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DRAFT - Rapid Response
Alternatives to Isocyanate-based Marine Coatings
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August 2011

Request

A local ship servicing facility uses isocyanate-based polyurethane (PU) for above-waterline coatings. Are there safer alternatives to isocyanate-based marine coatings?

Key Findings

- Non-isocyanate polyurethane (NIPU) coatings are available, but these are quite new and little performance data is available. Limited MSDS information suggests that these NIPU materials are skin sensitizers. Further study is required to determine whether or not these products are safer than PU during application and use.
- One- and two-component polysiloxane coatings are available from major marine coating manufacturers. Polysiloxanes appear to offer suitable durability and weathering, but the technical data were not complete enough to make thorough comparisons.
- A list of significant specifications was developed based on coating literature and product information sheets. These can be used as prompts for conversations with ship-servicing facilities and product suppliers.
- More detailed data on specification requirements (required gloss, weathering performance, durability, re-coat time, cost issues, etc.) are needed to understand whether the polysiloxane coating materials are suitable replacements for the PU coatings. PPRC recommends contacting the major suppliers and requesting head-to-head data on the existing PU coatings and polysiloxane offerings from the same companies.
- Some or all of the polysiloxane materials have hazardous ingredients. Health and safety comparisons will involve a great deal of data gathering and analysis and a clear definition of the objectives of PU replacement.

Background

Two-component polyurethane (PU) coatings have been widely used for decades as protective topcoats for automobiles, airplanes and ships. PU coatings have a reputation for good aesthetic performance (no-fading/yellowing, high gloss retention), good durability, and good water, solvent and chemical resistance. Two PU coating formulations from different manufacturers were provided as a baseline for material specifications. Both formulations were generic, high-gloss PU coatings containing hexamethylene diisocyanate and/or polymeric forms of hexamethylene diisocyanate.

PU coatings are generally spray-applied, leading to a risk of isocyanate exposure to workers during application. Isocyanate exposure is the leading cause of occupational asthma (NIOSH 2006). Studies also indicate that exposure to diisocyanates can cause contact dermatitis, skin and respiratory tract irritation, and immune sensitization.

Given the hazards of isocyanate-containing coatings, PPRC was asked to identify possible isocyanate-free materials that might be safer for use in marine-coating applications. A full alternatives identification and

assessment is well beyond the scope of a Rapid Response, however, an effort was made to identify possible candidates and some of the important specifications for marine coating alternatives.

Specifications for Current PU Products

A wide range of properties may be relevant to any given coating application. Product information sheets and marine coating literature were surveyed to identify specifications that might be important to ship-servicing facilities. Common specifications include:

- Aesthetic performance – a PU coating is generally applied as a topcoat. One or more underlying layers serve to provide some functionality (corrosion resistance, etc.) and the topcoat is most important for appearance. Specifications include gloss level (or finish) and how well gloss level is retained with exposure to the weather and sunlight, available colors and colorfastness. Tests may include accelerated aging for gloss retention (QUV accelerated weathering tests), UV stability, or colorfastness.
- Durability – the topcoat must also protect the underlying layers and withstand some degree of physical attack. The ship hull flexes with stress, which is especially challenging to coatings where different surfaces meet; the "work" of the vessel may involve equipment that bumps into the painted surfaces; it is normal to have contact with docks, or other structures for accessing the vessel. Specific tests may include abrasion resistance, direct impact resistance, flexibility and pencil hardness. Marine environments also challenge coatings with temperature excursions, water and salt spray, fuel and lubricant spills, etc.; specific tests may include humidity resistance, salt fog resistance, moisture condensation resistance, dry heat resistance, chemical spot resistance, etc.
- Product characteristics needed for coating application – Time is important to several aspects of the coating process. Time in service is time away from work. If a coating requires too much time to dry, it may affect the length of time out-of-service. A coating must remain fluid long enough for successful application but dry fast enough for additional coats, when needed. Some coatings require specific surface preparation steps to guarantee performance and compatibility with other surface layers is important. Specific tests include cure time, re-coat time, pot life, surface preparation requirements, statements of compatibility with surfaces or other coating layers. Temperature of cure may also be important if work must be done in cold climates.
- Environmental performance – due to changes in regulation, coatings have undergone transformation over the decades to reduce the volatile organics and hazardous air pollutants. Specific tests include VOC level, percent solids, and solvent content & type.
- Other characteristics – some applications may also specify a variety of other factors, including shelf life, flash point, health and safety requirements for workers, etc.

Two isocyanate-coating formulations provided as a baseline, a Sherwin-Williams Hi-Solids Polyurethane and International Marine Coating's (Akzo-Nobel) Interthane 990 polyurethane. Both products are two-component, aliphatic PU, with high gloss and "good protective qualities." Both products mentioned either "offshore structures" or "marine applications" as recommended uses. A request from the ship-servicing facility for additional specifications indicated the following requirements:

- The coatings are for metal sections exposed to very wet conditions,
- The ship-owners expect a minimum two year life in marine conditions in Alaska,
- The coating is used above the water line (e.g., decks, sides, railings, doors, and steps) [aka topside or freeboard applications].

Product MSDSs and information sheets offered some typical results for standard industry tests of product performance and product application information (drying time, etc.). No specific details were provided by the ship-servicing facility on requirements for coating compatibility, surface preparation or the characteristics described above. It could be that a certain base level of characteristics is assumed for PU coatings based on experience. Additional discussions are with the ship-servicing facility are needed to identify both major

concerns and less important factors. Gloss retention and durability tests such as abrasion resistance or impact resistance may be good bases for first-pass comparison of products.

