

3rd Nurnberg Congress

New Technologies for Coatings and Inks

Title

High Solids Polyurethane Coatings Using
Oxazolidine Reactive Diluents

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Summary

Oxazolidine technology has been around for quite a long time but advances continue to be made in the variety of species available and the end uses to which they are put(1). Oxazolidines may be used as drying agents, latent hardeners for polyurethane resins, reactive diluents and even as polyols in urethane/urea synthesis. These areas of research will be discussed in this paper.

Introduction

Oxazolidines are now called oxazolanes under the IUPAC naming system but are still widely known by the traditional name. They usually comprise a five membered heterocyclic ring containing a nitrogen and oxygen atom. They may be described generally as: **(figure 1)**

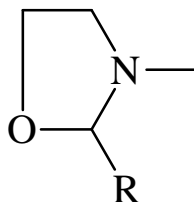


Figure 1 A five membered oxazolidine heterocycle

Oxazolidines are classically synthesised by the dehydration and ring closure of aminoalcohols by aldehyde or ketone species. The aminoalcohol and aldehyde or ketone are chosen depending on the application in which the final oxazolidine is to be used. As an example if an oxazolidine is to be synthesised from diethanolamine and isobutyraldehyde (IUPAC 2-methyl 2 propanal) the resultant product **(figure 2)** has an OH group which can react with an isocyanate terminated prepolymer in a single pack system and cause an almost immediate exothermic reaction which results in a viscosity increase and loss in crosslink density. **(Figure 3).**

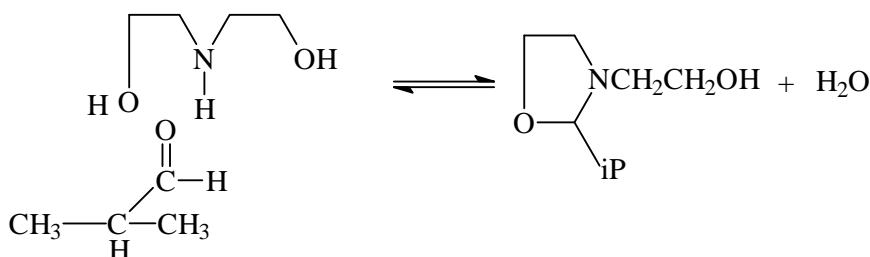


Figure 2 Classical cyclodehydration synthesis of an oxazolidine species (Incozol 3) from diethanolamine and isobutyraldehyde.

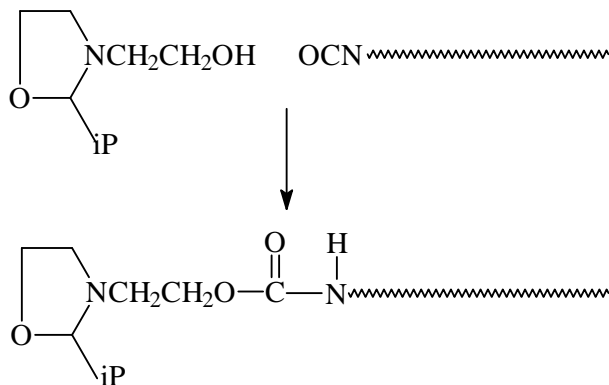


Figure 3 Reaction of an hydroxy terminated oxazolidine species (Incozol 3) with an NCO terminated urethane prepolymer

To overcome viscosity problems in single pack systems, hydroxy ethyl oxazoline should not be used. High viscosity usually means lower solids and hence another combination of starting materials would be chosen. If the product is to be used as a drying agent only however, a relatively small amount would be required and hence the ensuing viscosity increase could easily be tolerated.

