Polyurethanes, polyurethane dispersions and polyureas: Past, present and future

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Summaries

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The chemistry of polyurethanes, polyureas, polyurethane dispersions and their reaction partners such as oxazolidines continues to grow judging by the number of patent applications and papers published. The application areas of these products also continues to increase. This paper presents a review of past and current technology including examples of the synthesis of the above species. Hybridisation of these systems is in vogue and this trend will continue. Some chemical synthesis pathways are suggested for the modification of the above-mentioned species to enhance properties. A few predictions are made as to what the future might hold. Fast and slow reacting systems are discussed along with their uses in coating structural steelwork, floors and other substrates.

Les polyuréthanes, les polyuréthanes en dispersion et les polyuréas: hier, aujourd'hui et demain.

La chimie des polyuréthanes, des polyuréthanes en dispersion et de leurs réactifs tels que les oxazolidines va toujours croissant à en juger par le taux des demandes de brevets et des articles publiés. Le cadre d'application de ces prodits continue également à s'accroître. Cet article présente un examen de la technologie du passé et de nos jours et comprend des exemples des synthèses des espèces ci-dessus. L'hybridation de ces systèmes est à la mode et cette tendance va continuer. Des voies de synthèse chimique sont suggérées pour faciliter la modification des espèces ci-dessus afin d'améliorer leurs propriétés. On a fait quelques prévisions en ce qui concerne l'avenir. Des systèmes à réaction vite et à réaction lente sont discutés aussi bien que l'utilisation de ceux-ci dans le cadre du revêtement des tôleries de construction, des planchers et d'autres substrats.

Polyurethane, Polyurethandispersionen und Polyharnstoffe: Die Vergangenheit, Gegenwart und Zukunft

Die Chemie, die mit Polyurethanen, Polyurethandispersionen und Polyharnstoffen und ihren Reaktionspartnern wie Oxazolidinen durchgeführt wird, wächst ständig zu, gemessen an der Anzahl der Patentanträge und der Forschungsarbeiten. Die Anwendungsgebiete dieser Stoffe werden auch stets größer. Diese Arbeit bewertet die Technologien der Vergangenheit und der Gegenwart in diesem Gebiet. Die Hybridisierung der verschiedenen Systeme ist im Moment sehr in Mode, und dieser Trend wird sich weiter fortsetzen. Einige Syntheserouten für die Modifizierung und Verbesserung der obengenannten Stoffe werden vorgeschlagen, und wir machen ein paar Vorhersagen für die Zukunft. Wir beschreiben schnell und langsam reagierende Systeme und ihre Verwendung in Anstrichfarben für Baustahl, Fußböden und andere Substrate.

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Introduction

Polyurethanes (PU) are a very useful class of polymers and exhibit many desirable properties that can be exploited by chemists designing coatings. Examples of the diverse range of applications include their use in clear coatings for glass; as a scrap tyre binder for sports surfaces; as the main binder in anti-corrosive paint topcoats; in aliphatic single-pack roof coatings; as very high quality, light-stable line marking paints; and as encapsulants for weathered asbestos. Many review documents are available.[1] The commercial availability of new isocyanates has also contributed to the continuing growth of the technology of PUs.[1,2] PUs have excellent resistance to chalking, good abrasion and impact resistance, and cure well at low temperatures. Aliphatic PUs are more expensive than aromatic versions and it is thus more usual to see aromatic PUs and epoxies specified for use in primer, base and tie-coats, and aliphatic PUs in topcoats.

There are many examples of using aliphatic PUs as topcoats and other materials as primer/base coats. One example is in anticorrosive coating specifications for structural steelwork where an epoxy system is used as the primer and basecoat.[1,3] Other examples include flooring systems where a variety of basecoats are used. The floor may also be finished by applying a PU topcoat.

Polyurethanes and polyureas for floors

In flooring applications there are many technologies used which are based on two basic types. One is thin film technology where one or more thin coats of paint are applied. The total thickness of the coating would be in the order of 50 to 125 microns. The main features here are to mark out areas of floor; to seal it and thus reduce dust; and for purely aesthetic or decorative reasons. Examples of resin systems used with this type of floor coating include alkyds, water- and solvent-based epoxies or epoxy esters, water-borne polyurethane dispersions and hybrids, and acrylic latex types. The ideal is that these coatings should have good chemical- and water-spotting resistance. Obviously with alkyd coatings, the resistance to caustic alkali will be very poor as the polyester backbone is very prone to saponification even with a urethane modification. The urethane modification is introduced by reacting toluene di-isocyanate with the residual OH groups on the alkyd backbone. The course of the reaction may be followed by analysis of the OH number of the resin, which decreases as the isocyanate reacts.

