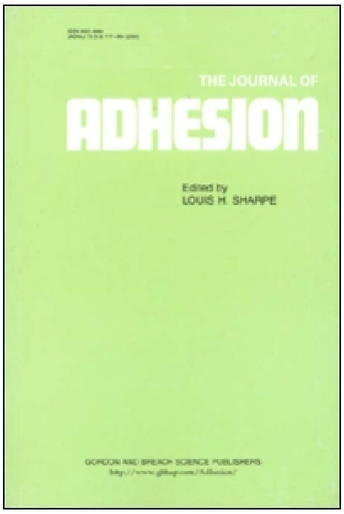

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Isocyanates as Wood Binders—A Review

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Isocyanates as Wood Binders— A Review

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The chemistry of isocyanate reactions is reviewed. Theories on the mechanisms for reactions with wood are developed. The reactions of isocyanates with various reactive sites on wood are offered as the most probable explanation for the excellent bonding efficiency of isocyanates in particleboard. Experimental evidence is cited which suggests that the formation of polyurea compounds provides the necessary link between urethane-to-wood anchored MDI molecules.

INTRODUCTION

Isocyanates are a relatively new type of wood binder which has demonstrated a fascinating capability for bonding wood. Particleboards can be manufactured which demonstrate excellent board properties and hydrolytic stability at resin levels far below those required for similar properties using urea-formaldehyde (UF) or phenolformaldehyde (PF) resins. Relatively little is known about the nature of the chemical and physical reactions which lead to the bonding of wood.

It is the intention of this report to review the chemistry of isocyanates and to consider the possible reactions that ultimately yield a particleboard.

CHEMICAL CONSIDERATIONS

Isocyanates, characterized by the —N=C=O group, are by themselves not that new, having first been made by Wurtz in 1849, as noted by Sayigh *et al.*[1]

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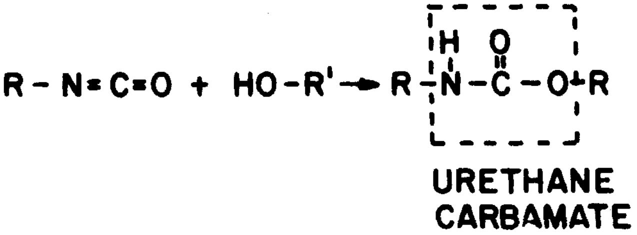
They remained a laboratory curiosity until 1937 when Bayer synthesized the first urethane. Since World War II, isocyanate/polyurethanes have enjoyed a remarkable growth. Today, many foams, both flexible and rigid, coatings, polymeric castings, and adhesives are based on isocyanate chemistry.

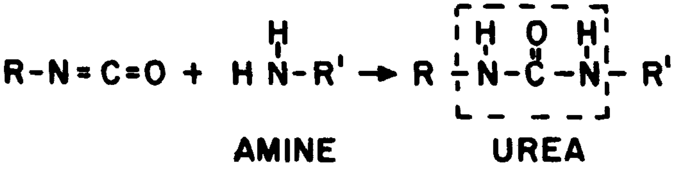
The —N=C=O group is capable of reacting with almost any active hydrogen under either acid or, preferably, alkaline conditions. The most commonly utilized reaction of isocyanate chemistry is with a hydroxyl group to yield a urethane.



$$R-N{=}C{=}O + HO-R' \rightarrow R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R$$

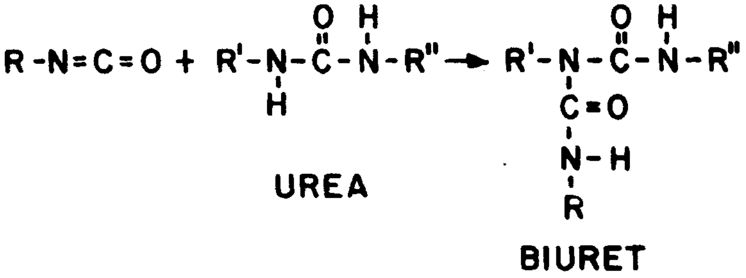
The urethane structure, also called a carbamate, is fundamental to many polymers utilizing isocyanates. Polymeric substances are formed when a difunctional isocyanate reacts with a difunctional alcohol.

Amines react with isocyanates to yield the familiar chemical structure of a urea.



