



With even lower viscosity requirements than overprint varnishes, the formulator understands that the composition of the UV curable ink jet vehicles will involve different components, as shown later in this paper. With these components, the pigment dispersion will have to show good compatibility and resist flocculation after the final let-down step.

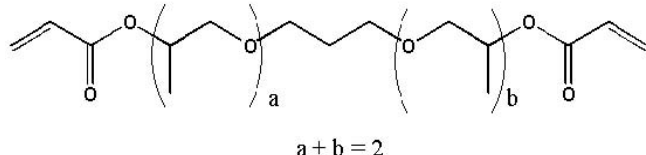
In order to offer solutions to the above challenges, Ciba Inc. has developed a range of pigment preparations to facilitate the cumbersome dispersion manufacturing process and provide wider versatility as regards other key ingredients, in particular monomers and oligomers. These new preparations are essentially stir-in materials when incorporated with a high speed mixer and provide inks with the following benefits:

- High color strength, gloss and transparency
- Small particle size and extremely narrow particle size distribution
- Long-term dispersion stability
- Wide acrylate-monomer compatibility
- No organic solvent requirements that reduce viscosity

Some results on formulations using one of these new generation pigment preparations and a review of monomers and oligomers by SARTOMER Europe will be presented in this paper.

## Strategy for vehicle and film-forming material selection

The predominant species in a UV or EB curing ink jet ink is the acrylate 'monomer'. This is the low viscosity material which acts as a binder for the pigment whilst fulfilling several other important functions in the formulation. A typical acrylate monomer for an ink jet ink would be a substance such as SR9003 (propoxylated neopentyl glycol diacrylate - NPG(PO)DA).



This particular monomer has several properties which are ideal for UV curable ink jet inks. It has a viscosity of around 25cps and a surface tension of 30 MJ/N2. It is a diacrylate and so will have reasonable cure speed when exposed to UV light or EB radiation. The cured film based on SR9003 (NPG(PO)DA) will show some resistance to solvent and also exhibit good adhesion on a wide variety of plastic and paper substrates. It also possesses reasonable pigment wetting properties for such a low viscosity material and gives good stability in an ink jet ink.

There are many other acrylate monomers apart from SR9003 (NPG(PO)DA) which are commercially available and are suitable for use in ink jet inks. Each one will vary slightly from the molecule above in its properties, depending on its chemical structure. Some are considerably less reactive but give better adhesion, some are faster curing, some have lower viscosity. But all are generally compatible and by selecting a combination of acrylate monomers the required properties can be achieved. For the purposes of this paper a selection of acrylate monomers covering a broad spectrum of properties were chosen for the technical work.

Another type of raw material used in UV/EB curable ink formulations are the 'acrylate oligomers'. These tend to be higher molecular weight acrylate species based on well known chemistries such as urethane or polyester. Though possessing a high viscosity, small additions of these materials can considerably enhance the pigment wetting and stability of that dispersion in an ink as well as the product resistance of the cured ink.

Thus a UV/EB curable ink jet ink is normally a mixture of several different materials. However for the purposes of this paper the individual materials have been highlighted in order to clarify the underlying trends.

## Practical examples of raw materials selection and benefits

As discussed above, an efficient way of preparing UV curable ink jet inks is to incorporate by mixing (Figure 2 below), in the acrylate based carrier, pigment preparations that exhibit stir-in properties and the desired small and controlled narrow particle size distribution.

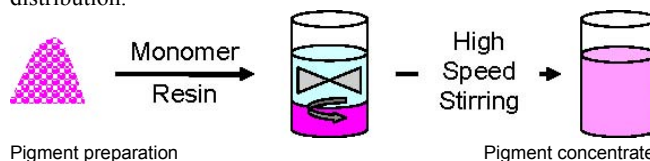


Figure 2 – Mixing scheme

Such preparations are already used in solvent-borne ink jet inks and belong to the Ciba® MICROLITH® range of pigment preparations [2], manufactured using a proprietary finishing technology. These preparations can also be used to formulate UV curable ink jet inks but with certain limitations of viscosity, monomer compatibility and/or the addition of a small amount of an organic solvent.

In the examples below, a new generation of pigment preparations containing a specially designed acrylic dispersant has been introduced. This process magenta is based on a quinacridone pigment and contains circa 70% of this chromophore.

It will be compared to Ciba® MICROLITH® Magenta 5B-K pigment dispersion.

First and foremost, the particle size and distribution of particles are well below the micrometer, narrow and with minimum tailing (Figure 3).