Oxazolidines as latent hardeners

The above mentioned oxazolidine though is a very useful synthetic precursor for a range of oxazolidines. US patent 3,743,626 disclosed a number of these synthetic pathways back in the late 1960's and early 1970's. GB patent 1463944 also disclosed a method for joining two hydroxyethyl oxazoline rings together with a diisocyanate and then using the product as a latent hardener for curing isocyanate terminated polyurethane prepolymers without the evolution of carbon dioxide gas.(figure 4).(2,3)

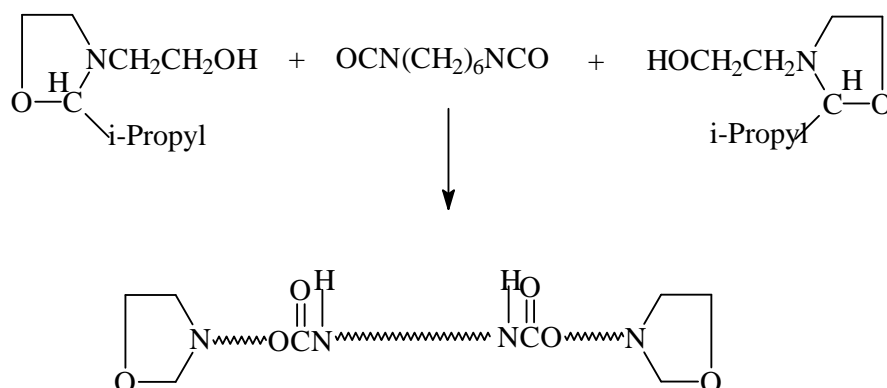


Figure 4 Synthesis of a urethane bisoxazolidine from an hydroxyethyl oxazoline and a diisocyanate

This type of product has been on the market for a number of years now and is available as Incozol 4 ex Industrial Copolymers Ltd. When blended with urethane prepolymers it is very stable but on exposure to moisture in the atmosphere, the water reacts preferentially with the oxazolidine rings. This yields a four functional species which then reacts with the urethane prepolymer producing a tough flexible crosslinked species but without the evolution of carbon dioxide gas which is produced with normal moisture curing urethanes (Figure 5).

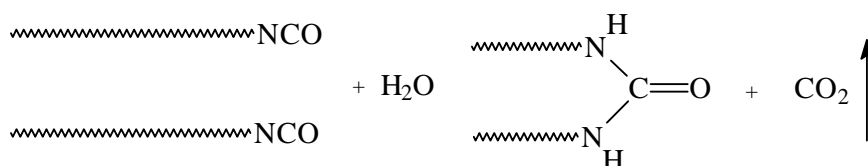


Figure 5 Traditional moisture curing polyurethane with the production of carbon dioxide gas

A comparison of these methods of cure can be seen by examining figures 5 & 6.