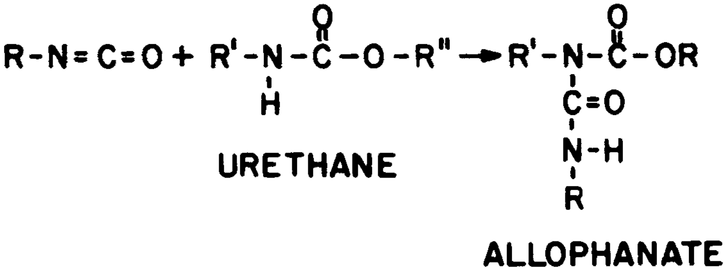
$$R-N{=}C{=}O + H\,\overset{H}{\overset{|}{N}}-R' \rightarrow R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R'$$

When the isocyanate group acts with a urea, a biuret group is formed.



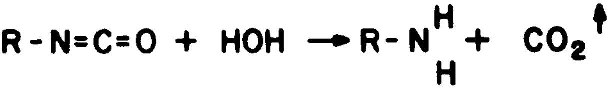
$$R-N{=}C{=}O + R'-\underset{\overset{|}{H}}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R'' \rightarrow R'-\underset{\substack{|\\ C{=}O\\ |\\ N-H\\ |\\ R}}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R''$$

Isocyanates can react with urethanes to yield an allophanate.



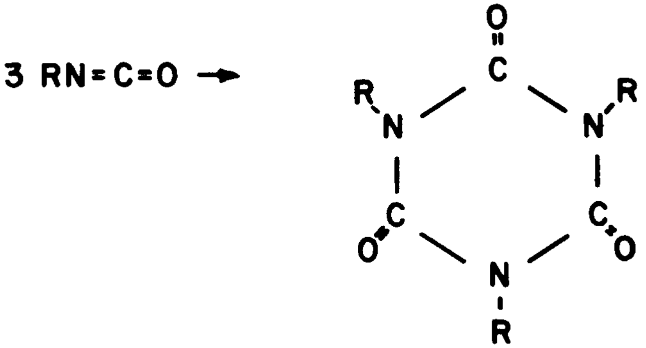
$$R-N=C=O + R'-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R'' \rightarrow R'-\underset{\underset{\underset{R}{|}}{\underset{N-H}{|}}}{\underset{C=O}{|}}{N}-\overset{O}{\overset{\|}{C}}-OR$$

Isocyanates react very readily with water to form primary amines and carbon dioxide.



$$R-N=C=O + HOH \rightarrow R-N\overset{H}{\underset{H}{}} + CO_2\uparrow$$

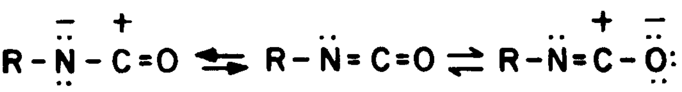
This is important because the amine itself is quite reactive with isocyanate and ureas, as shown earlier. Finally, isocyanates react with isocyanates to form various cyclic structures.



ISOCYANURATE

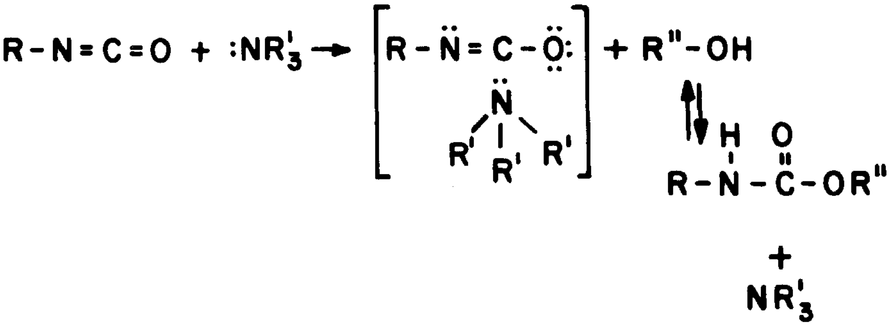
The reactions of isocyanates are strongly influenced by catalysts and temperature. The subject of catalysts in isocyanate reactions has been reviewed by Saunders and Frisch[2] and more recently by Sayigh, Ulrich, and Farrissey.[1]

The isocyanate group can resonate as follows:



$$R-\overset{-}{\ddot{\underset{..}{N}}}-\overset{+}{C}=O \rightleftarrows R-\ddot{N}=C=O \rightleftarrows R-\ddot{N}=\overset{+}{C}-\overset{-}{\ddot{\underset{..}{O}}}:$$

This resonance predisposes the carbon to electron donors and the oxygen or nitrogen to electron acceptors. A tertiary amine is thought to act as a catalyst as in the following scheme:[2]



In general the reaction is thought to follow the sequence:

$$\mathrm{R\text{-}N{=}C{=}O} + \text{CATALYST} \longrightarrow$$

$$\text{COMPLEX} \xrightarrow[\text{COMPOUND}]{\text{ACTIVE H}} \text{PRODUCT} + \text{CATALYST}$$

Catalysts can include most base metal complexes, including the organic compounds of tin, titanium, cobalt, and lead.

