STRAINING AT A GNAT AND SWALLOWING A CAMEL: SAFETY AND PERFORMANCE ISSUES WITH TWO - PART URETHANE FINISH COATS

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ABSTRACT

An escalating amount of negative press on the tried-and-true polyurethane finish coats has arisen due to concerns with their free-isocyanate content. This paper explores performance aspects of polyurethanes with respect to their UV resistance properties, and safety issues associated with polyurethanes as a function of their precursor isocyanate molecules.

A brief exploration is undertaken to ascertain whether or not the perceived assault on polyurethanes is justified when certain non-isocyanate replacement technologies deserve more careful scrutiny.

Ironically, could it be that industry might be "straining at a gnat and swallowing a camel" (biblical: highly concerned about an arguably small matter while ignoring or unwittingly ignorant of something far bigger)?

INTRODUCTION

Two-component polyurethanes have largely been the de facto finish coats of choice for much of the past fifty years. Aside from their famed UV resistant, aesthetic and non-yellowing wet-look properties, polyurethanes have also been formulated to possess excellent water, chemical and solvent resistance (1).

As a generic coatings class polyurethanes are a versatile resource to help protect a wide variety of substrates in the fight against corrosion (2). Applications are diverse, ranging from finish coats for zinc/epoxy systems applied to structural steel, to rugged anti-skid systems on ships and car park decks, gas proofing for digesters in waste treatment plant, and protection of buried pipelines.

With a proven track record that spans decades, why are polyurethanes apparently under the gun so much these days, notably at a time when there is a clarion call by some to avoid polyurethanes? The answer has to do with safety implications, at times both perceived and real, associated with the functional group –N=C=O. It is this highly reactive –N=C=O, or isocyanate group, that co-reacts in a polyisocyanate molecule with the hydrogen atoms of a polyol to form a two-component polyurethane.

There is a critical necessity to understand key elements of the chemistry of polyurethanes. Other things being equal, the impetus for cost reduction and optimization of life cycle costs in both new construction and maintenance painting necessitates a good understanding of primers, mid-coats and finish coats. It cannot be overemphasized that particular attention must be paid to

understanding the chemistry of the finish coats. In broad terms, better understanding the safety and performance issues of finish coats will ultimately lead to an owner obtaining a better net return on his investment.

This paper will largely focus on two-component polyurethanes used as finish coats applied to anticorrosive mid-coats and primers. A brief reconnaissance of recent non-isocyanate finish coats will prove helpful before examining two-component polyurethanes.

ALTERNATIVE FINISH COAT TECHNOLOGY

A key driver in any coatings company is the need to reduce volatile organic compounds (VOC's) and meet increasingly stringent environmental regulations. Some of the new or modified topcoat technologies include:

- polysiloxanes – old and new generation
- polyaspartic esters
- proprietary water-based polyurethanes
- acrylic epoxies

A good overview of these and other recent innovations in topcoat technologies has been given elsewhere (3).

Polysiloxane chemistry has afforded some excellent types of non-isocyanate finish coats and is a relatively new generic classification in terms of aesthetic finishes (4, 5). Introduced in the mid-90's, some of the earlier types of organically modified polysiloxanes were very brittle and occasionally failed in service. More recently, newer generation polysiloxane coatings have been developed with improved weathering, improved stability, less internal stress, and greater flexibility. But their track records are of the order of a few years compared to decades for polyurethanes (6, 7).

Since polysiloxane coatings are a hybrid inorganic-organic system, the key touted feature of the earliest types was their high build characteristics and compatibility with zinc rich primers to offer a cost competitive (two coats vs. three coats) exterior system. However, since this new technology has not been fully explored under real field painting conditions, several catastrophic failures have occurred, and the real cause has not been fully understood.

Polyaspartic esters are precursors to the manufacture of excellent modified polyurethanes. They are a new class of amine-functional polymers that contain secondary aliphatic diamines that co-react with aliphatic polyisocyanates (8-10). Although the resulting coating films can be considered as modified polyurethanes, they are essentially polyaspartic-based polyureas. Polyaspartic topcoats can be formulated to have superior weathering, fast cure, abrasion resistance, and water and chemical resistance properties (11). The track record for polyaspartic coatings is around six years.

