Hydrothermal Degradation Study of Phenolic Polymer Coatings by Advanced Analytical Methods

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Resole-type phenolic polymer coatings were deposited on carbon steel panels, and then were exposed for 15 days to a simulated geothermal brine with pH 1.6 at 150°, 175°, and 200°C. The phenolic polymers were hydrothermally oxidized. To comprehensively understand the mechanisms of this oxidative degradation of the coatings, the modern analytical techniques of XPS, contact angle, TGA, SEM-EDX, and EIS were used in combination. The oxidative degradation of polymer took place in the three-step oxidation routes: first, the bridging methylene linkages in the network polymer structure were replaced by the benzlhydrol-type linkages; second, the benzlhydrol-type linkages were transformed into the benzophenone-type linkages; and finally, the C–C–C linkage in the benzophenone derivative ruptured to form salicylic acid derivatives as the ultimate degradation products. Hydrothermal temperatures of >175°C promoted the degree of such oxidative degradation, causing the coating surface to become susceptible to moisture, to absorb more brine, and also to allow corrosive electrolytes to permeate easily. Consequently, iron oxides as the corrosion products from the underlying steel were yielded at a critical interfacial zone between the coating and steel. The excessive growth of iron oxides led to the generation of internal stress-induced cracks in the coating film, thereby resulting in the failure of these corrosion-preventing barriers.

INTRODUCTION

Two factors are key in successfully using organic polymer coatings to mitigate corrosion of the interior surfaces of heat exchanger tubes made of carbon steels, which are used in geothermal power plants with low pH hot brines at temperatures up to 180°C. One factor is that the coating's surfaces should not be susceptible to hydrothermal oxidation; the other is that these surfaces should resist abrasive wear and tear.[1-3] Regarding the former, once coatings undergo severe oxidation, they allow the corrosive electrolytes to infiltrate through the film layer. Furthermore, oxidation introduces functional oxygen derivatives, such as hydroxyl, peroxide, carbonyl, and carboxylate, on the outermost surface sites of the coating film. The topographical configuration of coating's surfaces then changes from a smooth texture into a rough one. The major concern here is that these functional organic groups occupying the rough surface sites have a strong chemical affinity for the alkali metals, such as Na and K, and alkaline earthmetals, such as Ca, Mg, and Ba present in the geothermal brine, thereby promoting the rate of fouling by brine-induced scale deposits. A layer of scales linked chemically to the coating surface is undesirable, not only because it lowers its heat-transfer performance and increases flow pressure losses, but also because scales are difficult to remove from the coating's surface.

Phenolic resin is categorized as a thermosetting polymer and is commonly used in high-temperature performance coatings in the plastic processing industry.[4,5] The solid phenolic polymer has a covalently bound carbon-carbon crosslinked network that confers thermal stability over a wide temperature range, and is responsible for the development of the desirable physical properties of its surfaces, such as a very slippery glassy face and a ceramic-like hardness. These characteristics of phenolic polymers prompted us to assess their usefulness as a corrosion-preventing barrier for the carbon steel substrates. However, as is well documented by several investiga-

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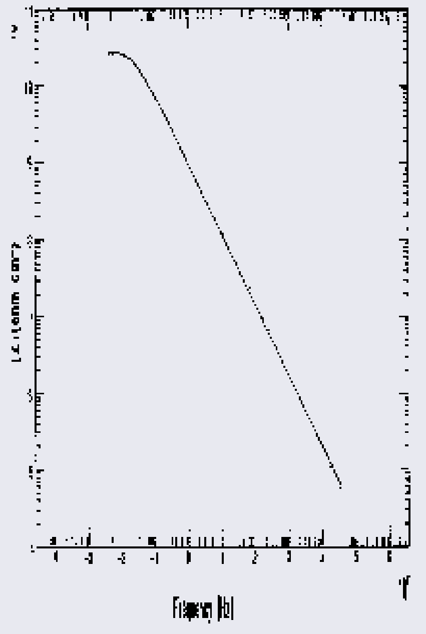

Figure 1—C_{1s} core-level spectra for (a) "as-received" coating, and (b) 150°C-, (c) 175°C-, and (d) 200°C-15-day-autoclaved coatings.

