Coatings for Elevated Temperature Service in Process Facilities

Heated surfaces on stacks, boilers, and similar equipment require the highest levels of coating technology to withstand corrosive fumes, cyclic heating operations, thermal expansion, and atmospheric weathering.

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For many operating power generating facilities, chemical plants, and refineries, the painting of heated surfaces represents one of the most problematic and challenging applications for the coatings engineer. Heated surfaces found on stacks, breaching, boilers, heat exchangers, reactors, stills, crackers, furnaces, and engine exhaust manifolds have traditionally required the highest levels of applied coating technology to achieve successful coating installations (Fig. 1). Once installed, the coatings may be subjected to the rigors of corrosive fumes, cyclic heating operations, thermal expansion, and atmospheric weathering. Each of these factors can contribute to the incipient failure of the elevated temperature coating system.

The consequences of a less-than-optimal coating selection and installation can include elevated maintenance costs throughout the life of the facility, along with expensive downtime for repairs of the substrate. This article presents a generic survey of the formulation technology found in contemporary coating products for elevated temperature, and outlines surface preparation requirements to ensure acceptable coating service life. Also included are design and material alternatives to liquid coatings for protecting heated surfaces.

Determining Operating Conditions

The most important step in the successful use of protective coatings at elevated temperatures is the correct determination of the nominal temperature level that the equipment or structure will be subject to during operation. Temperature data taken from active recording devices is the most reliable basis for determining the temperature range during both normal operation and transients. In the absence of instrumentally recorded data, contact thermometers or infrared pyrometers can be used to determine point readings on the heated surfaces. When direct temperature data are difficult to obtain, data derived from process and equipment diagrams or equipment data sheets may be used as a guide to estimating operating temperatures. Plant process engineers may also be sources for temperature data, but the estimates should always be subject to review for accuracy. In the absence of hard data, process plant personnel may overestimate temperature levels in the interest of conservatism. Unfortunately, this process can impose unreasonable constraints in the selection of high temperature coatings, forcing the coating specifier or engineer to eliminate some normally acceptable materials.

Steady or Cyclic Temperature

The rate at which heat flows into or through a substrate can affect the performance of an attached coating. The steady state temperature represents an important design point for coating specification. It effectively characterizes the mean level of temperature at which the coating will be expected to perform. However, where the temperature cycles through a range of values, then the expansion and contraction of the coating system, its substrate, and any structural joints over which the coating has been placed will impose additional stress on the coating. Low alloy steels subjected to cyclic temperatures in atmospheric exposure undergo accelerated oxidation, scaling, and pack rusting that rapidly deteriorate the substrate. The failure to adequately protect these surfaces can result in costly metal cleaning and repair operations.

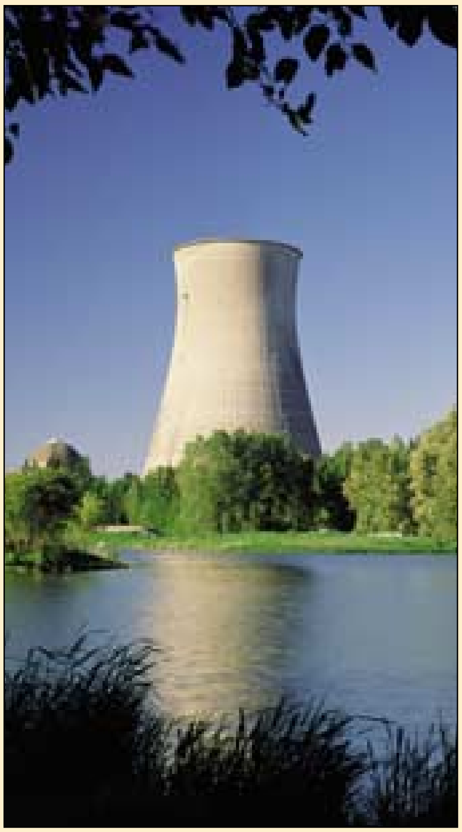

Fig. 1 - High heat coatings are needed on hot surfaces on boilers, heat exchangers, and other operating equipment in power plants