The other main type of floor coating is thick film technology. Here the coating is typically a minimum of 200 microns and sometimes 10 millimetres or greater in thickness. The functions of the coating in this case are to provide levelling and filling of large defects, and heavy-duty wear. Examples include cement-based coatings and solventless epoxies. The cement and optionally aggregate may be mixed with a variety of resins including epoxies, aromatic polyurethane (here the binder is essentially castor oil and MDI (diphenylmethane-4,4'-di-isocyanate)), and even acrylic or SBR (styrene butadiene) latex. They may be sprayed out with suitable equipment or poured out and then the application assisted with a hand trowel, power trowel or spiked roller. Thick film floor coatings also include unsaturated esters, vinyl esters and 100% solids epoxies. These are poured onto the floor and then the application further assisted with a roller or squeegee blade.

Aromatic PUs based on MDI have been used in large quantities for flooring applications because MDI is a relatively low-cost isocyanate. However, UV radiation is easily absorbed by the molecule and by polymers synthesised from it because it is chromophoric in nature. This gives rise to yellowing. To overcome this problem, their aliphatic counterparts may be used. However, aliphatic PUs are more expensive than aromatic PUs, and cure very slowly as a straight moisture-cure system. The cure-rate is much faster if two-component systems or oxazolidine technology is utilised.[1] Aliphatic PUs have a major advantage in that they only yellow over a long period of time. Examples of aliphatic isocyanates in common usage include isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), TMXDI™ and hydrogenated MDI (H12 MDI). TMXDI™ has two hindered tertiary isocyanate groups in the molecule and is shown in Figure 1.
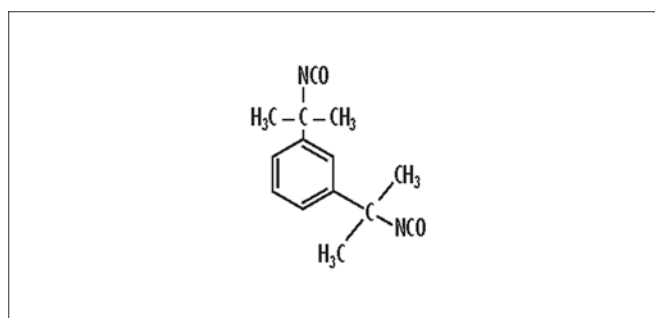

Figure 1: Structure of TMXDI™ isocyanate

It should be noted that although there is an aromatic ring present on the TMXDI™ molecule, its behaviour and reactivity closely resemble aliphatic types because of the shielding effect of the methyl groups. The structure is asymmetrical, the NCO groups are tertiary and very sterically hindered meaning that PUs derived from it are much less reactive and slower in drying than other aliphatic systems. To obtain good drying rates with aliphatic PU, especially those based on TMXDI™, the use of oxazolidine technology is strongly recommended. Another possibility is to utilise TMXDI™ in polyurea technology.

Although TMXDI™ can give advantageous properties, it has a price disadvantage. This is the case in North America as well as in Europe. IPDI, for example, is approximately $3.50 per pound commercially in the USA whereas TMXDI™ is approximately $5.50/lb and that is before the in-built disadvantage of molecular weight is taken into consideration. TMXDI™ has a molecular weight of 244 and that of IPDI is 222, so that on a mole-for-mole basis TMXDI™ is 244/222 x 100 = approximately 110% of the price of IPDI even if the headline costs were the same.

Relative reaction rates for the most reactive NCO group on the di-isocyanate molecule are shown in Table 1. These are approximate values based mainly on the author's experience. Some model kinetic studies have been carried out on most isocyanates by other authors.