In a review of the influence of isocyanate reaction at elevated temperatures, Saunders[3] noted that many reactions which are normally of consequence at room temperature can become dominant at higher temperature. He specifically pointed out the increased potential for reaction between isocyanate and isocyanate derivatives such as urethane and ureas. Also of importance are the homopolymerization reactions of isocyanates, which lead to the formation of cyclic dimers and trimers. Here the formation of the trimer (isocyanurate) is important because of its excellent thermal stability relative to the dimer. The order of decreasing thermal stability of isocyanate reaction products as reported by Fabris[4] is:

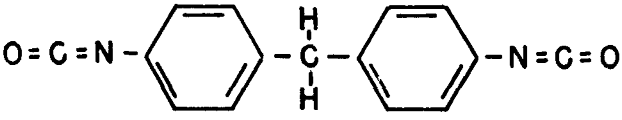
isocyanurate > urea > urethane > biuret > allophanate

Isocyanurates are stable at temperatures in excess of 250°C, whereas biurets and allophanates decompose at temperatures as low as 100°C.

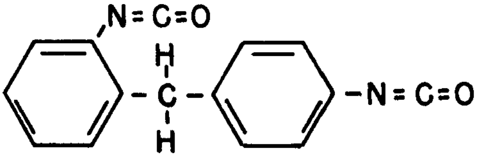
WOOD BONDING CONSIDERATIONS

Isocyanates have been used for wood bonding in two ways: first, as an isocyanate currently being used in the particleboard industry, and second, as the new generation of isocyanate-polyol reaction products or urethane prepolymers which are finding increased use as laminating resins. The following discussion will be limited to particleboard isocyanates rather than to the polyol/isocyanate type urethane technology, for which several reviews are available.[5–7]

The type of diisocyanate normally used for particleboard manufacture is 4-4′-diphenylmethane diisocyanate, or MDI. MDI was recognized early as the preferred type of diisocyanate for particleboard manufacture. It has a very low vapor pressure at room temperature, has a viscosity range which in the low molecular weight ranges is consistent with the needs of the particleboard industry, and as diisocyanates go, it is relatively inexpensive. MDI is made in two general isomeric forms.



4,4' MDI, PARA-PARA



2,4' MDI, ORTHO-PARA

The reactivity of 4-4′-MDI is much higher than other forms, and this has led to manufacturing procedures to maximize this particular form. Typically, a crude MDI will be in excess of 90% in this form.

In addition to diphenylmethane diisocyanate (often referred to as a dimer), a typical binder as supplied by a manufacturer will also include a fraction of higher molecular weight materials. Oligomeric fractions up to a DP of 6 will normally account for approximately one-half of the total mass of a volume of diisocyanate. Thus, as supplied, the binder will consist of approximately 40% 4-4′-diphenylethane diisocyanate, with the other 60% comprised of isomeric forms of the dimer and higher molecular weights.

Whether or not MDI bonds wood is not a question. In reviewing the history of isocyanates used as adhesives, Ball and Redman[8] have cited references dating to 1951, which show that isocyanates are effective binders. Work by Deppe and Ernst[9] helped to demonstrate the possibilities of this new resin for particleboard manufacture. Since then, there have been many workers identifying and characterizing the uses of MDI in particleboard manufacture. The question, then, is how does it work?

In an attempt to identify a model for the chemical nature of the bonds formed, one must account for the characteristics of isocyanates in particleboard. Isocyanates are fast, have good water resistance, and can be used at very low levels of application. Further, it is possible to make boards at furnish moisture contents much higher than is possible with UF or PF resins, with 20–25% often being given as an upper limit. An outstanding characteristic is that isocyanates will adhere to virtually everything. A final factor to consider is assembly time. Isocyanates are somewhat more sensitive to extended assembly time than the PF resins.

Another important characteristic of isocyanate is its ability to react with hydroxyl groups to form the urethane structure. One of the first models to help explain the excellent properties of isocyanate boards at the very low resin levels was a direct covalent bond with cellulose and lignin hydroxyls.[10]

There are a large number of inferences that this, in fact, happens. Recently, Rowell and Ellis[11] have modified wood with methyl isocyanate, and the efficiency of treatment was measured by weight percent gain (WPG) on oven-dried wood. Many of the properties of wood were changed with increases in WPG. Hartman[12] discussed the manufacture of polyurethane foam using bark and isocyanate.

