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Polyurethanes in Roofing Applications

How chemistry improves rooftop performance

by Jason Smith

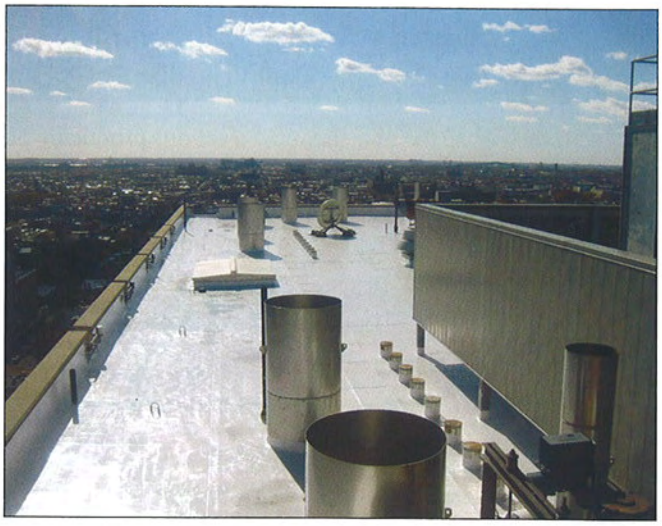
For many people, the mention of the word 'polyurethanes' immediately conjures images of something one paints on patio decks for protection from the rain. While this particular application provided the original proving ground for polyurethanes, these reactive waterproof systems have found their way from the patio to the roof in many different forms.

Polyurethane and polyisocyanurate insulation products were introduced in the 1970s in direct response to the oil embargo. Heating costs were rising, and consensus had it that up to a quarter of the heat lost in a single-family home went—no pun intended—through the roof. Prior to this time, traditional forms of insulation (*e.g.* fiberboard, cork, perlite) were mainly used on low-slope roofs as a means of leveling the surface underneath the membrane. To some extent, this is still the case, but from the 1970s onward, the issue of heat loss could no longer be ignored when evaluating insulation.[1]

Around this same time, it was discovered polyurethanes are very strong when manufactured into a closed-cell rigid foam. When the polyurethane is heated to a much higher temperature than usual during manufacturing, the urethane groups react with themselves to form a very strong, cross-linked network called an isocyanurate.

Insulation manufacturers also noticed the polyurethane foams had a very high R-value, which is a measure of the insulation's thermal resistance. For this reason, polyisocyanurate boards are the most popular insulation used today, regardless of whether the roof is built-up (BUR) or single-ply.

Since polyurethane technology emerged so much later than more traditional roofing products, systems such as BURs continued to dominate the roof market. However, BURs were not a panacea, and leaks continued to occur. On a built-up system, seams can be a major source of water intrusion when not properly addressed during installation. A leak in the top of a BUR or single-ply membrane disperses water and saturates insulation. Consequently, where the leak ends is not necessarily where it begins.



Introduced in the 1970s, polyurethane and polyisocyanurate products have helped revolutionize roofing. The material has become one of the most popular insulation components for U.S. projects.

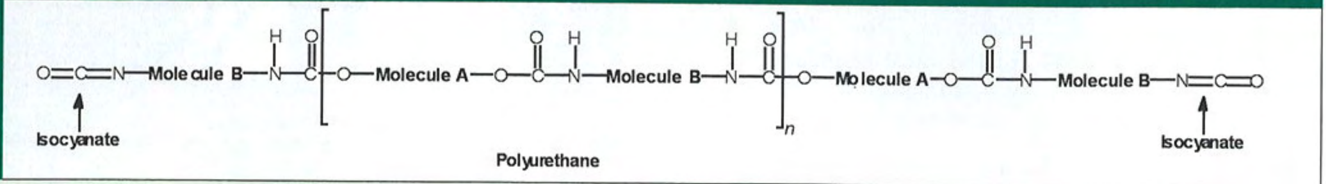
SPF success and challenges

It was discovered when a 51-mm (2-in.) layer of polyurethane foam was applied to a roof deck, water movement was restricted to the hole, even if a hole was punched through the