Technical advances have been made in two component water-based urethane technology (12). Both hydrophilic and hydrophobic isocyanate curatives have gained recognition in this technology. However, their use has chiefly been limited to the light duty industrial side of the protective coatings market. Being water-based and over indexed with NCO, the total mileage is limited to ca. 2-3 mils DFT as heavy films cause inordinate CO_2 formation. Additionally, a new

tint system to generate new colors further complicated the use of these water-based polyurethanes in the heavy duty market.

About thirty years ago, acrylic epoxies received good market acceptance as a non-isocyanate finish coat. One of the key features offered in this technology was the toughness of epoxies coupled with good color retention of acrylics. Actual field use indicated their performance was somewhere in-between a pure epoxy finish coat and an aliphatic polyurethane. Additionally, this technology offered excellent self-aged recoatability.

POLYURETHANES

Polyurethane Coating Performance:
Aliphatic polyurethane coatings have a well established place in the world of coating finishes. They possess excellent gloss and gloss retentive properties, especially the polyester polyurethanes, or acrylic polyurethanes formulated with super-antioxidant hindered amine light stabilizers (HALS) (13).

Under intense UV conditions such as on the Eastern seaboard of the US, gloss retention of the more expensive polyesters has traditionally been superior to the acrylics and markedly better than the alkyd modified polyurethanes. The latter, though seldom used nowadays, have good recoatability characteristics unlike the polyesters types.

Certain aliphatic polyurethanes have been judiciously dosed with HALS to give finish coats with markedly superior gloss retention and comparable aesthetic qualities to polyester polyurethanes. The mode of action by which HALS work can be explained with an analogy to the human body. In order to forestall the ravages of physical aging and degeneration, people will take *antioxidants* such as Coenzyme Q10, Selenium, Vitamin C and Vitamin D. The antioxidants behave as molecular mercenaries with the ability to scavenge unpaired electrons from free radicals. Otherwise, if free radicals such as hydroxy (OH˙) or peroxy (ROO˙) species are able to roam unchecked they can attack cellular DNA and cause oxidation and degenerative disease (14).

In the same way that the human body is helped by antioxidants to scavenge free radicals, so in the sphere of protective coatings, high performance polyurethanes are helped by HALS. The latter neutralize free radicals arising from UV induced degradation of the polyurethane binder. Just a small dose of HALS in a polyurethane coating (ca 1%) can make a considerable difference in terms of the coating's gloss retention.

Testing protocols for polyurethanes in many laboratories include UV exposure according to ASTM D523 "Standard Test Method for Specular Gloss" as well as field exposures in UV intense geographical regions. Figure 1 compares the gloss retention in a 34 month period where different aesthetic finishes were exposed to intense UV irradiation in New Zealand (15). It can be seen that the gloss retention obtained from polyurethanes depends on the particular polyurethane tested, where those doped with HALS have superior gloss retention than the same coating without HALS.

Figure 1 shows that in a 30 month period the gloss level of the best acrylic polyurethane with a HALS addition had dropped approximately 14%, from 90 to 77 gloss units. Interestingly, as seen in Figure 2 the field gloss loss results of the same polyurethane finish coat correlates well with its gloss loss in an accelerated UV laboratory exposure (QUV-313B). Although the laboratory exposure was a relatively short test period of 2000 hours (and is still ongoing) the gloss level of

the polyurethane had dropped approximately 19% from 91 to 74 gloss units. Furthermore, it can also be seen in Figure 2 that when the highest performing HALS-doped acrylic polyurethane is compared with more expensive proprietary polysiloxanes, it is evident that under the conditions tried the polyurethane had superior gloss retentive performance compared to the epoxy polysiloxanes, and slightly superior performance than the acrylic polysiloxane.

It is noteworthy that there is a far greater latitude for the coating's formulator to prepare different polyurethane finishes than there is to prepare many non-isocyanate finishes. For instance, the large number of hydroxy-terminated molecules that can be reacted with isocyanates, varying the polyol:isocyanate stoichiometry, and judiciously combining HALS and UV absorbers, gives the formulator greater versatility in developing high-performance finishes.

<u>Polyurethane Coating Safety:</u>
Protective coatings are sophisticated materials that are invariably composed of binders, pigments, additives and solvents. Each constituent introduces its own hazard and hygiene implications. The manufacturer's material safety data sheet (MSDS) provides essential information with respect to the coating's chemical and physical dangers, associated safety procedures and safety protocol in case of an emergency (16).