tors,[6,7] phenolic polymers can undergo oxidative degradation at temperatures of > 300°C in air. Therefore, assuming that the phenolic polymer coatings suffer hydrothermal-catalyzed oxidation, our emphasis in the current study was directed towards a better understanding of the mechanisms of hydrothermal degradation of the coatings: for this, we combined the modern analytical techniques of X-ray photoelectron spectroscopy (XPS), contact angle measurement, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX), and AC electrochemical impedance spectroscopy (EIS). XPS that provides information on the chemical composition and states occupying the outermost surface site of the materials[8,9] was used to investigate the degree of hydrothermal oxidation of the coating's surfaces, to identify the oxidation products of the polymer, and to reveal its oxidative degradation pathways. The combination of contact angle measurement and TGA gives data on the magnitude of coating's susceptibility to moisture, and the extent of absorption and uptake of brine by the coatings. Since EIS is a very useful tool for detecting the rate of permeation of electrolyte through the coating layer,[10,11] it was employed to measure the conductivity of corrosive ionic species passing through the oxidized coating layer. SEM coupled with EDX was used to explore alterations in microstructure at the critical interfacial zone between the coating and steel.

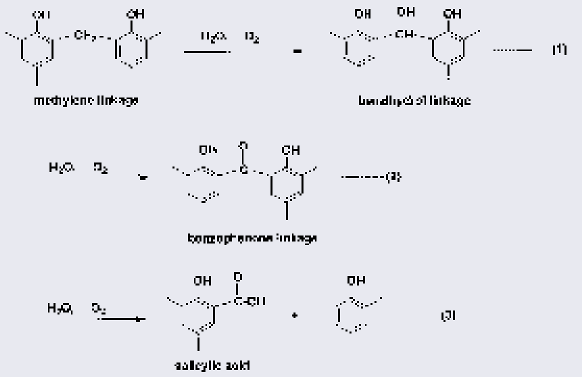

Figure 2—Schematic representation of a hypothetical hydrothermal oxidation route for a phenolic polymer.

EXPERIMENTAL

Materials

The metallic substrate used was commercial AISI 1008 carbon steel. Commercial resole-type phenolic polymer-based coatings were deposited on sand-blasted carbon steel panels (6.3 cm × 6.3 cm). The raw phenolic resin that covered the metal surfaces was baked for two hours in an air oven at 218°C to completely convert the resin into a solid polymer. The thickness of coatings ranged from 140 to 150 µm.

Measurements

The coated test panels were exposed for up to 15 days in an autoclave containing a pH 1.6, brine (1 wt% H_2SO_4, 13 wt% NaCl, and 86 wt% water) at 150°, 175°, and 200°C under hydrothermal pressures of 0.5, 0.9, and 1.6 MPa, respectively. XPS was used to investigate the degree of hydrothermal oxidation and to identify oxidation reaction derivatives at the surfaces of the exposed coatings. Using a contact angle analyzer (Model CAA-3, Imass Instruments), the extent of susceptibility of the film's surface to moisture was determined from the values of water contact angles which were measured within the first 20 sec after placing the drop of water on the surface. TGA was used to evaluate the amount of absorbed brine in the coatings after exposure, and to investigate the temperature of onset of their thermal decomposition. This analysis was run with the non-isothermal method at a constant rate of 10°C min over the range of 80° to 450°C.

The microstructure developed in the critical interfacial regions between the coating and metal and its chemical contributors were explored using SEM and EDX. AC EIS was used to evaluate the ability of the coating films to protect the steel from corrosion. The specimens were mounted in a holder, and then inserted into an electrochemical cell. Computer programs were prepared to calculate theoretical impedance spectra and to analyze the experimental data. Specimens with a surface area of 13 cm^2 were exposed to an aerated 0.5 M NaCl electrolyte at 25°C, and single-sine technology with an input AC voltage of 10 mV (rms) was employed over a frequency range of 10 KHz to 10^{-2} Hz. To estimate the protective performance of coatings, the poreresistance, Rp, (ohm-cm^2),

Table 1—Area Ratios of C(C–OH at 286.5 eV)/C(–CH$_n$- at 285.0 eV), C (C=O at 288.0 eV)/ C(–CH$_n$– at 285.0 eV), and C(COOH at 289.5 eV)/C(–CH$_n$– at 285.0 eV) for "as-received," and 150°C-, 175°C-, and 200°C-Autoclaved Coating Surfaces.

