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RESINS FOR SURFACE COATINGS

Volume III (Second Edition)

Polyurethanes
Polyamides
Phenolplasts
Aminoplasts
Maleic Resins

By

PKT Oldring
N Tuck

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VOLUME III

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CHAPTER I

POLYISOCYANATE CROSSLINKERS AND POLYURETHANE RESINS USED IN SURFACE COATINGS

POLYISOCYANATE CROSSLINKERS AND POLYURETHANE RESINS USED IN SURFACE COATINGS

1. Introduction

Polyurethane resins are reaction products of a polyisocyanate (materials containing more than one – N = C = O group) with at least one other species containing an active hydrogen, often a polyol (materials containing more than one – OH group). They are normally of relatively high molecular weights. Polyurethane resins can be prepared and used as a major binder in coating formulations or polyisocyanates can act as a crosslinking agent in their own right, thereby forming a polyurethane after cure. There is a very wide range of materials which can be used to form polyurethanes. Consequently, a very wide range of properties is possible. Polyurethane chemistry has essentially been commercially available only since the 1930s. Over the last 40 years or so, there have been many developments and polyurethanes are now used in foams, elastomers and coatings. Originally, polyurethanes were developed for foams and plastics. In practice, they have only been used in coatings since the 1950s. They are or have been used in[1]:

- Industrial wood and furniture finishing
- Plastics coating
- Original automotive finishing (OEM)
- Large-vehicle finishing and automotive repair
- Industrial coatings — air and force drying
- Industrial coatings — stoving
- Corrosion protection (civil and water engineering) — heavy duty
- Decorative coatings (trade and DIY)
- Coatings for mineral substrates, such as concrete
- Sealants, sealers and casting compounds
- Paper and foil finishing
- Printing inks

Table 1-1a contains an overview of some surface coating applications by substrate type of polyurethane and polyisocyanate crosslinked coatings.

TABLE 1-1a: EXAMPLES OF APPLICATIONS OF POLYISOCYANATE-BASED (AND POLYURETHANE-BASED) SYSTEMS

Substrate	Application	Coating type
Wood	Flooring, plank and cork, gymnasium and industrial floors, decks, windows, industrial fittings, frames, fittings	Wood stains, primers and varnishes, primers and finishes for apartments, semi-gloss and high gloss
Plastic	PVC — floors, moulded items, table coatings, credit cards, automobile interiors, airbag coverings, household electrical goods and computers, soft feel	Adhesives, coatings, migration resistant, adhesives for laminates, binder for metal particles, abrasion resistant
Aluminium	Packaging, aircraft coatings, facade sections	Decorative lacquers, protection against chemical agents, fuel, skydrol
Other metals	Automobile interiors, coil coating, application maintenance, interior of houses	Anticorrosion primers, metallic base coat, temporary protection, polishes
Masonry	Indoor floor varnishes, garages, terraces, foundations, walls, wires	Sealing coats, fuel and oil-resistant, abrasion-resistant, low temperature flexibility, anti-graffiti
Paper	Paper sizing, cardboard, paper to particle board	Improves application of ink, coatings and adhesives

Substrate	Application	Coating Type
Textile	Synthetic leather, improvement of weather resistance, antifray, nonwoven and woven fabrics	Microporous coatings, fibre and fabric sizes, fabric handle modifiers, pigment print binders
Leather	Shoes, clothing, bags, accessories, chairs and car fittings	Pigmented or clear bases, finishes and intermediates
Glass	Glass fibre reinforced plastics, glass tubes and bottles	Fibre sizing, shatter-resistant coating
Ink/varninsh	Printed texts and images, printing inks	Resins for high-gloss protective film

This chapter is an overview of the use of polyurethanes and polyisocyanates in coatings. For more detailed information, consult *Waterborne and Solvent Based Surface Coating Resins and their Applications*[(2)]. For coating applications, polyisocyanates are used in two different ways, namely:

1) As difunctional or trifunctional base monomers (alone or otherwise) for the production of polymers, in particular polyurethanes, polyureas, polyimides and polyhydantoins.
2) As chemical crosslinking agents for linear or branched polymers having a functionality of at least two groups which can react with the isocyanate functionality. Crosslinking is the final transformation, which gives the coating its mechanical characteristics (tensile strength, resistance to chemical reagents, to wear and to ageing).

The term polyurethane is nowadays widely used and sometimes arguably incorrectly, in the opinion of the author. Once a polyisocyanate is used to modify a product or a resin, the term polyurethane is often used to designate the final product obtained, even if this only contains urea or allophanate groups. For example, it is arguable whether alkyd resins modified with a diisocyanate can be considered as polyurethane resins, rather than as urethane-modified alkyd resins.

Note: Coating technologists often refer to materials in a loose generic sense rather than a strict scientific sense and provided everyone understands what is meant, it will be difficult to change this practice.

The ASTM (American Standards for Test Methods) D16 norm has 6 classifications of polyurethane coatings, which are shown in Table 1-1b.

