Oxazolidines and tetramethylxylene diisocyanate based polyurethanes in legislation-compliant anticorrosion coatings

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Introduction

There are only a few companies in the world that produce oxazolidines commercially. Fewer still produce low viscosity oxazolidines which are suitable as latent hardeners to enable production of single-pack moisture activated polyurethanes. There is, therefore, very little published data on their use, although the principles of manufacture have been published with suggested formulations. Their use in anticorrosion coatings has also been recently investigated as part of an MSc thesis. There are many papers and reviews of urethane technology and its use continues to expand. Urethanes are frequently used in anticorrosion coatings. However, the isocyanate chosen for this research, is tetramethylxylene diisocyanate (TMXDV M) which has been available commercially only since 1988. There is very little published information on polyurethanes based on this isocyanate. There is no published information about the use of TMXDITM in anticorrosion finishing coat applications. There are, however, a number of papers discussing the use of TMXDITM in water-borne polyurethane dispersions.

Polyurethanes are a very useful class of polymers which exhibit many desirable properties which those designing anticorrosive coatings can beneficially exploit. There is a large range of uses for this class of product. Examples of the diverse range of applications include their use in clear coatings for shatter-proof glass as a rubber crumb binder for sports surfaces as the main binder in anticorrosive paint finishing coats as the main binder in aliphatic single pack roof coatings and as encapsulants for electronic components. This wide range of uses continues to expand despite legislative constraints. The commercial availability of new isocyanates has also contributed to the continuing growth of the technology of polyurethanes.

Legislation

In 1990, spurred on by legislation in the USA, the Environmental Protection Act legislated in the UK to control further the use of Volatile Organic Compounds (VOC). This had European backing as all governments in the European Union likewise passed laws aimed at improving the environment. This legislation has further concentrated the thinking of resin and coatings formulators. PG6/23(95) published by HMSO gives a number of VOC figures that coatings must meet to conform to legislation. The alternative is to install an abatement plant to reduce the solvent emissions at source. This equipment, however, is expensive and has quite high running costs. Consequently, the research and development drive of most coatings and resin producers, is at the moment, the reduction of the solvent content of the paint and resin systems by the high solids route. Another drive is towards conversion to water-borne systems. The polyurethane resin industry is no exception. One method of achieving the environmental aims demanded by legislation in the polyurethane coatings industry is to use oxazolidines. The low viscosity oxazolidines are particularly useful.

Polyurethanes

Polyurethanes do not have quite the same degree of adhesion to metal substrates as epoxy resins. However, they have extremely high resistance to chalking and good abrasion resistance. It is, therefore, more usual to see epoxies specified for use in primer or base coats, and polyurethanes as finishing coats. The main disadvantage of polyurethanes is that isocyanates are used in their manufacture. With the exception of MDI and TMXDV M, all isocyanates are toxic. The polyurethanes produced from them are thus perceived to be toxic also. They are not necessarily so when based on MDI and TMXDV M. However, aromatic isocyanates are relatively cheap and, hence, the polyurethanes synthesised from them are also relatively low in cost and, therefore, are very popular. They do, however, suffer from yellowing due to the high degree of conjugation and the aromaticity present in the molecule. Aromatic polyurethanes cure very rapidly by moisture and are relatively cheap. Thus, formulators still use them in vast quantities. The yellowing is tolerated because of their low cost and very useful properties.

A classic example of an aromatic isocyanate used to manufacture aromatic polyurethanes is methylene diparaphenylenediisocyanate (MDI). Usually, ortho and meta isomers are also present. LW radiation is easily absorbed by the molecules because of the ease by which the energy can be spread (delocalised) over the molecule. This gives rise to the yellowing seen when aromatic polyurethanes are used...
resistance and weatherability, This is good for an anticorrosion finishing coat. To obtain good drying rates with aliphatic polyurethanes and thereby corrosion resistance, the use of oxazolidine technology is strongly recommended.

