New Materials for Radiation Curable Ink Jet Inks

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Abstract

Raw materials used in UV curable ink jet ink formulations are, not surprisingly, required to provide solid performance at three essential stages: to enable ink dispersion and preparation, as vehicles of color in the printing equipment and as part of the formed thin film, enhancing resistance. Ink jet, particularly UV curable ink jet, systems are mandatorily very low viscosity formulations, with demanding visco-stability and dispersion stability criteria. These criteria are best achieved if the ink system has optimal homogeneity. This makes selection of components a challenge and an opportunity, and is also an excellent example of inter-dependency between pigments, dispersants, resins, diluents, additives, etc. In this paper, Ciba and Sartomer have collaborated to study new materials offering formulators new latitude to adjust the performance of their inks from manufacturing to printing and the resistance required of the finished products.

Introduction

One of the most significant recent success stories of UV curable technology has been its introduction into ink jet printing applications [1]. The performance benefits of using UV curable systems are such that lightfast pigmented inks can be formulated with good adhesion to a variety of substrates, excellent film properties and of course the usual benefits of UV curable systems – solvent free, fast cure and excellent durability. The versatility of UV technology also allows significant improvements in other parameters such as print quality and production levels.

During the past few years the growth of UV curable ink jet inks has continued apace. It is now the technology of choice for several ink jet printing applications and has benefitted from other technological advances, such as print head improvements and computer software developments. The growth of UV ink jet applications in the market has averaged 20% per annum over the past few years and is expected to continue to grow at a similar rate for several years to come.

In a dynamic market such as this, the technical performance of the inks will also be expected to develop. This means that ink makers face extra demands and challenges over and above those of an already difficult technology. UV ink jet inks are very low viscosity systems with high sensitivity to variations in rheology, pigment dispersion and stability. This paper describes a novel way of improving ink performance by combining the benefits of both pigment dispersion technology and acrylate technology. These improvements will allow ink makers to meet the challenges of the future growth this exciting technology.

Strategy for colorant selection and dispersion preparation

The selection of colorants for UV curable ink jet inks shows evident commonalities with the preparations of inks used in other printing processes. To enable the reproduction of a defined color space, color targets for each process color have to be defined and, depending on the final application requirements, additional resistance criteria (to light, to chemicals, to process constraints such as temperature exposure, etc.) of the printed materials will be added. This will result in a selection of adequate available chemistries.

Soluble dyes are an option mostly used in water-borne ink jet inks for small office/home office printing. Although they are easy to prepare and reduce the risk of stability problems, sedimentation or aggregation, they are barely an option for UV curable systems. They often lack the resistance required for industrial applications. In addition, they sometimes impair the curing performance of free radical curing systems and also start to fade when exposed to UV light during curing.

Therefore, pigments are the main source of colorants used to prepare UV curable ink jet inks. This implies careful management of the dispersion of pigments in the ink jet vehicle to obtain a highly chromatic and transparent ink and reduce the average particle size in the ink to well below one micron. This is where the preparation of pigmented ink jet inks differs from other ink systems requirements. In ink jet, tolerance to small amounts of coarse particles or aggregates is very much reduced, as they can immediately damage the ink jet heads (nozzle blocking).
As a consequence, industrial milling or dispersion methods have to be adapted. Milling cycle times are increased, higher quality and consistency milling equipment is necessary and elimination of coarse particles requires additional filtration, frequent recycling of some off-spec dispersions, etc.
These are the challenges arising at the ink preparation stage. Additionally the long term stability of ink jet Inks has to be maintained until jetting since the formation of aggregates subsequent to the dispersion step could destroy the effect of the manufacturing procedures. Any pigment aggregates present will cause severe problems with the ink jet printing heads.

The low viscosity requirements inherent in the ink jet process are an additional obstacle to achieving a long-term stable ink dispersion. In figure 1 below, the viscosity requirements of various UV curable systems are shown.