Chemistry Lesson

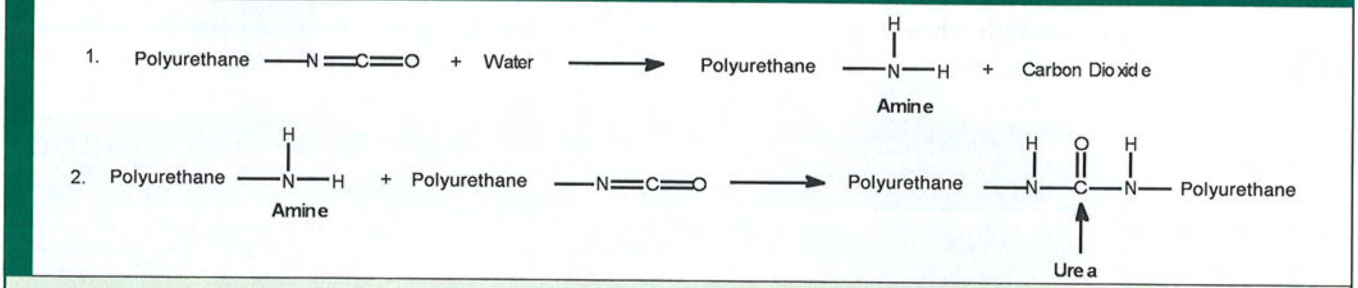
In the 1950s, the first chemical reactions producing polyurethanes were performed by Otto Bayer, PhD, during his employment for I.G. Farben Industries in Frankfort, Germany. A polyol—a chemical containing two or more terminal hydroxyl (-OH) groups—was blended with a polyisocyanate, a chemical containing two or more terminal isocyanate (-N=C=O) groups. The hydroxyl group reacts with the isocyanate group and forms a urethane.

Figure 1



In a typical reaction, there are statistically more isocyanate groups than hydroxyl groups, so by the time the polyurethane is formed, there are no more of the latter, leaving a small excess of unreacted isocyanate groups. This is what gives the polyurethane its moisture-cure properties (Figure 1).

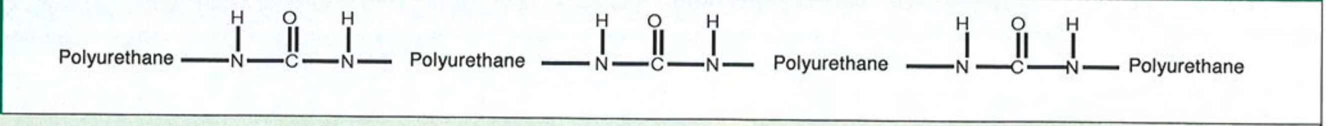
Figure 2



In its simplest form, the moisture-curing process is a two-step reaction, as illustrated in Figure 2.

1. Water reacts readily with the unreacted isocyanate (-N=C=O) at the end of the long polymer chain. The isocyanate converts to carbon dioxide gas and an amine ($-NH_2$).
2. The amine reacts rapidly with another unreacted isocyanate group at the end of another long polymer chain, becoming a urea, and forming a very strong bond.

Figure 3



Like boxcars in a train, the polyurethane polymers continue to link up with the urea linkage, until a large cross-linked network is formed (Figure 3). This is what gives polyurethanes their toughness and water-repellant nature.

entire 51 mm. Beginning in the late 1960s and early 1970s, polyurethanes were sprayed onto roofs in the form of two-component foams called sprayed polyurethane foams (SPF). When mixed in a specified ratio—typically 1:1 by weight—a chemical reaction occurs expanding the SPF up to 30 times its size and forming a solid, seamless, closed-cell, fully adhered roof system for residential, commercial, institutional, or industrial projects.[2]

With polyurethane foams, seams around flashings and other protrusions on a roof are sealed, eliminating a common source of leaks. SPF roofs provide excellent water resistance and thermal insulation capabilities. The foam coating itself is lightweight, typically 22.7 kg (50 lb) per square (*i.e.* 9.3 m^2 [100 sf]), versus 363 kg (800 lb) per square for a BUR or about 500 kg (1100 lb) per square for a ballasted single-ply roof.[3] In short, SPF has the best insulating properties available in commercial construction today. However, despite these properties, sprayed polyurethane foams have their limitations.