Wet or Dry Heat

Moisture and other chemical vapors can have an adverse effect on the performance of a coating system operating at elevated temperatures. All coatings are permeable to the movement of vapors through their matrix. In the case of coatings exposed to boiling liquids, an elevated oxygen concentration at the vapor/liquid interface can place additional stress upon an attached coating. In many cases, wet heat can cause blistering and adhesion loss of an attached coating, whereas the same level of dry heat will have no effect. In almost every case, there is a reduction in temperature tolerance when coatings are exposed to wet heat. Heated surfaces that are allowed to cycle between ambient and some elevated temperature and that are exposed to the atmosphere can undergo accelerated corrosion through contact with oxygen and condensed moisture. In these applications, functional inhibitors must be present in the coating formulation to prevent substrate corrosion during periods of equipment downtime.

Binder Considerations

The selection of the binder, or resin, which constitutes the major portion of the coating system, generally governs the temperature resistance or temperature tolerance of the coating. In practice, the binder is combined with an appropriate selection of pigments that, when blended together, will achieve a desirable level of performance at elevated temperatures. In general, many of the resin systems used in conventional coating systems can also be used at some level of elevated temperature. Because they are composed of organic molecules, they are heat sensitive. The limiting factor for each of these resins will be the temperature at which the resin (binder) will begin to degrade.

Air-Oxidizing Resins

Atmospherically reactive resin systems, like oil-modified and alkyd resins that cure by solvent evaporation and slow oxidation, exhibit relatively low levels of heat resistance. The input of heat to these systems accelerates binder oxidation and produces a corresponding degree of brittleness and inflexibility to the cured coating matrix. Additional heat influx will cause initial discoloration of the binder. As the coating matrix is exposed to continued heat flux, destructive distillation (or thermal decomposition, the boiling off of lighter hydrocarbons in formulation) and mechanical breakdown of the organic binder matrix will occur, leading to charring and eventual coating delamination. Coatings of this type can be used safely only to maximum temperatures in the range of approximately 140 F to 250 F (60 C to 121 C).

Thermoplastic Resins

Most binders utilizing thermoplastic addition polymers or dispersion resins, like acrylics, styrene, chlorinated rubber, and vinyl acetate or vinyl chloride, also exhibit relatively low thermal resistance. Coatings incorporating these binders undergo decomposition with increased heating caused by the weakening of bonds between the aliphatic hydrocarbons in the binder matrix. The breakdown temperature is also lowered through formulations that introduce unsaturation and ester linkages into the resin structure. Resins that contain chlorinated hydrocarbons, like vinyl chloride, may also release chlorine as a decomposition product. Chlorine is corrosive to most metal substrates, and in the case of some stainless steels, will cause stress corrosion cracking. The practical range for elevated temperature use of coatings employing these resins is from approximately 140 F to 250 F (60 C to 121 C).

One notable exception is with fluorocarbon resins, which are thermoplastic in nature but have excellent heat resistance. Coatings formulated with fluorocarbon resins can exhibit heat resistance to 750 F (399 C).

Chemical and Heat-Cured Resins

Multifunctional organic resins that cure through chemical reaction can exhibit higher levels of heat resistance because of enhanced cross-link density. Resins in this group include epoxies and phenolics, along with blends like novolac epoxies and phenolic novolacs. Epoxy systems based upon bisphenol A epoxy resins and a variety of curing agents can survive service temperatures in the 140 F to 300 F (60 C to 149 C) range. With the addition of heat curing or baking, blends of epoxies with phenolic novolac resins and a variety of curing agents develop extremely high cross-link densities. Such formulations can survive service temperatures up to 500 F (260 C). They do, however, tend to become more brittle with increased cross-linking. The higher temperature materials are well suited to heat exchanger service, transfer piping, and storage tanks where hot liquids

