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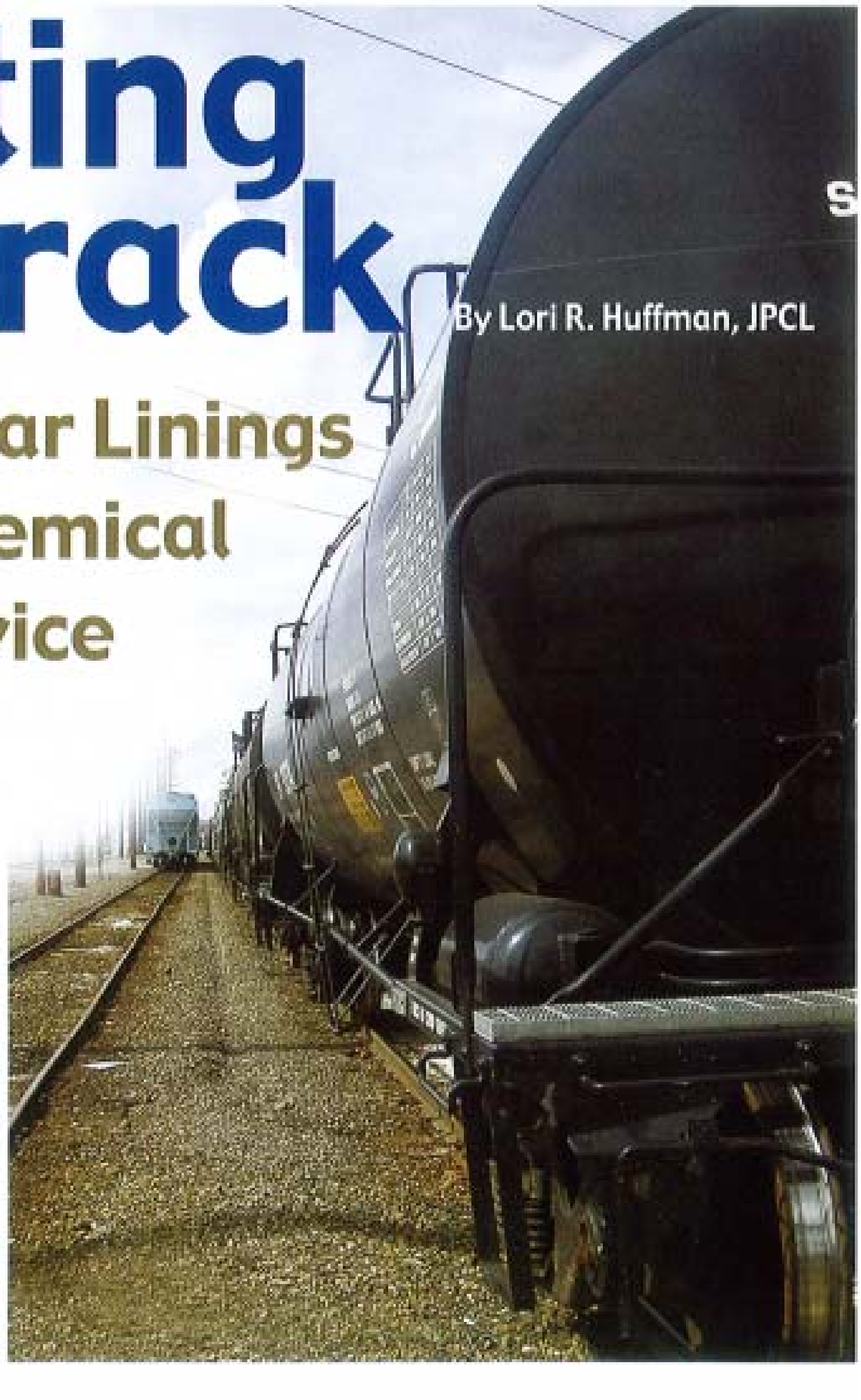
with Railcar Linings for Chemical Service