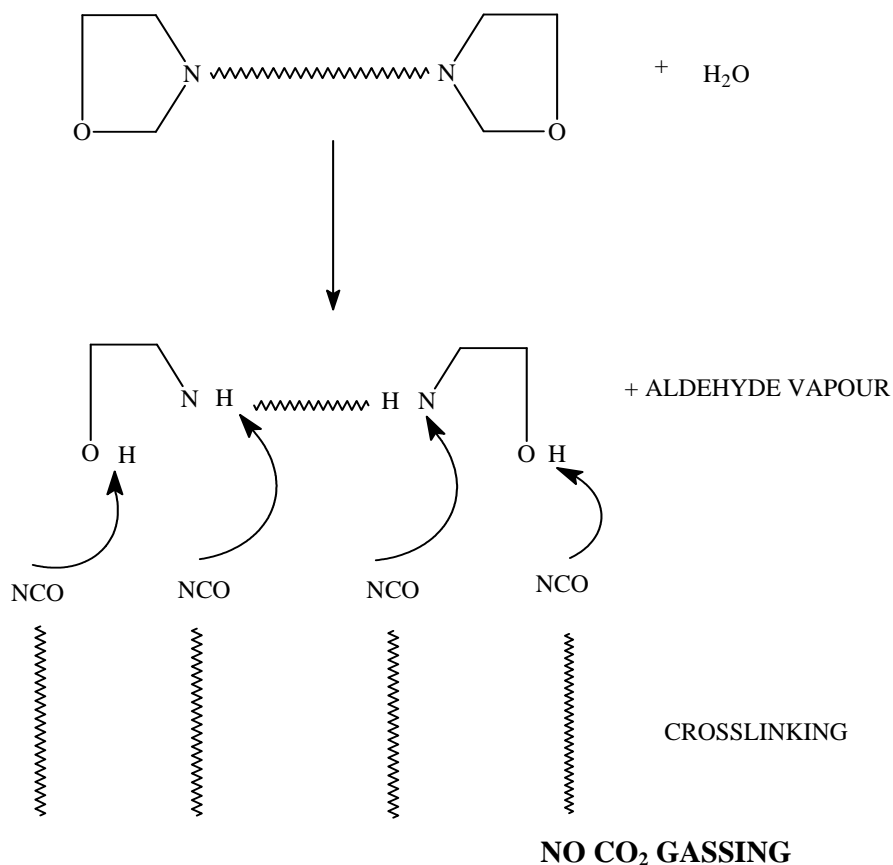


Figure 6 Curing mechanism of a urethane bisoxazolidine with an NCO terminated prepolymer

Both very soft and very hard systems may be produced using oxazolidines depending on how they are formulated. An example of this may be seen by reference to formulation 91/806/AC23 in table 1.

Table 1 Hard anticorrosive topcoat reference 91/806/AC23

Incorez 806/007	31.23%	trifunctional PU resin
Xylene	17.36%	
Tego Flow	00.43%	additive
Tego Glide	00.43%	additive
Titanium Dioxide	23.42%	TR92
Ircogel 906	04.34%	thickener
DBTL	00.06%	catalyst
Incorez 701	10.41%	Flexible PU resin
Incozol 4	12.32%	Oxazolidine latent hardener
TOTAL	<u>100.00%</u>	

Paint properties

PVC	18.46%
Wt. Solids	71.33%
Vol. Solids	60.82%
SG	1.206
Persoz Hardness	285

The Incorez 701 is a relatively soft and highly flexible prepolymer which is present to provide some flexibility in the finished system. This illustrates that hard systems can be produced with oxazolidines. Careful examination of the structure produced from the reaction of a diisocyanate with oxazolanes i.e Incozol 4 shows that urethane linkages are produced which in turn can hydrogen bond (**figure 7**). Hydrogen bonding produces some excellent properties such as toughness but it also increases the viscosity of the product.

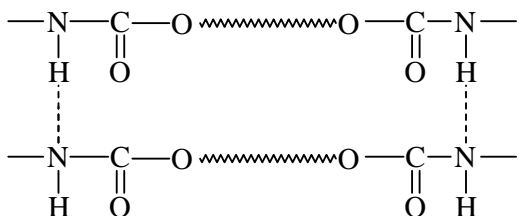


Figure 7 Hydrogen bonding in a urethane bisoxazolidine

This viscosity increase makes the production of high solids (Low VOC) systems difficult and hence there was a need seen in the market place to produce oxazolidines without the potential to hydrogen bond to give low viscosity and hence high solids and low VOC. It should be noted that high solids isocyanate-oxazolidine coatings are not new but there are number of ways of meeting this objective (4).

Newer Oxazolidines

The word “newer” is deliberately used in the title of this section because the possibility of using a range of chemical linkages was covered in US patent 3,743,626 but commercially available products have not been available until now for single pack systems (5,6). As well as urethane linkages to join two or more oxazolane rings together, it is possible to have ester or carbonato links (**Figures 8 &9**)

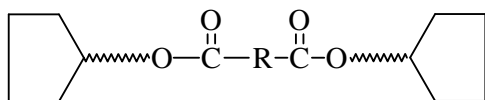


Figure 8 Ester bisoxazolidine

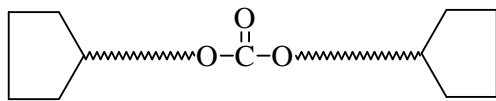


Figure 9 Carbonato bisoxazolidine.

Industrial Copolymers produce bisoxazolidines both with and without the hydrogen bonding to give customers choice and flexibility but it is with non-hydrogen bonded

systems that high solids coatings are usually made. For example in Table 1 a formulation was presented which contains the urethane bisoxazolidine Incozol 4 which is a hydrogen bonded species. If that same formulation is made with Incozol LV a reasonable reduction in solvent content can be made to give a higher solids coating (**Table 2**).

