Title

Reactive diluents to overcome challenges in UV curable inkjet inks and coatings applications

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Abstract

Solving the challenges facing UV-EB curable applications such as regulatory pressure for favorable toxicological profiles and enhanced technical performances of UV curable formulations are addressed herein by oxazolidinone based reactive diluent structures. Compared to traditional reactive diluents in the industry, vinyl methyl oxazolidinone in specific offers significant technical benefits and formulating capabilities over incumbent technologies such as being liquid at room temperature, with a very low viscosity of 4 mPa/s (at 20°C), a low color and odor and favorable toxicological profile.

Introduction

Vinyl methyl oxazolidinone (VMOX) is a newly launched BASF vinyl monomer, which, since the beginning of 2020 is available in commercial quantities also in North America. It is particularly suited to be used as a reactive diluent in UV-curing coatings and inks applications, for example in UV inkjet printing. In these applications, the monomer has distinct technical benefits when compared to conventional reactive diluents: high reactivity, very low viscosity, good color brilliance, low odor and performance characteristics such as adhesion on plastic substrates are concerned. Furthermore, it allows innovative formulations with a favorable toxicological profile which has been recently a challenge and increasingly difficult to overcome with current chemistries. Herein, an overview of the effects on formulating capabilities, characteristics and registration status will be discussed.

Discussion

In general, vinyl-ether and/or -amide monomers along with other industry standard monomers such acrylates have been used extensively in photoinitiated co-polymerization reactions with acrylate oligomers, epoxy and unsaturated polyester resins in both radical and cationic UV curing systems.[1,2,3] They have shown to efficiently decrease viscosity at low levels, increase conversion of acrylate oligomers and improve performance properties of the cured system such as adhesion, shrinkage, flexibility, scratch, thermal and chemical resistance.

In recent years, current technologies such as N-vinyl pyrrolidone (NVP) and N-vinyl caprolactam (NVC), although technically well performing and competent, they have come under regulatory scrutiny and are in danger of being phased out due to restrictions, reassessment and potential reclassification. As an example, in Europe, EuPIA (European Printing Ink Associations) has banned products with mutagenic or carcinogenic profile like NVP in all printing formulations and NVC is following the same route. Thus, both regulatory pressure and the need for materials which are readily available and easily handled in formulations at the same time have created a substantial hurdle for the industry players to overcome. Our new monomer vinyl methyl oxazolidinone is particularly suited to solve these challenges.

VMOX in its physical state, has a melting point of 20°C and is liquid at room temperature without the need of melting equipment, reducing costs and thus enabling easier handling of the monomer. In contrast for example, NVC is solid at room temperature and needs to be heated in order to be liquified and dosed into the formulations. Furthermore, with its very low viscosity (4 mPA*s) imparts significant diluting effect while enabling high performance of UV ink formulations in which significant viscosity reductions are needed and are below of 10 mPA*s.

In Figure 1 the viscosity effect of traditional reactive monomers such as NVC and acryloyl morpholine (ACMO) is compared to that of VMOX in typical formulations for inkjet inks, coatings and 3D printing respectively. The compositions are described in Table 1. The formulations with VMOX consistently show the viscosity reduction compared to other monomers and prove its excellent diluting power.

Figure 1: Viscosity Comparison

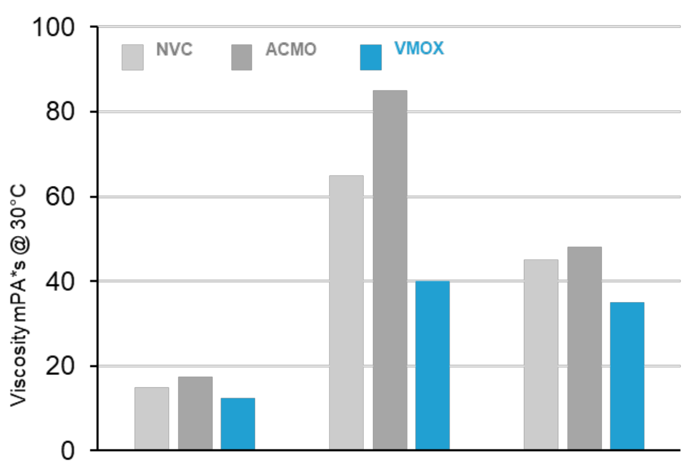

Table 1: Formulations/Compositions

Formulation / Composition	Inkjet	Coating	3D Printing
Reactive Diluent	34	60	30
Other monomers	60	–	35
Oligomers/Resins/Cross-Linkers	–	39	20
Others (incl. Photo-Initiators)	6	1	15

In terms of reactivity, the monomer shows a very high co-polymerisation reactivity with all state-of-the-art acrylate monomers (i.e. DPGDA, IBOA, TBCH, POEA, CTFA, etc.) and N-vinyl amides, and a high affinity for traditional acrylate oligomers being used in the industry. In Figure 2 the reactivity of VMOX is compared with standard technologies such as N-vinyl pyrrolidone (NVP), N-vinyl caprolactam (NVC) and acryloyl morpholine (ACMO). The reactivity was measured based on a standard protocol where ink formulations are cured on a belt which runs under a LED or Mercury lamp at a speed of 15m/min. Subsequently the number of runs to fully cure the formulation is determined and compared. Subsequently the number of runs to fully cure the formulation is determined. VMOX achieves very similar ratings (3) compared to other monomers.