Table 1: Relative reaction rates for some common isocyanates

Isocyanate	NCO groups	Relative reaction rate
TMXDI™	2 tertiary	1
H$_{12}$MDI	2 secondary	6
IPDI	1 primary, 1 secondary	7
HDI	2 primary	10
MDI	Aromatic	3000
TDI	Aromatic	4000

Polyurea coatings

Polyurea technology has come to the fore over recent years.[4-6] The main advantage with coatings based on this technology is a very fast cure speed. In fact, even using a polyurea system based on TMXDI™, the slowest reacting of the commonly available isocyanates, the coating will cure in under 20 seconds when sprayed over a block of ice. This may be very useful if a coating is needed, for example, on an oil pipeline in the Artic circle region. The advantages of coating pipelines are well known. They include the reduction of cathodic current required for cathodically-protected pipelines. This is the case whether the cathodic protection is afforded by sacrificial anode or impressed current.[1,3]

The basic chemistry of the polyurea polymer system is the reaction of an amine-functional species with an isocyanate-functional compound to produce a polymer with urea links. This is shown schematically in Figure 2.

In many ways a polyurea is very similar to a two-component polyurethane. The usual procedure when manufacturing a polyurethane coating system is to have a polyol as the 'A' side of a formulation, pigmented as required. The 'B' side, sometimes called the hardener or curing agent, is not an isocyanate monomer but an oligomerised isocyanate. Polyureas are similar. The A side is an oligomerised amine or blend. Various pigments and additives may also be added. The B side is an isocyanate oligomer(s) or quasi-prepolymer. This is manufactured by reacting a large excess of isocyanate with an amine or amine blend, and more usually with an amine-tipped oligomer.

The speed of reaction, as already mentioned, is extremely fast and so most applications utilise specialised spray equipment.[4] When first introduced the isocyanate portion was based on MDI as the monomer. This produced low-cost systems with excellent properties. Later in the early 1990s, aliphatic systems were introduced and researched by a number of companies in the UK and USA.[4,5,7] These systems gave improved light stability, and when TMXDI™ was the monomer, a slight reduction in reaction rate. However, even using TMXDI™ as the isocyanate the systems were so fast that laboratory research was difficult. If a hand mix was attempted, the system became unusable within a few seconds and certainly with insufficient time to cast a film on a QUV' panel. Plural component spraying equipment was required which consumed large quantities of raw material and were in effect a pilot scale batch each time and not a laboratory batch. Even cooling the components down in a freezer gave materials that were very difficult to handle. Sample for-
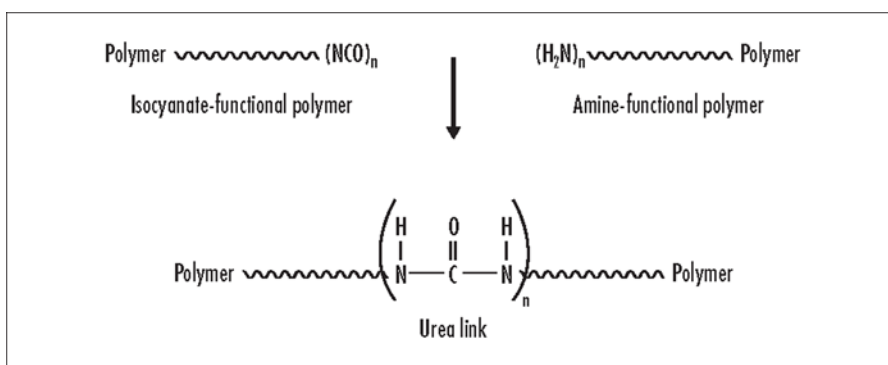

Figure 2: Schematic reaction of polyurea formation

mulations of the sort of systems investigated are shown in Tables 2 and 3

Manufacturing instructions

Disperse the pigment into a portion of the amine and additives to make a mill-base. When the Hegman grind is achieved add the balance of the amine. If organic pigments are used a horizontal bead mill or sand mill should be used instead of a high-speed disperser.

Allow to cool to below 35°C and can off.

Table 3: SPI UREA 001B simple quasi prepolymer formulation

Component	MWt	Moles	Weight
TMXDI™	244	1.47	360.0
Jeffamine™ D-2000	2000	0.32	640.0
Total			1000.0
Viscosity at 25°C	6200 mPas		
NCO	9.20%		
Equivalent weight	457		

Manufacturing instructions

- Run in the amine to the isocyanate slowly over 30 minutes under a nitrogen blanket and with efficient stirring.
- Allow to exotherm, cool to below 35°C and can off.

The B side shown in Table 3 is an unusual formulation. It is more usual to see a formulation with a much higher level of isocyanate and hence lower viscosity. The viscosity is fairly easy to handle with the correct spraying equipment. The system parts are designed to give a 1:1 by volume mix ratio.

