Technical Paper

VMOX – Answering the Challenges in UV-Curable Inks and Coatings Formulations

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OCCA: BASF has entered the market with a new monomer VMOX. Tell us something about the background.

In all industrial areas, there is a constant drive to improve – from regulatory pressure for favorable toxicological profiles to enhanced technical performance and improved handling – and concerning UV-/EB-curable formulations, all application fields face similar challenges. BASF is the market leader in the supply of specialty vinyl monomers and is thus intrinsically motivated to support our 'UV curing' customers. Our new monomer VMOX (vinyl methyl oxazolidinone) is a reactive diluent that helps address the current challenges. Compared to traditional reactive diluents in the industry, VMOX offers a favorable toxicological profile together with technical benefits and improved formulating capabilities. This includes it being liquid at room temperature, with a very low viscosity of 4 mPa/s (at 20°C), a high reactivity with acrylates, and low colour and odour characteristics.

Overall, VMOX is particularly suited for use as a reactive diluent in UV curing coatings, inks and 3D printing applications. While providing the beneficial technical performance vinyl monomers are known for, VMOX allows innovative formulations with a favourable toxicological profile, which recently has been a challenge and is increasingly difficult to overcome with current chemistries.

OCCA: Why would your customers be interested in using VMOX?

Sustainable product/formulation labelling of a reactive system is a challenge for formulators. In recent years, current technologies such as N-vinyl pyrrolidone (NVP) and N-vinyl caprolactam (NVC), although technically well performing, have come under regulatory scrutiny and are in danger of being phased out due to restrictions, reassessment and potential reclassification. As an example, the European Printing Ink Association (EuPIA) has banned products with mutagenic or carcinogenic profiles, such as NVP, in all printing formulations. Thus, continued regulatory pressure – and the need for materials to be readily available and easily handled in formulations – has created a substantial hurdle for the industry to overcome. The new monomer, VMOX, has been explicitly developed to solve these challenges and was found to meet the criteria after intensive evaluation and testing.

Figure 1 summarises the Globally Harmonised System (GHS) pictograms for VMOX and compares them to those of the standard vinyl monomers, revealing the absence of acute toxicity and health hazard labels. Labelling is one key aspect,

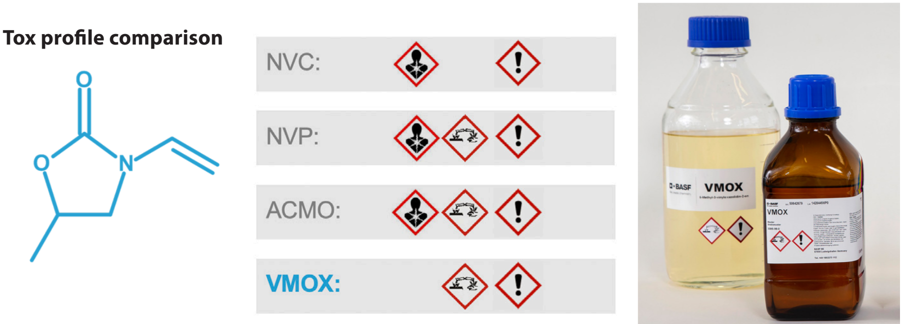

Figure 1: VMOX structure and GHS pictogram comparison with other monomers

but there are inherent chemical properties, such as odour, that are also very important to those handling chemicals and using formulations. Even after printing, VMOX-based formulations are virtually odourless. To expand the scope beyond use in UV inkjets, VMOX testing has demonstrated success as a reactive diluent in UV coatings, UV adhesives and 3D printing applications.

OCCA: How has VMOX been tested?

Our focus for the technical evaluation of VMOX has been clearly on UV cured formulations, specifically UV curable inks, coatings and 3D printing (Table 1). Our aim was to ensure that VMOX performed well compared to the industry standard vinyl diluents as well as a compatibility with acrylate standards.