Table 1 lists four common isocyanates, both aliphatic and aromatic. They are hexamethylene diisocyanate (HDI), diphenylmethane diisocyanate (MDI), MDI-based polyisocyanate (PMDI), and toluene diisocyanate (TDI), all of which are used to manufacture polyurethane coatings. The former, HDI, is aliphatic and suitable for aesthetic finishes. The degree of irritation and sensitization that these isocyanates can inflict is also provided (17). The toxicological properties of a given isocyanate are a function of the –N=C=O group and the molecular structure. Polymeric isocyanates do not have a measurable vapor pressure whereas the diisocyanates do (see Tables 2 and 3).

Table 4 provides exposure limits to the isocyanates listed (17). Three exposure limits are of interest. They are the TLV-TWA or Threshold Limit Value, Time Weighted Average, the TLV-STEL, or Threshold Limit Value, Short Term Exposure Limit and TLV-C, or Threshold Limit Value, Ceiling Exposure Level. Airborne exposure limits of different constituents are set by the MSDS, ACGIH (American Conference of Governmental Industrial Hygienists) TLV's, and OSHA PELs (18).

Scrutiny of polyurethanes would appear to be higher than that of other finish coats. This is beneficial in that polyurethanes are well understood from the perspective of toxicological, medical, hygiene and overall safety vantage points.

Described as toxic due to the presence of very small amounts of "free" monomeric isocyanate, two-component polyurethanes often contain less than 0.2% free isocyanate. This percentage is then reduced still further when the typical 4 to 9 parts of base portion (polyol) are added to the catalyst portion (isocyanate) and polymerization begins to take place. Health hazards do not occur when the polymerization is complete and monomers have fully reacted.

It is known that overexposure hazards from isocyanates are more likely to occur from inadvertent inhalation during spray application of polyurethanes. Common symptoms that indicate overexposure are irritation of the eyes, nose, and respiratory tract. In extreme cases sensitization may occur, where individuals can experience severe breathing problems and asthma. Once an individual is sensitized the asthma attacks can be induced by isocyanate levels even below the occupational exposure limits (19-25).

In contrast, acute or chronic isocyanate exposure rarely causes any skin damage although redness and swelling may arise.

Good hygiene practices and minimizing worker exposure to isocyanates has been thoroughly discussed in the literature (22). Isocyanate concentrations can be determined using different techniques, some of which are more sensitive than others. As with all chemicals and alternative isocyanate-free finish coats, appropriate respiratory protection (organic cartridges or supplied air-fed masks), personal protective equipment and safe handling are all of paramount importance (26-28).

Over the years the author's have encountered well-meaning people that perceived a greater worker and public health risk with isocyanates compared to alternative isocyanate-free finish coats and epoxy mid-coats. This generalization is in error. For instance, isocyanates are not considered human carcinogens and yet the very word "isocyanate" conjures up all sorts of phobias whereas the degree of concern in some quarters with carcinogenic amine curatives has not been so great. Interestingly, the hazards posed from the use of amino functional reagents and solvents may well be greater than those associated with isocyanates.

GENERAL DISCUSSION:
STRAINING AT A GNAT AND SWALLOWING A CAMEL

What, one may reasonably ask, distinguishes polyurethanes from other two-component finish coats to have emerged in the past decade? In a nutshell, the answer is that professionals know so much more about the safety and performance aspects associated with polyurethanes. But this sometimes leads to "straining at a gnat and swallowing a camel". For instance, specification authorities sometimes dismiss a polyurethane in favor of a much-touted non-isocyanate alternative. Yet the latter may actually have more toxicological data, or "toxicological baggage", so-to-speak, be treated with less caution perhaps, and have some potentially deleterious, and unrecognized performance issues that can lead to premature coating failure.

One key presupposition, therefore, that encourages specification of a non-isocyanate finish is that it is safer to apply the non-isocyanate finish and less restrictive regarding testing for isocyanates in the application environment. After all, isocyanates legitimately raise safety issues with their use. The authors contend, however, that with safe handling of polyurethanes, and understanding their airborne particulate characteristics should they require removal at a future date, the judicious selection of polyurethane finishes is often preferred. In this context, the old adage, "better the devil you know than the devil you don't know" seems most appropriate.

