Introduction

The European legislation, VOC Directive 2004/42/CE, limiting the use of volatile organic compounds (VOC) in deco paints and automotive refinish paints was published in April 2004. The directive defines maximum levels of organic compounds (with a boiling point below 250°C) used as solvents in decorative surface coatings for a variety of coating categories.

The directive imposes significant challenges to the resin producer and coating formulator that include major reformulation efforts.

Croda has developed LoVOCoat polymeric emulsifiers that provide an easy solution to this challenge. The LoVOCoat products allow the incorporation of water in a solvent born alkyd based paint as partial replacement of solvent. This guide has been created to ease reformulation efforts and offers guidelines that will help you to develop VOC compliant high quality paints, varnishes and stains without compromising on performance or adding additional costs.

This document will discuss the following:

- Formulation guidelines on how to incorporate water into SB coating
- What to do if…
- Answers to FAQ’s

Formulation guidelines

Various strategies of water incorporation are possible and depend on possibilities/limitations set by the manufacturing sequence of the paint. Most important is to obtain a fine droplet size of the dispersed water phase as it enhances emulsion stability and minimises increase in drying time.

The following 3 approaches will be discussed:

- Water emulsified in resin solution
- Water in solvent emulsions
- Water incorporation in the pigment grind

Also some practical “What to do if” formulation tips are given.

For more information, please consult your Croda Polymers & Coatings sales contact, email coatings@croda.com or visit www.crodapolymersandcoatings.com
How to create low VOC alkyd formulations with LoVOCoat™ the W/O approach

1. Water emulsified in resin solution

The surfactant is mixed with the alkyd resin solution and allowed to homogenise. Water is slowly added to the resin while mixing. Mixing is continued for 30 minutes after complete water addition.

High mechanical shear is required for low viscous resins. Low speed stirring (even as low as 1 m/s peripheral speed) is sufficient for incorporation of water into high viscosity resins (10-15 kPa.s). Slow water addition is required to assure fine dispersion of the water droplets. It is recommended to emulsify the water into the resin as supplied by the resin manufacturer and adjust viscosity with solvent after emulsification. The viscosity of the resin helps to shear apart the water droplets.

2. Water in solvent emulsions

Stable water in solvent emulsions with high internal phase ratio can be prepared. Internal water levels up to 60% are accessible. These W/O emulsions can be mixed at low shear with basecoat or during let down stage.

Surfactants and solvent are mixed. Sufficient time is required to allow full dissolution of the surfactant in the solvent. Water is emulsified in the solvent using high mechanical shear. Homogenisation is continued for 30 minutes after complete water addition. (use a Silverson L4R rotor/stator type stirrer for efficient emulsification at 6000rpm).

3. Water incorporation in the pigment grind

Water can also be incorporated in the pigment grind, before let down stage.

Pigment is grinded in the presence of a fraction of the binder. The LoVOCoat surfactants are added after grinding and allowed to homogenise. Water is slowly added to the grind. Mixing is continued for 30 minutes after complete water addition. Add the letdown.

Again, the viscosity of the grind contributes to the shear required to emulsify the water droplets. As during grinding, a viscous resin phase is needed for efficient de-agglomeration of the TiO2, comparable conditions are required for emulsification.

Generic formulation

The required amount of surfactant depends on the amount of water incorporated. Recommended level of LoVOCoat is at about 16% on internal water phase, in which the ratio of LoVOCoat Form 100 : LoVOCoat Stable 100 ratio is 60:40.

For example, for the incorporation of 20% water in the paint formulation, we recommend a total surfactant level of 3.2%, of which 1.9% LoVOCoat Form 100 and 1.3% LoVOCoat Stable 100.

Water can be emulsified in a resin solution and mixed at low shear with the pigment grind/concentrate.