The need for keeping reactive raw materials separate means special equipment is needed to bring the components together in the required ratio. If not mixed properly, the product will not cure (too much polyol) or cure very slowly with little or no foaming (too much diisocyanate). Due to the respiratory risks associated with the scattering foam during application, this author heavily advises operators wear respirators fitted with special diisocyanate filters to optimize worker health and safety.[4]

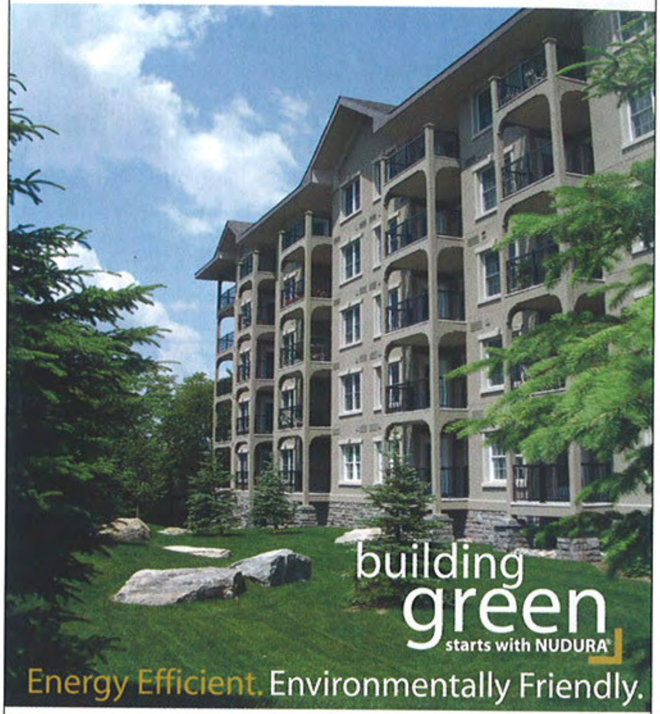
In addition, SPFs are best applied in ideal conditions (*i.e.* warm, sunny, little or no wind, and no threat of rain), which makes them very touchy to apply in cooler northern climates or hot and humid southern climates.

For all its strength and superior water barrier properties, the foam roof's biggest drawback is its lack of ultraviolet (UV) resistance. In the presence of sunlight, a decomposition reaction chemically breaks down the polyurethane polymer, turning its surface to a discolored brown dust. UV absorbers can be added to slow (but not eliminate) this process. Coatings can also be used to dramatically reduce, or in some cases eliminate, this degradation, while improving the aesthetics of the browned SPF surface. Such coatings are primarily water-based acrylic systems. However, polyurethane coatings are rapidly becoming a popular alternative for ensuring watertight protection, whether over SPF surfaces or other substrates.

White polyurethane roof coatings

With the advent of California's Title 24 mandate, and incentive programs built around the U.S. Department of Energy's (DOE's) Energy Star, the U.S. Green Building Council's (USGBC's) Leadership in Energy and Environmental Design (LEED), and Cool Roof Rating Council (CRRC) guidelines, sustainability has become front of mind for many building owners and design teams.[5] For pre-existing, restored, and new roofs, white coatings have become one of the most popular means of reducing rooftop energy loss. With easy spray or roller application, the contractor need not bother with cumbersome equipment at the job-site.

Acrylic and acrylic-latex roof coatings provide UV stability and are relatively inexpensive. As they are water-based,



flammability is not an issue on-site. However, acrylic coatings may not be a wise choice if rooftop ponding is a concern. The acrylic roof coating is subject to reversion in areas where water collects. This is especially true during the drying process, when the water is being evaporated and the coating is forming its coalesced film. The acrylic coating eventually softens and lifts when immersed in ponding water.

In such cases, polyurethane coatings are a great alternative. Polyurethanes come in one- or two-component packaging. Products in the first category contain the reacted polyurethane (with excess isocyanate groups), and are commonly used in the roof coatings discussed in this article. One-component polyurethanes require external moisture (typically from ambient air or a misting station) to cure, but are easy to apply, often only requiring a paint roller.

