyester has been tested with various pigment commonly used in printing inks, such as Blue 15:4, Yellow 14, and Red 57:1. New polyester PEA6 is here compared to PEA3 (same type of polyester) which already show excellent rheology with black pigment.



The graphs here above show the improvement in term of rheology when newpolyester PEA6 is used to disperse pigments. PEA6 offer better flow properties which imply a better pigment wetting in the blends. Improvements are particularly noticeable on Blue15:3 and Yellow 14.

Conclusion

In this paper we reviewed the parameters having a contribution / impact on a pigment dispersion. An evaluation of a wide variety of UV raw material highlighted that apart from physical properties, specific building blocks can improve pigment wetting.

This selective approach lead to the development of an new polyester acrylate enhancing flow properties in dispersions based on commonly used pigments.

These results open the door to several new structures or molecule conformations to move forward in the field of pigment dispersion.

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