Another straining at a gnat and swallowing a camel has been the underestimation of well known polyurethane performance in contrast with an overestimation of less well-known isocyanate-free finish performance. Critically, a lack of awareness of certain properties of an alternative finish coat can lead to an unexpectedly vicious bite from the proverbial camel.

A first-hand tale of woe noted by the authors was an overcoat application to the alkyd-coated externals of a large steel structure. The gnat that was strained (amongst other considerations), was that the engineer writing the specification was led to believe that the gloss retention of a candidate polyurethane finish was inferior to that of a polysiloxane finish coat. Working on behalf of the owner, the engineer's intent included the desire to have a better gloss retentive finish in the service environment. In all fairness to the specifier the gloss retentive properties of lower performance polyurethanes can indeed be poorer than certain non-isocyanate finishes. But it does

not help matters when the gloss retention data purported to represent a polyurethane coating is based on so-called "typical urethanes" with poor gloss retention which make polyurethanes look decidedly inferior to several types of polysiloxanes. As Figure 2 shows, if a well-formulated high-performance polyurethane with HALS was used instead to represent the generic class of polyurethanes vs polysiloxanes, the lower cost polyurethanes with their excellent UV properties would make the specifier scratch his baldspot! That is to say he would probably think again.

To reiterate, what was not appreciated was that this was no low-performance polyurethane. In fact, unbeknown to the engineer, it actually had superior gloss retentive properties than the polysiloxane finish coating. But compounding things beyond measure this was not the problem in the field. The camel unwittingly swallowed was the alternative coating's proclivity to elevated stress levels under post-project conditions. This was due, in part, to the effect of intrinsic coating stresses in the coating exacerbated by extrinsic hygrothermal stresses due to inclement weather.

In another project, the curing mechanism in one particular polysiloxane finish was speculated to be rather problematic. It was believed that the curing continued longer than first expected. The result? Large internal stress development within the coating system. Even after a couple of years this very good gloss retentive finish system was prone to come away from sharp edges. Some argued that the specification was at fault given that a two coat system with a potentially problematic finish (especially if overbuilt) was specified. Others argued that the problem would never have happened if a proven thin film polyurethane finish with HALS had been used. Conjecture on all sides.

Substrate geometry can also have a bearing in the success or failure with coating systems utilizing gloss-retentive finish coats. If the latter are properly applied to large flat surfaces, such as tank externals, the coating system will almost surely do well. In contrast, if the coating system is applied to structures with numerous angular surfaces, all sorts of problems of coatings coming away from edges in a few years could be envisioned. Agreed, the project rationale from the outset would likely be to save time and money using a two-coat zinc/alternative finish system. Mission accomplished. At least in the short term. But perhaps not in the long term. Failures might loom large with a lot of maintenance money required to fix things. Not good! How can the coating failures be inexpensively fixed if the substrate geometry is complex and way up in the air? And with some types of polysiloxanes that possess extremely low surface free energies and antigraffiti-like properties, the self-self recoat scenario can also be problematic. The question is did the engineer factor potentially significant rehabs and self-self recoats into the equation? A camel probably just got swallowed.

Compare and contrast these coating situations with tried-and-true high-quality polyurethane systems that virtually all coatings companies have, where internal stresses are not so much of an issue, and where treatment of aged polyurethanes with adhesion promotion liquids readily assures self-self recoats, and the scenario looks excellent based on a good history of success.

The moral of these stories? Caveat emptor: buyer beware. Seek not to know the answers but to understand the questions. In the final analysis, it is all about understanding the chemistry of each coating and having an appreciation of that chemistry within the context of safety and performance. Generalizations within coating classes can sometimes lead to painful consequences.

And don't forget the gnats and camels.

CONCLUSIONS

- Performance expectations from polyurethane aesthetic finishes are well known because the technology is mature and has a proven track record spanning several decades. The same cannot be said for many non-isocyanate finishes.

- Compared to many non-isocyanate aesthetic finishes, superior UV protection can be obtained from well-formulated, high-performance acrylic polyurethane coatings with hindered amine light stabilizers (HALS).