Two-component polyurethanes, on the other hand, are more stable because the diisocyanate is kept separate from the polyol until the moment of use. This packaging is typical for polyurethane foams discussed in this article. These types of coatings can be useful in areas with low humidity, since everything the polyurethane needs to cure is contained within the two components.

Two-component polyurethane coatings present the same application issues as polyurethane foams. To apply properly, a special two-component spray unit capable of metering out the right weight ratio of components is necessary. One-component polyurethane coatings can be applied in the same ways as acrylics, using traditional spray units or by paint roller.

The big difference between a polyurethane and an acrylic coating is the fact the former undergoes a chemical reaction with moisture. In other words, it cures. During this reaction, carbon dioxide is released (as bubbles), and the polyurethane polymer chains become linked together through very strong urea bonds. Additionally, a secondary bonding phenomenon—hydrogen bonding—takes place between the urethane chains rubbing along each other (akin to spaghetti in a bowl). This secondary bond also contributes to the coating's incredible strength.

In contrast, most acrylic coatings undergo a drying process and do not cure, despite often being described as curing systems. In an acrylic or acrylic-latex water-based coating, droplets of polymer are suspended in an emulsion surrounded by surfactant and water. Once the coating is applied, the water begins to evaporate, reducing the space between the droplets, causing them to bump against other droplets. Soon, enough water evaporates that the walls of the droplets cannot maintain their shapes and break against other droplets. The polymers within the broken droplets intermix, forming a film that hardens with continued drying. This film-forming process is known as 'coalescence.' Both the strength and durability of water-based coatings can be increased with additives that induce chemical cross-linking within the polymer once the droplets break. Nevertheless, the process is still a film-forming one.

Cured polyurethane roof coatings remain one of the most water-resistant and resilient films, protecting the roof against water penetration even under ponding water. Depending on their formulation, the UV stability of a white polyurethane coating is a bit better than that of sprayed polyurethane foams, but some yellowing still occurs.

Polyurethane coatings use titanium dioxide and UV stabilizers to help shield them from the degrading effects of UV radiation. To be Energy

Urethane coatings that meet current emissivity and reflectivity requirements are becoming increasingly popular.

Star-qualified, white polyurethane roof coatings must have, after three years, a reflectance of at least 0.5 for low-slope roofs, or 0.15 for steep-slope roofs. Initial reflectance requirements are at least 0.65 and 0.25 respectively.

Aromatic polyurethanes, such as those based on methyl diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) eventually yellow, even with UV stabilizers. Aliphatic polyurethanes, such as those based on hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI), do not undergo the same degradation reaction as aromatic diisocyanates in the presence of UV radiation. This makes them very UV stable, but relatively more expensive than their aromatic counterparts.

Polyurethane coatings are available in solvent-borne and water-borne versions. Flammable solvents such as mineral spirits or aromatic solvents are commonly used. However, the use of solvents such as glycol ether DB acetate help keep volatile organic compound (VOC) levels acceptable (in some cases, less than 250 g/L [2.1 lb/gal]).

Waterborne polyurethanes, also known as polyurethane dispersions (PUDs), are used mostly for wood flooring and concrete protection, although there have been advances in two-component water-borne coating technologies because of the desirability of reduced-VOC formulations.

A major focus of polyurethane research has been on lowering these volatile compounds while keeping the attributes that have made polyurethane coatings desirable. For example, new raw materials are being developed that require less solvent to make the coatings easy to apply, while still maintaining the strong physical properties of polyurethanes.

Polyurethane sealants and adhesives

After World War II, there was an increase in the use of building components with higher expansion coefficients, versus the traditional brick and mortar buildings. The existing polysulfide and silicone sealants were unable to seal the joints of buildings constructed with these new components. However, polyurethane sealants and sealant adhesives were ideal for such applications.[6]

Polyurethane-based sealants and adhesives met existing specifications better than polysulfide counterparts at a lower material cost. Additionally, their superior hydrolysis-resistance to substrates such as concrete helped polyurethanes gain market share in the face of competition from conventional silicone sealants.[7]

Polyurethane sealants display high strength, have outstanding elasticity, and exhibit high recovery. These properties make them ideal for use on:

- roofs to bridge expansion and control joints;
- flashing reglets;
- precast panels;
- tilt-up walls;
- metal curtain walls;
- panel bedding;
- glazing details; and
- traditional sealant applications (*e.g.* windows and door perimeters).