TABLE 1-1b: CLASSIFICATION OF POLYURETHANES

ASTM-D16 Classification	Category	Curing process
1	Oil-modified urethanes	Oxidation of double bonds
2	Moisture-cure urethanes	Reaction with moisture
3	Blocked urethanes	Thermal unblocking
4	Prepolymer plus catalyst	Reaction with moisture
5	2 pack urethanes	NCO + OH reaction
6	Urethane lacquers	Physical drying

However, when viewed from a purely chemical rather than a coating viewpoint, this is not necessarily the most logical or useful classification. An alternative classification[(2)] which covers all types of polyurethanes encountered in coatings is:

- 2 component polyurethanes (2K PUs) — polyisocyanate to crosslink other components with active hydrogens
- 1 component polyurethanes (1K PUs) — normally a blocked polyisocyanate
- 1 component moisture cured polyurethanes — residual isocyanate groups react with moisture in the atmosphere
- Non-NCO containing polyurethanes — normally thermoplastic

It should be noted that as polyurethanes are generally more expensive than many alternative systems and because they impart many desirable properties, it is not unusual for companies to promote urethane-modified resins or coatings, even when the actual amount of urethane in the resin or coating is minimal.

In addition to the above classification, radiation-curable (UV and EB) materials based on urethane acrylates are available. Polyisocyanates are normally reacted with hydroxy functional acrylic monomers and other saturated polyhydroxy materials, either a polyol or low molecular weight polyester resin, with a large hydroxyl excess. The resulting resin, containing acrylic unsaturation, is then diluted in the radiation-curable monomers, such as TPGDA (tripropylene glycol diacrylate). Additives etc. would then be added to form a coating and pigments for inks. For a UV-curable system, a photoinitiator package (photoinitiator and synergist(s)) would be added. Cure is achieved through free radical polymerisation of the acrylate unsaturation. The resulting urethane containing films are tough and durable. It is not the intention of this book to discuss radiation curable materials. Consult Oldring[(3,4)] for further details.

Urethanes are esters of carbamic acid ($NH_2 - COOH$), or rather of substituted carbamic acids of the general formula RNHCOOH. Hence they are prepared by reaction of an alcohol with an isocyanate, with an example being shown in Figure 1-1a

$$C_6H_5 - NCO + C_6H_5 - OH \rightarrow C_6H_5 - NH - CO - O - C_6H_5$$
$$\text{phenyl isocyanate + alcohol} \rightarrow \text{phenylurethane}$$

Figure 1-1a: Preparation of a polyurethane from a isocyanate and an alcohol

The formation of the polyurethanes is classified as a polycondensation reaction, although there is no liberation of by-products. In the view of many people, it has long been regarded as a polyaddition reaction.

For an effective crosslinked network, it is essential that the isocyanate has as a minimum two NCO groups per molecule and the polymer being crosslinked has at least two groups per molecule which will react with an NCO group. Isocyanates with more than one NCO group are often referred to as polyisocyanates. Under certain conditions it is possible for NCO groups to react further, resulting in a higher than theoretical crosslink density.

The urethane functional groups can develop a strong dipole moment, which in the case of polymers with a high degree of symmetry will result in excellent mechanical characteristics accompanied by marked resistance to solvents and chemical agents. The formation of lateral electrostatic forces, which are due to hydrogen bonds between the CO groups of one chain and the NH groups situated on an adjacent chain, should also be noted. Particular use is made of this property in thixotropic (antidrip) resins, and thixotropic agents are also called SCA (sagging control agents).

i) History of synthesis of isocyanates

Isocyanate chemistry is about 150 years old. In 1849, Wurtz, for the first time, synthesized an aliphatic isocyanate (Equation 1.1)

$$R_2SO_4 + 2KCN \rightarrow 2RCNO + K_2SO_4 \quad \textbf{(Equation 1.1)}$$

Furthermore, in studying these compounds, a certain number of reactions which are of industrial importance today (Equation 1.2 and Equation 1.3) were observed.

$$Et - NCO + HO - Et \rightarrow Et - NH - CO - O - Et \qquad \textbf{(Equation 1.2)}$$

where $Et = C_2H_5$

$$Et - NCO + H - N(Et)_2 \rightarrow Et - NH - CO - N(Et)_2 \qquad \textbf{(Equation 1.3)}$$

In 1850, Hoffmann prepared the first aromatic isocyanate, phenyl isocyanate, by the pyrolysis of diphenyl oxamide (Equation 1.4).

$$(C_6H_5 - NH - CO -)_2 \rightarrow 2C_6H_5NCO + H_2 \qquad \textbf{(Equation 1.4)}$$

In 1884, Hentschell developed a synthesis which is still used today (Equation 1.5). This is essentially the reaction of phosgene with aryl amines.

$$R - NH_2 + COCl_2 \rightarrow RNHCOCl \rightarrow RNCO + 2HCl \qquad \textbf{(Equation 1.5)}$$

In 1937, Carothers and his team successfully studied the superpolyamides. These encouraging results prompted the company I G Farbenindustrie to study systems which were similar, but not protected by the Du Pont De Nemours patents.

O. Bayer discovered polyaddition, which allowed the synthesis of polyurethanes and polyureas, which led to fibres (Perlon U) and to plastics (Irgamid U).

During the 1939 – 1945 war, the IG Farbenfabriken subsidiary of Bayer was directed to develop this chemistry with important applications in plastics, adhesives and coatings.

In 1938, Linke patented a linear polyurethane in the USA. It was at this point that work on the isocyanates began in the USA.

In 1942, Du Pont introduced an isocyanate into alkyd resins to improve their curing — drying and resistance characteristics.

In 1945 – 1947, after the end of the war, teams began to publish the work done by the Germans during the war in the form of reports. The Americans became very interested in this wo especially the US Air Force.