Balancing Stability & Cure in Cationic UV Jet-inks

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Abstract

UV free-radical jet-inks are well established as the UV ink chemistry of choice for a variety of industrial printing applications. However, curing is inhibited in air and for high speed applications an inert atmosphere is required. In addition, cured films may exhibit shrinkage and have limited adhesion to media such as plastics and metals; in many cases a coating or surface treatment is needed.

Cationic UV jet-inks have emerged as a new technology that can compete with free-radical in several areas. The curing mechanism is such that it is not affected by the presence of oxygen and can offer satisfactory adhesion, lower shrinkage, to plastics and metals. In contrast to the free-radical case, the inks are very sensitive to the presence of acids and bases. The former help propagate curing while the latter tend to have an inhibiting effect. Therefore, in terms of storage stability and end-use performance, such as speed of cure, it is important to balance the acidity and basicity of the inks. This paper examines some of the factors involved in stabilising cationic UV jet-inks, looking specifically at the role of acids and bases on storage and curing properties.

Cationic curing mechanism

UV free-radical ink-jet printing has grown in popularity in many traditional markets such as packaging and labeling.[1] However, to fully compete with conventional printing techniques, the inks need a fast curing response to print at similarly high speeds. This may be difficult due to their sensitivity to atmospheric oxygen, which can slow or terminate the curing mechanism.[2] This can be circumvented through formulation changes, such as high loadings of photo-initiator, or alternatively by printing in an inert environment. These approaches can cause residual odour and engineering considerations, respectively.

Cationic UV curable formulations have been used for several years in applications such as adhesives, coatings and inks.[3] Beneficially, their curing mechanism is not inhibited by air and so an inert environment is unnecessary. As such, odour may be less through lower usage of photo-initiator, and in many cases, adhesion and film shrinkage on plastics are superior to free-radical. Although not influenced by air, the curing mechanism is very much affected by the presence of acids and bases. As the mechanism in **Figure 1** shows, the photo-initiator releases a proton on exposure to UV light. This then reacts with monomer to create an active cationic species which grows with further monomers to form a polymer chain. It is clear that the propagating cation is susceptible to attack by base at various stages of chain growth. This can lead to low monomer conversion, high residual odour and ultimately inadequate film properties. This may necessitate the application of a high cure dosage or undesirably high photo-initiator levels. On the other hand, if a proton donating species (acid) is present, the reaction may initiate earlier than desirable and possibly in the absence of UV light. The ink could therefore be storage unstable due to the effect of acids or insufficiently reactive due to the presence of base.

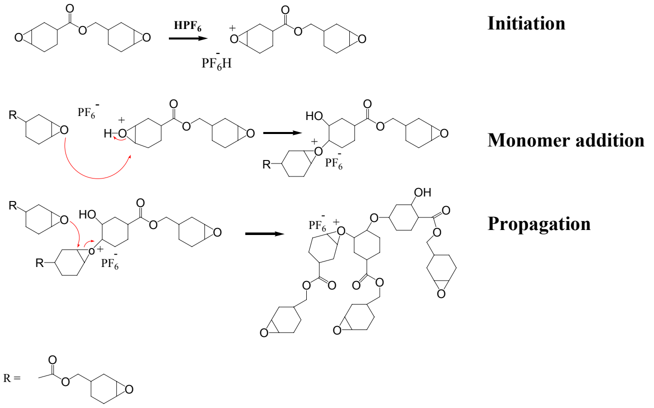

Figure 1: Schemactic diagram of cationic UV curing of epoxy

An obvious way to avoid this situation when formulating, is to exclude basic and acidic materials. However, when taking into account traditional pigment stabilisation, a polymeric dispersant or surfactant is often used.[4-6] In the case of free-radical UV jet-inks, this usually contains a long inactive tail and a functionalized end group. The role of the end group is to interact with the pigment surface such that in combination with the dispersant tail, pigment flocculation is avoided. In some cases, the dispersant functions the other way round with the functionality pointing away from the pigment surface and toward the other ink components. In either event, the chemistry of the end groups are often acidic or basic and hence how they interact in a cationic matrix is of interest. The amount of dispersant needed for such purpose varies according to pigment surface area and is a function of oil absorption number. In any case, it is difficult to ensure that there is only sufficient dispersant to anchor to the pigment and that there is none free in the ink matrix. Should this occur, it is important how the dispersant interacts with the bulk of the ink components, such as photo-initiator and monomer, for the curing and storage reasons described above. There is therefore a careful match needed between dispersant and cationic ink chemistry. In order to do this, some understanding of dispersant chemistry is required. In general however, this information is not disclosed in any detail by commercial dispersant suppliers, often with acid and amine values quoted as the main means for differentiating them. Little is known about the structure of the acid or amine and its acidity or basicity. Therefore, it is difficult to rationalize their impact on storage and curing performance in the cationic formulation.

