Catching the Polyurethane Train

By Jason Smith

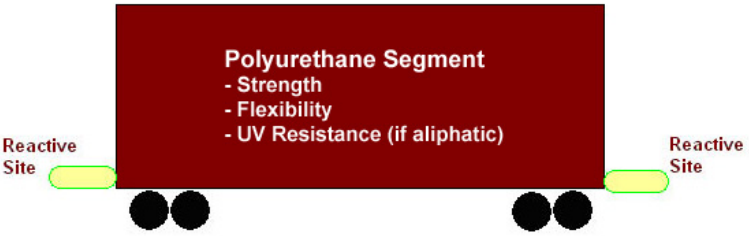
Why have urethanes become one of the fastest growing segments of rooftop coatings? Understanding how urethane chemistry works is the best way to identify when and where to use it. Did you know that:

- Unlike acrylics, which undergo a drying process, urethanes actually “cure” in a chemical reaction that links their polyurethane polymer chains with very strong urea bonds.
- Humidity accelerates the curing process of polyurethane coatings.
- Polyurethane films outperform acrylic roof coatings in ponding water.
- Film strength is critical for withstanding rooftop stresses such as:
- Freeze/thaw cycles
- Flash cooling on hot days
- Building expansion and contraction

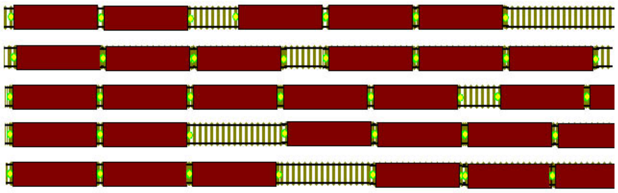
Have you ever wondered what is meant by the curing process of polyurethanes, and why they become an effective water barrier once cured? Ever needed a better way of explaining how polyurethane coatings work without resorting to a chemistry book? Here is a useful analogy that will help explain what is going on with that film that comes out of a can of polyurethane.

In The Pail

For the purposes of this article, our primary subject is polyurethanes that that are used to protect built up, modified, and single ply roofs. We can illustrate what is going on with this class of polyurethanes at the molecular level by imagining a railroad yard. Our rail yard is made up of boxcars of identical length and build. The boxcar represents one segment of polyurethane polymer, which is where the majority of the properties of the film (flexibility, strength, etc.) reside. The couplings on either end of the boxcar represent the isocyanate reactive sites.



In a large rail yard, the tracks split off into many different spurs via side tracks. Picture our identical boxcars (polyurethane segment) on each track connected to each other in various lengths (chains). This boxcar-boxcar coupling is very strong, so once coupled, it doesn’t come apart. One spur may have a chain of five boxcars, then a chain of thirteen, and maybe a chain of three, and so on, with each chain of boxcars independent of the others. Another spur will have four boxcars attached to one another, followed by a separate chain of 24, and so on. The number of individual boxcars is not important; what is important is the image of random chain lengths.



Now, picture this rail yard spreading out for miles and miles with spur after spur of variously sized couplings of identical boxcars, and you get an idea of what is inside each pail of polyurethane. In actuality, the tracks and subsequent boxcar chains would be weaving in and out of each other in random 3-dimensional ribbons of polymer chains (more like spaghetti in a bowl), but to keep things simple, let’s assume everything is linear and parallel, although at intervals, to help our illustration, there are switch tracks to go from one track to another.

On The Roof – The Curing Process

Once the polyurethane coating is poured out onto the roof, another component is added…atmospheric moisture. Moisture is represented by the train engine. So, our rail yard of identical boxcars coupled at various lengths on miles and miles of spurs are gradually peppered with train engines that weave from spur to spur using the switch tracks. The engine’s sole job it is to link with either end of the long boxcars chains. The first engine links with any boxcar coupling it comes across; whichever is closest to it at the time.

Likewise, the moisture reacts with the isocyanate end group on the polyurethane chain. This process releases carbon dioxide gas — those bubbles you sometimes see on the surface of the coating — and forms an amine. An amine group is very reactive, and will link rapidly with any other isocyanate reactive site in its vicinity.

By way of illustration, the train then pulls the coupled boxcars to another line of boxcars to form a funny looking train where the engine is between two sets of boxcars. The engine becomes a urea once it has been coupled on either side with boxcars. The ends of the two chains of boxcars can be coupled further with other engines.

The fast-reacting amine and isocyantate form a urea, a very rigid strong bond.

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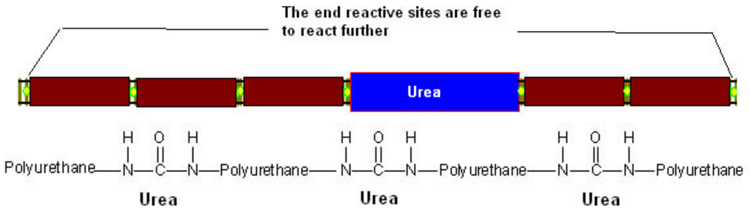


The amount of train engines (moisture) present dictates how often the coupling occurs. The fewer the engines, the slower the coupling; the more engines, the faster the coupling, that is:

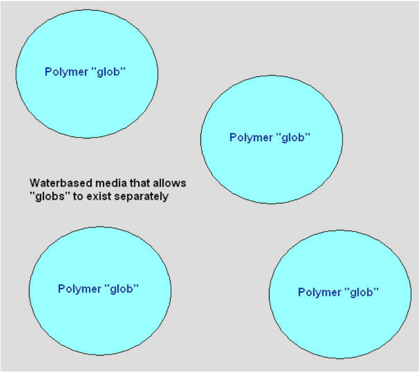
The less moisture, the slower the cure, while more moisture speeds up the cure.