Coating	C(C–OH)/C(–CH$_n$-)	C(C=O)/C(–CH$_n$–)	C(COOH)/C(–CH$_n$–)
"As-received"	0.30	—	—
150°C-autoclaved	0.49	0.20	—
175°C-autoclaved	0.51	0.25	0.06
200°C-autoclaved	0.54	0.29	0.10

was determined from the plateau in Bode-plot scans that occurred in low frequency regions.

RESULTS AND DISCUSSION

Hydrothermal Oxidation

To investigate the degree of hydrothermal oxidation of the phenolic polymer and the route of oxidation, we focused on the changes in chemical states of the coating's surfaces after exposure for 15 days at 150°, 175°, and 200°C. This survey was carried out by XPS. All XPS inspections were made at an electron take-off angle of 40°, which corresponds to an electron-penetration depth of ~5.0 nm,[12] implying that the XPS data reveal the chemical states present in a surface layer with a thickness of ~5.0 nm. *Figure* 1 compares the XPS C$_{1s}$ core-level photoemission spectra of the coating surfaces before and after exposure. In these spectra, the scale of the binding energy (BE) was calibrated with the C$_{1s}$ of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference standard. A curve deconvolution technique, using a DuPont curve resolver, was employed to substantiate the information on the carbon-related chemical states from the spectrum of the carbon atom. The spectrum (a) of "as-received" coating surfaces can be deconvoluted by three resolvable Gaussian components at the BE positions of 285.0, 286.5, and 291.0 eV. In a study on curing resole-type phenolic resins, Katovic[13] reported that those cured at temperatures around 150°C involved two different bridging groups, methylene (–CH$_2$–) and methylene ether (–CH$_2$–O–CH$_2$–), which act to link between the phenolic rings. However, raising the curing temperature to 210°C eliminated the bridging ether linkages by cleaving C–O–C bonds, while the –CH$_2$– linkages remained intact. Since this coating was prepared by heating it at 218°C, the principal contributor to the major peak excited at 285.0 eV is due to the C in the bridging –CH$_2$– linkages and the phenolic rings. According to the literature,[14,15] the second intense peak at 286.5 eV reflects the C in C–OH bonds of the phenolic hydroxyls, while the weak signal emerging at the highest BE of 291.0 eV is assignable to the $\pi \rightarrow \pi^*$shake-up satellite of conjugated C=C bonds in the phenolic rings. When this coating was exposed to hot acid brine at 150°C, the spectral features (b) were different from those of unexposed specimens; in particular, there were (1) an emergence of additional peak at 288.0 eV in the C$_{1s}$ region, and (2) a decreasing intensity of the principal –CH$_2$– linkage- and phenolic-related carbon peak at 285.0 eV. The carbon signals corresponding to both the hydroxide group and the $\pi \rightarrow \pi^*$ shake-up satellite were retained. A possible contributor to new signal at 288.0 eV is the C in carbonyl, C=O, groups.[14] Increasing the temperature to 175°C resulted in the incorporation of another peak at 289.5 eV in the spectrum, (c) and also caused a further decay of the signal intensity at 285.0 eV. This new peak, emerging at 289.5 eV, originated from the C in carboxylic acid, –COOH, groups.[14] In comparison with that of the 175°C-autoclaved coatings, the curve structure (d) of the 200°C-autoclaved coatings was characterized by some growth of the C–OH peaks and an attenuation of the principal hydrocarbon-type carbon peak; meanwhile, the $\pi \rightarrow \pi^*$satellite signal still emerged at 291.0 eV. Since this satellite signal was related directly to the phenolic rings, it is possible to assume that a striking decay of the principal signal at 285.0 eV with the increase in the brine's temperature is more likely to be associated with conformational changes in the bridging –CH$_2$– linkages in the polymers, rather than the disintegration of the phenolic rings. If this interpretation is valid, the methylene bridges might be substituted for the functional oxygen derivatives, such as hydroxide, C–OH, C=O, and COOH groups by hydrothermal oxidation. Regarding the formation of C–OH groups, the peak at 286.5 eV might involve the C in both the phenolic hydroxyl and the benzlhydrol derivative with a structure in which two phenolic rings are linked by a > CH–OH substituent. Nevertheless, it is apparent that the degree of hydrothermal oxidation of the phenolic polymer can be estimated from the identification of oxidative derivatives; namely, a highly oxidized polymer provides the COOH substituent.