Ways were then developed by Wicks et al, to slow polyurea systems down in order to make them easier to handle and to remove the need for plural spray equipment – though it still may be used if desired.[8,9] It requires making the amines secondary rather than primary, sterically hindering them and generally making the molecule more bulky, thus altering the kinetics. This can be achieved by making a poly aspartic ester (PAE) by means of the Michael addition reaction. This reaction is shown schematically in Figure 3. A simple formulation is shown in Table 4.

The hindered amine species has a higher viscosity than the amine. The molecular weight has now been increased considerably. One way to reduce this viscosity and enhance properties is to utilise a low-viscosity oxazolidine. One drawback of this type of system is that they still require isocyanate-functional species. There is a long-term trend in the coatings industry to move to isocyanate-free technology.

Table 2: SPI UREA 001A simple amine A side for polyurea

Ingredient	Weight (g)
Additives (eg Disperse aids)	50
Pigment	80
Jeffamine™ D230	300
Jeffamine™ T403	200
Jeffamine™ D2000	370
Total	1000
Nitrogen equivalent weight	432
Active hydrogen equivalent weight	216
Viscosity mPas (cps) at 25°C	400

Table 4: Polyurea coating based on poly aspartic esters (PAE)

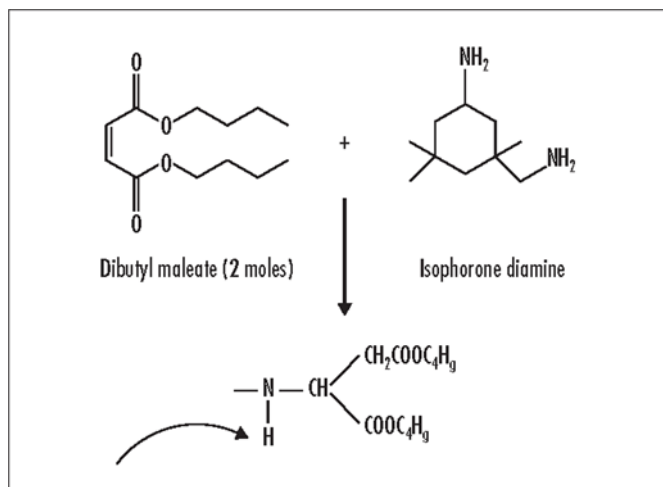| A side	Weight %
PAE 1	54
PAE 2	23
PAE 3	13
Additives	1
Pigment	9
B side	
HDI oligomer	80
Low viscosity oxazolidine	20

Figure 3: Production of a hindered amine as part of a polyurea system

Oxazolidine technology

There has been much written in the last few years about oxazolidine technology including papers, patents and theses for higher degrees.[1,3,10-16] Oxazolidines are a useful species that may be used in both one and two-component PU as moisture scavengers, reactive diluents and latent hardeners to name a few applications. They have also been used successfully with epoxy resins to simultaneously cure and plasticise. They have even been used as chain extenders in polyurethane dispersion technology but no advantages were noticed which would be needed to justify the increased costs.[12] In view of this, it was an obvious step in many ways to use them in combination with polyurea species. This has now been researched with great success. Low-viscosity multi-functional oxazolidines have been commercially available for a number of years now. One such product links two oxazolidine groups with a carbonate bridge. There are other methods of linking the molecules but often the result is more hydrogen bonding which increases the viscosity.[10]

The manufacture of bis-oxazolidines proceeds as follows: an intermediate is first made by reacting diethanolamine and isobutyraldehyde. The materials reach equilibrium with the evolution of much heat. A slight excess of isobutyraldehyde is used and the water is driven off azeotropically to drive the equilibrium forward in line with Le Chetalier's Principle. A hydroxyethyl oxazolidine intermediate is produced (see Figure 4). This may be vacuum distilled if very high purity is required but this increases the crystallisation tendency in a urethane bis-oxazolidine. Low colour is achieved by using a material such as cyclohexane as the azeotroping solvent rather than xylene or toluene. The use of cyclohexane would not be necessary if the material was going to be vacuum distilled, toluene being suitable.
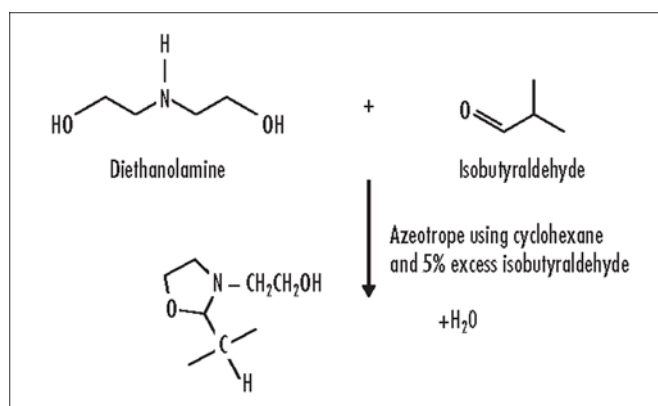