To help address this, some work was undertaken with model amines in simplified cationic UV jet-ink formulations. This paper looks at the effect of these models, with known structures, on the thermal stability and curing characteristics of some non-pigmented "clear" cationic UV formulations. It is hoped from this work, that the findings can be extrapolated to the development of new pigment dispersants, that may be better placed to work successfully in such inks. To begin with, some pigmented formulations are discussed to highlight the stability/ curing issue.

Experimental

Stability: defined herein by <10% change in viscosity measurement after storage for 1 week or greater at 50 ^{o}C. In the case of pigmented inks, there should be no evidence for particle growth, with all particles < 1 micron in size.

Viscosity: Brookfield DV-II. Spindle 18.

Particle size: Malvern Mastersizer S.

Curing: UV Fusion rig equipped with an "H" bulb. 12 micron draw downs were made on Lenetta card and the minimum cure dosage required to form a non-tacky, hardened film noted.

Cationic UV jet- ink formulations:

	wt %
Epoxy	0-40
Di-oxetane	0-50
Mono-oxetane	0-50
Photoinitiator	0-20
Pigment magenta	0-10
Dispersant	0-10

Amine number measurements: according to method number SMS 2358 available from Resolution Performance Products.

Pigment dispersion stability

A known, storage stable free-radical and a developmental cationic UV jet-ink were formulated concurrently with the same pigment and amine headed dispersant. Initial, 1 week and 1 month storage data points for particle size and viscosity were taken from the mastersizer and viscometer, respectively. **Figure 2** shows the particle size measurements for the two inks.

The control free-radical sample gave little variation in particle size over time. Similarly, the cationic ink showed no particle growth above 1 micron. It was noted that there is some unexplained particle movement below 0.2 micron after 1 month storage but this is considered insignificant to jetting performance. Therefore, in overall terms of particle stability, the inks appear to be satisfactory. In this respect, the dispersant is functioning effectively at stabilizing the pigment in both the free-radical and cationic matrix. This contrasts with the results found from viscosity measurements over the same period (**Table 1**).

The free-radical ink does not vary significantly over 1 month storage, indicating excellent stability. However, the cationic version shows a high and rapid viscosity increase. The source of this is most likely due to polymerization of the cationic monomers, rather than pigment flocculation, as there is no sign of particle growth from the mastersizer measurements. This suggests the curing mechanism is being activated on storage. As discussed above, this could be triggered by a source of acid (or via base aiding the formation of acid), possibly contributed by the pigment or dispersant. To rule out the effect of pigment, some work followed in assessing a set of non-pigmented, clear formulations with a selection of added dispersants.

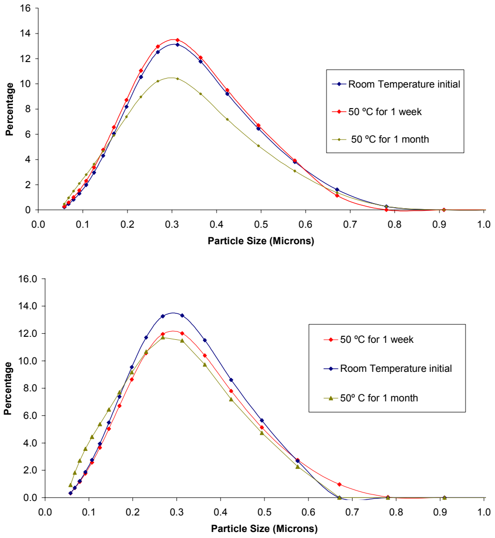

Figure 2: particle size of free-radical (top) & cationic (bottom) UV jet-inks.

Table 1: Viscosity stability of free-radical & cationic UV jet-inks.

