Feature

Specifying Polyurethane Products


All images courtesy Garland Co.

Understanding the chemical bonds that bind

By Jason Smith

For many people, the promise of polyurethanes was proven in the paints protecting patio decks from the rain.[1] These reactive waterproof systems have long since found their way from the backyard to the roof in many different forms—foam insulation, coatings, and various sealant and adhesive products. Despite the material's seeming ubiquity, not all design/construction professionals understand the building science behind these products. Knowing polyurethane attributes helps ensure products are properly specified.

Polyurethane foams

Introduced to the roofing realm as a direct response to the oil embargo, polyurethane insulation was intended as a way to curb heat loss and rising utility costs.[2] The polymers are very strong when manufactured into a closed-cell rigid foam. As the material 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.

The polyurethane foams have a very high R-value, which led to polyisocyanurate boards becoming the most popular insulation, regardless of whether it is a single-ply or built-up roof (BUR).

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 the hole was punched through the 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.[3]

With polyurethane foams, seams around flashings and other protrusions 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.[4] However, despite excellent insulating properties, sprayed polyurethane foams have their limitations.

The need for keeping reactive raw materials separate means special equipment must be used to bring the components together in the required ratio. If improperly mixed, the product either does not cure (too much polyol) or does so too slowly with little or no foaming (too much diisocyanate). Due to respiratory risks associated with scattering foam during application, this author heavily advises operators wear respirators fitted with special diisocyanate filters to optimize worker health and safety.[5]

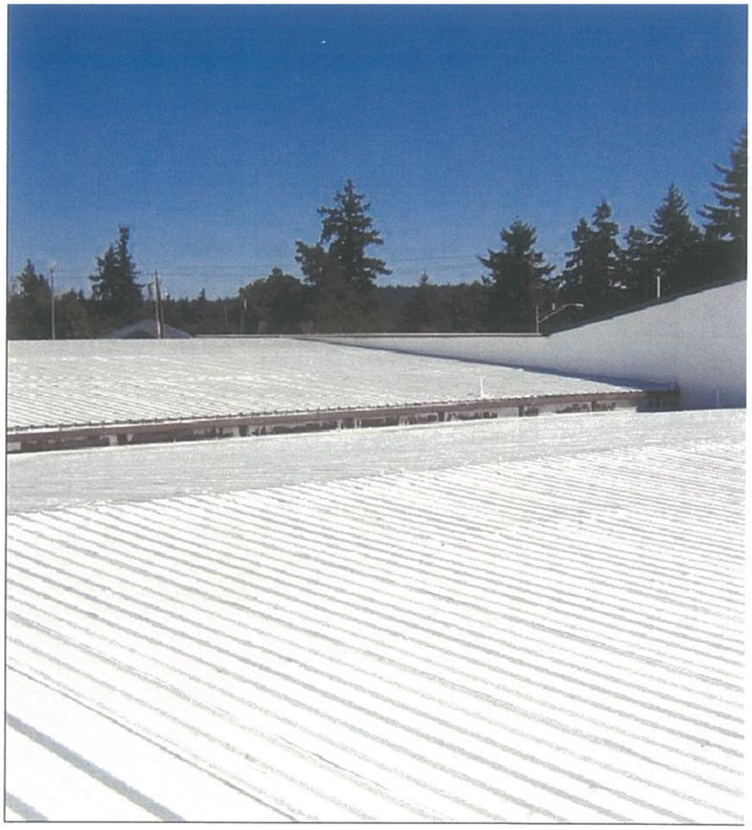
Since SPFs are best applied in ideal conditions (*i.e.* warm, sunny, little or no wind, and no threat of rain), they can be touchy to apply in Canada's cooler northern climates (likewise in hot and humid southern climates). For all its strength and superior water barrier properties, the foam roof's biggest 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 discoloured brown dust.

UV absorbers can be added to slow (but not eliminate) this process. Coatings can also dramatically reduce (or even eliminate) this degradation, while improving the esthetics 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.