Table 1
Thermal Resistance: Silicone Resin Formulations*

Resin System	Pigment	Silicone Content (percent)	Temperature Range Fahrenheit	Temperature Range Celsius
Organic	Aluminum	None	240-400	116-204
Silicone/Organic	Colored	15-50	240-400	116-204
Silicone/Organic	Aluminum	50-90	350-500	177-260
Silicone/Organic	Carbon/Aluminum	50-90	450-700	232-371
Silicone	Colored	100	450-700	232-371
Inorganic Silicate	Zinc	None	700-850	371-454
Silicone	Carbon/Aluminum	100	600-1,000	316-538
Silicone	Ceramic	100	800-1,200	427-649

** Data from reference 1.*

are used. These coatings also display high levels of corrosion resistance.

Moisture-Curing Polyurethanes

Another class of resins with moderate heat-resistant properties is the moisture-curing urethanes. They are single package formulations that cure by the reaction of atmospheric moisture with residual isocyanate groups, in either aromatic or aliphatic urethane resin bases. These resins have been represented to withstand elevated temperatures in the range of 220 F to 325 F (104 C to 163 C). With some commercial products, discoloration may occur at the upper limit of this range. While moisture-cured urethanes are formulated with colored, aluminum, and zinc pigments, the temperature tolerance of the urethane binder will be the limiting factor in elevated temperature service.

Silicone Resins

Because of a high degree of cross-linking with multi-functional silane groups, silicone polymers exhibit excellent thermal stability and a very strong resistance to oxidation. These properties make silicone resins, as a class, one of the most heat-resistant, and widely-used binder systems for elevated temperature service. Silicone resin systems often require heat rather than ambient cure.

Silicone resins are blended in increasing amounts with other hydrocarbon resins to impart heat resistance to a coating binder. Alkyd, acrylic, and phenolic resins are blended with moderate additions (15 percent to 25 percent) of silicone resin to produce improvements in heat resistance that add approximately 100 F to 150 F (38 C to 66 C) to the sustained heat operating range of the coating system. Through the addition of proportionately greater amounts of silicone resins (50 percent to 90 percent) and heat-resistant pigments, the operating range of the coating formulations can be extended to approximately 450 F to 700 F (232 C to 371 C).

The higher temperature formulations are color-limited because they incorporate carbon-based and metallic pigments. At the highest levels of thermal performance, formulations utilizing 100 percent silicone resins with ceramic pigments can survive sustained operation in the 800 F to 1,200 F (427 C to 649 C) temperature range. Finzel[1] has classified the many silicone resin-based formulations available for industrial use. Table 1 summarizes the thermal resistance of different silicone resin formulations.

Silicate Resins

Inorganic zinc-rich coatings are principally used as extremely effective corrosion-resistant materials. However, as a binder class, the inorganic, silicate-based resins used in these coating formulations also exhibit excellent resistance to elevated temperatures. The alkyl silicates, which cure through the incorporation of atmospheric moisture, or the alkali silicates, which cure by elimination of water, are robust binders in zinc-rich systems. They perform well because the inorganic constituents of the systems behave as refractory-like materials, exhibiting melting points in the 1,400 F to 1,600 F range (760 C to 871 C).

In practice, it is actually the zinc metal pigment, with a melting point of approximately 790 F (421 C), that is the limiting factor in the high temperature performance of inorganic, zinc-rich systems. Coating manufacturers list the service temperature of these materials at 750 F to 790 F (399 C to 421 C), with intermittent operation to 1,000 F (538 C).

Because of their heavy loading of zinc pigment, typically in the 80 percent to 90 percent range, inorganic zinc-rich coatings exhibit a gray, matte finish. In high temperature applications, they may be used without a topcoat. However, where the heated system may be shut down, cycled through lower temperatures, or exposed to moisture in the range of ambient to 200 F (93 C), the inorganic zinc-rich coating may serve as an anti-corrosion, high temperature primer. This primer can then be topcoated with a variety of high temperature coatings to provide a colored topcoat. Among compatible topcoats are silicone, silicone acrylic, and epoxy-based formulations.