Table 2 High solids hard anticorrosive topcoat reference 94/806/AC23/LV

Incorez 806/007	41.00%	trifunctional PU resin
Xylene	05.00%	
Tego Flow 300	00.47%	additive
Tego Glide ZG400	00.47%	additive
Titanium Dioxide	28.00%	TR92
Ircogel 906	04.00%	thickener
DBTL	00.06%	catalyst
Incorez 701	06.00%	soft PU resin
Incozol LV	15.00%	Low viscosity Oxazolidine

Paint properties

PVC	13.00
Vol Solids	71.80%
Wt Solids	80.40%
S.G	1.275
Persoz Hardness	270

In the system illustrated in Table 2 the solvent level is greatly reduced from the system in Table 1 but the hard to soft resin ratio has also been increased. Incorez 806/007 is a very hard trifunctional polyether/TMXDI based species whereas Incorez 701 is a very flexible bifunctional (approximately) species. The switch from urethane bisoxazolidine with the potential to hydrogen bond present, to the non-hydrogen bonded Incozol LV whilst giving much lower viscosity also affects other properties such as tensile strength, elongation and flexibility and hence the hard/soft resin ratio is usually adjusted to compensate. Incozol LV as a general rule gives lower tensile strengths and higher elongation than an equivalent system with Incozol 4. This is not usually very important when formulating a 100 micron thick anticorrosive topcoat but can be more important when formulating a thicker elastomeric type system. This can be illustrated very well using a flexible system based on a flexible polycarbonate based polyurethane system again based on TMXDI, Incorez 805 (**Table 3**). Though it should be stressed other systems such as polyester/IPDI may be used also.

Table 3 Flexible polycarbonate based polyurethane coatings-comparison of Incozol 4 and Incozol LV

	Incozol 4	Incozol LV
	<u>% by Wt</u>	<u>% by Wt</u>
Incorez 805	72.23	87.00
Incozol 4	12.22	-
Incozol LV	-	12.94
DBTL catalyst	00.05	00.06
Methoxy propyl acetate	15.50	-
Total	<u>100.00</u>	<u>100.00</u>

Properties

Tensile strength (MPa)	13.02	8.61
Elongation at break	295%	364%
100% modulus (MPa)	4.05	1.93
Solids by weight	63%	74%

From these results it can be seen that although there are major benefits in terms of higher solids and solvent reductions to be gained from a switch to the newer oxazolidine technology, other properties are affected and some formulation work is required to optimise the system. As has been seen from previous examples there are advantages in using resin blends as more formulation flexibility is then available.

Formulation calculations

A number of questions often arise when formulating oxazolidine based systems such as how does one calculate the hardener to prepolymer resin ratio. The %NCO of the polyurethane resin(s) must be known, but this data is invariably given on the data sheet by the supplier. Using Incorez 805 as an example:

$$\text{Incorez 805 \%NCO} = 3.7\% \text{ therefore equivalent weight} = \frac{42 \times 100}{3.7\%} = 1135$$

The molecular weight of the urethane bisoxazolidine Incozol 4 is approximately 500 and since the species will have four functions on ring opening, the equivalent weight is 125. There is a lot of formulating flexibility however and some chemists choose to allow for only the NH groups reacting and hence the bisoxazolidine would then have an effective equivalent weight of 250. The vast majority of formulators choose somewhere between these figures usually 130-160 i.e an average of 145. These ratios are illustrated in Table 4.

Table 4 Polycarbonate PU and Oxazolidine hardener resin ratios

	<u>Resin Weights Kg</u>	<u>Ratio PU:Hardener</u>
Incorez 805	1135	
Incozol 4		
250 eq wt	250	1135/250 = 4.5:1
145 eq wt	145	1135/145 = 7.8:1
125 eq wt	125	1135/125 = 9.0:1

Incozol LV on the other hand has a molecular weight of circa 380 and an equivalent weight of between 95 and 190 depending on the formulator. A good average to use would be 113 and hence the ratios would be:(**Table 5**)