So, drier areas like Arizona will cause a polyurethane coating to cure slower than in relatively more humid areas like Georgia in the summer. Gradually, with enough of this type of coupling, the rail yard becomes full of very large connected (crosslinked) chains. The side tracks become full and the engines (moisture) that arrive fresh on the scene are finding it more and more difficult to find any boxcars to couple with. In the coating, this is called the cure process. Pretty soon, the rail yard becomes so saturated with boxcars coupled to engines that everything grinds to a halt. The film is cured and will not allow water to pass through.

It should be noted that temperature also plays a role in curing, but its effects are less dramatic. Generally speaking, the warmer the temperature, the faster the cure rate; with colder weather, the cure rate slows.

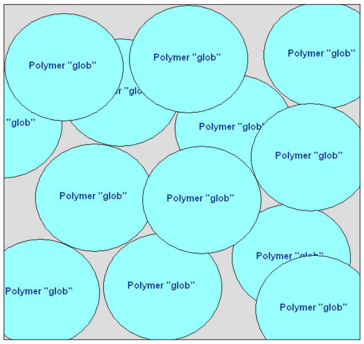
How does the polyurethane curing process compare with the acrylic drying process?

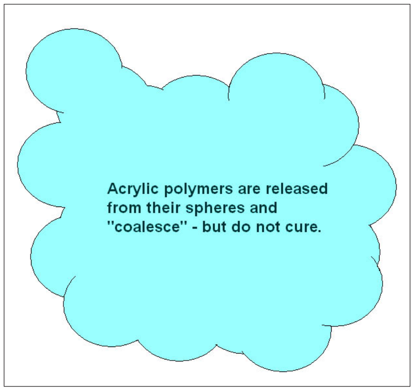
The big difference between a polyurethane and an acrylic coating is the fact that a polyurethane coating undergoes the chemical reaction previously described. In other words, it cures. During this reaction, carbon dioxide is released (bubbles), and the polyurethane chains become linked together with very strong urea bonds. Additionally, a secondary bonding phenomenon, hydrogen bonding, takes place between the polyurethane chains that are rubbing along each other like 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, although they are often incorrectly 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, and causing them to bump against other droplets (below at left). 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 called coalescence (below at right).





The strength and durability of water-based coatings can be increased with performance-enhancing additives that induce chemical cross-linking when the "globs" break and release the polymer. However, this is often done as a post-addition on the job site, which involves wasted time for mixing. Furthermore, if the mixing is not thorough, spotty coalescence will occur. The "cure" occurs because a chemical reaction is taking place with the polymer, which causes linkage to another polymer.

The upside to acrylic coatings is that they are inexpensive, water-based (no solvent), and are relatively more UV stable than aromatic polyurethane coatings. The downside is that acrylic roof coatings are not as strong as cured polyurethane and will fail eventually in ponding water. Additives and other chemistry can be employed to slow the process, but in ponding water, acrylic-based coatings inevitably will begin to delaminate from their substrates. Properly formulated polyurethanes, once cured, maintain their integrity under ponding water. They are also much stronger than most acrylic roof coatings on the market — a testament to their curing ability. A strong polyurethane film will withstand freeze/thaw cycles, flash cooling during a hot summer day's rain storm, and the day-to-day movement of a building.

Conclusions

To summarize, consider these points when evaluating a "cured" rooftop waterproofing solution:

- Polyurethane systems provide an authentic "cure;" the film-forming process that takes place in acrylic systems is more accurately described as "coalescence."
- A cured polyurethane film provides a strong, resilient, waterproof surface.
- The only true "curing" achievable with acrylic coatings most often occurs after their manufacture, as a second step, when an additive is stirred into the bucket of acrylic at the job site. Incomplete mixing will lead to spotty curing on the surface. In contrast, the only additive a single-component polyurethane coating needs to cure is moisture, which is supplied by the atmosphere.
- Acrylic roof coatings tend to fail in ponding water; polyurethane films do not.
- The more moisture in the air, the quicker the cure rate of polyurethane coatings. As a result, the polyurethane film cures more quickly in humid environments; in drier areas, polyurethanes will cure more slowly.

Jason Smith is the Sr. Research & Development Chemist for The Garland Company, Inc. He has multiple US and foreign patents directly related to roofing and has written several articles related to coatings applications and solvent regulations. Jason is a member of the Roof Coatings Manufacturers Association and serves as the co-chair for its Technical Committee.
Smith received his undergraduate degree in Chemistry from The University of Pittsburgh and his Masters Degree in Polymer Chemistry and Coatings from DePaul University in Chicago.