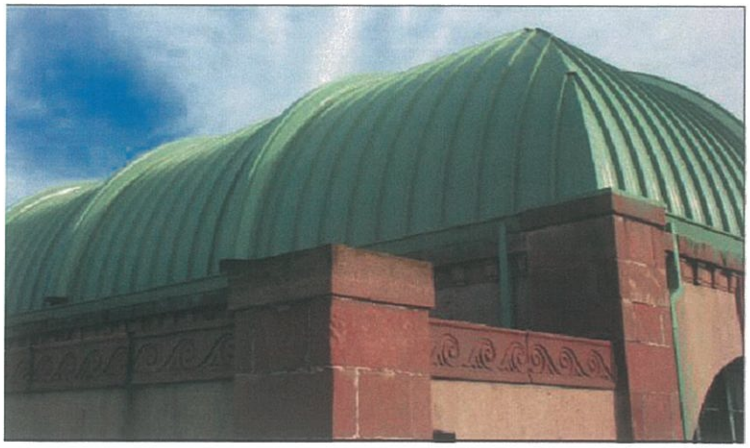
White polyurethane roof coatings

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, contractors need not bother with cumbersome equipment at the job-site.

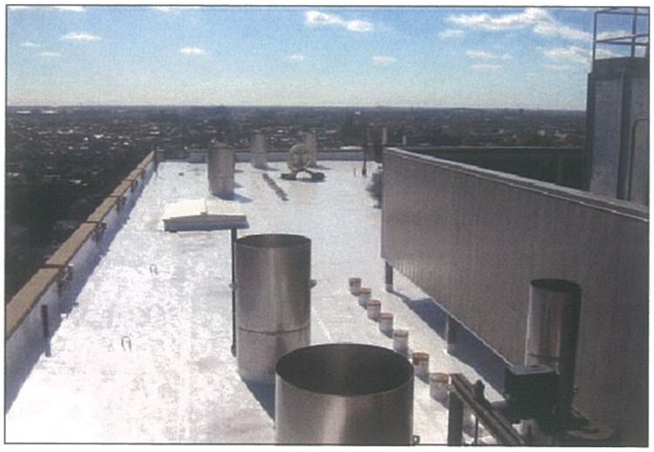
Acrylic and acrylic-latex roof coatings provide UV stability and are relatively inexpensive; further, since they are water-based, flammability is not a site issue. Nevertheless, acrylic coatings may not be a wise choice if rooftop ponding is a concern. The acrylic roof coating is subject to reversion in areas where water collects. This is especially true during drying, when the water evaporates and



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



Advances in reduced-solvent, and even water-based, polyurethane systems enable reductions in offgassing while maintaining the performance properties that make the materials so desirable.



Introduced in the 1970s, polyurethane and polyisocyanurate products have helped revolutionize roofing. The materials have become among the most popular insulation components for building projects.

the coating forms its coalesced film. The acrylic coating eventually softens and lifts when immersed in ponding water.

In such cases, polyurethane coatings can be an 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 and often only require a paint roller.

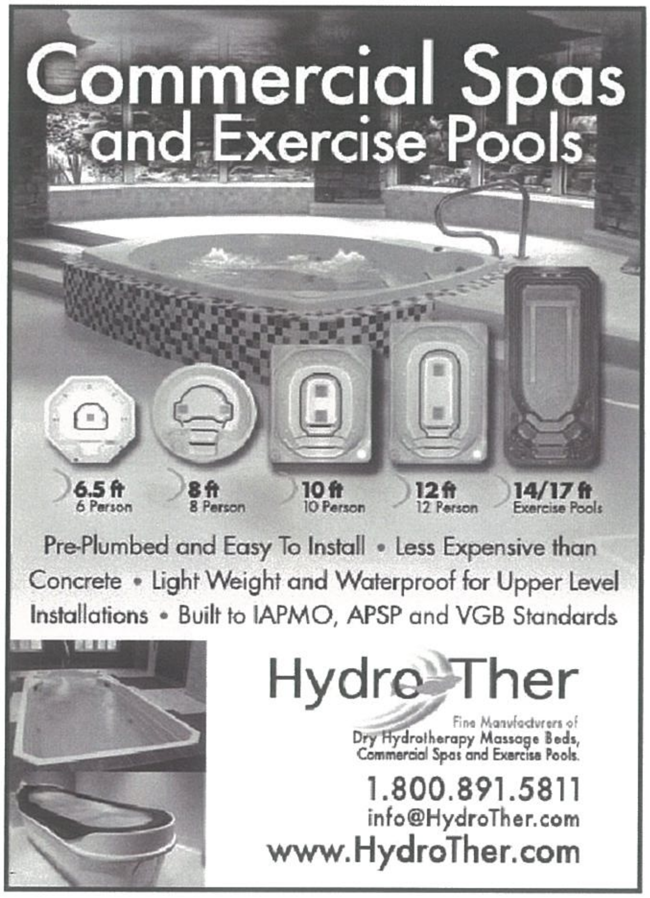
Two-component polyurethanes, on the other hand, are more stable because the diisocyanate is kept separate from the polyol until the moment of use. This packaging is typical for polyurethane foams discussed in this article. These types of coatings can be useful in areas with low humidity, since everything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