A covalent bond has a bond energy in the range of 70–100 kcal per mole while a secondary bond, the type most normally associated with adhesion, is in the range of 5–10 kcal per mole. Direct chemical bonding to the wood substance accounts for the excellent dry bond properties at low resin spreads.

This reaction model seems reasonable, yet two important observations should be kept in mind. The surface of wood is often perceived as hydroxyl-rich. This is understandable since carbohydrates make up perhaps 70% of the total weight of wood. Recently developed information tends to dispute this perception, however. Nguyen and Johns[13] investigated the polar and dispersion force contribution to the total surface free energy of Douglas fir. Interestingly enough, polar forces were responsible for one-third or less of the total surface free energy. More recently, Young[14] and co-workers used ESCA to characterize the surface of wood. What was seen was a surface rich in carbon and hydrogen and poor in oxygen. If, in fact, the isocyanate is reacting with wood hydroxyls, there may be less opportunity for a direct urethane formation than was previously thought. This is not to suggest that the urethane linkage is not taking place. Both ESCA and contact angle research are typically thought of as measuring surface phenomena. The depth of penetration of MDI or methyl isocyanate into the wood structure has not yet been determined, but is presumed to be substantial.

Having anchored the isocyanate to the wood surface chemically, the model must now permit a gap-filling quality based on the isocyanate. While many potential reaction mechanisms can be envisioned, two seem most likely.

The first is the formation of a polyurea. This is considered a possibility because of the large volume of water present in a mat during pressing. By simple calculation it can be shown that for wood at 5% MC the amount of water available for reaction with isocyanate is many times the amount needed to convert all isocyanate to form a polyurea. There is experimental evidence for this reaction. Wittmann[15] measured the CO_2 released from isocyanate-treated wood during the pressing of a mat. He concluded that if each amine group formed *via* the gas reaction reacted with an NCO group, more than 50% of the substance introduced for bonding would lead to the formation of polyureas. Other researchers[10,16] have also expressed the opinion that polyurea formation is of substantial importance to the bonding of wood with isocyanates.

Most recently, Farrissey[17] used FT-IR to investigate the surface of isocyanate-treated flakes. He was able to readily show the presence of polyurea bonds with a strong absorption band at 1650 cm^{-1}. Also seen, but less obvious, was the presence of a urethane absorption band at 1725 cm^{-1}. Both of these bands are associated with the relevant carbonyl group. A band at 1530 cm^{-1} was also noted. This band is associated with an amide II group and is unique to the binder and not the wood substance. The relative strength of the urethane bands could be changed by the use of various catalysts which promote the formation of urethane structures.

The second potential reaction mechanism for filling the gap between urethane chains is the development of an isocyanurate linkage.[18] This reaction sequence does not involve any secondary reactions, but takes place directly between NCO groups. The presence of a large release of CO_2 indicates the presence of a comparable amount of amine, which would favor the formation of polyurea; a portion of NCO is probably still available for further reaction. While isocyanurates are normally somewhat difficult to form, the high temperature of the mat adjacent to the platens may very well cause this reaction.

The formation of a significant polyurea base mat suggests a susceptibility to water deterioration. The excellent hydrolytic stability of these resins seems to be related to the chemical proximity of aromatic rings stabilizing the structure of the crosslinked network.

Thus, evidence gathered to date suggests that the excellent board performance at low resin levels is most likely related to the formation of urethane linkages between isocyanate and wood hydroxyls. The very fast press cycles may be caused by the water-NCO reaction, yielding an amine which would tend to react very quickly with available isocyanate, yielding urea bonds. Structural strength is probably related to the crosslink network made possible by secondary reactions leading to polyurea and, in some cases, isocyanurate linkages.

Recent observations have extended both the practical use of and the knowledge of isocyanates in combination with wood. Lambuth[19] recently noted that the compatibility of isocyanates with aqueous mixtures was directed at developing lower cost alternatives to meet MDI. An advantage of this approach is that pulping residues such as ammonium lignosulfonate can act as very efficient emulsifiers for isocyanates, a fact confirmed by Johns.[20]

Another recent observation[21] is related to the use of 1,8-diazabicyclo (5,4,0)-undecene-7 as a catalyst for MDI mixtures. This compound, when used as the acid salt of 2-ethyl hexoic acid, can act as a catalyst for the formation of urethane bonds in lieu of polyurea bonds in particleboard. The reduction of either press time or press temperature can be used. Within the constraints of a production line, such modifications may be of value.

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