Table 5 Polycarbonate PU and low viscosity Oxazolidine resin ratios

	<u>Resin Weights Kg</u>	<u>Ratio PU:LV Hardener</u>
Incorez 805	1135	
Incozol LV		
190 eq wt	190	1135/190 = 6:1
113 eq wt	113	1135/113 = 10:1
95 eq wt	95	1135/95 = 12:1

The use of Incozol LV illustrates the advantage of being able to formulate at the high end of the equivalent weight spread. With a ratio of 1 part low viscosity oxazolidine to 6 parts PU as opposed to 1 part LV to 12 parts PU there is much greater scope for viscosity reduction and hence solids increase. Formulations tend to be very tolerant to these wide ranges of oxazolidine ratios but the tensile properties would be altered. As more low viscosity oxazolidine is formulated into the system, the extensibility increases and the ultimate tensile strength reduces.

Oxazolidines as Drying Agents

Strictly speaking when oxazolidines are used as drying agents their use does not directly contribute to attainment of high solids, but indirectly they do. Urethane/urea prepolymer resins are sensitive to moisture and therefore all pigments, solvents, plasticizers and other additives are usually dried with monomeric isocyanate. The toxic properties of these species means they are being gradually phased out. With high solids systems there is inevitably more moisture present. This is more likely to cause a noticeable viscosity increase and hence there is a greater need to dry all the species present in the system. As a high solids system is generally already heavily loaded with pigments, use of molecular sieves is not a realistic alternative but oxazolidines offer a convenient and more environmentally method of drying. As an added bonus they are often cheaper than other methods.

Usually bisoxazolidines are not used for drying but monomeric bifunctional species are. It has already been pointed out that it is generally better not to use hydroxyethyl oxazolane e.g. Incozol 3 as the OH group present makes this product a three functional species which will produce an almost immediate reaction with any NCO terminated species present increasing the viscosity and lowering the reactivity even though the drying efficiency is excellent. To manufacture a bifunctional species the starting raw materials are chosen from species with only one amine and one hydroxyl functionality and then reacted with an aldehyde or ketone in the usual way. Incozol 2 is an example of such a species and the structure is as shown in (**figure 10**).

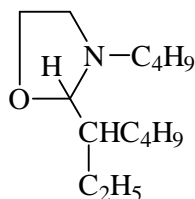


Figure 10 Incozol 2 - an oxazoline drying agent

It has been experimentally determined and reported that the structure of the oxazoline ring and the nature of the side groups and particularly the leaving group affects the drying rate.(7) This is the main reason for the bulky 2 ethyl hexyl species which has been used to ring close. Ketones may also used as leaving groups and their efficiency in drying is excellent(8). Calculation of the amount of drying agent required is by following the manufacturers instructions or by going from first principles. One mole of a mono-oxazoline reacts with one mole of water, so the quantity required is calculated from the molecular weight which can in turn be calculated from the structure but is usually supplied by the manufacturer. In the case of Incozol 2 the molecular weight is 230.

As an example, suppose a formulation contains 1000 Kg of pigments and solvents and the water content is determined to be 500 parts per million by Karl Fischer. There is therefore:

$$1000 \times 500/1000000 \times 1000 = 500\text{g of water present}$$

$$500/18 \times 230 = 6.4 \text{ Kg Incozol 2 drying agent required}$$

To illustrate how the drying efficiency varies with the type of oxazolidine an investigation was conducted using an industry standard polyol and adding various oxazolidines as drying agents with a paratoluene sulphonyl isocyanate drier as a control. After a fixed length of time the water was remeasured and the results compared. The data is presented in table 6.

Table 6 Effect of Oxazolidine structure on drying efficiency for a Polyether Polyol

<u>Side Group</u>	<u>Leaving Group</u>	<u>Initial Water Content</u>	<u>Water Content After 1/2 Hour</u>
methyl	isobutyl	500 ppm	400 ppm
hydroxy ethyl	isobutyl	500 ppm	250 ppm
butyl	2 methyl pentyl	500 ppm	230 ppm
butyl	2 ethyl hexyl	500 ppm	180 ppm
paratoluene sulphonyl isocyanate		500 ppm	450 ppm

A problem of attempting to dry polyols with tosyl isocyanate is the competing reaction between the NCO and the terminal OH groups of the polyol. This does demonstrate though, the advantages of drying polyols with oxazolidines. The best results in this series came from the butyl side chain species with 2 ethyl hexanal as the leaving group. This is the species Incozol 2. Again it is fair to point out that excellent results have been reported with the use of ketones as leaving groups (9).