By Lori R. Huffman, JPCL



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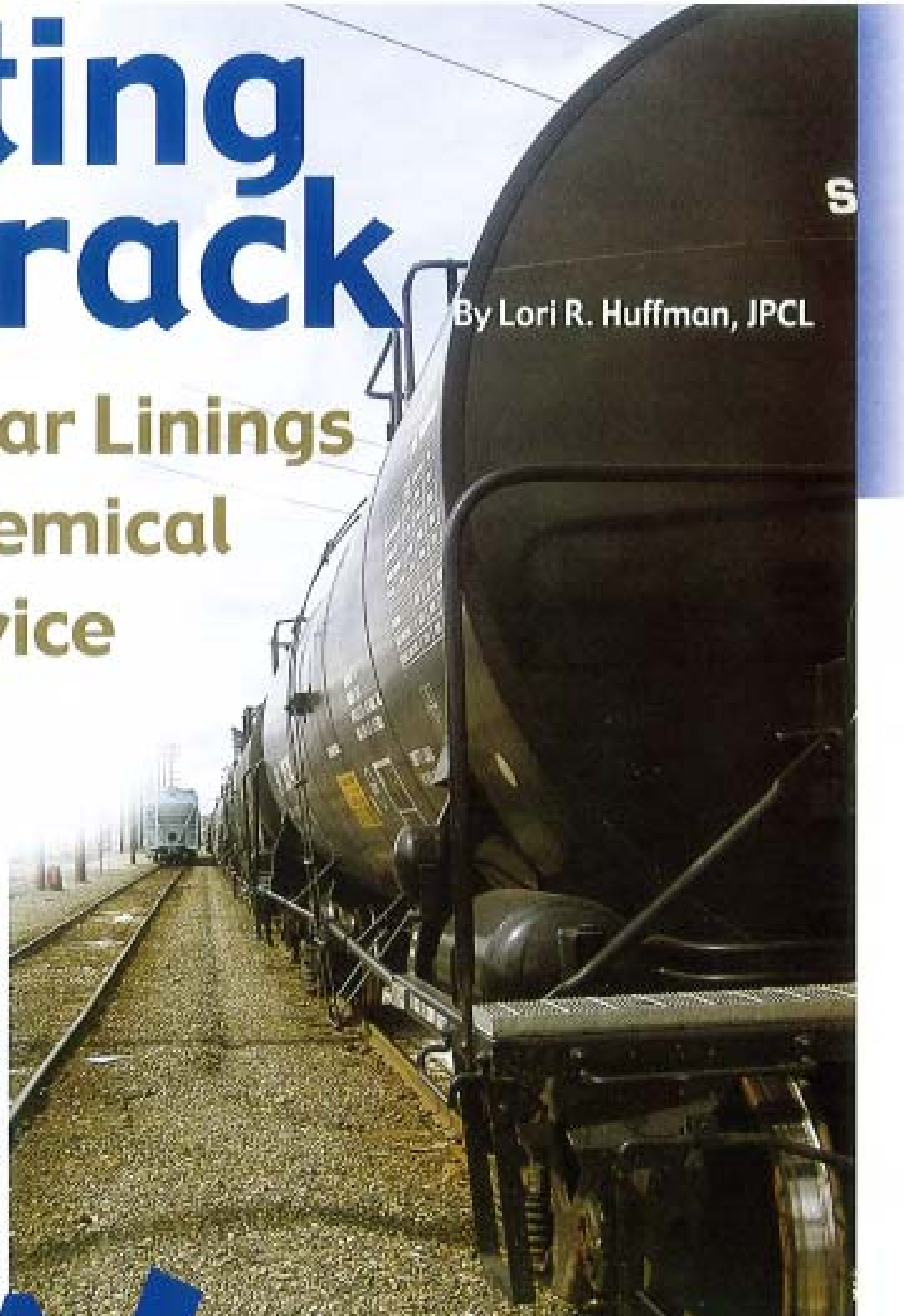

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With railways crisscrossing the United States, it's nearly impossible not to spot a train during the daily commute. Chances are the train you see is towing quite a few tank cars, which are probably carrying a variety of ladings. Jim Molnar of Union Tank Car estimates that an approximate total of 300,000 tank cars are in service in the U.S. And, adds David Clayton, senior chemical engineer with GATX, "The range [of ladings] is limited only by what the Department of Transportation allows." He rattles off

Blistering, such as that shown in the rubber lining at left, has a variety of causes, including proprietary additives in the lading and steam cleaning.
Courtesy of Jim Molnar, Union Tank Car

David Clayton, GATX

just some of the products carried by his company's tank cars: chlorine, ammonia, hydrochloric acid, nitric acid, methyl ethyl ketone, pesticides, and sulfur dioxide.