Figure 4: Production of a hydroxyethyl oxazolidine intermediate

This intermediate can now be converted to a urethane bis-oxazolidine or a carbonate-bridged version. If a urethane bis-oxazolidine is required, one mole of HDI is added to about 2.1 moles of the intermediate over a few hours. Efficient reactor cooling is required as the reaction is very exothermic. The reaction is complete when there is no NCO peak on an infrared spectrum of the product. The species is shown in Figure 5 along with the reasons for the higher viscosity encountered than with the lower viscosity version discussed below.

When the intermediate oxazolidine species shown in Figure 4 is linked by HDI to produce a urethane bis-oxazolidine, the resultant viscosity is fairly high, approximately 5000mPas at 25°C. This is because of inter-molecular hydrogen bonding and other electrostatic forces illustrated in Figure 5.[10]
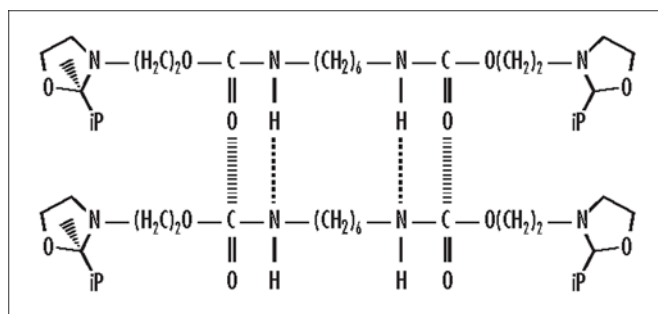

Figure 5: Urethane bis-oxazolidine showing H-bonding and electrostatic forces

A low-viscosity carbonate-bridged version may be manufactured by reacting the intermediate under transesterification conditions using a dialkyl carbonate and a powerful base such as potassium tertiary butoxide (see Figure 6). If dimethyl carbonate is the reactive species, methanol is produced which is distilled along with any excess carbonate. The mole ratios of the dimethyl carbonate and hydroxy ethyl oxazolidine intermediate along with condenser efficiency and a number of theoretical plates, all affect the colour of the final product and its composition. Although a schematic product is shown in Figure 6, in reality there is some mono oxazolidine-terminated species present in commercially available products and also free hydroxy ethyl oxazolidine.

When the level of hydroxy ethyl oxazolidine is high and an efficient reflux condenser used, the colour of the final product will be higher, but the level of mono-terminated species lower. When the level of dimethyl carbonate is high, the level of mono-terminated oxazolidine will also be high, but the colour of the final product is lower. The level of mono-terminated oxazolidine may be important, because when the species is ring-opened, it will only be difunctional and will limit cross-linking,
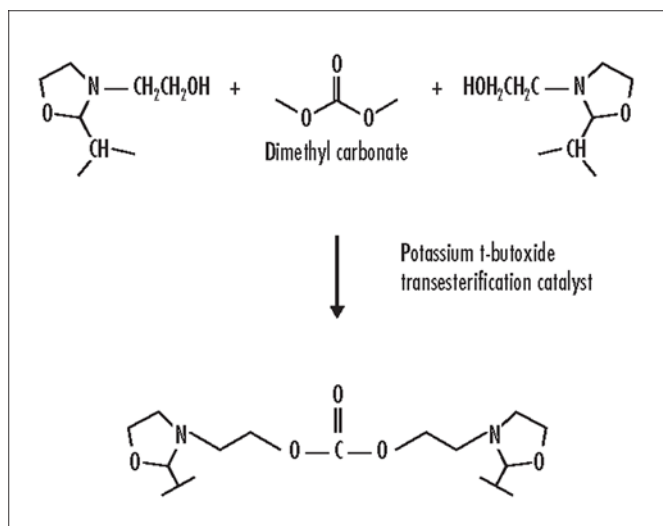
Figure 6: Production of a low-viscosity carbonate-bridged bis-oxazolidine

acting as a chain extender instead. On the other hand, the colour is important especially when used in automotive OEM and refinish coatings.