The major 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 space between the droplets, causing them to bump against each other. Once enough water evaporates, the droplet walls cannot maintain their shapes and break. The polymers within the broken droplets intermix, coalescing into a film that hardens with continued drying. 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 still forms a film.

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 slightly better than that of sprayed polyurethane foams, but some yellowing still occurs.



Adhesion: Sticking to the Basics

When considering polyurethane sealants, adhesives, and coatings, it is important to understand the building science basics of adhesion. This is, in larger terms, the same property allowing dew to cling to a blade of grass, a spider web to sway in the morning breeze, or a stain to be applied to a wood deck.

The five mechanisms

There are five basic mechanisms commonly used to describe this phenomenon.

Chemical

Two substrates can form a chemical compound at their interface, either through:

- swapping or sharing atoms (which creates a very strong bond); or
- hydrogen bonding—a weaker interaction for substrates containing oxygen, nitrogen, or fluorine atoms. (This is also called 'dispersive adhesion.)

Mechanical

Mechanical adhesion is best evidenced by the grip of Velcro, and can also be seen in rough or etched substrates. Coatings using mechanical adhesion actually penetrate into the pores or voids of a rough surface, then interlock onto the substrate. Applying a coating to polyurethane foam roofs is one example of mechanical adhesion. In addition to some chemical interaction occurring at the coating-foam interface, the coating flows (or 'wets out'*) into the nooks and crannies of the foam, then locks into place once the coating has dried or cured.

Electrostatic

When an electrostatic charge is applied over a substrate, it can create an attractive force, drawing in the other substrate. One example of this adhesion can be demonstrated by forgoing the softener sheet when using the dryer. When one tries to pull apart the clothes, a static charge dissipates, creating a crackling or snapping noise.

Diffusive

When one substrate's molecules move and intermingle (*i.e.* diffuse) with that of the other, the result can be adhesion. This mechanism is used when building polystyrene models—since the model pieces do not adhere to one another by themselves, a toluene-based clear adhesive is employed, enabling a portion of Part 105 to intermingle or diffuse into a portion of Part 32, thereby creating a single-welded piece. Polyvinyl chloride (PVC) pipe bonded to another PVC pipe with solvent-based pipe adhesive is another example of this mechanism.

Dispersive

Dispersive adhesion occurs between atoms or molecules of two substrates in close proximity of each other. While the interactions are not very strong individually, their combined bond strength can become significant. This process enables the bonding of polar and non-polar surfaces and coatings.

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

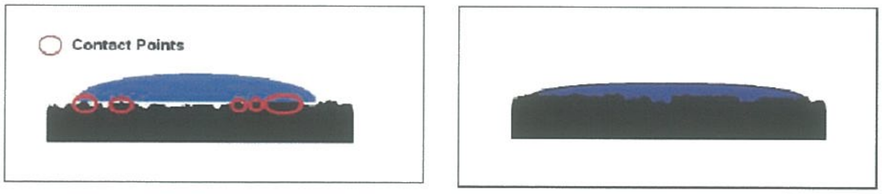
Polyurethane coatings are available in solvent-borne and water-borne versions. Flammable solvents (*e.g.* mineral spirits or aromatic solvents) are most commonly used. However, use of solvents such as glycol ether DB acetate helps keep volatile organic compound (VOC) levels acceptable (less than 250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

Waterborne polyurethanes, also known as polyurethane dispersions (PUDs), are mostly specified 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 attributes that made polyurethane coatings desirable. For example, new raw materials are being developed that require less solvent to ease coating application, while at the same time, maintaining the strong physical properties of polyurethane products.