- Dismissing polyurethanes in favor of non-isocyanate aesthetic finishes can introduce performance problems that have yet to be fully resolved.

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FIGURE 1

Gloss Values vs. Time
Polysiloxane & Polyurethane
QUV- 313 B (Laboratory)
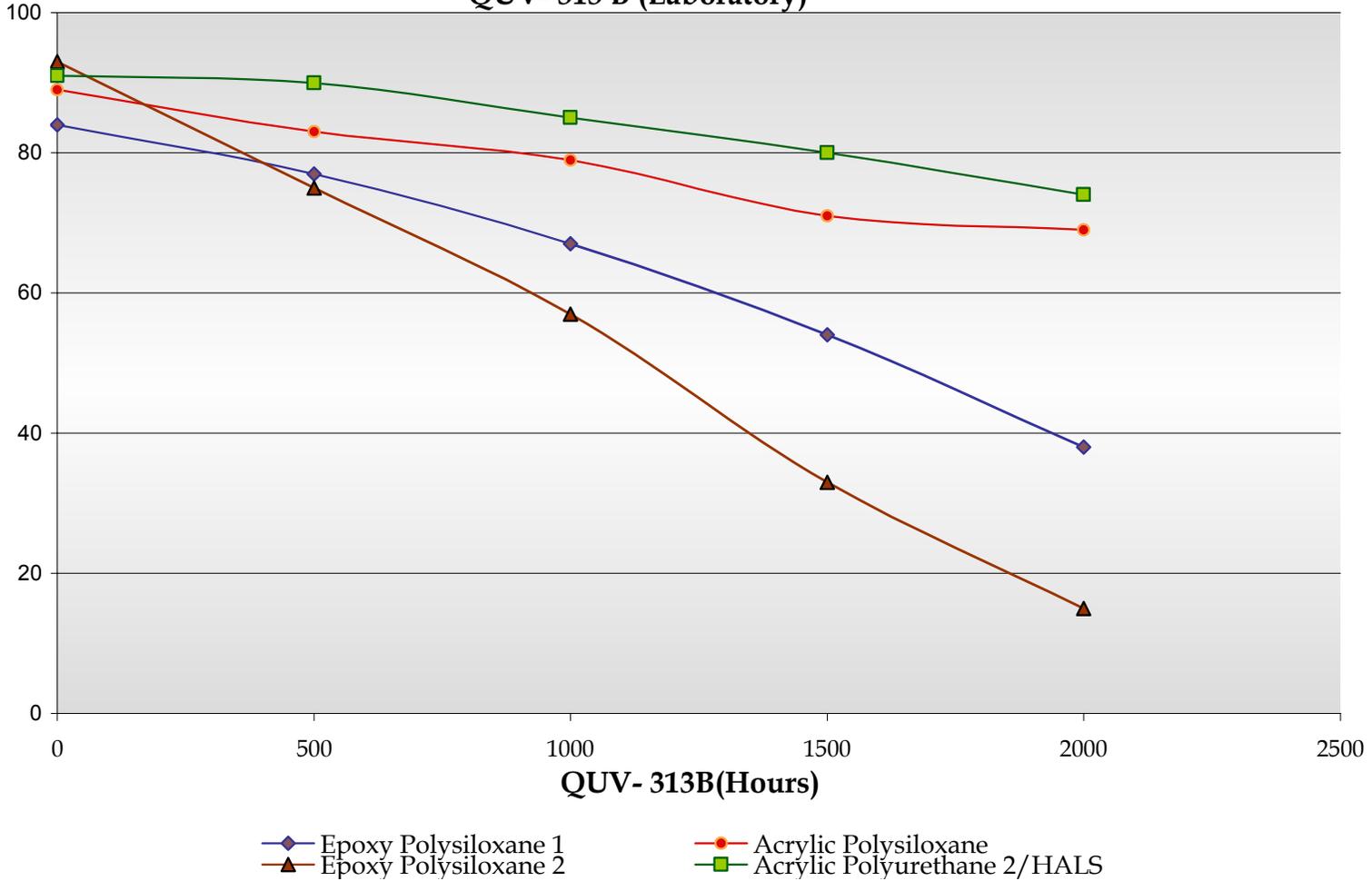
FIGURE 2

