

RESINS FOR SURFACE COATINGS

VOLUME III
Polyurethanes
Polyamides
Phenoplasts
Aminoplasts
Maleic Resins



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**Volume III
(Second Edition)**

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Maleic Resins**

TABLE OF CONTENTS

CHAPTER I

POLYISOCYANATE CROSSLINKERS AND POLYURETHANE

RESINS USED IN SURFACE COATINGS	1
1. Introduction	3
i) History of synthesis of isocyanates	7
2. Principal Diisocyanate Monomers for Surface Coatings	9
i) Principles of manufacture of diisocyanates	14
ii) Aromatic diisocyanates	19
iii) Aliphatic diisocyanates	21
iv) Summary of commercially available diisocyanate monomers	25
3. Principal Reactions of the Isocyanate Group	27
i) Nucleophilic addition reactions with compounds of the type H – X	29
ii) Self-polymerisation	36
iii) Other reactions	37
4. Modified Polyisocyanates	37
i) Polyol adducts	37
ii) Biurets	39
iii) Oligomers	41
5. Blocked Polyisocyanates	44
i) Nature of blocking agent on dissociation temperature of blocked isocyanate	48
ii) Structure of isocyanate on dissociation temperature of blocked isocyanate	51
iii) Influence of presence of nucleophile on dissociation temperature of blocked isocyanate	53
iv) Influence of catalysts on dissociation temperature of blocked isocyanate	53
6. Materials Used for Reaction with Polyisocyanates	55
i) Polyesters	55
ii) Polyethers	56
iii) Hydroxylated polyacrylates	57
iv) Various resins	62

7. Aqueous Dispersions of Polyurethanes	64
8. Chemistry of the Different Systems	71
i) General remarks and classification	71
ii) Two-component systems	74
iii) One-component systems for moisture cure, physical drying and stoving	79
9. Examples of Formulations	85
ii) Automobile industry	95
iii) Plastic materials	108
iv) Construction and public works	122
v) Miscellaneous applications	126

CHAPTER II

POLYAMIDES 131

1. Introduction	133
2. Raw Materials	134
i) Dimer acid	134
ii) Di functional acids (excluding dimer)	135
iii) Mono-functional acids	137
iv) Amines	139
3. Preparation of Polyamides	140
i) Preparation of reactive polyamides	140
ii) Preparation of polyamino amides	143
iii) Non-reactive polyamides	143
4. Polyamine, Fatty Acid Based Curing Agents for Epoxy Resins	144
i) The epoxy amine reaction	145
ii) Selection of type of amine epoxy curing agent	146
Reactive Polyamides	150
ii) Poly amino amide epoxy curing agents	156
iii) Imidazolines formation in polyamides or poly amino amides	157
iv) Waterborne systems	160
5. Principles of Formulating Solvent-Based Epoxy Polyamide Coatings	161
i) How much polyamide resin to use	161
ii) Effect of temperature on rate of cure	168
iii) Accelerators and catalysts	170
iv) Pot-life	171
v) Solvent	173
vi) Reactive dilutents	176
vii) Pigment selection	176

6. Principles of Formulating Waterborne Polyamide Epoxy Coatings	177
i) General principles	177
ii) Pot-life and film formation	182
7. Non-Reactive Polyamides	184
i) Polyamides for thixotropic alkyds	184
8. Formulations	186
i) Solvent-borne coatings	186
ii) Solvent free coatings	193
iii) Waterborne coatings	194
iv) Raw material suppliers	196
9. Commercial Sources of Polyamide and Poly Aminoamide Resins	197