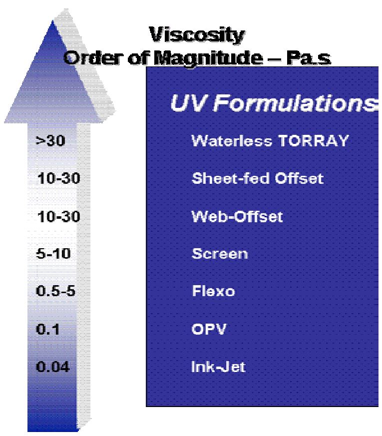


Figure 1.

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.

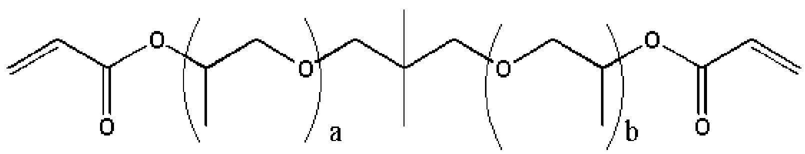
In order to offer solutions to the above challenges, Ciba Inc. has developed a range of pigment preparations to facilitate the cumbersome dispersion manufacturing process and provide wider versatility as regards other key ingredients, in particular monomers and oligomers. These new preparations are essentially 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)



$$a + b = 2$$

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.

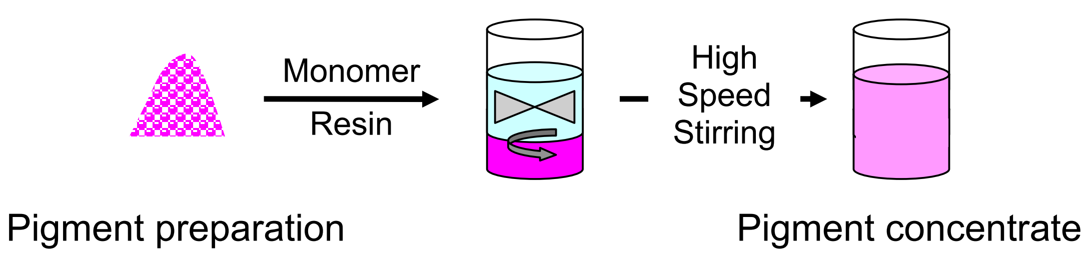
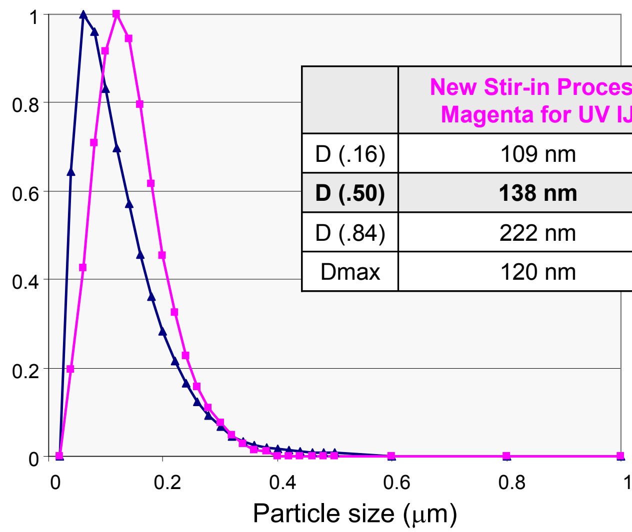


Figure 2 – Mixing scheme

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).



	New Stir-in Process Magenta for UV IJ	MICROLITH® Magenta 5B-K
D (.16)	109 nm	59 nm
D (.50)	**138 nm**	**109 nm**
D (.84)	222 nm	202 nm
Dmax	120 nm	60 nm

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).