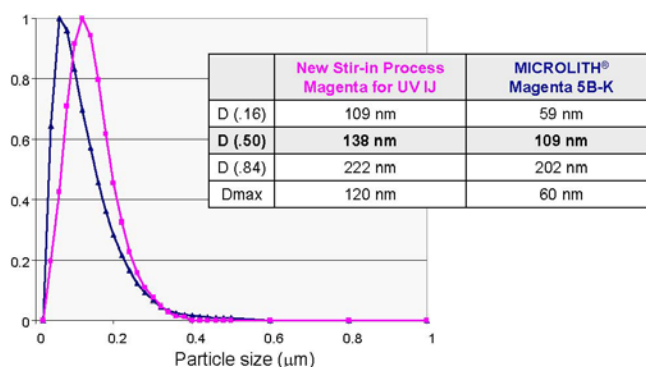


Figure 3 – Particle size distribution after re-dispersion in a strong solvent system

Ink concentrates will be produced as described below.

The high speed mixing is firstly done in the presence of a first monomer, at higher concentration, to allow enough shear for good and rapid dispersion. More monomer or a second monomer is then added with further mixing to finish the concentrate (see Figure 4).

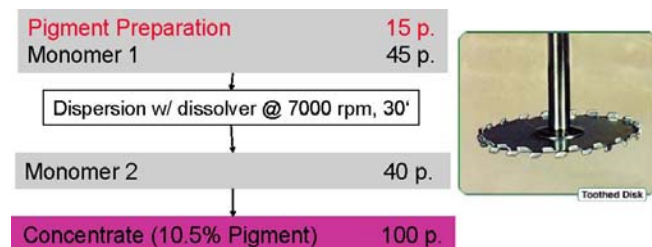
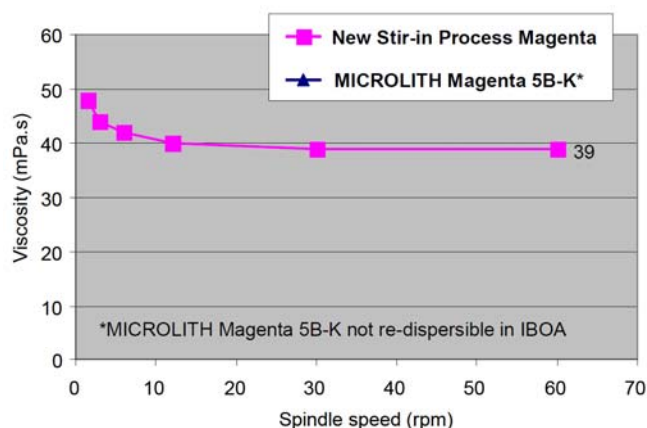


Figure 4 – Ink Jet Ink concentrate composition

The newly developed pigment preparation provides wider compatibility in acrylate monomers (see also next section). For instance, in IBOA (SARTOMER® 506), it allows rapid incorporation whereas Ciba® MICROLITH® 5B-K is not stir-in. The viscosity level and the “newtonicity” are also outstanding at this pigmentation level and at room temperature (Figure 5).

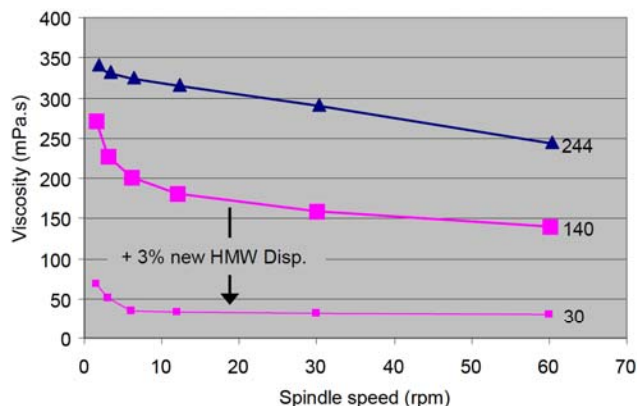


<b>Concentrate 1</b>	
MICROLITH® p.p.	15%
IBOA	45%
2PO NPGDA	40%

IBOA = Isobornyl Acrylate  
2PO NPGDA = Propoxylated Neopentyl Glycol DiAcrylate

Figure 5 – Rheology of concentrates in IBOA

In another monomer, HDDA, the superior performance of the new generation pigment preparation is confirmed. It is important to note that Ciba® MICROLITH® 5B-K contains only 50% pigment and therefore will not exhibit the same high chromaticity as the new process magenta dispersion. This is shown in Figure 6, which also illustrates the benefit of the addition of high molecular weight dispersants with a special architecture. Such a combination allows extremely low rheology and also long term stability (experiments and results not shown here).