Oxazolidines as Reactive Diluents in Single Pack Systems

Oxazolidine species without the potential to hydrogen bond are generally of very low viscosity -typically 50 mPa.S (10). Once the heterocyclic ring(s) has opened NH and OH functionalities are present. Both of these features make them attractive propositions for use as reactive diluents. The OH & NH functionalities are effectively blocked when ring closed and unblocked when ring opened. Although the reaction may be catalysed by metal salts, organic acids are particularly effective and often used. To get the best of both worlds formulators sometimes use metal soaps solubilised in fatty acids. The acid is particularly effective at catalysing the ring opening and the metal salt is a good catalyst for the OH/NCO reaction. The NH/NCO reaction is almost instantaneous and does not need catalysing.

A potential problem to bear in mind is that if only two functions are available when the heterocyclic ring is opened, chain extension with the NCO terminated urethane prepolymer will occur rather than crosslinking. This will not be a problem if a very thermoplastic system is required but could be a problem if tough thermosetting properties are needed. There are various ways to formulate round this. One way is to use a multi (i.e greater than 2) functional NCO terminated prepolymer which will give higher crosslink density. Another way to improve thermoset properties would be to use low viscosity oxazolidine species which give more than two functions or indeed to use a blend of oxazolidine resins. . As there are both NH & OH functionalities present the resulting system would be a hybrid polyurethane/urea as the products of the NH/NCO and OH/NCO reaction are a urea and urethane group respectively (**figure 11**).

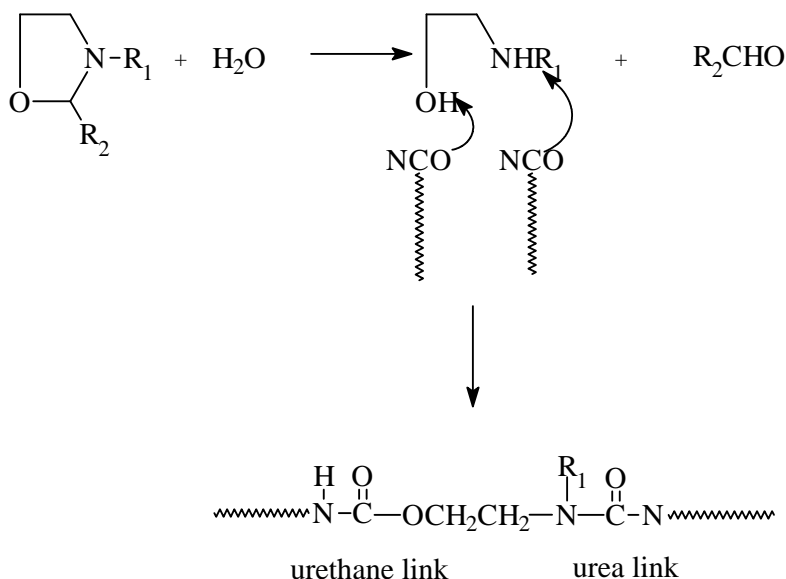


Figure 11 Oxazolidine ring opening followed by NCO/OH/NH reaction to give urethane and urea groups.

Oxazolidines as Reactive Diluents/Polyols in Two-Pack Systems

Feedback from the market indicates that a number of formulators are using oxazolidines in two-pack systems. Although not as convenient as one pack systems, these two pack products give excellent performance. A typical two-pack system of acrylic polyol and trifunctional cross-linker is given in Table 7. This is a brushing

grade so further solvent would be required to give a viscosity suitable for spray application.