The most important issues in maintaining these steel vessels are, therefore, the compatibility of the lining with the transported product and the service life that the lining offers in that environment, says Tim Schaffer, plant manager and corporate coating manager of Rescar Companies.

Service Environment Influenced by Many Factors

The service environment of tank cars is affected by more than just the chemical composition of the ladings. According to Molnar, railcars are subjected to the extremes of ambient temperatures. Tank cars may begin their journey in sub-zero conditions in Alaska and arrive to tropical conditions in Mexico. "Although the majority of tank cars have some weather insulation, it doesn't make much of a difference," he says. "They reach ambient temperature quickly."

In addition to temperature extremes, tank cars can be subjected to hot loading and unloading, depending on the product transported, says Molnar. At their final destination, tank cars might be heated—with steam coils—up to 350 F (177 C), a high temperature for typical epoxy linings, he says. Therefore, knowing how a lining will react with the chemicals at elevated temperatures is important.

Jim Molnar, Union Tank Car

Tank car linings are also subject to mechanical damage during offloading, when tools or ladders may be accidentally dropped into the tank, Clayton says. Rubber linings are particularly susceptible. The cause of accelerated failures in these linings "can be difficult to pinpoint," he says. Clayton suggests that rubber linings may also be damaged in transit; for example, a pipe may become dislodged from a sump in the tank car and may then cut into the lining. Likewise, loading hoses dropped into the car can cause damage.

When the tank cars are cleaned, the linings must withstand more abuse. Typically, water jetting and mechanical or hand scraping are performed, followed by neutralization using a pH extreme that may be the opposite of what the lining is designed to resist, says Molnar. In addition, steam, often used in cleaning operations, can cause linings to blister.

Another problem with lining service exposures is the potential for ladings to contain small amounts of proprietary additives that can adversely affect the linings, says Molnar. The effects of these "mystery" additives can range from blistering, peeling, and flaking to the appearance of a "bathtub ring" in the tank car, he says.

Changing the ladings of tank cars can also cause problems with the existing linings, says Clayton. In certain instances, changing the lading of a tank car after several years of service with a different commodity can decrease the life of the lining. For instance, he says, rubber-lined cars that alternate between transporting hydrochloric acid and transporting hydrofluorosilicic acid show accelerated deterioration. The hydrochloric acid leaves a chloride layer on the rubber lining, which breaks down upon exposure to hydrofluorosilicic acid, weakening the lining and allowing the hydrofluorosilicic acid to permeate the lining more quickly, according to Clayton.

Federal regulations require periodic inspection of lined cars that carry corrosive materials. Molten sulfur service is among the most corrosive environments for railcars. Coating failure at the manway is shown here. Courtesy of Jim Molnar, Union Tank Car

Regulation Mandates Inspection of Tank Car Linings

As laid out in federal regulations on the qualification and maintenance of tank cars (49 CFR 180), the tanks of lined cars that transport corrosive materials must be inspected every 10 years. The regulation was issued in 1998 for uninsulated cars and in 2000 for insulated cars. The rule assigns the lining owner the burden of determining periodic inspection intervals, test techniques, and acceptance criteria for linings. The lining owner is defined as the entity whose lading is being shipped.

According to the Association of American Railroads' (AAR) guideline on corrosive products, any lading that has a corrosion rate of 2.5 mils per year or more is considered corrosive. However, the DOT's open-ended list of hazardous materials is the basis for the federal regulation. Should the AAR's definition of corrosive products be used as the benchmark for triggering lining inspection, the DOT's list is bound to expand, says Clayton.

Tim Schaffer, Rescar Companies

Who's Responsible for Determining Inspection Intervals?

The regulation requires the lining owner to set inspection intervals based on the owner's data on the performance of the lining in service. Although the regulation gives responsibility for this task to the lining owner, railcar owners have a vested interest in compiling their own data and calculating inspection intervals, says Schaffer. In addition, the lining owner may defer to the car owner's experience concerning inspection intervals. "The vast majority of customers don't have data on chemical ladings," says Clayton. Molnar agrees, stating that his company compiles service data to determine inspection and maintenance procedures "by default." "Customers keep tabs [on their linings], but with 70,000 tank cars we have the benefit of having [a more complete] overview," he says.