Figure 2: Reactivity Comparison

	NVC	NVP	ACMO	**VMOX**
Reactivity (Exposure runs at 15 m/min)				
LED Lamp	3	3	3	**3**
Mercury Lamp	4	3	3	**3**

Another very critical technical performance characteristic of reactive diluents and UV formulations for printing applications is the adhesion to all common substrates. VMOX promotes excellent adhesion of the ink or coating. As shown in Figure 3, the adhesion of formulations containing VMOX, NVC and NVP is compared based on a standard peel test protocol. The ratings are determined with 0 peel being the best and 5 peel being the worst. Five peels were contacted on each entry and recorded for failure. VMOX based formulated inks displayed similar adhesive properties compared to NVC and NVP, even in lower concentrations compared to the other monomers listed in Figure 3.

Figure 3: Adhesion Comparison on Various Polymer Substrates

Adhesion (1d/3d)	NVC	NVP	ACMO	**VMOX**
PE Foil *(not Corona treated)*	0/0	0/0	0/0	**0/0**
PP Foil *(not Corona treated)*	0/0	0/0	0/0	**0/0**
PET Foil	0/0	0/0	0/0	**0/0**
PVC Panel	0/0	0/0	0/0	**0/0**
PA Panel	0/0	5/5	5/5	**0/5**
PC Panel	0/0	0/0	0/0	**0/0**
PS Panel	0/5	0/0	0/0	**0/0**
Glass	5/5	5/5	0/5	**0/5**

Yellowing and color related issues along with odor have been always a challenge to overcome in the discussed applications. Formulations containing NVP or NVC are prone to yellowing due to auto oxidation and decomposition. To that extent, NVP or NVC monomers are usually stabilized with various amines which tend to slow the yellowing, but not cause it to disappear. In Figure 4, a worst-case scenario example of VMOX, although exhibits the highest APHA color (>350) compared to NVC, NVP and ACMO results in the lowest color factor after curing. In clear lacquer formulations, it seems that the yellowing was lowered to comparable levels with the other monomers, while it also exhibited good color response (when it comes to higher vibrancy of printed or coated products, particularly when compared to NVC for white and clear coatings).

Another advantage of the monomer is the very low odor. Even after printing VMOX-based formulations are virtually odorless. To expand the scope beyond the use in UV inkjets, VMOX testing has demonstrated to be successful in UV coatings (as a reactive diluent and monomer), UV adhesives (as a reactive diluent and additive for adhesives) and 3D printing (as a photo-monomer) applications.

Figure 4: Color Comparison

	NVC	NVP	ACMO	**VMOX**
Reactive Diluent (APHA)	68	35	304	**> 350** (worse case scenario)
Clear Lacquer Formulation# (Gardner)	6,0	5,6	5,8	6,2
L*	92,15	93,28	93,07	93,39
a*	-3,35	-1,25	-0,66	-1,21
b*	**8,64**	**0,99**	**1,34**	**0,55**

VMOX is fully registered with REACH and recently listed in TSCA inventory in USA for use in UV printing inks and 3D printing applications. In contrast to commonly used reactive diluents, such as NVC, NVP and ACMO and in accordance with the classification of the European Chemicals Agency (ECHA), VMOX is not mandated to be labeled with the “Serious health hazard” and “Acute toxicity” warning labels. There was a very limited range of choices and virtually no technically comparable alternatives for those formulators whose formulations largely do without the use of products carrying the “Serious health hazard” and “Acute toxicity” warning labels. BASF has been able to meet this demand with this newly launched product. Figure 5 summarizes the pictograms and compares them to those of the above-mentioned monomers. Further registrations for countries such as Switzerland and the Philippines have already been published, while those for China and Japan are in in progress

Figure 5: VMOX Structure and Pictograms

Conclusion

With VMOX, we have added to the global industry’s most comprehensive portfolio of functional vinyl monomers offered by BASF as an exceptional alternative that meets both the technical and regulatory challenges in UV inks and coatings applications. Furthermore, it has been shown that VMOX has excellent diluting power and can be used effectively for reducing viscosities below 10 mPA*s, is liquid at room temperature without the need of melting it, results in low or no yellowing in the cured formulations and causes no odor to emit. Its favorable tox profile complies with the most recent regulatory restrictions and expand the range of toolbox for new and highly demanding new formulations.

References

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