In general, vinyl-ether and/or -amide monomers – along with other industry-standard monomers such as acrylates – have been used extensively in photoinitiated copolymerisation reactions with acrylate oligomers, epoxy and unsaturated polyester resins in both radical and cationic UV curing systems. In general, they have been shown to efficiently decrease viscosity at low incorporation levels, accelerate the conversion of acrylate oligomers and improve performance properties of the cured system, such as adhesion, shrinkage and flexibility, along with scratch, thermal and chemical resistance. In our evaluation, VMOX had shown the same positive effects that we know from other vinyl-ether and/or -amide monomers.

OCCA: Besides the labelling advantage, what are the technical benefits of using VMOX as a reactive diluent?

In terms of performance, we believe the efficient viscosity reduction and good adhesion on plastic substrates are two stand-out parameters.

Before VMOX even reaches a formulation, it shows an advantage in handling properties compared to the standard viny-ethers and vinyl-amides. The liquid state of VMOX at room temperature (melting point of 20°C) makes the need for melting equipment obsolete, reducing time and handling complexity. In contrast, for example, N-vinyl caprolactam (NVC) is solid at room temperature and must be heated to be liquified and dosed into the formulations, potentially leading to undesirable yellowing effects. Furthermore, the low viscosity of VMOX (4 mPa*s) imparts a significant diluting effect, while enabling high performance of UV ink formulations in which significant viscosity reductions are needed and are below 10 mPa*s.

Figure 2 compares the effect of several reactive diluents on the viscosity of a typical inkjet ink, coating and 3D printing formulation (as shown in Table 1). VMOX consistently achieves superior viscosity reduction when compared to NVC or acryloyl morpholine (ACMO) in all three example formulations.

Another critical technical performance characteristic of reactive diluents and UV formulations, especially in inks and coatings, is adhesion to different substrates. As VMOX is monofunctional, it helps control the curing shrinkage, whilst its high Tg positively impacts the physical resistive properties of a cured film. VMOX promotes excellent adhesion, presumably due to its high polarity. As shown for the various plastic substrates in Table 2, the adhesion of formulations containing VMOX, NVC and NVP is compared, based on a standard peel test protocol. VMOX-based formulated inks displayed similar adhesive properties compared to NVC and NVP. This is a great result as one of the key reasons for NVC and NVP usage is plastic adhesion.

OCCA: How does VMOX perform in combination with acrylate functionality?

We found a high affinity with traditional acrylate monomers, and particularly VMOX shows a high copolymerisation reactivity with all state-of-the-art acrylate monomers (i.e. DPGDA, IBOA,TBCH, POEA, CTFA, etc.) and N-vinyl lactams, and a high affinity for traditional acrylate oligomers being used in the industry. In Table 3, the reactivity of VMOX is compared with NVC, NVP and ACMO. The reactivity was measured based on a standard protocol in which ink formulations are cured on a belt that runs under an LED or mercury lamp at a speed of 15 m/min. Subsequently, the number of runs to fully cure the formulation was determined and compared among the different monomers. VMOX performed similarly to the other tested materials (rating of 3).

Table 1: Composition comparison of example inkjet, coating and 3D printing

Formulation/Composition	Inkjet	Coating	3D Printing
Reactive diluent	34	60	30
Other monomers	60	-	35
Oligomers/Resins	0/0	39	20
Others (incl. Photoinitiators)	6	1	15

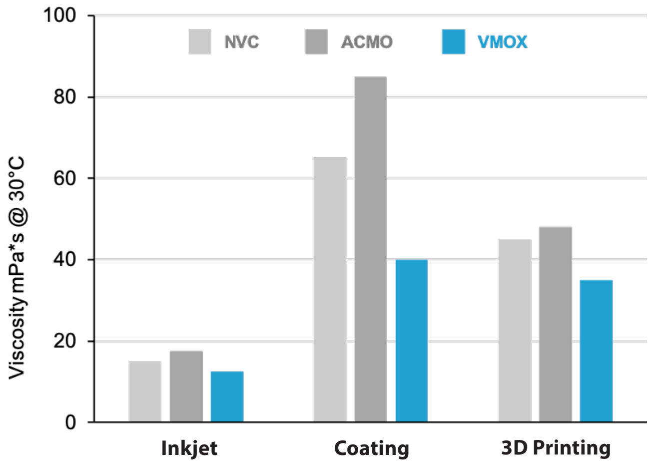

Figure 2: Comparison of example inkjet, coating and 3D printing formulation viscosity

Table 2: Adhesion comparison on various polymer substrates: 34% reactive diluent, 60% other monomers and 6% others (including photoinitiator). Manual scratch and tape test three days after curing : 0 for full adhesion; 5 for completely peel-off.