Gathering data on lining performance, like the failure and pitting above, is crucial to improving long-term protection. Courtesy of Jim Molnar, Union Tank Car

Building Service Histories

As an owner and lessor of a fleet of over 100,000 railcars (approximately 60% of which are tank cars), Clayton's company takes an active role in gathering lining performance data. "We are interested in long-term asset protection. We want a part in regulatory issues and [development of] inspection intervals," he says. "Typically, customers leave it to us to develop [inspection] criteria." To this end, his company offers an on-line regulatory reporting system through which railcar shops performing inspection and maintenance can fill out electronic inspection forms. Information gathered from the shops during coating inspection, such as lining age and the number of tank cars shopped and passing inspection, is then compiled in the company's database.

"In certain commodity services, such as molten sulfur, we've gotten much more specific about inspection criteria," says Clayton. This increased vigilance is the result of the negative effects of heat cycling and the presence of moisture in the sulfur-carrying tank cars.

Commonly Used Linings for Chemical Service

The roster of available tank car linings for chemical service has not changed greatly over the years, note the industry experts interviewed for this article. Epoxies and high-bake phenolics are widely used for a variety of ladings, while rubber linings and vinyl esters round out the list.

Epoxies

Epoxy linings came into common use to handle alkali exposures in tank cars. With a dry film thickness (dft) of 10 to 20 mils (250 to 500 microns), these medium-build linings offer ease of installation and field repair, and they don't require high baking, says Molnar. Amine epoxy is a workhorse lining for tank cars carrying less aggressive materials, such as food grade products, says Clayton, while epoxy phenolics are often used in cars that transport sulfur and caustic soda.

High-Bake Phenolics

High-bake phenolic linings have evolved into higher solids, two-coat systems, says Molnar. Calling them "mainstay" linings, Molnar notes that high-bake phenolics are relatively thin, with dfts below 10 mils (250 microns). These linings are suitable for sulfuric acid and phenol service, Clayton adds.

Vinyl Ester

Vinyl ester linings are high-build systems chosen to protect tank cars from ladings with corrosion rates higher than epoxies can handle but not high enough to require a rubber lining, says Molnar. Compatibility of the vinyl ester resin with potential ladings is an important consideration in the selection of this lining, he says. Vinyl esters are typically used in cars carrying sodium bisulfite and sodium chlorate, says Clayton.

Natural and Halobutyl Rubber

Thousands of tank cars are lined with natural rubber, probably more than are lined with any other elastomeric lining, says Larry DeLashmit, sales manager of Polycorp. Natural rubber linings are used for hydrochloric acid ladings, which are incompatible with chlorobutyl rubber linings.

Chlorobutyl rubber, one type of halobutyl rubber, is widely used for tank cars carrying phosphoric acid, ferric and ferrous chloride, hydrofluoric acid, and sodium hypochlorite (bleach), says DeLashmit. The lining is applied in overlapping sheets that are between 5/32 and 1/4 inch thick (4 mm and 6 mm). Joints in the lining are held together with "tack cement." The lining is vulcanized (heated to between 230 F and 280 F [110 C and 138 C] for approximately 6 hours) after installation.


Larry DeLashmit, Polycorp

For ferrous and ferric chloride service, blended chlorobutyl rubber linings are chosen. Blended chlorobutyl rubbers are typically composed of 80 to 85% chlorobutyl rubber and 15 to 20% natural rubber. Because these ladings don't require heating to high temperatures before loading, the diminished heat resistance of the blended chlorobutyl rubber linings (versus pure chlorobutyl) is not a concern, says DeLashmit. The blended chlorobutyl rubber linings typically give 20-year service lives in these exposures.

According to Molnar, his shippers are now looking more to rubber linings as an alternative to vinyl ester and other liquid-applied linings for corrosive ladings when the liquid-applied linings have short service lives (5 years or less) and are fairly expensive to install and maintain. Liquid-applied linings in such corrosive services usually require repair before the five-year point, and the cost of shopping, cleaning, decontaminating, and spot repairing the tank cars can approach the cost of performing a complete relining job, says Molnar. By using rubber linings, Molnar believes that shippers can often get a solid five years' performance before requiring work. The catch, however, is that the tank cars have to be designed specifically for rubber linings, not least because these materials add weight (more than a ton) to the railcar. In addition, the nozzles and fittings on the car must be designed to accommodate the lining or must be eliminated, and all interior edges must be rounded to a 1/32-inch (1 mm) radius. Because of these requirements, the choice to use rubber linings has to be planned. "It's best to order new cars, which can take one and one-half to two years [to manufacture]," he says.