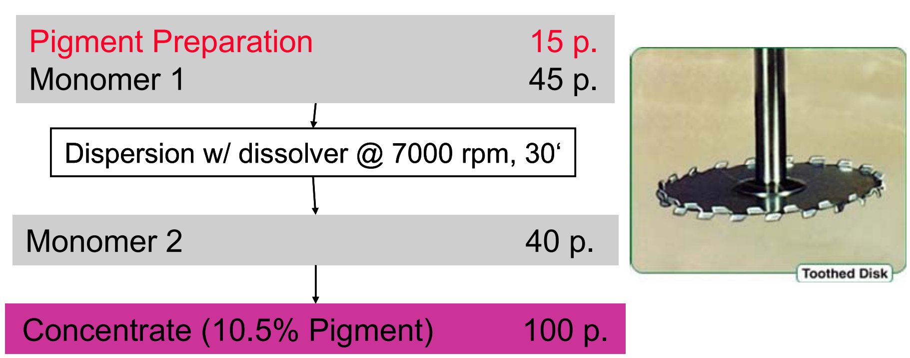
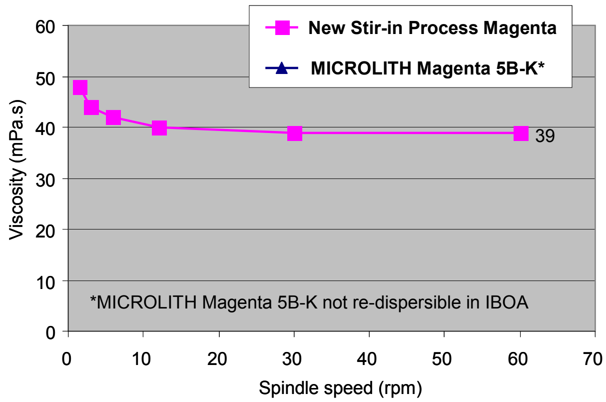


Figure 4 – Ink Jet Ink concentrate composition

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).

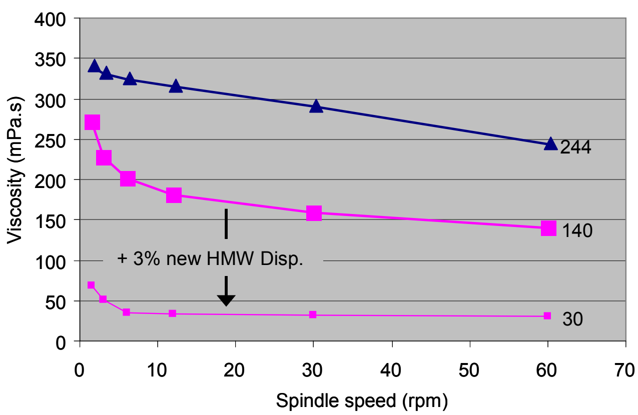


Concentrate 1	
MICROLITH® p.p.	15%
IBOA	45%
2PO NPGDA	40%

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).



Concentrate 2	
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 alkoxylated 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 below)