<b>Concentrate 2</b>	
MICROLITH® p.p.	15%
HDDA	45%
2PO NPGDA	40%

HDDA = HexaneDiol DiAcrylate

Figure 6 – Ink rheology of concentrates in HDDA

## Monomer selection

The previous section demonstrates that it is possible to achieve excellent dispersibility with the new pigment preparation with mixtures of three basic monomers. For the pigment preparation to be of substantial benefit to industrial applications, it must be shown that it is effective with other monomers as this will allow the ink formulator greater flexibility. Therefore this section looks at a wider range of monomers in order to establish the versatility of the preparation whilst also highlighting any specific monomer which shows greater advantage.

As can be seen from the initial evaluation three monomers (HDDA, IBOA, 2PO NPGDA) show suitability. These monomers have specific structures. For the purpose of formulator flexibility, the testing regime was expanded to include the effect of several other types of structure thus

- TMPTA and alkoxyated versions - TMP(EO)TA, TMP(PO)TA
- Aromatic cyclic monomers - PEA
- Aliphatic cyclic acrylates – Isophorylacrylate, CTFA and DOGDA
- Branched acrylate – MPDA

For the purpose of testing 2PO NPGDA was used as standard.

Apart from chemical structure, each monomer varies in solubility parameter and surface tension thus allowing several trends to be observed.

Dispersions were prepared in each of the above monomers and tested for suitability as a stir-in monomer. One basic method of evaluating the compatibility of the stir-in dispersion is to assess the increase in viscosity subsequent to pigment dispersion. Three monomers proved to be particularly suited to the new pigment

preparation. These were TMP(PO)TA, Isophoryl acrylate and the standard product 2PO NPGDA. (See figure 7)

#### Cutting power of various monomers with the magenta pigment preparation (in 40p. NPOPGDA)

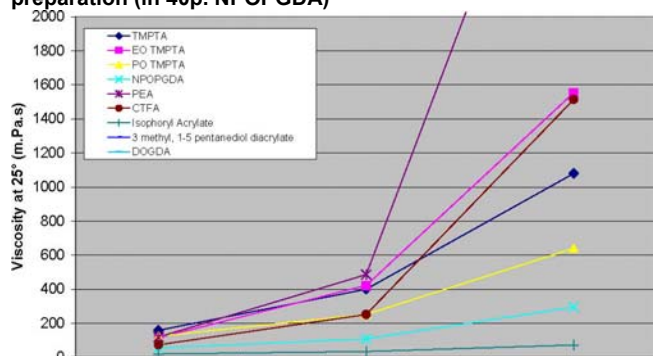


Figure 7 : Acrylate monomer cutting power

#### Testing in basic formulations

The next stage in the evaluation process was to study in greater detail the pigment dispersions in a simulated ink environment. The pigment dispersions based on three monomers thus selected (TMP(PO)TA, isophoryl acrylate and 2PO NPGDA) were then further evaluated for two of the key elements of UV curable Ink Jet formulation - stability and film properties.

The 2PO NPGDA was used as the basis for the formulations and then each monomer was introduced to evaluate its effect .

#### Stability

Stability testing was considered first. DSC tests on each of the dispersions was performed and the results are shown in Figure 8.

- Formulation 1 : 15% Magenta Preparation, 85% NPOPGDA
- Formulation 2 : 15% Magenta Preparation, 45% NPOPGDA, 40% PO TMPTA
- Formulation 3 : 15% Magenta Preparation, 45% NPOPGDA, 40% Isophoryl Acrylate

As can be seen the dispersion based on Isophoryl acrylate shows the highest onset temperature (206°C) and thus potentially the best long term stability. However all three systems are quite stable. It is interesting to note the benefit of this cyclic aliphatic acrylate here.

#### Film properties

In order to assess the film properties of the pigment preparations in the selected monomers a further variable was introduced, a higher molecular weight oligomer. The introduction of an oligomer into the system further evaluates the performance of the pigment dispersion with the selected monomers in a more realistic environment. The impact of the oligomer could be adverse if the compatibility with the ink formulation is compromised.

Careful selection of suitable oligomers finalized on the use of a medium molecular weight polyester acrylate. This was then evaluated in each of the three monomer types (Figure 9).