To support this information, the integrated peak areas of these four groups, –CH$_n$–, C–OH, C=O, and COOH, at 285.0, 286.5, 288.0, and 289.5 eV, respectively, were computed in the deconvoluted Gaussian curves for each of these peaks. We then calculated three integrated carbon-

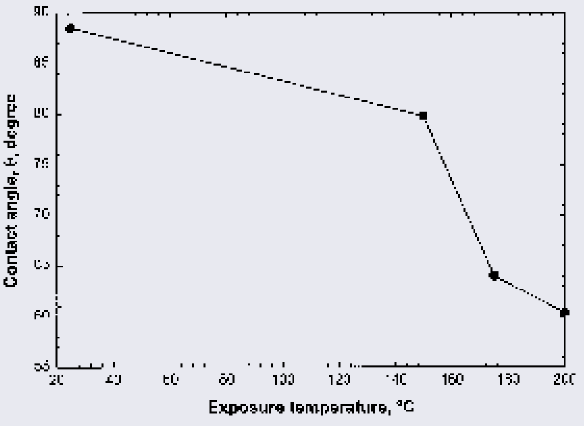

Figure 3—Changes in the contact angle of a water droplet on the coating's surfaces as a function of exposure temperature.

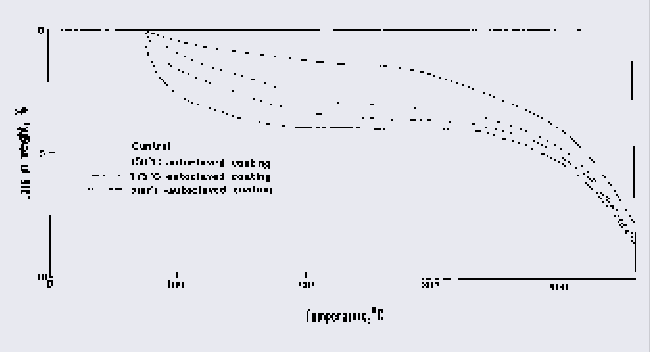

Figure 4—TGA curves for the "as-received," and 150°C-, 175°C- and 200°C-autoclaved coating films removed from the steel substrates.