Table 7 A typical two-pack Acrylic Polyol/PU lacquer

<u>PART A</u>		<u>Lacquer Properties</u>
	<u>parts by weight</u>	
Acrylic Polyol (400 eq wt)	53.50	Vol Solids 42.06%
Tinuvin 292	0.60	Wt. Solids 45.16%
N-ethyl morpholine	0.20	Gloss = excellent
Butyl acetate	6.50	Persoz Hardness 250
Bannersolve 125**	3.14	Viscosity A=550 mPa.s
10% DBTL in solvent	0.06	B=550 mPa.s
**=trimethyl benzene/xylene blend		Pot life >4 hours
<u>PART B</u>		
Trifunctional cross-linker	17.40	eg Tolonate HDB 75 MX
Butyl acetate	12.60	
Bannersolve 125	6.00	
	<u>100.00</u>	

Thinning solvent Butyl acetate/xylene is added to aid spraying

There is a large amount of solvent in a formulation of this nature and therefore a corresponding scope for solvent reduction by the use of oxazolidines. The drying mechanism in this type of system is by solvent evaporation and coalescence followed by a crosslinking reaction between the OH groups on the polyol in the part A of the formulation and the NCO groups on the trifunctional crosslinker in the part B. If oxazolidines are incorporated into the system there is the additional mechanism of ring opening of the oxazolidine species by atmospheric moisture followed by crosslinking and reaction with the NCO groups. There is no problem in this instance in using an OH terminated oxazolidine to replace solvent in the part A. In the part B a non OH terminated oxazolidine would have to be used to avoid premature reaction with the NCO functionalities. To summarise what is possible refer to table 8.

Table 8 Areas of use for Oxazolidines in Two-pack Systems

Part A Acrylic polyol portion

Part B NCO terminated trifunctional cross-linker

<u>Part A</u>		<u>Part B</u>
Incozol 2	OK	OK
Incozol 3	OK	Not recommended
Incozol LV	OK	OK

The formulation given in table 9 is an example of the sort of solvent reductions that can be achieved by the judicious use of oxazolidines.

Table 9 Two-pack Acrylic/PU Lacquer with oxazolidines replacing some solvent

PART A

	<u>parts by weight%</u>	<u>Lacquer properties</u>
Acrylic Polyol	48.64	Wt solids 63.72%
Tinuvin 292	00.55	Vol solids 61.16%
Incozol 3 (see fig 3)	04.55	Gloss = excellent
10% DBTL in solvent	00.06	Persoz Hardness 250
Butyl acetate	01.94	Viscosity A 650 mPa.s
Bannersolve 125	01.53	B 580 mPa.s
		Pot life>4 hours

PART B

Trifunctional cross-linker	31.64	eg Tolonate HDB 75 MX
Incozol 2	07.27	
Butyl acetate	03.82	

100.00

Thinning solvent added to desired spraying viscosity

Conclusion

There has been much activity in developing the field of oxazolidine technology in the last 20 years in particular. This activity has been further driven by legislation aimed at reducing solvent emissions which can be achieved by increasing solids contents of the various systems. New oxazolidines have appeared on the market to give chemists greater latitude in formulating both high and lower solids systems. Oxazolidines were once thought to be only of real use in one-pack systems but there has and is much research being done on their use in two component systems. Judging by the amount of literature which is being published there is no doubt that oxazolidine technology is very versatile and will continue to help in the trend towards higher solids elastomers, coatings and sealants and other non traditional areas.

References

- 1) US patent 3,743,626
- 2) Ibid. from ref. 1
- 3) GB patent 1,463,944
- 4) Emmons W.D. , Mercurio A. , Lewis S.N. , "High Performance Isocyanate Oxazolidine Coatings," Journal of Coatings Technology, August 1977, Vol. 4, No 631
- 5) Ibid. from ref. 1
- 6) Schall D.C. "High Solids Isocyanate-Oxazolidine Coatings" Proceedings Water-Borne & Higher Solids Coating Systems Symposium 1985 page 120
- 7) Robinson G.N , Alderman J.F. , Johnson T.L. , "New Oxazolidine-Based Moisture Scavenger for Polyurethane Coating Systems," Journal of Coatings Technology, May 1993 Vol. 65, No 820 pages 51-55
- 8) Ibid. from ref. 6
- 9) Ibid. from ref. 6
- 10) Industrial Copolymers Technical Data Sheet for Incozol 2 and 3