Isocyanate-Free Polyurethane Alternatives

Two isocyanate-free polyurethane suppliers were identified in internet searches. Hybrid Coating Technologies markets a "green polyurethane," also referred to as a hybrid non-isocyanate polyurethane (HNIPU) coating. Hybrid Coating Technologies claims that the HNIPU product is more durable than conventional PU coatings. No detailed safety information was found at the Hybrid Coating website. Hybrid Coating Technologies is a licensee of Nanotech Industries, Inc. MSDSs at the Nanotech website (http://www.nanotechindustriesinc.com/nipu-msds.php) suggest that components of the "green polyurethane" are skin sensitizers. Further study would be required to verify whether these products are substantially safer than standard PU materials. While marine applications were mentioned, no detailed application information was found.

Cray Valley offers a broad-range of coating materials, including isocyanate-free marine coatings. No US distributor could be identified. Application information can be found at: http://www.crayvalley.com/en/images/gammes_produits/resines_liquides/documentations/brochure_protective_march_11.pdf. In general, it appears that non-isocyanate PU coatings are in an early stage of development and may not be widely available.

Polysiloxane Alternatives

The main competitor for PU topcoats appears to be polysiloxane coating materials. Polysiloxanes are a blend of epoxy (organic) and siloxane (inorganic) materials and use no isocyanates. Major marine coating suppliers, including Sherwin-Williams, International Marine Coatings (Akzo-Nobel), and PPG Industries have lines of polysiloxane coatings offered for marine applications. Product performance data was available from several polysiloxane alternatives via information data sheets. Unfortunately, each coating material offered a slightly different set of characteristics and often in different units (SI vs English).

PPG Materials

PPG's materials appear to be single-component formulations (http://ppgamercoatus.ppgpmc.com/). PSX 700 Epoxy siloxane coating is said to have "exceptional gloss retention, corrosion resistance, and abrasion resistance." A second material, PSX® 1001, "gives you…better long-term weatherability and gloss retention than the best aliphatic polyurethane." Little technical data was available in the product data sheets for comparisons of durability or weathering performance.

The PPG MSDS system produced hundreds of possible MSDS sheets. In general, it appears that most of these products contain hazardous ingredients and it is not possible to evaluate their safety in this brief review.

Sherwin-Williams Materials

Sherwin-Williams has both one- and two-component polysiloxane formulations (http://protective.sherwin-williams.com/search.jsp?Ntt=polysiloxane). Interestingly, these are not mentioned in Sherwin-Williams Marine Systems brochure (http://protective.sherwin-williams.com/pdf/systems-by-industry/marine-systems.pdf).

Polysiloxane 1K is a single-component finish coat. The product data sheet suggests somewhat poorer abrasion resistance when compared with the Sherwin-Williams Hi-Solids PU, but otherwise similar mechanical properties. The MSDS suggests irritation upon exposure to eyes, skin or respiratory system.

Polysiloxane XLE-80 is a two-component system. Product data sheets suggest similar performance with PU coatings on tests of adhesion and abrasion (XLE-80 vs Sherwin-Williams Hi-Solids PU).The MSDS suggests skin irritation and presence of a probable human carcinogen (ethylbenzene).

International Marine Coatings' Materials

International Marine Coatings offers a two-component polysiloxane topcoat, Interfine 979 (http://www.international-marine.com/products/productsearch/pages/Interfine_979_922.aspx). Qualitative comparisons in their "High Performance Cosmetic Finishes" brochure (see Resources below) suggest good

performance when compared with typical PU coatings. Interfine 979 contains skin sensitizers and other potential hazards.

Summary

PPRC reviewed a number of potential isocyanate-free marine coatings. While isocyanate-free PU coatings are becoming available, they do not appear to be in broad use for marine applications. Polysiloxanes appear to offer good durability when compared with PU coatings, but more detailed data is needed to determine whether they meet the requirements of the ship-servicing facility. Suppliers may be able to recommend other coating materials to meet application requirements.

Safety data obtained from MSDS (or REACH-directed SDS) sheets was suggestive of serious health issues with components of many of the alternative coatings. An analysis of their comparative safety is beyond the scope of this Rapid Response and it is not clear at this point that polysiloxanes offer a significant safety advantage over PU coatings.

The coating field is a diverse and complicated arena, and this work offers only a glimpse at some alternatives. A significant effort will be required to address PU alternatives, including access to test data from suppliers on relative performance. To advance further, more information is needed from the ship-servicing facility to determine the important specifications for these coating materials (reference can be made to the major specification areas described in the "Specifications" section above). These data should be used in conversations with major coating suppliers (PPG, International Marine, and Sherwin-Williams) to determine whether polysiloxanes are suitable alternatives from a performance standpoint. Direct questions about the relative safety of these products should also be addressed to supplier representatives.

Resources

Possible sources for safer, non-isocyanate polyurethane coating materials

- Hybrid Coating Technologies, a green polyurethane manufacturer. Marine application product data may be available by contacting them directly: http://www.hybridcoatingtech.com
- Cray Valley offers a broad-range of coating materials, including isocyanate-free marine coatings. Application information can be found at: http://www.crayvalley.com/en/images/gammes_produits/resines_liquides/documentations/brochure_protective_march_11.pdf

Marine Coating Information/Brochures

- International Marine's High Perfomance Cosmetic Finishes - http://www.international-marine.com/Literature/High_Performance_Cosmetic_Finishes.pdf
- PPG literature on polysiloxane coatings - http://ppgamercoatus.ppgpmc.com/products/Products.cfm
- Sherwin-Williams Marine Coating Systems brochure - http://protective.sherwin-williams.com/pdf/systems-by-industry/marine-systems.pdf