Silicon Oxide Resins

Recent advances in coating technology include the advent of organo functional, silicon oxide-based resins that have a substituted organic-cyclic structure. These materials are capable of forming highly cross-linked organic/inorganic polymers possessing high heat and chemical resistance. The materials are reported to withstand dry heat service temperatures in the range of 1,000 F to 2,000 F (538 C to 1,093 C). They cure at ambient temperatures and require no extended heat cure prior to service.

Pigment Type

Pigments That Impart Color

Pigments selected for elevated temperature use frequently have better overall temperature resistance than the binders with which they are blended. Pigments utilized in high temperature coatings are generally inorganic (mineral-based) or metallic. In the case of the mineral-based pigments, materials like clay, fumed silica, mica, and ceramic particles will have melting or decomposition points that are significantly higher than the resins with which they are blended. Mineral pigments can typically withstand temperatures in the range of 1,500 F to 2,000 F (816 C to 1,093 C).

Aluminum, zinc, and stainless steel are also used in high temperature coating systems. The upper limits of metallic pigments are principally defined by their melting points. The melting points are approximately 1,220 F (660 C) for aluminum, 790 F (421 C) for zinc, and 2,500 F (1,371 C) for stainless steel. Due to their high thermal conductivity, these metals aid in the transfer of heat away from the coated substrate and in the ability of the coating system to survive at elevated temperatures.

Pigments used to impart color to high temperature coatings must be stable in the range of intended temperature usage. Within the range of thermal-resistant coatings, certain colored organic and inorganic pigments exhibit good-to-excellent resistance to heat loading in the range of 200 F to 500 F (93 C to 260 C).

Coatings utilizing some form of car-

Table 2
Coloring Pigments for High Temperature Coatings

Color	Type	Pigment Name
Red	Inorganic	Cadmium Red, Red Iron Oxide
Orange	Inorganic	Cadmium Orange
Yellow	Inorganic	Yellow Iron Oxide, Nickel Titanate
Green	Organic	Phthalocyanine Green
Blue	Organic	Phthalocyanine Blue
White	Inorganic	Zinc Oxide, Titanium Dioxide
Black	Inorganic	Lampblack, Carbon Black
Metallic	Metal	Aluminum Flake, Zinc Dust, Stainless Steel Powder

bon, such as lampblack or carbon black, or metallic pigment, such as aluminum, zinc, or stainless steel, will maintain their color over a usable range that exceeds 500 F (260 C) and approaches their respective melting points.

Coatings that use finely divided carbon or metal as pigments are usually only available as black or metallic in appearance, respectively. Table 2 lists pigments used to color heat-resistant coatings.

In addition to pigments used as primary colorants, other pigments are added to high temperature coatings to impart specific resistance to corrosion, increase film build, and enhance physical integrity of the cured films. Materials such as inhibitive pigments, fiberglass flakes, and ground ceramics have been used for these purposes.

Temperature-Indicating Pigments

There is often a need in chemical processing operations to identify hot spots, insulation failures, and temperature transients on tanks, vessels, and reactors. Temperature-indicating pigments are added to some high temperature paint formulations that have service temperatures in the range of ambient to 600 F (316 C). One modified silicone product displays 3 different colors as substrate temperatures of 400 F, 600 F, and above 600 F (204 C, 316 C, and above 316 C) are reached.

Other coating products undergo a single color change as a predetermined substrate temperature is attained. The color changes are irreversible as the equipment cools, and the surfaces must be repainted to restore the temperature-indicating capability.

Surface Preparation

Next to the proper selection of resin system, proper surface preparation is the most important factor in the successful application and performance of high temperature coating systems. The failure to remove mill scale, rust, and old coatings from a steel surface will be problematic to all coatings subjected to elevated temperatures. Mill scale and rust, as oxides of iron, have different rates of thermal expansion than steel and iron. When a steel or iron substrate containing these surface contaminants is heated, the contaminants will expand at a different rate than the substrate, creating stresses that will result in the delamination of the mill scale and rust. Coatings applied over these materials will also become dislodged, creating discontinuities in the corrosion protection afforded by the applied coating.