Polyurethane chemistry can help ensure long-term watertight protection. In some cases, it can help delay tear-off, prolonging the assembly's life.

As with their coating counterparts, polyurethane sealants are available in one-, two-, and even three- part systems, and are packaged in cartridges, buckets, or drums.

There are some polyurethane sealants on the market designed for firestopping applications. While the sealant itself provides no hindrance to fire (the hydrocarbon chains support combustion), when backed by organic insulation such as organic fibers, polyurethane sealants can act as smoke barriers.

Another factor driving the increasing popularity of polyurethane-based sealants and adhesives is the demand for reduced- and zero-VOC sealants and adhesives. Unsurprisingly, manufacturers of polyurethane sealants have found ways of reducing VOCs by using exempt solvents such as N-Methyl-2-pyrrolidone (M-Pyrol), without sacrificing the product's performance properties.

Conclusion

For more than 40 years, polyurethanes have been successfully used in the roofing industry. Urethane insulating foams remain a competitive player in the roofing market. Urethane coatings that meet current emissivity and reflectivity requirements, while ensuring long-term watertight protection, are becoming increasingly popular, and in some cases can delay tear-off, prolonging the working life of existing roofs.[8]

Advances in reduced-solvent and even water-based polyurethane systems enable reductions in VOCs while maintaining the performance properties that make polyurethanes so desirable. As new catalyst systems that will

Additional Information

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Abstract

This article covers the basics of the chemistry behind polyurethanes, and the trends that have driven the roofing industry toward their use in the form of foams, coatings, and adhesives. It also explores the features and benefits in relation to specific application requirements.

react with aliphatic systems become available, formulators will be able to produce UV-stable, 100 percent solids, zero-VOC topcoats with very short open times. These and other technological advances will ensure polyurethanes continue to play a significant role in roofing, as the design/construction industry evolves to meet ever-changing challenges.

Notes

[1] See the first volume of H.O. Laaly's *The Science and Technology of Traditional and Modern Roofing Systems* (Laaly Scientific Publications, 1992).

[2] For more, see *The Polyurethane Foam Book* created by the Monolithic Dome Institute. Visit www.monolithic.com/foam/book/addendum/index.html.

[3] Foam roofing history can be found on the Foam Roofing Contractors Web site at www.foamroofing.com/aboutSPF.html.

[4] In the open air of a roof, vapors will not become concentrated, making the need for respirators unnecessary. However, when the foam is being sprayed into a surrounded corner or a well space where the diisocyanate vapors in the Part B component could concentrate, the operator is at risk. Typical foam roof supplier material safety data sheets state if the diisocyanate vapors are exceeded or expected to exceed the threshold limit value, an Occupational Safety and Health Administration/National Institute for Occupational Safety and Health (OSHA/NIOSH)-approved, positive pressure-supplied air respirator with a full-face piece of an air-supplied hood should be used. Contractors applying these foams should have these safety measures in place.

[5] Title 24 is the State of California's energy efficiency standards for residential and nonresidential buildings.

[6] See Robert Evans' *Polyurethane Sealants: Technology and Applications* (Technomic, 1993).

[7] See note 6.

[8] For other resources on polyurethanes, see Michael Szycher's *Handbook of Polyurethanes* (CRC Press, 1999) and Edward P. Squiller's "Polyurethanes: High-Performance Coatings Technology for Architectural Applications" (*Journal of Architectural Coatings,* January 2006). Another source would be C. Angeloff et al's "Two-component Aliphatic Polyurea Coatings For High-productivity Corrosion Protection Applications," which was presented at the 2002 Society for Protective Coatings (SSPC) Conference in Tampa, Florida.