Linings That May Offer Improved Performance

A few products may broaden the available choices for tank car linings in chemical service.

Bromobutyl Rubber

While chlorobutyl rubber is a common lining material, another type of halobutyl rubber known as bromobutyl may offer improved performance in the same services, says DeLashmit. Bromobutyl rubber has been available for more than a decade, but the material has not found use as a tank lining until recently. This rubber lining displays better resistance to heat and chemicals than chlorobutyl rubber, he says.

Typically, chlorobutyl rubber linings fail over time due to hardening and cracking. In the past, a service life of 20 years for chlorobutyl rubber linings was not unheard of. However, service life is now typically 15 to 20 years in phosphoric acid service, says DeLashmit, because manufacturers of super phosphoric acid are heating their product to higher temperatures to avoid the solidification of the chemical, which occurs at 140 F (60 C). The effect of loading the heated chemical into the unheated, chlorobutyl rubber-lined cars leads to hardening of the lining, which can reduce its service life.

To test the performance of the bro-

Tank cars must be specially designed for rubber linings to prevent premature failure. Pictured above is a failed and delaminating rubber pad. Courtesy of Jim Molnar, Union Tank Car

mobutyl rubber, DeLashmit applied the lining to a shipping tank where phosphoric acid was stored before being loaded into tank cars. The shipping tank was heated to 210 F (99 C), 10 degrees Fahrenheit (approximately 6 degrees Celsius) warmer than phosphoric acid is typically shipped, he says. One sheet of the bromobutyl rubber was applied over a newly installed blended chlorobutyl rubber lining, directly under the heating coil on the bottom of the tank. After six years of service, the chlorobutyl rubber lining had begun to harden significantly, whereas the bromobutyl rubber was unaffected. Extrapolating on the results of the field test, DeLashmit says that the bromobutyl rubber linings may offer as much as a 50% gain in service life over blended chlorobutyl rubber in super phosphoric acid service.

According to DeLashmit, the increase in service life makes the bromobutyl rubber lining a good choice, and its price is competitive with chlorobutyl rubber linings. In terms of cost, bromobutyl rubber linings are sandwiched between pure chlorobutyl rubber and blended chlorobutyl rubber.

Other Possibilities

"We don't see a lot of new [lining] products coming into the rail market," says Clayton. "There's downward pressure on R&D to minimize costs." Although the railcar industry experts interviewed for this article agreed with this opinion, a few newer products have raised some interest, including chlorinated polyethylene.

According to DeLashmit, chlorinated polyethylene, a thermoset material, offers significantly better performance than other linings for sodium hydrochlorite service. One snag, however, is the lining's more difficult installation and higher cost. DeLashmit predicts that this lining will catch on with the tank truck industry sooner than with the railcar industry.

Wrinkled rubber lining on tank car head Courtesy of Jim Molnar, Union Tank Car

Rubber linings typically consist of thin plies of rubber that are laminated together on a calender. Some of the linings fail due to delamination between plies, says DeLashmit. Extruded rubber linings have a much better surface appearance and may offer longer service life because there are no plies to separate, he says.

Molten Sulfur Cars

The corrosive environment of molten sulfur cars makes for a real maintenance challenge, says Schaffer. Many factors contribute to lining failures in the cars. Among the causes are sulfur residues in the tank cars following unloading, irregular cleaning, and atmospheric conditions that can introduce moisture into the tank.

The typical lining for molten sulfur service has been a two-coat epoxy system, says Molnar. Modified epoxy, epoxy phenolic, and high-bake phenolic linings are also used. However, tank car owners and customers are finding that the heat cycling issues inherent to sulfur service are extremely damaging to these linings. Sulfur melts at 240 F (116 C) and is handled at up to 320 F (160 C), Molnar explains. In addition, when moisture is present, tank linings can be attacked by sulfide vapors.

Thick linings in sulfur service tend to mudcrack and allow sulfur to etch the substrate, says Larry Hopper, rail fleet maintenance coordinator of PCS. Most lining manufacturers advise that their linings be applied no thicker than 12 to 14 mils (300 to 350 microns) in sulfur cars, he says.

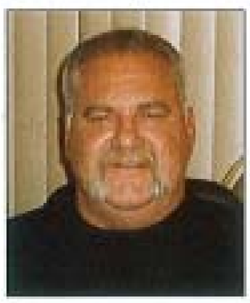
Clayton says that special attention must be paid to inspecting lined areas around attachments to the tank shell, including the manway nozzle, the bolster areas, and the bottom of the car near the outlets. When molten sulfur is unloaded, these areas cool faster than the rest of the tank car, and residual sulfur can harden and be retained on the steel, laying the foundation for corrosion.

Ken Thurman of Chevron notes that retained, hardened sulfur is problematic for molten sulfur tank cars. However, careful tank design can minimize "retains" and lengthen the service life of the lining and tank car. For example, tank cars his company designed specifically for molten sulfur feature twice as many heating coils than typical tank cars. Built in 1982, the tank cars are still in use, owing to the minimization of heat transfer areas and the improved drainage that the design permits, he says.

Guidance on Lining Selection

Given the challenges of molten sulfur service, Task Group 067 of NACE International is working to devise more rigorous testing procedures for the selection of appropriate linings, says Molnar. His company has been active in researching test procedures and has developed an accelerated test similar to an Atlas cell to simulate the environment inside sulfur cars.

After being asked by AAR to write a consensus standard, the task group initially developed and published the Standard for Coating Selection and Application for Tank Cars in Molten Sulfur Transportation in 2002, says Thurman, who chairs the task group. In 2004, the task group began to revise the document to develop a thermal cycling test. The standard's scope is also being broadened to address linings for requalified tank cars, not just linings for new molten sulfur cars, he says.



Ken Thurman, Chevron

In addition, NACE is working on a state-of-the-art report on inspection intervals, procedures, and rationales for lined cars in corrosive services including molten sulfur cars, says Molnar. The report may be completed and published within the next year, he says.

What's Coming?

According to Hopper, the most promising lining for tank cars in sulfur service may well be a product that isn't new. The lining, a low-bake, high-solids, modified epoxy, was manufactured by a company that recently went out of business. The good news, he says, is that another company acquired the product with plans to make it again.

As part of the development of the NACE standard for testing linings for molten sulfur service, laboratory testing of potential linings has indicated that vinyl ester is a promising candidate. Molnar notes, however, that these 30- to 50-mil linings (1,000- to 1,250-micron) are expensive to install. The linings perform well in laboratory testing, but variables in the field—such as the formation of acids from cooling sulfur in high heat flux, mechanically damaged areas at the bottom of the tank, and corrosion in the vapor zone—may produce a different outcome, he says.

The Problem with Plastic Pellet Cars

Although this article focuses primarily on tank cars, several persons interviewed also pointed to another issue that garners attention in the railcar industry: the performance of linings in hopper cars that carry plastic in pellets and other granulated forms. According to Molnar, the box-like hopper cars tend to shimmy in transit, causing the linings to crack at areas of stress. Lining manufacturers are looking into the unique demands of this service, says Molnar, but the problem has yet to be completely solved.

Tougher Regulations May Restrict Future Choices

Future reductions in the limits for volatile organic compounds (VOC) and hazardous air pollutants (HAPS) in coatings may narrow the choice of chemical- and heat-resistant linings for railcars, says DeLashmit. In the case of rubber linings, some shops in California are phasing out their use in favor of liquid-applied linings—not because of the VOC content of the rubber linings themselves but because of the high VOC levels of the tack cements needed for lining installation. Installers of these linings must file for VOC exemptions in California, says DeLashmit.

Schaffer points out that changing VOC regulations will also make the learning curve steeper for those responsible for determining lining inspection intervals. Linings with established performance records may no longer be acceptable for use or even available due to their VOC/HAPS content, and new or reformulated products will require lining owners—and, by extension, tank car owners—to start from scratch to develop performance histories on which to base inspection intervals.

Given the variety of chemical exposures and harsh operating conditions, the owners of linings and the lessors of tank cars have a dizzying job in selecting and maintaining linings for corrosive chemicals. Increased regulatory attention toward railcar inspection and maintenance will spur the railcar industry to continue to search for better products and procedures. The hope is that lining manufacturers will develop more products to meet railcar industry needs.

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