Coating manufacturers almost universally require a surface cleanliness corresponding to at least an SSPC-SP 10/NACE 2, Near-White Blast Cleaning, for coatings subjected to elevated temperatures in atmospheric service.

For coatings subjected to elevated temperatures in wet heat service, the substrate should be cleaned in accordance with SSPC-SP 5/NACE 1, White Metal Blast Cleaning.

Using coatings in a wet heat condition also requires that the metallic substrate be free of soluble chemical contamination in the form of chlorides, sulfates, and ferrous ions. If not removed, each of these contaminants can precipitate the blistering of applied coating films through osmotic effects. For this reason, a pre-cleaning step, performed in accordance with SSPC-SP 1, Solvent Cleaning, using steam or aqueous media, should be completed before abrasive cleaning is attempted if the presence of these materials is suspected.

The decontaminated surface should, at a minimum, comply to condition SC-2 of the Joint Surface Preparation Standard SSPC-SP 12/NACE 5, Surface Preparation and Cleaning of Steel and Other Hard Materials by High- and Ultrahigh-Pressure Water Jetting Prior to Recoating. The SC-2 cleaned surface should have less than 7 $\mu g/cm^2$ of chloride contamination, less than 10 $\mu g/cm^2$ of soluble ferrous ions, and less than 17 $\mu g/cm^2$ of sulfate contaminants as verified by accurate analysis.

However, it should be noted that field methods for the surface sampling of steel contaminated by soluble salts, such as swabbing or surface-cell extraction, vary in their transfer efficiencies for extractive sampling. The works of Trimber[2] and Flores[3] discuss these parameters as they relate to such detection means as ion-sensitive, paper chromatography.

Fig. 2 - Abrasive blasting may not always be acceptable in operating plants because it may interfere with equipment or cause safety hazards.

Under certain conditions in operating plants, it may be impossible to use abrasive blast cleaning to prepare the metal surfaces (Fig. 2). In these situations, it may be possible to employ SSPC-SP 11, Power Tool Cleaning to Bare Metal. This cleaning method is suitable where a roughened, clean, bare metal surface is required, but where air-driven abrasive cleaning cannot be used.

A final area requiring specific attention lies in the surface profile of the metallic substrate. To avoid the problem of thermally induced coating stresses, high temperature coatings are generally specified for application at lower film thickness than conventional coatings. A dry film thickness (dft) range of 3 to 6 mils (75 to 150 micrometers) is common for these materials. Within this thickness range, a 1- to 2-mil (25- to 50-micrometer) surface profile would ordinarily be appropriate. However, due to the high incidence of failure among defective coating applications, many high temperature coating applications are made over previously corroded surfaces. After cleaning, these surfaces may be pitted and roughened, conditions that will be problematic to uniform coating deposition. Care should be taken to both cover the existing metal profile with the specified dft and avoid the accumulation of excessive coating in substrate pits. That is, the applied coating should conform to the surface profile and not fill deep pits; otherwise, undue coating stress may develop upon curing and placing into service.

In some situations, equipment cannot be shut down for cleaning and painting, and all work must be done directly on hot surfaces. While this is not an ideal condition under which to carry out such operations, a limited number of high temperature coatings can be used successfully. These coatings are generally single-component, self-priming silicone copolymer formulations that will tolerate application to surfaces at temperatures up to 500 F (260 C). However, the hot surfaces must initially be cleaned in accordance with SSPC-SP 1, Solvent Cleaning, to remove adherent dirt, oil, and grease. Weld flux must also be removed. This operation should then be followed by abrasive blast cleaning in accordance with SSPC-SP 10. The coating should be applied before visible oxidation forms on the hot surfaces.

Curing Cycle Considerations

High temperature coatings cure by a variety of mechanisms. The curing mechanism will be closely tied to the binder system employed in the coating formulation. Coatings that cure at ambient temperatures use mechanisms such as oxidation, reaction with atmospheric moisture, and chemical curing. Coatings that cure by these mechanisms must reach a state of full cure before heat is applied.