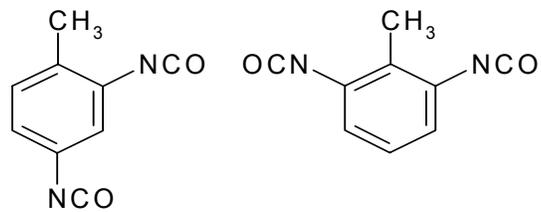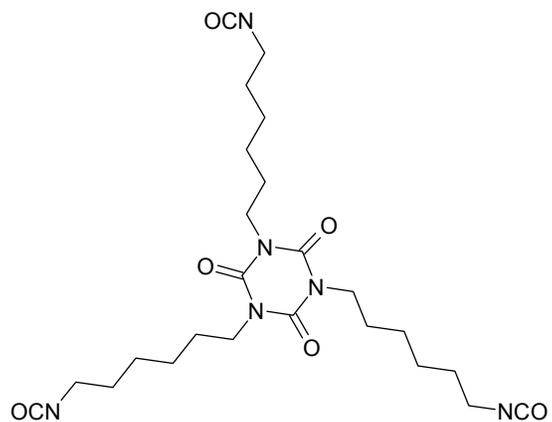| SYSTEM	DE 2000HR-QUV-B
Epoxy Polysiloxane (1)	4.1
Acrylic Polysiloxane	4.58
Epoxy Polysiloxane (2)	1.65
Acrylic Polyurethane	0.71
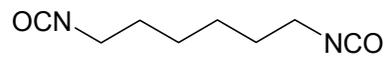
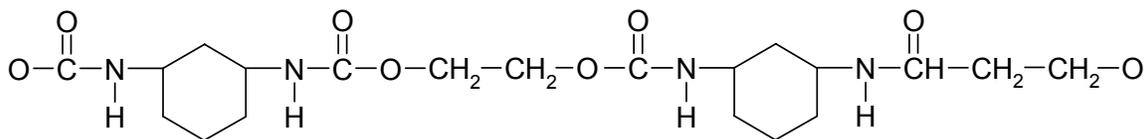**FIGURE 3 HDI Hexamethylene Diisocyanate**
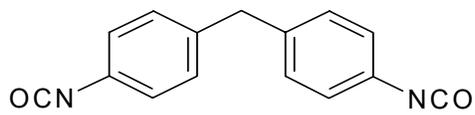
FIGURE 4 MDI Methylene Diphenylisocyanate

FIGURE 5 TDI Toluene Diisocyanate

FIGURE 6 HDI Trimer Polyisocyanate

FIGURE 7 A Polyurethane

TABLE 1

IRRITATION AND SENSITIZATION

	Irritation (Eye or Skin)	Sensitization Skin	Respiratory
HDI	severe	weak	positive
MDI	mild to moderate	weak	positive
PMDI	mild to moderate	weak	positive
TDI	moderate to severe	weak	positive

TABLE 2

PHYSICAL DATA OF ISOCYANATES

Isocyanate	Vapor Pressure mm hg, 20^0C	Saturated Vapor Concentration, ppm	Relative Vapour Pressure
MDI	$<1 \times 10^{-5}$	<0.013	1
PMDI	$<1 \times 10^{-5}$	<0.013	1
HMDI	1×10^{-5}	0.013	1
HDI polyiso.	7.5×10^{-5}	0.099	7.5

TABLE 3

ISOCYANATES DATA COMPARISON

Isocyanate	Vapor Pressure mm Hg, 20^0C	Saturated Vapor Concentration, ppm	Relative Vapour Pressure
TDI	0.025	33	2.5×10^3
HDI	0.01	13	1.0×10^3
Phl	2	2631	2.0×10^5
nBl	16	21053	1.6×10^6
Water	18	24259	1.8×10^6
MIC	390	513162	3.9×10^7

TABLE 4

ISOCYANATES

Exposure Limits/Guidelines

	Exposure Limits/Guidelines					
	OSHA		**ACGIH**	**Manufacturers Guidelines**		
Isocyanate	TWA	Ceiling	TWA	TWA	STEL	Ceiling
HDI	None	None	5 ppb	None	None	20 ppb
MDI	None	20 ppb	5 ppb	None	None	None
HDI Polyisocyanates	None	None	None	0.5 mg/m^3	1 mg/m^3	None