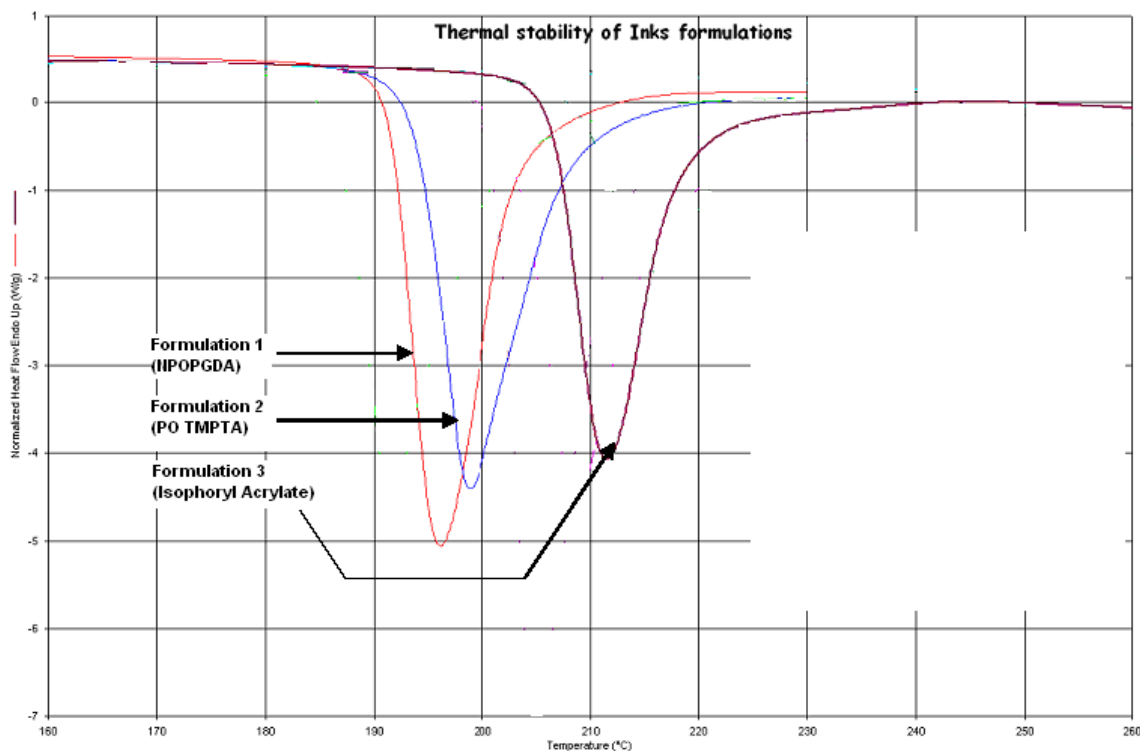


Figure 8 : Thermal stability of Magenta concentrates

	Composition (%)		
Magenta Concentrate (Based on PO TMPTA)	33		
Magenta Concentrate (Based on NPOPGDA)		33	
Magenta Concentrate (Based on Isophoryl Acrylate)			33
NPOPGDA	51	51	51
Polyester acrylate	10	10	10
Photoinitiator standard mix	6	6	6
<b>Film Properties</b>			
Cure speed (m/min) (12µm on a leneta card)	5	5	5
Acetone resistance (s) (12µm on glass panel)	140	130	57
Adhesion on metal (tape test-6µm)	5	5	5
Adhesion on hard PVC (tape test-6µm)	2	3	5
Flexibility on metal (mm) (6µm)	3	3	3
Gloss (60°)	91,9	95,5	95,8

Figure 9 : Film characterization based on Magenta concentrates

As it can be seen from Figure 9, there are some differences in the film properties when formulating with the different monomers. However these are in line with expectations for the differences expected from the various monomers. There is also no adverse effect from incorporation of oligomer into the system thus demonstrating the robustness of the pigment preparation in these particular monomers.

Thus by evaluation it can be shown that the pigment preparation is suitable for use in several monomers, that some monomers such as 2PO NPGDA, Isophoryl acrylate and TMP(PO)TA are particularly suited and offer optimal stability and dispersion properties. Also it is shown that when incorporated into an ink system, the overall benefit of such a pigment preparation/monomer selection is harmonized and produces inks that can be formulated with a number of materials.

## Conclusion

In this paper, Ciba Inc. and SARTOMER Europe have reviewed some of the materials that allow the formulation of low viscosity and stable pigment concentrates and ink jet inks. Very encouraging progress has been made toward achieving solvent-free “jettable” systems, which are no longer outperformed by solvent-borne systems. Further work could be to investigate in more detail the influence of the selected materials on cure speed and cured film performance (resistance and adhesion for instance), etc.

## References

- [1] Alan Hudd, Xennia Technology Ltd, The proof is in production - Inkjet comes of age for industrial applications, IMI Lisbon Conference, 2008.
- [2] [www.ciba.com](http://www.ciba.com) – Solution Finder