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**

Table 3: Reactivity comparison of inkjet formulations: 34% reactive diluent, 60% other monomers and 6% others (including photoinitiator). Irradiation at 395 nm, 550 W/cm².

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

This is a great result, because this cross-compatibility leads to VMOX usability as a drop-in problem solver in all standard UV formulations.

Alongside these practical tests, we also ran quantum mechanical simulations on our super-computer *Quriosity* to explore the fundamental principles of VMOX reactivity. We found that the copolymerisation ratios between VMOX and an acrylate functionality fully support the experimental findings.

OCCA: *Quriosity* sounds interesting – what is *Quriosity* and how does it work?

Some years ago, BASF decided to use *Quriosity*, a super-computer with 1.75 quadrillion computing operations per second, to develop new products and push the frontiers of chemical R&D. *Quriosity* offers ten times more computing power than we previously had for scientific computations. In our approach, we simulate the molecular structure of the monomers and reactive species on a quantum mechanical level. By calculating activation energies for the reactions involved, we can derive the reaction speed, which then result in the experimentally known copolymerisation ratios. As a rule of thumb: the lower the activation energy, the faster the reaction.

With these simulations, we can explain how our existing and potential new BASF products work on a molecular level. And that's exactly what we have done with VMOX in combination with other reactive molecules.

OCCA: How should VMOX be used?

We think of VMOX as a drop-in problem solver for all standard UV formulations and we tested it at various levels up to 60% without issues.

The ideal pH for using any vinyl monomer is neutral to slightly basic, whereas acidic formulations will need more detailed formulation work.

Table 4: Colour comparison of example formulations containing different reactive diluents (50% reactive diluent, 42% other monomers and 8% others (including photoinitiator).

	NVC	NVP	ACMO	VMOX
Reactive diluent (APHA)	68	35	304	**>350** (worst 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**

OCCA: The sample looks a little yellow – is that a concern?

Yellowing and colour are significant issues in this industry. NVP and NVC can be prone to yellowing due to auto-oxidation and decomposition and as a result, monomers they are usually stabilised with various amines, which tend to slow the yellowing, but do not eliminate it. While pure VMOX exhibits the highest APHA colour value among the set of monomers shown in Table 4, the colour of the cured coating is in line with NVP, NVC and ACMO (cf. Clear Lacquer Formulation). Additionally, VMOX showed an improved colour response, as indicated by the CIELAB colour space measured on a white plastic substrate. VMOX-containing formulations resulted in higher brightness whites (L*) and more neutral colour deviations (a*, b*).

OCCA: What is the registration status of VMOX?

VMOX is registered with the European Union's Registration, Evaluation, Authorisation and Restriction of Chemicals regulation (REACH) and was recently listed in the Toxic Substances Control Act (TSCA) inventory 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 labelled with the "serious health hazard" and "acute toxicity" warning labels. Prior to VMOX, there was a very limited range of choices and virtually no technically comparable alternatives for those formulators whose materials require the absence of such labelling. Our goal is to make a VMOX registration available in all relevant countries of the world to support our customers in their development of sustainable new products.

OCCA: How would you summarise the value of VMOX to a formulator?

VMOX is the newest addition to BASF's vinyl monomer portfolio. It provides a drop-in solution to help meet both technical and regulatory challenges in UV printing inks and coatings applications.

Furthermore, it has been shown that VMOX has handling benefits, a low inherent odour, excellent diluting power and contributes to adhesion.

OCCA: Thank you

Thank you.

References

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