Formulation examples

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (1% MgSO4)</td>
</tr>
<tr>
<td>LoVOCoat Form 100</td>
</tr>
<tr>
<td>LoVOCoat Stable 100</td>
</tr>
<tr>
<td>Long Oil Alkyd, 78% in</td>
</tr>
<tr>
<td>Exxsol D40</td>
</tr>
</tbody>
</table>

Wt%

| Water (1% MgSO4) | 60 |
| LoVOCoat Surfactants | 10 |
| Solvent | 30 |

(LoVOCoat Form 100 : LoVOCoat Stable 100 ratio is 60:40)
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4. Practical formulation tips

Q: What do I do in practice?
A: Mix the surfactant with the resin solution (or pigment grind), allow homogenising for 30 minutes and gradually adding the required amount of 1% Magnesium sulphate solution to the resin while stirring at ambient temperature. It is advisable to adjust the viscosity with solvent after emulsification process, since the emulsification process is more efficient when the viscosity of the continuous phase is high.

Q: What is the required mixing speed?
A: Mixing speed will depend on the viscosity of the medium. High shear mixing is required for finely dispersing the water droplets. If the medium (resin (or pigment paste) and solvent) has low viscosity, high speed mixing is required. We used a Silverson L2R rotor stator high shear mixer at 6000 rpm for our experiments. Overhead stirrers with cowles blades or Intermig impellers can be used at lower stirring speeds when resin viscosity is sufficiently high (peripheral speed can be as low as 1 m/s for resin viscosity around 10-15 Pa.s). The viscosity of the medium is sufficient to shear the water droplets apart. Grinding conditions (‘donut effect’) should be sufficient to incorporate the water.

Q: What is the preferred rate of water addition?
A: Fast water addition (in approx. 30 minutes) is possible with high speed mixing. If only low speed mixing (3-400 rpm) is available, more care is necessary. This method is only applicable when the resin viscosity is sufficiently high (see opposite).

Q: How do I upscale production with LoVOCoat?
A: Similar formulation advice can be followed to produce the paint formulation with LoVOcoat. The viscosity of the medium will influence the speed of water addition (see section “what is the required mixing speed”). More efficient emulsification conditions are obtained when the viscosity of the medium is high. Therefore, it is advised to adjust viscosity with solvent addition after the emulsification. Water can be added to the vessel within 5 minutes whereafter stirring is continued for another 10-15 minutes. Mixing with an impeller at a tip speed of 15-20 m/s should be sufficient to obtain a good quality emulsion.

Q: What type of packaging should be used for the end formulation?
A: Due to the presence of water in the paint formulation, it is advised to use lined cans for packaging. This is to avoid corrosion in the can.
### What to do if ..?

“What to do if …” tips in the process of developing new formulations are always helpful. The tips opposite will support you in achieving the desired properties of a formulation quicker and easier.

<table>
<thead>
<tr>
<th>Issue</th>
<th>Probable cause</th>
<th>Possible solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water separation</td>
<td>Too big water droplets were created</td>
<td>Increase mechanical shear by increasing stirring speed.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Increase surfactant level. Recommended surfactant levels can vary from between 15 - 40% on dispersed water phase.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Change the ratio between the LoVOCoat form and LoVOCoat stable surfactants. Depending on the polarity of the solvent and resin other ratio’s then 60:40 might be required.</td>
</tr>
<tr>
<td>Oswald ripening – water diffusing from the small to bigger droplets that will eventually separate out</td>
<td>Make use of osmotic pressure regulators such as salts or water soluble polymers to avoid Oswald ripening.</td>
<td></td>
</tr>
<tr>
<td>Water separation upon tropical storage</td>
<td>Insufficient stabilisation</td>
<td>Increase surfactant level. Recommended surfactant levels can vary from between 15 - 40% on dispersed water phase.</td>
</tr>
<tr>
<td>High viscosity</td>
<td>Resin has a high viscosity</td>
<td>Increase solvent volume and use less water. The amount of water that can be incorporated depends on the viscosity of the alkyd. Use if possible an alkyd with lower viscosity Use a different solvent.</td>
</tr>
<tr>
<td>Drying time increase</td>
<td>Incorporation of water affects drying time</td>
<td>Particle size of water droplets has an impact on drying time. If the water is dispersed in smaller droplets increase in drying time is minimised. Use less water. Experiments with a formulated paint have shown a direct link between water levels and drying time.</td>
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<tr>
<td>Loss of hardness</td>
<td>Plasticizing effect of the surfactant</td>
<td>If stability is not affected reduce amount of surfactants. To counter the plasticizing effect of the surfactant use a less oil containing alkyd</td>
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</tbody>
</table>
Answers to FAQ

Q: What is the Water in Oil (W/O) concept?
A: Water is used as liquid filler for partially reducing solvent levels in solvent borne alkyd based coatings.