UV jet-ink	Viscosity stability (cPs)		
	Initial	1 week 50 ^{o}C	1 month 50 ^{o}C
Free-radical	12.2	12.2	12.1
Cationic	16.3	22.5	27.4

Effect of dispersant in non-pigmented formulations

In the case of free-radical UV inks, amine or acid headed dispersants that are unattached to pigment are of little or no consequence, as curing is not influenced by these materials. It is of interest to see if this is true for the cationic case, where it is expected that amine stops or slows down curing and one might predict good storage stability but slow cure. Similarly, acid headed dispersants might tend to promote cure speed to the detriment of storage performance. To examine this, the effect of the dispersant was assessed in a cationic matrix by making a set of non-pigmented formulations with monomers and photo-initiator, doped with dispersants. Viscosity stability and curing performance was monitored. This included the same dispersant "A" as used in the above inks as well as a range of alternative commercial dispersants. In general, the chemistry of these dispersants is not given but they were chosen because of their ability to effectively stabilise a range of pigments. Two of these dispersants were amine headed with moderate and low amine numbers. Two were acid headed with low and high acid values. **Table 2** shows the initial and 1 week viscosities for the fluids and their UV curing performance.

The control, made in the absence of dispersant, shows a small drop in viscosity but is essentially stable, so any difference in viscosity in the other samples is due to the dispersant's influence. The formulation containing dispersant "A" shows a small increase in viscosity, again within acceptable limits. In comparison with the pigmented ink in **Table 1**, this rise is negligible. Alternative dispersants "C" and "D" show large viscosity rises whilst "B" is steady. These results show that the acid headed dispersants contribute to thermal instability of the formulations whilst the amine headed analogues have little influence.

Table 2: dispersants added to non-pigmented cationic UV formulations & their effect on viscosity stability & cure response.

Dispersant description					
	Control	"A"	"B"	"C"	"D"
Head type	None	amine	amine	acid	acid
Amine no.*		42	20	0	0
Acid value*		0	0	10	100
Viscosity (cPs): 10 wt% dispersant added to clear formulation					
Initial	10.08	13.04	10.22	9.51	10.85
1 week 50 °C	9.05	14.21	10.08	13	15.5
wt (%)	**Cure dose (mJ/cm^2) for varied dispersant weight in clear cationic UV formulations**				
0	100				
0.50%		100	100		
1%		100	100		
2%		100	100		
5%		>1000	200		
10%		>1000	>1000	200	200

*(mg/g KOH)

In the absence of dispersant, a UV cure dose of 100mJ/cm^2 is sufficient to form a well cured film. Surprisingly, at 10% dispersant addition, the acid headed dispersants have some inhibiting effect on UV curing. However, this inhibition is far less than the amine containing examples at the same weight of addition. In these cases, a cure dosage of >1000mJ/cm^2 was required to cure effectively. Addition of such a high level of dispersant is perhaps excessive and so in two amine cases involving dispersants "A" and "B", lower amounts were assessed. Looking at these examples, the lower amine numbered dispersant had a smaller effect on curing inhibition at 5% addition than the higher amine version. Below this value, it was possible to obtain the same degree of UV curing as found in the dispersant-free case. This shows it is possible to use amine in the formulation and have only a small effect on curing. Care is needed, however, to ensure the amount of amine is controlled or severe inhibition may occur.

Hence, as one might expect, the amine headed dispersants can inhibit cure and do so according to their amine number and concentration. In general, these are preferable to acid headed for thermal storage stability, as shown in the viscosity data. The latter impart poor thermal storage with only a moderate inhibiting effect on cure. These results clearly show that dispersant can strongly influence curing and thermal stability of the cationic matrix in the absence of pigment. At the optimum addition level, it should be possible to use dispersants "A" and "B" in conjunction with appropriate pigment.

The amine number of these dispersants was shown to have an effect on curing in these examples but in terms of specific amine chemistry, we have no information. So, to address this, several low molar mass model amines were tested in clear formulations and their viscosity stability and curing properties tested.

Low molar mass model amines

2-Benzyl pyridine, 1-methyl imidazole and 1-naphthyl amine were chosen as "model" amines for testing in clear cationic UV formulations. These materials offer a range of basicities and have structures that could conceivably be useful end groups on polymeric dispersants. Their structures are shown in **Figure 3**.