**Figure 2: Common usage aliphatic isocyanates**

- **Isophorone Di-Isoyanate (IPDI)**
- **Hexamethylene Di-Isoyanate (HDI)**
- **Tetramethylxylylene Di-Isoyanate (m-TMDI)**

**Figure 3: Structure of m-TMDI™ isocyanate curing mechanism of polyurethanes**

- **Tetramethylxylylene diisocyanate**
- **m-TMDI™**

(Figure 1). To overcome this problem, their aliphatic counterparts can be used.

Aliphatic isocyanates are considerably more expensive than their aromatic counterparts. Consequently, polyurethanes made from aliphatic isocyanates are also more expensive. Aliphatic isocyanates cure comparatively much more slowly. However, the yellowing performance of aliphatic polyurethanes is far superior to aromatic polyurethanes. They yellow only over a long period of time, much more slowly. However, the yellowing performance of aliphatic polyurethanes made from aliphatic isocyanates are also offer lower water absorption than the other aliphatic isocyanate groups. These then react with the aliphatic polyurethane isocyanate and thereby corrosion resistance, the use of oxazolidine technology is strongly recommended.

**Figure 4: Curing reaction of a polyurethane with moisture**

![Curing mechanism of polyurethanes](image)

**Curing mechanisms of polyurethanes**

Polyurethanes cure by reaction with atmospheric moisture forming an amine and then a substituted urea with the release of carbon dioxide gas.

The hydrogen atoms which are attached to the nitrogen atoms can undergo a further reaction with NCO groups on other urethane pre-polymer molecules. Eventually, a tightly cross-linked structure results. The disadvantage with this type of polyurethane system is that carbon dioxide can get trapped in a drying paint film. This causes blisters and hence paint film voids. These then become areas of unfavourable anode/cathode ratios and very high localized corrosion can result, especially where cathodic protection systems are in use or where there are stray currents. An explanation of this phenomenon is worthwhile.

The anodic and cathodic reactions involved in the dissolution of a metal are illustrated below. An appeal to logic will show that a metal of 1 square millimetre corroding at a rate of say 10^{13} electrons per second will dissolve completely before the same metal of an area of 1 square centimetre corroding at the same rate of 10^{15} electrons per second. The corrosion rate is related to current density. Corrosion is, thus, an electrochemical reaction (Figure 5).

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**Figure 5: Anodic and cathodic reactions in metal dissolution**

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M \rightarrow M^{\text{II}} + 2e^{-}
\]

Anodic corrosion reaction

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2H_{2}O + O_{2} + 4e^{-} \rightarrow 4OH^{-}
\]

Balancing cathodic reaction

in neutral/alkaline conditions

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When defects occur in paint films, on structures where there is a stray current, corrosion is greatly accelerated because all the anodic reaction occurs at the defects. This results in a very large current density and pinholes can occur in the metal itself, completely weakening structural integrity.

A method of simultaneously overcoming both potential carbon dioxide gassing and slow cure problems with aliphatic polyurethanes, is to use oxazolidine technology.

**Curing mechanism of polyurethanes with oxazolidines**

Oxazolidines are heterocyclic rings containing both nitrogen atoms and oxygen atoms. They are synthesised by the cycloaliphatic reaction of an amino alcohol and an aldehyde or ketone. The reaction proceeds by the removal of water which drives the reaction forward because of Le Chatelier’s Principle. Oxazolidines can be further reacted to produce a species illustrated in Figure 6. When in the presence of an aliphatic isocyanate, the oxazolidine species is very stable and in-can stabilities of nearly two years have been observed. However, when a coating containing the oxazolidine species and the aliphatic polyurethane is exposed to atmospheric moisture, the water vapour reacts preferentially with the oxazolidine species. This causes the oxazolidine rings to open yielding –NH and –OH functional groups. These then react with the aliphatic polyurethane species to give a highly crosslinked coating with no carbon corrosion.