Another group of high temperature coatings requires the application of heat to complete the cure cycle. To fully cure, this class of coatings typically requires a one- to two-hour baking period at an intermediate temperature that is 40 percent to 60 percent of the peak operating temperature. The curing cycle is related to the time/temperature relationships during the cycle. Higher temperatures will shorten the time necessary to accomplish a full cure. The baking period completes the curing by driving off residual solvents, sets the binder, and improves its weathering characteristics.

A third type of high temperature coating formulation utilizes single-component resin binders that hold dispersed metallic pigment, like aluminum, in suspension and facilitate the pigment transfer to the metal surface. Simple oleoresinous, coumarone-indene, and pure silicone resins are used in these formulations. As the substrate is elevated to the operating temperature, the binder resin is boiled off to allow the metallic pigment to melt and fuse to the substrate, or, in the case of the higher boiling silicone resins, to create a complex fusion product of resin, ceramic colorants, and additives. By these methods, coating service temperatures of 900 F to 1,500 F (482 C to 816 C) are attainable.

Alternatives to Conventional Liquid Coatings

Several alternatives are available for protecting hot surfaces. Although these alternatives have high installation costs, they may greatly reduce the costs of periodic maintenance painting with conventional high temperature liquid coating systems.

Thermal Spraying

Metals—like stainless steel, aluminum, zinc, 85/15 zinc/aluminum, and 90/10 aluminum/alumina—have been used successfully in high temperature service to protect metallic substrates from additional oxidation and corrosion. The coatings are applied directly to the metallic substrate by passing the coating media, in the form of a wire or powder, through a high energy source consisting of a high intensity flame, plasma arc, or electric arc. As the coating materials pass through the energy zone, they are heated to a molten or plastic state and propelled by a stream of compressed gas toward the substrate. As the particles strike the surface, they flatten and form thin platelets. In this manner, molten coating droplets are fused directly to the metallic substrate. The process requires a substrate cleanliness equivalent to SSPC-SP 5.

The initial cost of these coatings is higher than most of the liquid coatings surveyed in this article, but they can provide service lives of up to 20 years, with minimal maintenance. The service temperatures of the thermal sprayed metallic coatings are a direct function of their melting points, and are in the range of 750 F to 1,000 F (399 C to 538 C).

Sheathing

An alternative means of addressing the poor aesthetics presented by oxidizable heated surfaces is to clean them and cover them with aluminum metal sheathing. To avoid potential galvanic coupling, an insulating layer should be inserted between the 2 metals. If necessary, cooling fins can be added to the aluminum sheathing to dissipate additional heat from the protected surfaces. The option of covering the heated surfaces eliminates the need for periodic repainting. If the skin temperature is low enough, or reduced through additional insulation, aluminum sheathing covered with custom-colored, factory-applied coil coatings can be used as exterior sheathing material.

Alternative Materials of Construction

The materials used to construct breaching and stacks can be changed to eliminate the need for painting with high temperature coatings. Metals like stainless, weathering, or galvanized steel can be substituted during facility design to eliminate the use of conventional carbon steel. Although the substitution of these materials will increase initial construction costs, their use will be accompanied by a corresponding savings in future maintenance painting requirements.

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Summary

Elevated temperature operation is one of the most rigorous environments for liquid-applied coatings. The successful corrosion protection of hot substrates in operating plants depends upon an understanding of the capabilities and limitations of the many coating formulations that are available to the coatings specifier or engineer. Armed with an understanding of the thermal and physical parameters associated with the heated equipment, coating personnel can choose from commercially available products that meet most coating and substrate protection requirements.

The degree of success attained through the use of these products will depend upon the implementation of some common sense principles commonly identified with good coating practices. Among these are proper surface preparation, adherence to the manufacturer's recommended curing cycles, and periodic repairs to maintain coating integrity during field use. It is also important not to exceed the technology envelope for which these products are designed. If these basic rules are followed, successful coating performance can be realized. **JPCL**

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