Q: For which types of alkyds is this concept applicable?
A: The surfactants are compatible with long, medium and short oil alkyds. The choice of solvent is more relevant. The surfactants are compatible with aliphatic and aromatic hydrocarbons.

Q: How much water can I incorporate in the formulation?
A: That entirely depends on the viscosity of the resin. Water is not a solvent for the resin. Low viscous resin solutions in hydrocarbon solvents permit high levels of water incorporated. It is even possible to formulate stable water in solvent (xylene or Exxsol D40) emulsions with internal (water) phase ratio of 50-60%.

Experiments with long oil alkyd resin allow us to incorporate water levels of roughly 20-30%. At low water levels (up to 20%), the water does not cause an increase in viscosity or change in flow properties of the formulation. Some viscosity increase and a shear thinning flow are observed at higher water loadings (25-32%).

Q: What is the advantage of using LoVOCoat polymeric surfactants?
A:
- Shelf life of the formulation is maximised and water separation prevented.
- High levels of water can be incorporated with minimal effect on viscosity and flow.
- Effects on drying time and dry film properties are minimal

Q: How come?
A:
- The LoVOCoat emulsifiers show high affinity to the oil water interface and at the same time provide superior (steric) stabilisation to the dispersed water droplets. This prevents water droplet growth through coalescence and assures good shelf life of the emulsion.
- The superior steric stabilisation of the water droplets prevents weak flocculation of the water droplets. This keeps formulation viscosity low.
- Diffusion of the surfactant to the film surface during/after drying is minimised thanks to the molecular weight of the surfactants and their compatibility with the resin.

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Answers to FAQ

Q: Why use two products for emulsion stabilisation?
A: Typically a combination of surfactants gives better emulsions stability than single components. LoVOCoat Form 100 is the principal water in oil stabiliser. It is a product with a low HLB (hydrophilic/lypophilic balance). LoVOCoat Stable 100 is a hydrophilic co-surfactant. Experimental work on water in solvent and water in long oil alkyd/exxsol D40 has shown that a LoVOCoat Form 100 to LoVOCoat Stable 100 ratio of approx. 60:40 pbw gave optimum stability. Preferred surfactant ratio will depend on polarity of the solvent and resin and might require optimisation.

Q: What are the LoVOCoat products chemically?
A: These are non-ionic polymeric emulsifiers, with high molecular weight. These amphiphiles are typically used in applications where shelf life is critically important.

Q: What is the composition of the LoVOCoat emulsifiers?
A: The surfactants are supplied as solutions to facilitate handling:
- LoVOCoat Form 100 is supplied as a 20% solution in Exxsol D80
- LoVOCoat Stable 100 is supplied as a 20% solution in water.

Q: Why using Magnesium sulphate in the water phase?
A: The salt is present as an osmotic pressure regulator. The salt can be replaced with water soluble polymers if needed. The salt is present to avoid a phenomenon known as ‘Ostwald ripening’. A diffusion of water molecules from the dispersed phase to the continuous phase and back causes shrinkage of small molecules and growth of large molecules. This will eventually cause the water phase to separate.

Q: How much stabiliser is required?
A: Required surfactant level is calculated on the amount of water incorporated. W/O Emulsions using from 3 to 8% surfactant on dispersed waterphase have been formulated. Experiments show that even with a level as low as 3.1% (by weight) surfactant (active matter) on dispersed waterphase, an excellent tropical storage stability of the emulsion is obtained. Since the emulsifiers are 20% active solutions, the recommended usage level of LoVOCoat products is 15.5% on internal waterphase, or 9.6% LoVOCoat Form 100 and 5.9% LoVOCoat Stable 100 on water. Shelf life of the emulsion is proportional to the level of stabiliser used.

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