area ratios, C(C–OH at 286.5 eV)/C(–CH_n– at 285.0 eV), C(C=O at 288.0 eV)/C (–CH_n– at 285.0 eV), and C(COOH at 289.5 eV)/C(–CH_n– at 285.0 eV), for the unexposed, and 150°C–, 175°C–, and 200°C–15-day-autoclaved coating surfaces (see *Table* 1). The area ratio of C(C–H) to C(–CH_n– for the "as-received" coating was 0.30. When this coating was exposed to hot acid brine at 150°C, the value of the area ratio rose almost 63% to 0.49, suggesting that some –CH_n– groups were substituted for the >CH–OH substituents to yield the benzlhydrol derivative. Since the –CH_n– groups governing such substitution are more likely to be associated with the methylene bridge, rather than the phenolic rings, it is conceivable that the >CH–OH substituent was introduced by the oxidation of the –CH_2– bridge into the phenolic polymer. The extent of such substitution is enhanced as the temperature increases; in fact, this ratio of 0.54 at 200°C was ~ 10 % higher than that at 150°C. The area ratio of C(C=O)/C(–CH_n–) ratio at 150°C was 0.20. The trend toward an increase in this area ratio with an increasing temperature is similar to that from the C(C–OH)/C(–CH_n–) ratio; the value of the area ratio at 200°C was 0.29, corresponding to a 45% increase over that at 150°C. For the C(COOH)/C(–CH_n–) ratio, a value of 0.06 was obtained from the 175°C-autoclaved coating surfaces. At 200°C, this value has risen ~67% to 0.10, implying that an extensive oxidation of the –CH_2– linkages resulted in a growing number of COOH substituents. In their study of the thermal degradation of phenolic polymers in an air oven at temperatures ranging from 140° to 1000°C, Jackson[16] and Conley[17] reported that the pathway of oxidative degradation begins with the primary oxidation of the bridging methylene linkages. The typical oxidation of –CH_2– linkages then led to their substitution for the carbonyl moiety attributed to benzophenone-type linkages at the end of oxidative degradation. Relating our results to this information, a similar degradation route, except for a possible substitution of C=O for the COOH, can be proposed in the autoclaved phenolic polymers. *Figure* 2 gives a schematic representation of its hypothetical hydrothermal oxidation route. As is seen, when the phenolic polymer was exposed to a hot acid brine, it underwent the hydrothermally oxidative degradation in the three steps. The first step was the substitution of the bridging methylene linkages for the benzlhydrol-type linkages in the oxidation-inductive stage; the second step was related to the formation of benzophenone as ketonic-type linkages derived from the oxidized benzlhydrols; and the third was the transformation of benzophenone into salicylic acids as the final degradation products brought about by incorporating more oxygen into the polymer, reflecting the rupture of C–C–C linkages connecting two phenolic rings. Thus, the methylene → benzlhydrol → benzophenone → salicylic acid transition is defined as the main route for the hydrothermal degradation of the resole-type phenolic polymers. Consequently, this degradation route can be taken as exemplification that the degree of the polymer's oxidation depends primarily on the oxygen substituents. Its magnitude is ranked in the following order, COOH > C=O > >CH–OH. Nevertheless, the salicylic acids formed at the end of this route might be detrimental to the maximum efficacy of the coatings in mitigating corrosion of the steel because of the disintegration of the network polymer structure by breakage of C–C–C linkages.

Based upon this information, our focus was then turned to assessing the magnitude of susceptibility of the oxidized coating surfaces to moisture. The hydrophobic characteristic that the assembled film surfaces are not sensitive to moisture is among the important factors that are indispensable for good protective coatings. To gain information on this characteristic, the contact angle made by a water droplet falling on the coating surfaces before and after exposure for 15 days at 150°, 175°, and 200°C was measured using the contact angle analyzer. Before taking this measurement, the surface of all exposed coatings was rinsed with deionized water to remove any salt contaminants. If the contact angle was low, the coating surfaces were judged to be susceptible to moisture, corresponding to a high surface energy. A high degree of susceptibility may allow moisture to permeate through the coating film easily. A plot of the average value of contact angle, θ, (degree), for five water droplets, as a function of the exposure temperature is shown in *Figure* 3. The resultant θ-temperature relation data reveals that the θ value of an unexposed coating plotted at a temperature of 25°C markedly declined as it was exposed to brine, especially for the 175°- and 200°C-autoclaved coatings. By comparison with the θ value of 88.5° for the unexposed one, it fell 9.8%,

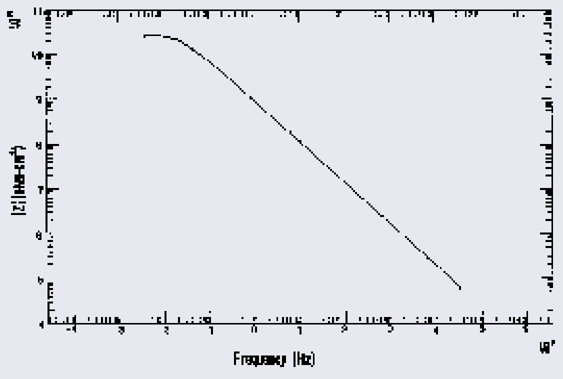

Figure 5—Bode-plots for an unexposed coating panel.