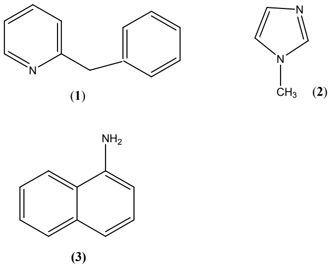

Figure 3: structures of model amines (1) benzylpyridine, (2) methylimidazole, (3) napthyl amine

Taking molecular weight into account, amine numbers were made relative, showing that methyl imidazole contributed most amine and 2-benzylpyridine least (see **Table 4**).

Table 4: Amine numbers, molecular weight and "relative" amine number for model amines.

Material	Measured amine no.	Molecular weight (g/mol)	"Relative" amine no.
Benzylpyridine (1)	366	169	2.16
Methylimidazole (2)	809	82	9.85
Napthylamine (3)	445	143	3.11

The amines were introduced to pigment–free formulations at 0.1%, 0.2%, 0.3% and 0.5% by weight and initial viscosities measured. **Figure 4** shows a plot of the percentage increase in viscosity after 1 week storage at 50 °C against the amount of amine added. Benzyl pyridine and naphthyl amine proved to be effective at stopping the thermal polymerisation when added at concentrations above 1%. In contrast, methyl imidazole gave better stability at concentrations lower than 1%, showing large viscosity increase at 1.5% and 2%. These results show that it is possible to control the thermal stability of the cationic clear formulation to a good degree. However, there does not appear an obvious relationship between amine structure and performance.

In terms of UV curing characteristics (see **Table 5**), methyl imidazole gave the greatest inhibition effect, followed by benzyl pyridine and naphthyl amine.

Unlike, the amine dispersant case where amine number and concentration could broadly account for inhibition performance, this relationship does not hold in all cases with the model amines. For example, napthyl amine inhibits the least here but has a higher "relative" amine value than benzylpyridine.

Instead, these observations can be rationalised somewhat according to amine structure.[7] Broadly speaking, the amines can be grouped in two sets; heterocyclic and non-heterocyclic. Within this, it is known that primary amines may be weaker than tertiary, ignoring effects such as solvent and hydrogen bonding contributions. In this respect, non-heterocyclics are considered as less basic. This means that benzyl pyridine and methyl imidazole would be expected to perform more effectively as inhibitors than the non-heterocyclic examples. The results show this is the case. One can account for the superior inhibiting effect in imidazole versus pyridine due to the presence of two nitrogen atoms in the former with only one in the latter.

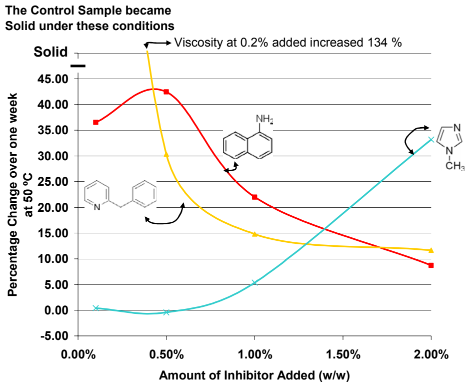

Figure 4: plots of viscosity increase vs amount of amine added over 1 week at 50 °C.

Table 5: model amines added to non-pigmented cationic UV formulations & their effect on curing.

	Model amine description			
Head type	None	2-benzylpyridine	naphthyl amine	methyl imidazole
Relative amine number	0	2.16	3.11	9.85
wt (%)	**Cure dose (mJ/cm^2) for varied amine weight in clear cationic UV formulations.**			
0.00	100			
0.10		100	100	100
0.20		100	100	>1000
0.30		>1000	100	>1000
0.50		>1000	>1000	>1000

Conclusions

Both acids and bases have a strong effect on thermal storage stability and UV curing speeds in cationic UV jet-inks. When it is not possible to avoid these materials, such as when acid or base-headed pigment dispersants are needed, care is needed in their selection. Results show that amine basicity and amine number, together with the amount used in the formulation are important in achieving a satisfactory balance between storage and curing response. Within this, work with model amines has shown that certain structures such as heterocyclic imidazoles can perform to a lesser degree than non-heterocyclic examples such as napthylamine. In turn, these findings may be useful in the design of new pigment dispersants for cationic UV jet-inks.

Acknowledgements

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