The production may be monitored by using gas chromatography utilising a 3% OV17 on a chromosorb W-packed column with a thermal conductivity detector. The conditions can be either isothermal at170°C or ramping to 280°C. Alternatively, a 0.53 ID capillary on a RTX-50-phase column may be used with a flame ionisation detector.

The absence of hydrogen bonding in the carbonate-bridged species gives very low viscosities in the region of 50mPas at 25°C. This can be used to great advantage in polyurea systems that have been adducted to make them less reactive but of higher viscosity.

Hybrid systems

A logical step is to utilise oxazolidines with polyurea technology to produce hybrid systems. Sometimes it is useful to have them to balance stoichiometry, so that exactly 1:1 by volume systems may be produced. They also introduce a moisture-activated aspect to the cure which may be desirable in certain instances. Adhesion is often enhanced due to the presence of the OH groups when the oxazolidine rings are open. Tolerance to the NCO:OH/NH ratio is also introduced to this hybrid system (see Table 4).

Water-borne floor coatings

A large floor area painted with a solvent-borne paint system will release a large amount of VOC (volatile organic compound) in to the atmosphere. Flooring applications are thus a big market for solvent-less and water-borne systems. Polyurethane dispersions (PUDs), PUD/acrylic hybrids and blends have already gained a share of the market in Europe. An acrylic emulsion polymer (or more correctly latex) will tend to be of relatively low cost. Acrylic emulsions have thus been viewed for a number of years as almost commodity items. They have found an increasingly large use in decorative coatings, including those for floors, but often lack the required abrasion resistance. PUDs, on the other hand, impart excellent abrasion resistance to a floor coating but are generally more expensive than acrylic emulsion polymers and thus many formulators have investigated ways of reducing costs.

Polyurethane dispersions

The usual method of manufacturing a water-borne PUD is to make an isocyanate-terminated prepolymer and to incorporate carboxylic acid functionality in the backbone with a modifying polyol. This is then dispersed into water with a tertiary amine to produce ionic centres thus stabilising the polymer particle. The species is then chain-extended with a polyamine. There are many good reviews and articles available since the early work by Dieterich.[17-21] Patent applications over the last ten years seem to concentrate on the application. A simple PUD formulation is shown in Table 5.

Table 5: Guide PUD formulation based on a polyester backbone

Ingredient	MWt	Moles	Amount (g)
N-Methyl pyrrolidone (NMP)			120.0
DiMethylol propionic acid (DMPA)	134	0.24	33.5
Polyester polyol	2000	0.26	520.0
Isoporone diisocynate (IPDI)	222.3	1.00	222.3
Triethylamine	101	0.24	24.0
Water/ice			2250.0
Dytek™ A	116	1.00	116.0
Water/ice			120.0
Byk 022 defoamer			1.2
Total			3407.0

The formulation as shown has an NCO/OH ratio of exactly 2:1. To help incorporate the DMPA into other modifiers, this may be lowered. The closer the ratio gets to 1:1 the higher the viscosity and the more difficult it becomes to manufacture. There is also an increased risk of premature gelation with this almost being guaranteed below a ratio of 1.5:1. Also, in the formulation in Table 1, the quantity of triethylamine (TEA) neutralising agent is equimolar with the carboxyl group on the DMPA. This may be increased if desired.

Manufacturing instructions for PUD in Table 5

1 Add the NMP to the reactor which must be scrupulously clean because of the powerful cleaning action of this solvent.
2 Slowly sprinkle in the DMPA with stirring and gentle warming if required.
3 Add the polyol and continue stirring. Keep the temperature below 30°C.
4 Add the isocyanate as quickly as possible to avoid chain-extension and unwanted side reactions. Use vigorous stirring to ensure homogeneity.
5 Warm gently keeping the temperature below 60°C. Add the DBTDL catalyst and hold at this temperature for two hours and then check the NCO value.
6 Add the TEA to water and ice in a separate reactor ensuring the temperature is below a maximum of 7°C and ideally below 5°C.
7 With vigorous stirring add the prepolymer as quickly as possible.
8 Finally, add the chain extender in water/ice in a steady stream for about 10 to 20 seconds maximum. Stir for a further 30 minutes and stand to de-aerate.
9 A small amount of defoamer may be added if required. Drum off via a sieve to remove any polymerisation grit and other extraneous matter.