Polyurethane sealants and adhesives

After World War II, there was an increase in the use of building components with higher expansion coefficients compared to 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, newer polyurethane sealants and sealant adhesives were ideal for such applications.[6]



At left, an etched, non-polar, low-energy surface will bead a coating and limit the number of contact points at the coating/substrate interface. This adversely affects adhesion. At right, an etched, polar high-energy surface wets out a polar coating and adheres at an infinite number of contact points along its bond line, resulting in very strong adhesion.

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]

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

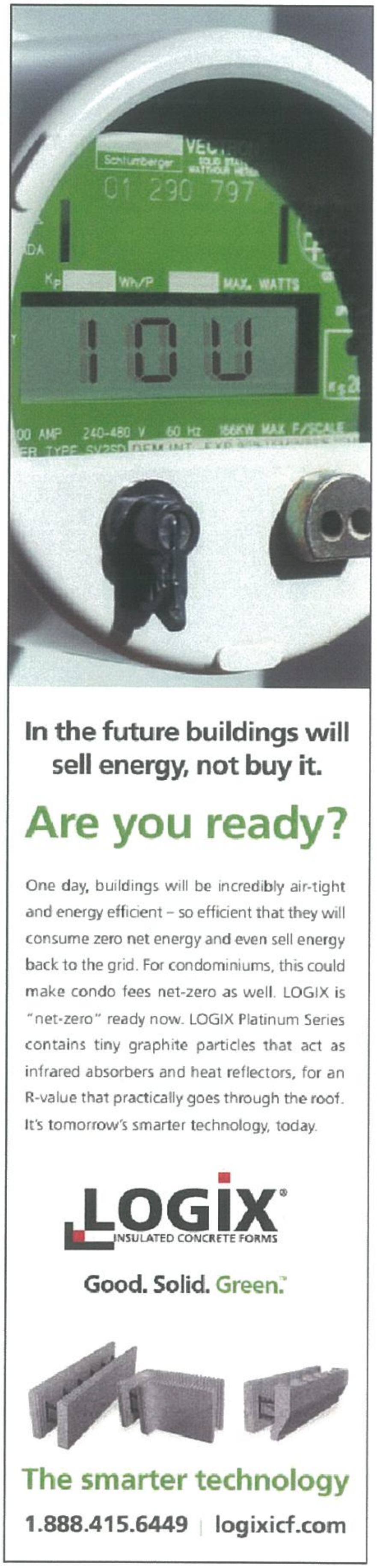
- roofs (in order to bridge expansion and control joints);
- flashing reglets;
- precast concrete panels;
- tilt-up concrete walls;
- metal curtain walls;
- panel bedding;
- glazing details; and
- traditional sealant applications (*e.g.* window and door perimeters).

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

There are some polyurethane sealants designed for firestopping applications. While it is important to remember the sealant itself provides no hindrance to fire (hydrocarbon chains support combustion), when backed by organic insulation such as organic fibres, 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, various polyurethane sealant manufacturers have found ways of reducing VOCs by using exempt solvents such as N-Methyl-2-pyrrolidone (*i.e.* M-Pyrol), without sacrificing the final product's performance properties.

When considering polyurethane products, it is important to understand the building science basics of adhesion. Water beading on a substrate provides a useful example.



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Factors influencing adhesion

Each of these five mechanisms of adhesion is affected by common factors. Regardless of the application, properly specifying an appropriate adhesive requires consideration of:

- surface energy and substrate polarity;
- surface area covered and contact points achieved;
- surface contamination;
- surface texture; and
- coating cohesive strength.

Surface energy and substrate polarity

The type of ideal coating depends greatly on the substrate's surface energy. Polar substrates carry a positive or negative charge and adhere best to other polar coatings. Non-polar substrates, on the other hand, are charge-neutral and have to rely on other adhesion mechanisms (*e.g.* diffusive or mechanical) for bonding.