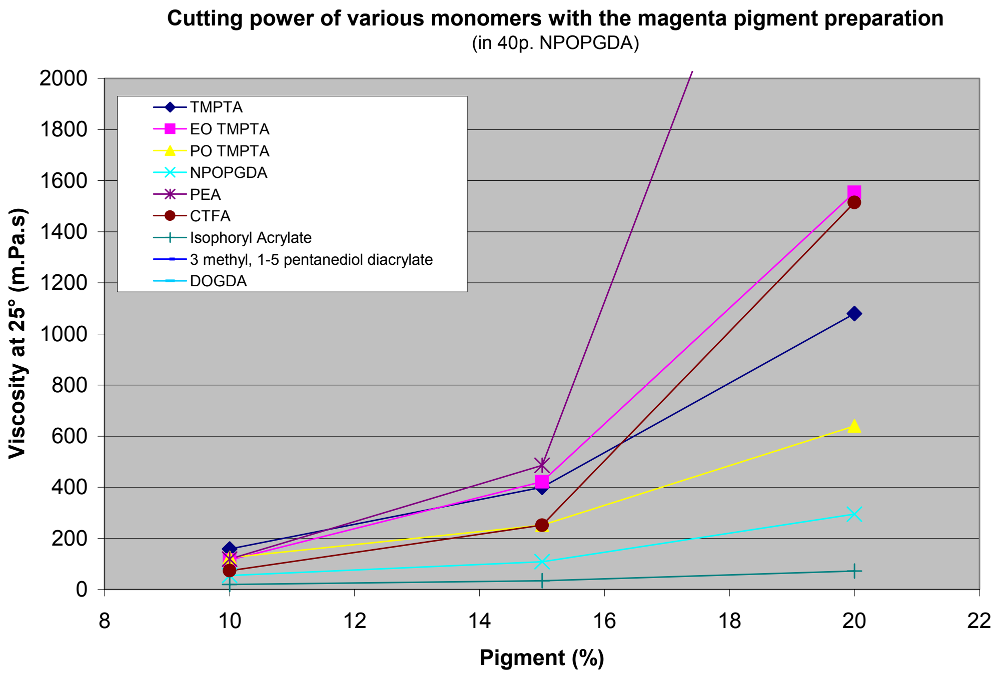


Figure 7 : Acrylate monomer cutting power

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

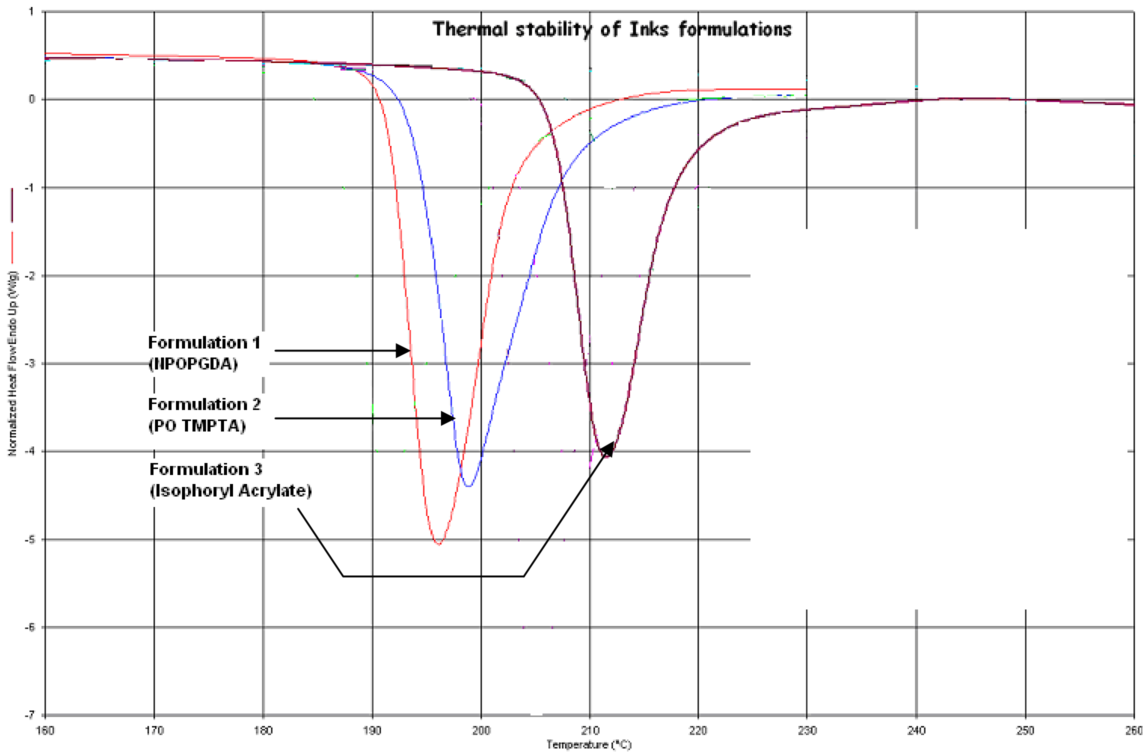


Figure 8 : Thermal stability of Magenta contentrates

As can be seen the dispersion based on Isophoryl acrylate shows the highest onset temperature (206C) 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)

	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
Film Properties			
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 – Solution Finder