The reason ice is used with water is to reduce the temperature quickly to slow down the reaction between water and iso-

cyanate groups. The ideal is that the NCO-terminated prepolymer is fully dispersed and neutralised in water and TEA, and the NCO groups react with the amine chain extender. However, it takes a finite amount of time and especially so in a production plant, to disperse the prepolymer in water. Whilst this is taking place the undesirable side reaction between water and isocyanate occurs. This can be minimised by cooling the neutralising mixture to less than 5°C.

Adhesion modifiers

There are many ways to modify the properties and performance of PUDs. This technology is often referred to as hybridisation. PUDs can be manufactured in the presence of other polymers, or indeed be simply blended. The pre-polymer precursor for the PUD may itself be modified before dispersion. The adhesion of the PUD may be enhanced by incorporating an epoxy modification into the pre-polymer precursor backbone. As an example a polypropylene oxide-based diglycidyl ether of molecular weight >700 may be reacted at about 60°C with diethanolamine in a 1:1 molar ratio to give an epoxy-terminated moiety with three OH groups on the molecule. The viscosity would need to be controlled with some NMP co-solvent. This intermediate would then be added to the polyol and DMPA blend before the isocyanate addition (ie between stages three and four in the guide formulation shown in Table 4). The terminal epoxy group does not react appreciably with either the isocyanates or with the polyamine chain extender. This is because the reaction with isocyanate and amine is vastly quicker, especially if the temperature is kept low. The synthesis of the adduct is shown schematically in Figure 7.

The theoretical molecular weight is approximately 900 and a maximum of 0.2 moles is usually sufficient to give considerably enhanced adhesion to a substrate such as concrete and even plastic. For an example, a suitably modified PUD may be used to coat various automotive plastics, and can even be made into a water-based aerosol format.[21] This would obviously need a suitable propellant such as dimethyl ether.

One cost reduction method is simply to blend PUDs with acrylic polymers. A water-based pigmented coating based on a 50:50 blend of a PUD and an acrylic emulsion has already been used on floors in Europe. The system dries to give a white semi-gloss finish suitable for use as a concrete floor coating or decorative finish on a wooden floor where alcohol and/or water resistance are particularly important (see Table 6).
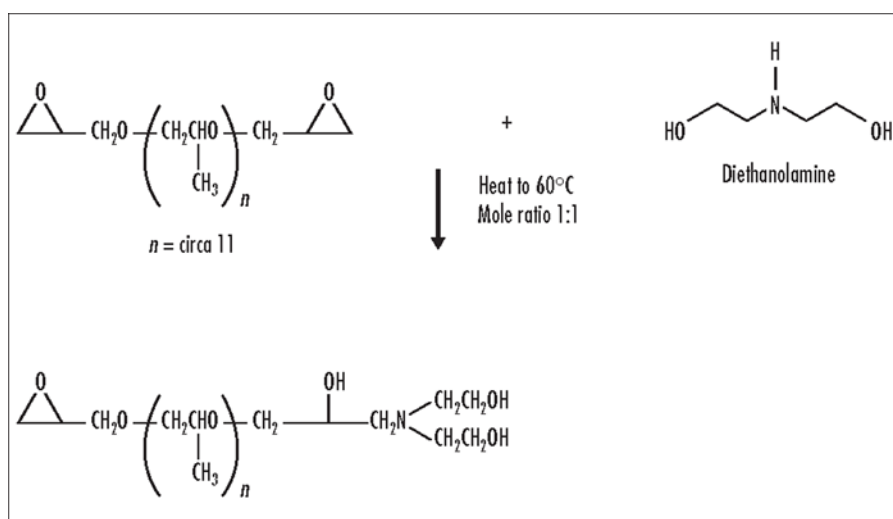
Table 6 PUD/acrylic water-based floor coating and properties22

Floor coating

Ingredient %	Wt
Des W-based PUD	30.00
Acrylic latex emulsion	30.00
Pigment dispersion	38.00
Butyl glycol	2.73
PU thickener	0.26
Bubble breaker	0.01
Total	100.00

Pigment dispersion

Ingredient %	Wt
Water	31.00
Titanium dioxide	68.17
Poly-acrylate dispersant	0.50
Ammonia	0.13
Cellulose thickener	0.10
Preservative	0.10
Total	100.00

Manufacturing procedure

1 Stir the PUD into the acrylic under a high-speed disperser.
2 Add the pigment dispersion slowly.
3 Increase speed then add half the thickener dispersed in the glycol; stir for five minutes.
4 Reduce speed and add remainder of thickener.
5 Stir for two minutes then fill off. Use a bubble breaker if necessary.

