Feature: Environmental

Oxazolidine diluents: Reacting for the environment

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Introduction

Over the last decade, there has been a considerable change in the market for solvent-borne industrial coatings. Significant developments have taken place in water-based coatings, that have now expanded from the consumer housepaint market into industrial sectors. Increasingly stringent VOC regulations have led to the development of a more viable water-based alternative to solvent-borne materials. However, some limitations still exist, particularly with the key properties of chemical and abrasion resistance in coating performance.

Alongside the advances in water-based technology, there has been the development of high solids coatings. These are usually formulated with lower molecular weight components to achieve the lowest possible viscosity with the minimum of solvent. However, there is a limit to molecular weight reduction, as this can lead to problems associated with loss of coating performance.

An example of the trends described above is two-pack polyurethane OEM coatings. Typically, these systems consist of an acrylic (or acrylic and polyester) polyol and an HDI-based polyisocyanate (usually biuret or trimer). These forms polyurethanes possessing unique properties including excellent chemical resistance and weather exposure as well as good abrasion resistance.

One possible solution to maintaining the coating benefits of solvent systems, whilst reducing the content of VOC, is to incorporate a reactive diluent. Incozol LV, a low viscosity bisoxazolidine reactive diluent has been designed specifically to produce high performance coatings that comply with even the strictest environmental legislation.

Incozol LV: Reactive diluent

Incozol LV (Figure 1) is a low viscosity bisoxazolidine designed as a co-reactant in polyurethane coatings to achieve a low content of VOC. Incozol LV consists of two oxazolidine rings (five membered heterocyclic rings containing nitrogen and oxygen) linked by a carbonato bridge, which affords low viscosity by restricting intermolecular hydrogen bonding.

Figure 1: Incozol LV – Reactive diluent for 2K PU coatings

Incozol LV has the ability to reduce the viscosity of the polyol component of the two-pack system in which it’s to be incorporated, in a way similar to solvent (Figure 2).

Figure 2: Viscosity reducing effect of Incozol LV

Incozol LV possesses the key properties demanded of a good reactive diluent, namely:

- Good polyol and solvent compatibility
- Low intrinsic viscosity – 50 mPas @ 20°C
- Reasonably high equivalent weight – 90 (functionality of 4)

Summaries

Oxazolidine diluents: Reacting for the environment

Incozol LV is a low viscosity bisoxazolidine reactive diluent that is activated by moisture present in both the polyurethane coating components (polyol and solvent) and in the atmosphere during application. The moisture triggered ring opening allows Incozol LV, by chemical reaction with polyisocyanate, to be successfully incorporated into the polyurethane coating. Incozol LV offers the benefit of reducing the VOC content of polyurethane coatings to below the present legislative demands without adversely altering the cure and coating properties.

Diluents Oxazolidines: Reagents for the environment

Incozol LV is an additive that is active at low concentrations of bisoxazolidine, that reduces the film viscosity of polyurethane coatings. Incozol LV is activated by moisture present in the polyurethane coating system components and in the atmosphere at ambient temperature. The moisture triggered ring opening allows Incozol LV to function as a reactive diluent in polyurethane systems.

Incozol LV improves chemical compatibility and film formation without affecting the physical properties of the coating.

Diluents Oxazolidines: Reactant for the environment

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Oxazolidinediluents: Reacting for the environment

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- Low colour (essential for clear lacquer finishing)
- Workable pot life and cure
- No adverse effect on coating properties (including film hardness and resistance, gloss and weathering properties)

Chemistry of oxazolidine diluents

Activation of oxazolidine reactivity with polyurethanes: Ring opening hydrolysis reaction

The ability of Incozol LV to enter into the polyurethane backbone of the coating is activated by the ring opening hydrolysis of the two oxazolidine rings, resulting from the reaction of water present as moisture in both the solvent and polyol components. Moisture in the atmosphere during spraying application also aids the activation of the oxazolidine rings. Consequently, the inclusion of Incozol LV has the benefit of scavenging moisture, as well as lowering the VOC. Polyurethane coatings can be affected adversely by moisture, through the reaction of water with the polyisocyanate, giving rise to carbon dioxide gassing. Often this can result in pinholing in the coating or hazing problems with clear lacquer finishes. Hence, pre-mixing Incozol LV with the polyol and solvent component to scavenge the moisture prior to polyisocyanate mixing is clearly an advantage towards improving the coating. Indeed, repeated opening of containers will serve to further activate the oxazolidine prior to hardener (polyisocyanate) mixing.

Activation of Incozol LV results from the hydrolytic ring opening of the oxazolidines yielding hydroxyl and amino functionality on each ring. Consequently, with Incozol LV, four sites (two hydroxyl and two amino) are available for reaction with polyisocyanate (Figure 3).

![Figure 3: Hydrolysis reaction ring opening Incozol LV](image)

Recently, research has been conducted, in conjunction with the University of Central Lancashire, to determine quantitatively the hydrolysis reaction, both from the point of view of extent and rate of hydrolysis. Practically, this has been done by determining the residual concentration of Incozol LV, if any, by gas chromatography, with respect to the amount of water added in different stoichiometric amounts of Incozol LV. Furthermore, the rate of hydrolysis has been studied by following the residual Incozol LV depletion with respect to mixing time.

The extent of hydrolysis (Figure 4), indeed the driving force for reacting the diluent, indicates that Incozol LV ring was almost completely opened and available for reaction with isocyanate after only 30 minutes mixing; with 15% residual Incozol LV detected when a stoichiometric amount of water was mixed with the oxazolidine. At 0.5 moles of water, which would represent a more usual level of water present in polyol and solvent components, a majority (about 80%) of Incozol LV has been activated after six hours mixing. This indicates that some interaction with atmospheric moisture must also contribute to the oxazolidine ring opening.

The rate of hydrolysis (Figure 5) for 0.5 moles of water showed a large proportion of oxazolidine activated by the water present initially in the mixture. The rate of hydrolysis then declined as Incozol LV was consumed by the atmospheric moisture. After 12 hours the oxazolidine ring has fully opened and the amino alcohol generated is fully available for reaction with polyisocyanate.

![Figure 4: Extent of hydrolysis of Incozol LV](image)

![Figure 5: Rate of hydrolysis for 0.5 moles of water](image)

Reaction of ring opened oxazolidine (aminoalcohol) with polyisocyanate

Once activation of Incozol LV has been completed, the aminoalcohol generated is then available to enter into the polyurethane backbone. This takes place through the formation of urea linkages formed from isocyanate reaction with the secondary amine sites and urethane linkages through the terminal OH groups (Figure 6).

A second study by the University of Central Lancashire examined the interaction of the aminoalcohol with HDI polyisocyanates (Tolonate HDT™) using Fourier Transform Infra-red spectrophotometry. Incozol LV was added to a large excess of Tolonate HDT™ (20% w/w Incozol LV to 80% w/w Tolonate HDT™). Quantitative FTIR analysis in absorbance mode of depleting NCO peak (Figure 7) was performed for the following reaction combinations: