Corrosion Prevention in Paints and Coatings

by Cynthia Challener
JCT CoatingsTech
Contributing Writer

When most people think about paints and coatings, they tend to focus on how the coating will affect the appearance of the substrate in question. While improving appearance is indeed a key attribute of paints and coatings, many also provide additional functionality. Paints and coatings that assist in the prevention of corrosion play a significant role in protecting valuable property for the military, government, industry, and the individual as well. Investment in innovation has enabled suppliers of corrosion protection technologies to respond to the changing environmental regulations, increasing offshore competition, and rising raw material and energy prices that they face today.

Corrosion carries a very high price tag for the United States. In 2002, the total annual estimated direct cost of corrosion in the U.S. was estimated to be $276 billion, or about 3.1% of the nation's gross domestic product (GDP), according to a study initiated by NACE International—The Corrosion Society. A 2001 U.S. government-sponsored study estimated the costs of corrosion for military systems and infrastructure alone to be about $20 billion annually. The Department of Defense has since established a central corrosion control activity and strategy that includes a strong push to bring corrosion control to the forefront and an increased emphasis on training and specification.

Paints and coatings serve as one of the key methods for protecting metal surfaces from corrosion. "Corrosion protection is one issue that penetrates across all segments of the coatings market," notes Michael D. Brown, vice president of The ChemQuest Group, Inc., a management consulting firm located in Cincinnati, OH. Formulators use three basic strategies to provide corrosion protection: barrier technology to prevent oxygen and water from getting to the surface; passivation of the metal surface using corrosion inhibiting additives; and galvanic protection using a sacrificial metal additive.

Above photo courtesy of HALOX.

Barrier properties are often imparted by the use of platelet-like (micaceous) additives. Chromates have long been used as inhibitive pigments, but alternatives to their use are now being sought due to regulatory concerns. Zinc-rich primers are a prime example of coatings that provide corrosion protection at least partly galvanically.

The North American market for anticorrosion technology used in paints and coatings is estimated by ChemQuest to be approximately $210 million, with $75 million attributed to the cathodic protection technology, $70 million to barrier protection, and $65 million to inhibitors. Industrial maintenance accounts for 57% of the total, and OEM applications the remainder. The global market is valued at about $590 million by the consultancy, with barrier protection the largest segment ($270 million, 46%), followed by inhibitors ($200 million, 34%), and sacrificial additives ($120 million, 20%). "North America tends to use more sacrificial coatings than the rest of the world because the value of assets to be protected is greater and there is also more ready access to the high quality sand blasting equipment required to prepare the raw steel as compared to the rest of the world," notes Mr. Brown. Overall, the market is nearly evenly split between North America, Asia, and Europe. Global growth is pegged by ChemQuest at 3.5–4% per year.

This growth rate has been achieved despite several negative factors currently in play in the paint and coatings marketplace. Rising raw material and energy prices, introduction of new regulatory restrictions, and the potential for overcapacity in the near future are all impacting margins. Commoditization of specialty additives due to increased offshore and domestic competition is also a concern, particularly for inhibitor suppliers, according to Tony Gichuhi, Ph.D., R&D manager with HALOX. Increasing demand by customers for more extensive technical support will also result in some companies exiting the market because they lack the necessary resources.

"All of these difficulties can be seen as both challenges and opportunities," says Roger Avakian, chief technology officer with PolyOne Corporation. "The industry is responding by forming partnerships and alliances and developing closer relationships with paint and coatings formulators," he continues. Jim Hachtmann, business manager with Buckman Laboratories adds that, "Challenges are always opportunities and industry continues to rise to the occasion. The intent, however, continues to be inhibited by rising cost of raw materials, lower priced products from offshore manufacturing, and regional regulatory control." R&D efforts tend to be focused on cost reduction and increasing productivity. Part of the strategy of North American suppliers has been to place emphasis on exporting products to take advantage of the weak U.S. dollar, according to Dr. John Sinko, technical director with Wayne Pigment Corporation.

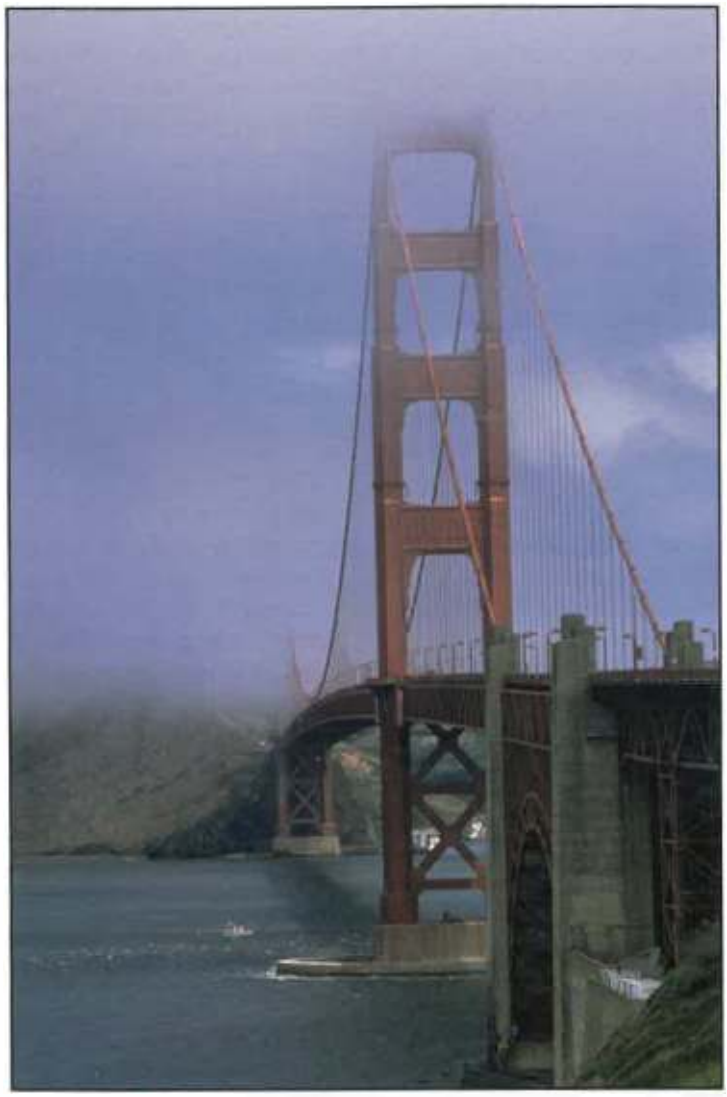
In the future, most manufacturers of corrosion control technology expect to be faced with continued raw material price increases. Some expect that supply and demand will come back into balance, while others predict that overcapacity will remain an issue. PolyOne anticipates that the growing use of bio-derived materials might affect the market. "Migration away from traditional inorganic chemistries to newer organic chemistries also leads to many questions," says Dr. Gichuhi. Concerns about whether or not existing manufacturing facilities will be able to handle the switchover, whether local jurisdictions will permit installation of new manufacturing equipment for organic technology, and how the marketplace will be able to absorb the higher cost of newer products all must be addressed. "Future market needs with regard to substrate protection will also vary as a result of evolving materials of construction," adds Gerald Witucki, coatings industry specialist with Dow Corning. Recycled metals, composites, and plastics will all have unique corrosion and degradation issues.

Economic expansion in China will have a positive impact for corrosion control suppliers say experts. "Currently, the infrastructure in China is new, but in a few years corrosion prevention will become an issue and provide tremendous opportunities for suppliers of this technology," explains Stephen Horton, technical manager with PolyOne. The company is currently working to get into place facilities that will be prepared to provide corrosion prevention materials to the Chinese marketplace when future demand has developed. The recently opened East-European market, with relatively relaxed environmental regulations and moderately sophisticated technology, offers commercial opportunities for U.S. manufacturers of corrosion inhibitors, according to Dr. Sinko.

Regulatory issues will remain a driving force for some time to come, particularly for corrosion inhibitors. Recent significant developments include special hazardous labeling of zinc oxide and zinc phosphate-containing products for the European Union (EU) and reduction in the Occupational Health and Safety Administration's (OSHA) permissible exposure limits (PEL) for hexavalent chromium inhibitors, according to Dr. Gichuhi. "The means by which to deliver the level of corrosion protection provided by traditional inhibitors such as chromates, while at the same time minimizing worker and environmental exposure, is central to ongoing studies," says Mr. Witucki. "Some innovations focus on the safe application and delivery of chromates, while others seek outright replacement."

Many are looking at the regulatory climate as an op-

portunity to differentiate themselves. "It is estimated that all industrial operations where airborne Cr(VI) appears are going to be more expensive in the near future. This situation is anticipated to make the paint and coatings industry more open to the introduction of new inhibitor pigment technologies, which automatically supports R&D," notes Dr. Sinko. Regulatory requirements for final formulations will also affect anticorrosion technology. "Since anticorrosive pigments are formulation specific, this will drive the need to look at inhibitors that have broad range applicability," notes Susanne Krieg, anticorrosive department director for Heubach GmbH.



Corrosion prevention is of greatest concern where substrates exist in harsh environments. Leading end use applications include general industrial, marine, automotive OEM and refinish, coil, and direct to metal coatings (DTM) for the household consumer (architectural or decorative). Each industry segment has its own performance standards, according to Mr. Brown. For industrial maintenance it is about 20 years, and for automotive applications it is about 10 years. Most corrosion prevention technology today can provide the level of protection required for these industries. There is little benefit to be gained by developing new additives that enable coatings to protect surfaces longer than the life expectancy of the object on which they are applied.

However, there are many ways that these technologies can be improved, and some must be replaced due to regulatory requirements. "The value proposition is in driving cost out of the system," Mr. Brown states. Lower costs can be achieved by reducing the amount of additive required in a coating formulation; improving the ease of formulating with these additives; reducing surface preparation time; reducing the number and/or thickness of required coats; reducing labor costs; and improving the ease of application.

"Unfortunately, improvements in technology do tend to be incremental in nature because there is such a long lead time for adoption of new technology. These coatings are applied to very expensive substrates, and it takes a long time to convince customers that a coating containing new anticorrosion technology will perform at an appropriate level," Mr. Brown adds. Dr. Sinko also notes that R&D in corrosion inhibitor pigment chemistry requires specialized and relatively complex interdisciplinary expertise, long-term investment into the intellectual property portfolio, and maintenance of that information. "Combined with the necessary marketing investment for launching new products, development of new anticorrosion technology can be prohibitively expensive, especially for small specialized companies," he states.

Replacement of toxic inhibitors has been a focal point for much of the recent R&D efforts in the anticorrosion industry. Investigation of complexes of rare earth metals such as cerium has been one approach, according to Dr. Martin W. Kendig, senior scientist with Rockwell Scientific. He adds that a trivalent-chromium based conversion coating, although most likely not as effective, is now being used as a replacement for this specific application, but the technology would not be applicable for inhibitors for paints.

Inherently conducting polymers (ICPs), such as those introduced by PolyOne Corporation, have also attracted much interest. "Despite the limited understanding that the industry has with regard to their role as inhibitors, and the problems ICPs have with processing, these products have significant potential," says Dr. Kendig. "The most important role of ICPs will en-

tail their use as 'smart' inhibitors that can give coatings the ability to release inhibitors 'on demand'; for example, as a result of the galvanic coupling of a defect in the coating to the coating material."

Hybrid organic/inorganic and ion exchange or other host/guest compounds also appear quite promising as chromate replacement compounds, according to Dr. Kendig. These materials include hydrotalcite, an anion exchange material, which can be exchanged with various organic and inorganic anionic inhibitors. "Interestingly, ICPs can also act as ion exchange compounds and may be doped with inhibiting anions," he notes. Cation exchange minerals have also been considered as corrosion inhibiting pigments.

Nanotechnology also has the potential to strongly impact the development of novel corrosion prevention technology. "Nanotechnology will play a role in the future of corrosion inhibitor technology by virtue of its novel and new application opportunities," notes Mr. Hachtmann. "We expect that nanotechnology will provide new insights into understanding inhibitive mechanisms and perhaps shed some light on how the increased surface area of nanomaterials can boost anticorrosive efficiency in, for example, metal surface pretreatment," says Dr. Cichuhi. Mr. Witucki believes that nanotechnology offers the potential for creating abrasion resistant and self-healing coatings. Heubach finds the technology interesting due to the electrochemical properties of nanoscale materials, but believes that the cost and difficulty of handling are obstacles that have yet to be overcome.

According to Dr. Kendig, nanomaterials that enable the controlled release of corrosion inhibitors should play a role in new corrosion inhibitors for paints and coatings. "Although there is no inherent reason why a nanotech approach will be required to achieve a practical system that releases inhibitors or otherwise provides protection as a result of a galvanic coupling to a coating defect, new developments in nanoscience represent a promising area to look for the tools for this technology," he comments. Nanotechnology is already being applied in select cases. Nanoscale ICPs are used as inhibitors in Europe and Japan to passivate the metal surface, and are expected to be adopted in North America as well, according to Mr. Horton. PolyOne is also developing a new product based on carbon nanotubes.

Most galvanic cell technology relies on zinc dust as the sacrificial additive. In North America, major suppliers include Gulf Zinc, Eagle Zinc, and US Zinc. PolyOne has introduced an alternative technology based on ICPs to the North American market. The coating additive, called Catize®, is based on the highly conductive polymer polyaniline, which works in conjunction with zinc or aluminum metal to provide both barrier and active rust protection. When a break in the coating system containing Catize corrosion-control additives occurs, the additives protect the underlying metal substrate from moisture and oxygen. The sacrificial coating acts as the anode and the metal substrate becomes the cathode. Catize additives are available for two-part epoxies and urethanes. PolyOne is currently developing versions of the product for use in waterborne coatings.

Also under development at PolyOne is its CarbOne™ additive that utilizes carbon nanotubes instead of ICPs to increase the conductivity of the galvanized cell. As with Catize, addition of the CarbOne additive to a primer creates a passive galvanic cell that protects the substrate. The carbon nanotubes provide higher temperature capabilities and are also more environmentally tolerant than ICPs. The CarbOne additives are being designed for use in acrylics and two-part epoxies and urethanes. As with the ICP based products, these additives from PolyOne containing carbon nanotubes provide both barrier and cathodic protection in one coating and also enhance the durability and stress resistance of the coating. "Advantages provided by both of these offerings include lower loading levels for zinc and other heavy metals, improved integrity of the barrier film, easier application, improved performance, and better aesthetics, and enhanced appearance," says Mr. Avakian. Because of the reduced zinc amounts, the cost for coatings containing these additives is equivalent to traditional zinc rich primers. Often fewer coats are required, and there is less surface preparation needed as well.

Traditional barrier technologies continue to find wide application. Suppliers of aluminum flake for use as a barrier technology include Silberline and Eckart, which recently announced that it has agreed to be acquired by Altana Chemie for $765 million (Euro 630 million). For these companies, aluminum flake is a standard offering that faces significant offshore competition and has nearly become commoditized, according to Mr. Brown. Major providers of epoxy resins as barriers include Dow Chemical and Hexion Specialty Chemicals (recently formed with the merger of Resolution Performance Products, Resolution Specialty Materials, Borden Chemicals, and Bakelite).

There are, however, significant new developments occurring in the corrosion inhibitor segment. Inhibitors applied in organic coatings are typically inhibiting pigments. Today, zinc phosphates, modified zinc phosphates, and modifications to silicates, molybdates, and borates are the leading corrosion inhibitors for paints and coatings. This technology was developed due to the regulatory issues surrounding lead- and chromate-based pigments. The chromate salts of zinc, strontium, and barium, while the most effective inhibitors, are declining in use due to the toxicity issues associated with

them. Leading suppliers include Elementis, HALOX, Heubach, Rockwood, Sherwin-Williams, and Wayne Pigment Corp.

Traditionally, corrosion inhibitor pigments are solid electrolytes (inorganic salts of weak oxy-acids) that have limited but effective solubility in water. "The contemporary selection/qualification paradigm for corrosion inhibitor pigments concerns toxicity, efficiency, and price," says Dr. Sinko. The CrO_4^{2-} anionic species is the most effective, versatile, and least expensive corrosion inhibitor, with the strontium complex the most valuable derivative. Due to human and environmental toxicity concerns, however, chromates are being phased out of most organic coating applications.

Chromate-free pigments available today are typically phosphates, silicates, borates, molybdates or cyanamides of Zn, Ca, Sr, Al, Ba, Mg, or Ce, and in many cases are mixtures thereof. "In these chromate-free inhibitors, except for those containing cerium or zinc, which exhibit some degree of corrosion inhibition ability, the anions of these complex pigments are the active inhibitor species, while the cations regulate important physical properties of pigments such as solubility, pH, and specific gravity," Dr. Sinko notes. Other toxic corrosion inhibitors that are declining in use include those based on nitrites and heavy metals, and aquatic toxins such as zinc-based products, which are regulated in Europe.

In response to the increasing regulation of corrosion inhibitors, there has been a steady growth in the value of nontoxic additives that are synergistic or multifunctional, according to Dr. Gichuhi. "It has been documented that synergy can produce positive effects with various corrosion inhibitors," adds Ms. Krieg. "It is only natural to look for combinations or hybrids of pigment types considering the modifications that have been necessary to achieve desired degrees of solubility," she continues. Heubach has found that one of the most successful synergies has been the combination of inorganic and organic inhibitors.

Research efforts have focused on developing nonchromate inhibitors that provide the same level of performance. This work has been challenging specifically with regard to thin organic coatings with limited barrier functionality, such as coil and aircraft coatings. These thin coatings require highly effective inhibitor capacity packed into a limited volume, which is difficult with nonchromate inhibitor pigments, according to Dr. Sinko. Finding nonchromate inhibitors that are broadly effective on all metal substrates has been a challenge as well, particularly for inorganic additives.

"Organic inhibitors have significant potential, but in general they have been designed for noncoating applications and therefore are very soluble in water, or are volatile, or operate by incompatible mechanisms," Dr. Sinko adds. "As a consequence, application of organic corrosion inhibitors in organic coatings is not a casual exercise." Nevertheless, the most significant progress has been realized through the development of corrosion inhibitor pigment technology based on organic corrosion inhibitors, and, more specifically, in the area of pigment grade organic/inorganic hybrids. Hybrid corrosion inhibitor pigments operate with organic active constituents, yet are pigment grade, nonvolatile, thermally stable solid powders with limited but effective solubility in water and are essentially insoluble in organic solvents. These products are substrate specific, though.

Several factors in addition to substrate metal can impact the choice of a corrosion inhibitor. "Corrosion inhibitors are significantly influenced by the desired application performance as well as the resin used to achieve this goal," says Ms. Krieg. "Environmental concerns for VOCs, application, performance specifications, testing parameters, etc. all influence the binder utilized and, thus, the requirements of the anticorrosive pigment."

Heucotech, a member of the Heubach group, has introduced two new corrosion inhibitors designed for universal applications that are based on modified phosphates. These Heucophos Wide Spectrum Anti-Corrosive (WSA) pigments are designed for use in waterborne, powder, and high-solids formulations as well as conventional systems, according to Ms. Krieg. "We believe that this newest generation of inhibitors offers the broadest range of applications and the ability to meet desired performance criteria."

The company's strategy is to separate itself from the competition by developing new technology, providing increased customer support by qualified technical personnel, and offering economically efficient products. The recent announcement of plans to build a modern technical service laboratory in North America at its site in Fairless Hills, PA, reflects this approach. Heubach GmbH has also installed significant new production capacity in Germany.

HALOX® has launched a new line of pigment-type corrosion inhibitors including HALOX 300, 400, 430, 710, and 720, plus the new liquid products HALOX 510, 515, 630 HF, and 900. The company expects to launch an organic-inorganic corrosion inhibitor in the fall of 2005. "All of these products are nontoxic and fulfill specific market needs," notes Dr. Gichuhi. With regard to investments, HALOX recently acquired the organic corrosion inhibitor line of Ciba Specialty Chemicals. The company also plans to install a volatile liquid facility to manufacture its organic corrosion inhibitors.

Wayne Pigment Corporation has focused on development of effective, chromate-free, and, in general, environmentally benign pigment grade corrosion inhibitors for over a decade. The result of this effort was the launch of its Hybricor® organic-inorganic hybrid line of corrosion inhibitors. At the present time, the company offers several specialized hybrid pigment grade corrosion inhibitors that are mechanistically tuned for effective protection of high strength aluminum alloys, with typical application as replacement of chromate pigments in aircraft coatings. According to Dr. Sinko, Wayne Pigment is in the process of introducing hybrid inhibitor pigments specifically designed for galvanized steel protection as well.

Wayne Pigment's new Corrosperse® product line includes several high-solids, resin-free dispersions of strontium chromate in several different organic solvents. These dust-free products are easy to incorporate into paint systems and can result in increased productivity with no capital investment. Corrosperse Strontium Chromate dispersions are intended as "stir in" precursors compatible with all contemporary manufacturing technologies of high performance coil and aircraft primers, according to Dr. Sinko. "These products offer the possibility to practically eliminate the Cr(VI) dust exposure hazard and all associated expenses without additional investment at paint manufacturing sites. This technology also protects the environment by eliminating the disposal of Cr(VI) contaminated packaging materials, resulting also in considerable savings. We hope our investment in the Corrosperse technology will extend the commercial and technological life of this most valuable corrosion inhibitor pigment," he explains.

Buckman Laboratories has recently launched its new corrosion inhibitor Butrol 465M, an oxyamino phosphate salt of magnesium. This product is a heavy metal free inhibitor designed to meet the requirements of a variety of demanding applications. "The company continues to view corrosion inhibition as an area of importance and focus. Using global demand as a benchmark for development, Buckman endeavors to investigate opportunities to better current technologies and application needs," notes Mr. Hachtmann.

R.T. Vanderbilt Co. Inc. is a manufacturer of extender pigments that work in combination with other corrosion protection pigments to enhance their performance and extend the life of the coating, particularly water-based systems. According to Vergil Carlson, sales manager, Paint Dept. of R.T. Vanderbilt, the company has invested significant resources in developing effective formulations with these products. "Our extender pigments improve the level of waterborne coatings that approach the level of solvent coatings to the level of solvent-based systems with respect to corrosion protection, while not affecting key appearance properties such as gloss." R.T. Vanderbilt also manufactures talcs and Vancor organic corrosion inhibitors based on sulfonate chemistry.

Dow Corning is investing in the study of corrosion surface chemistry and the impact of silicon-based materials on the mechanisms of attack, according to Mr. Witucki. "Our goal is to develop products that meet the market needs for safer and more cost effective corrosion control technology," he notes. As a part of this strategy, the company has expanded its line of silane materials to allow greater formulation alternatives.

The variety of new corrosion prevention technologies designed for use in paints and coatings reflects the determination and capability of the industry to overcome the evolving business climate within which it functions. It is widely believed by players in this market that the industry overall will meet the future challenges. "The question of the future will be who remains and who is new," notes Ms. Krieg. "The entry barrier is significant due to the wide range of applications and testing criteria, necessary technical support, regulatory changes, and resin and additive technology advancement." Those companies that are prepared to respond quickly to these market demands and capitalize on the opportunities they present will continue to be successful. CT