Paint properties		Film properties
Viscosity (25°C)	4500 mPas	After 7 days at room temperature
% solids w/w	51.5%	Hardness (Persoz) ca 170
PVC	23.5%	Gloss (60°) ca 70
SG	1.29	Touch dry <30 minutes
		Taber abrasion CS17 500 cycles
		25mg loss

One key advantage with water-borne polyurethane dispersions is that they are fully reacted systems and hence do not contain isocyanate. In the long-term, as the coatings industry moves towards isocyanate-free systems, this will be an advantage. Two-component PUDs are a different matter.

Cement-based systems

Due to the expiration of a key patent,[23] research is now being undertaken in a number of companies to utilise and improve on polyurethane-modified cements for flooring applications. A simple urethane cement-based slurry system might consist of the following (see Table 7):

Typical properties of this formulation would include low carbon dioxide gassing, good leveling and a working time of about 30 minutes. All three ingredients affect the properties of the polymer-modified cement-based floor

Figure 7: Synthesis of an epoxy-terminated polyol for PUD modification

Table 7: Polyurethane cement slurry system

Ingredient	Quantity	Ref
Castor oil emulsion	1 volume	Table 8
Polymeric MDI	1 volume	
Cement/aggregate	3 volumes	Table 9

Table 8: Polyurethane cement slurry system – castor oil emulsion

Ingredient	Weight %
Castor oil	50
Water	20
Surfactant	5
Plasticiser	25

Table 9: Polyurethane cement slurry system – cement/aggregate

Ingredient	Weight %
Mixed graded aggregate	78
Ordinary Portland Cement	15
Lime	7

coating. A simple formulation for the castor oil emulsion is shown in Table 8, and for the cement-aggregate combination in Table 9.

The system works by the water reacting with the cement in the normal way,[24] but in addition water reacts with the MDI producing a urea matrix and CO2 gas. The MDI reacts with the hydroxyl groups on the castor oil which is the triglyceride of a hydroxy fatty acid. A complex polymer cement matrix is produced which is hard-wearing and may be overcoated with other liquid-applied coatings. The lime, as well as controlling hydration and setting rate of the cement, also helps to absorb some of the carbon dioxide gas from the MDI/water reaction.

$$CaO + CO_2 \longrightarrow CaCO_3$$

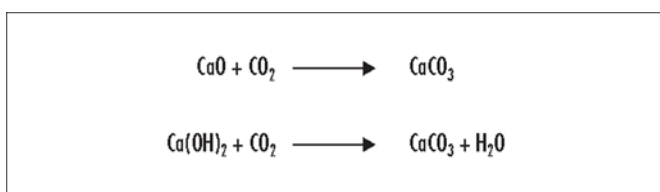$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Figure 8: Lime absorbing carbon dioxide by reaction

An innovative technology is to use cement as part of the pigmentation system in a coating. The binder is a proprietary resin mixture and the pigment is cement enhanced with fibres to improve the flexibility and, in particular, to control the crack propagation properties and hence to ultimately improve the tensile strength. Cementitious substances, like most ceramic materials, are weak in tension and strong in compression. Controlling the crack propagation properties by the addition of fibres or polymers improves this feature. When cement hydrates, the complex silicates hydrate and produce large quantities of OH-ions resulting in a large increase in pH. If this type of coating is used to protect steel, the alkaline environment prevents the steel from corroding in the same way rebars are protected in steel reinforced concrete.[25] This type of coating may even be brushed onto a vertical surface such as an oil pipeline. The result is a relatively low-cost anticorrosion system that is very tough and hard-wearing.

Conclusion

The use of PUs, polyureas, polyurethane dispersions and their reaction partners continues to grow. In particular they are popular in floor coatings. Legislation and other forces are driving the technology to no-solvent, high solids and water-borne systems. Long term, there will be a move towards isocyanate-free systems. This of course taxes the ingenuity of the formulators and in particular the designers of the resins and polymers. There is also a renewed interest in polymer-modified cementitious systems for floors and steel protection. New systems have come on the market and old patents have expired. This will renew the vigour of research in these areas resulting in advantages for the end-users. The future is bright for this class of polymer and type of coating.

Trade names

TMXDI™ is a trade name of Cytec

Jeffamine™ is a trade name of Huntsman

Dytek™ is a trade name of Du Pont

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