CHAPTER III

PHENOLPLASTS 199

1. Introduction	201
2. Raw Materials	203
i) Phenol	204
ii) Substituted phenols	204
iii) Aldehydes	207
3. Types of Phenolic Resin and Their Manufacture	208
i) Resole resins	208
ii) Novolac resins	216
4. Modifications of Phenolic Resins to Enable Their Use in Coatings	219
i) Modification with rosin	222
5. Crosslinking by Phenolplasts	224
i) Hardening reactions of epoxy-phenol (resoles/novolacs) systems	224
i) Catalysis of the epoxy-resole, novolac respectively reaction	228
ii) Structure-property relationship of epoxy-phenolic systems	228
6. Waterborne Phenolic Systems: Dispersions	230
7. Formulating Coatings with Phenolic Resins	231
ii) Corrosion protection — anti-corrosive coatings	231
ii) Coatings for metal packaging	238
Cold rolled steel (CRS) substrates	238
8. Suppliers of Phenolic Resins	255
i) Suppliers of phenolic resins	255
ii) Types of phenolic resins	256

CHAPTER IV

AMINOPLASTS 261

1. Introduction	263
2. Raw Materials	268
3. The Synthesis of Amino Crosslinking Agents	269
4. The Significance of Alkylation and Degree of Alkylation	272
i) Highly alkylated amino crosslinking agents	274
ii) Partially alkylated formaldehyde crosslinking agents	276
iii) High imino formaldehyde crosslinking agents	277
iv) Partially alkylated and high imino content aminoplasts	279
v) Affect of the nature of the alkylation alcohol	279
5. Significance of Degree of Polymerisation	283
6. The Chemistry of Aminoplast Crosslinking Reactions	285
i) Specific acid catalysis mechanisms	288
ii) General acid catalysis mechanism	292
iii) Self-condensation reactions	295
iii) Reversible and irreversible reactions during curing	300
v) Hydrolysis reactions	303
vi) Reactions of functional groups of the backbone resin and aminoplast	305
vii) Aminoplast considerations	308
viii) Catalysts	310
7. Commercially Available Aminoplasts	319
i) Urea formaldehyde crosslinking agents	320
ii) Melamine formaldehyde crosslinking agents	323
iii) Benzoguanamine formaldehyde crosslinking agents	330
iv) Glycoluril formaldehyde crosslinking agents	333
v) List of some commercially available aminoplasts	337
8. Principles of Formulating Coatings with Aminoplasts	353
i) Level and type of aminoplast	353
ii) Nature of backbone resin	360
iii) High solids coatings	362
iv) Backbone and aminoplast considerations for high solids coatings	363
9. Formulations and Applications	368
i) Lacquers	368

CHAPTER V**MALEIC RESINS 377**

1. Introduction 379
 - i) Uses 380
 - ii) Worldwide demand 381
 - iii) Reaction 381
 - iv) Catalysts 382
2. Use of Maleic Anhydride in Unsaturated Polyesters 384
3. Maleic Anhydride in Alkyds 385
4. Maleinised Rosins 390

INDEX 395

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, antifrayer, 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/varnish	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 ($\text{NH}_2 - \text{COOH}$), 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

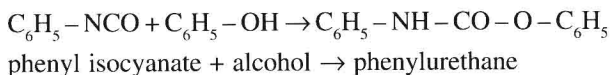


Figure 1-1a: Preparation of a polyurethane from a isocyanate and an alcohol

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

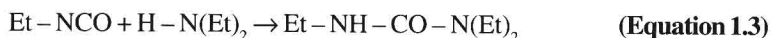
Isocyanate chemistry is about 150 years old. In 1849, Wurtz, for the first time, synthesized an aliphatic isocyanate (Equation 1.1)



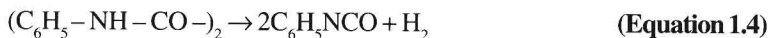
Furthermore, in studying these compounds, a certain number of reactions which are of industrial importance today (Equation 1.2 and Equation 1.3) were observed.



where $\text{Et} = \text{C}_2\text{H}_5$



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



In 1937, Carothers and his team successfully studied the superpolyamides. These encouraging results prompted the company IG 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 work especially the US Air Force.