For example, thermoplastic olefin (TPO) single-ply roofs are non-polar because they are made of polyethylene and polypropylene. TPOs can be very hard to coat, especially with polyurethanes (and other polar coatings like acrylic) because there is no charged surface with which it can interact. Consequently, the cured or dried film can be removed easily from the surface. To coat a TPO, a diffusive bond must form with a solvent-based primer, which then becomes a more compatible substrate.

In contrast, one can easily coat polar substrates (*e.g.* polyurethane foams) with acrylic or polyurethane products, which are also polar. In such cases, the coating interacts with the surface to create a dispersive force which, when taken over the whole area, is very strong. In addition, other factors such as surface contamination and surface texture further strengthen the bond.

Surface area covered and contact points achieved

Substrate polarity also affects surface energy (*i.e.* the factor enabling a coating to wet out or bead on a substrate. Simply put, the more the coating is able to wet out, the more surface area is covered. The more surface area covered, the more contact points achieved. The more contact points achieved, the better the adhesion to the substrate.

One can observe the phenomenon of beading and wet out when water is applied on a freshly waxed car. Before waxing, a car's paint is dusty and dirty. Chalky paint residue is blended into the dust and dirt as well. Dust carries a static charge, making the surface it coats polar (*i.e.* charged) with a high surface energy. The charged surface attracts more dust, dirt, and chalky paint residue onto itself. When water is applied to this surface, the beads of water spread out nearly flat, exhibiting wet out. In this case, each water droplet adheres strongly to the surface.

When the car is waxed, a non-polar (*i.e.* uncharged) hydrocarbon-based compound is deposited onto the paint surface. The once polarized surface is now replaced with a layer of non-polar hydrocarbons that have a low surface energy. As a result, dust or dirt does not stick well to the surface. Each drop of water (which is polar) is repelled by the low-energy surface, forming a bead. The lower the surface energy, the tighter, more spherical the bead; the higher the surface energy, the flatter the bead. Within a short time, the rain and sun dissipate the wax and make it necessary to wax the car once more.

Surface contamination

A substrate contaminated with dust, oil, debris, spores, or pollen, impairs coating adhesion. Areas with high concentrations of contaminates provide an alternate substrate over the intended substrate. Since the coating adheres so well to these polar contaminate particles, it has only partial or no contact with the intended substrate. An inadequate coating bond to the substrate can lead to blistering, peeling, or film delamination. (This is why coating manufacturers and distributors stress a clean surface before coating.)

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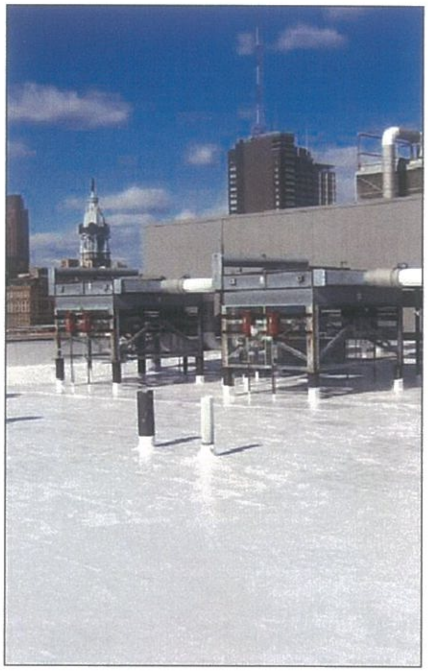

Urethane coatings that meet current emissivity and reflectivity requirements are becoming increasingly popular.

Conclusion

For more than 40 years, polyurethanes have been successfully used in the roofing industry. Urethane insulating foams remains a competitive player in the roofing market. Urethane coatings meeting current emissivity and reflectivity requirements, while ensuring long-term watertightness, 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 react with aliphatic systems become available, formulators will be able to produce UV-stable, 100 per cent 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] An earlier version of this article appeared in the August 2007 issue of *The Construction Specifier*, the official publication of the Construction Specifications Institute (CSI).