26.7%, and 29.5% at 150°, 175°, and 200°C, respectively, suggesting that coating surfaces autoclaved at > 175°C become more sensitive to moisture than at 150°C. Thus, the degree of surface oxidation appears to play an essential role in controlling the magnitude of susceptibility to moisture; a highly oxidized surface had an enhanced wettability and spreadability of water. In other words, the hydrophobic nature of a coating surface is converted into a hydrophilic one by enhancing the degree of its oxidation. Relating a considerable drop of θ value between the temperatures of 150° and 175°C to the oxidative degradation route of polymers described earlier, it is possible to rationalize that salicylic acids formed as degradation products from the rupture of C–C–C linkages in the benzophenone derivative at 175°C are the major reason for the drastic drop of θ value because of the conversion of hydrophobic surfaces into hydrophilic ones.

Characteristics of Coatings

The hydrophilic property of the oxidized coating surfaces led us to assess the coatings' uptake of water after exposure. In this study, coating films exposed in brine for 15 days at 150°, 175°, and 200°C were physically separated from the metal substrates, and then dried in an air oven for two hours at 70°C to remove any remaining moisture on the surface. The dried samples were examined by TGA to determine brine uptakes. *Figure* 4 depicts the TGA curves of these coating films over the temperature range of 80° to 450°C. The curves for all the samples represents a weight loss between 80° and 220°C, and then levels off between 220° to ~300°C. Beyond this temperature, a large reduction seems to take place. We believe that the weight loss incurred up to 220°C is due mainly to evaporation of all the water adsorbed and infiltrated into the films. Consequently, thermal decomposition of polymers is likely to begin at temperatures near 300°C. The weight loss of unexposed films denoted as "25°C" by dehydration was a 1.2%, implying that the "as-received" coatings have already included this amount of moisture. When this coating was autoclaved at 150°C, the dehydration-caused weight loss was a 2.8%, corresponding to more than two times over that of unexposed coatings. A further weight loss of 3.2% and 3.7%, respectively, was observed from the 175°- and 200°C-exposed coating films. This fact strongly verified that elevated hydrothermal temperatures promote the uptake of water by the exposed coatings. In other words, oxidative degradation of coating layers during exposure allowed the brine to infiltrate into them, seemingly causing the corrosion of underlying steel.

This information was supported by measuring the changes in ionic conductivity of the coatings using AC EIS. On the overall EIS Bode-plot curves [the absolute value of impedance |Z| (ohm-cm^2) vs frequency (Hz)] (*Figure* 5), particular attention was paid to the impedance value in terms of pore resistance, (Rp), which can be determined from the plateau in the Bode-plot occurring at a sufficiently low frequency of 1×10^{-2} Hz. *Figure* 6 represents the change in Rp value for the phenolic polymer-coated steel specimens as a function of exposure times at 150°, 175°, and 200°C. In the first five days of exposure, at 150°C, the coatings showed no changes in Rp value, compared with unexposed ones. By contrast, exposures at 175° and 200°C cause a declining Rp; at 200°C, the initial Rp value (2.0×10^{10} ohm-cm^2) of unexposed coatings had dropped almost two orders of magnitude to 4.5×10^8 ohm-cm^2. Since the Rp value reflects the magnitude of ionic conductivity generated by electrolytes passing through the coating layer, a higher value signifies a low degree of penetration of electrolytes into the coating film. Thus, the rate of permeation of electrolytes through the coating layer depended mainly on the exposure temperatures; an elevated temperature caused an increasing rate of their permeation. Afterwards, the Rp values for the 150°C-autoclaved coatings gradually decreased with an increase in time, inferring that extending the period of exposure promotes the uptake of some electrolytes by the coatings. However, the value of 1.0×10^{10} ohm-cm^2 after exposure for 15 days represented only a 50% decrease, suggesting that the coatings withstood the attack of hot acid brine at 150°C over a short-term exposure period. The trend toward a decrease with an increase in time can also be seen on the Rp-exposure time relation of the 175°C-autoclaved coatings. There was one marked difference from the 150°C ones; the Rp value conspicuously dropped in the exposure period between 10 and 15 days. Its value after a 15-day exposure was an 8.0×10^8 ohm-cm^2. At 200°C, the coatings failed catastrophically when the exposure time was prolonged to 15 days; consequently, the Rp value sharply dropped to 5.0×10^3 ohm-cm^2. The Rp at this level mainly reflects the corrosion of the underlying steel. In fact, rust stains were seen on the coating's surfaces due to the local corrosion of steel caused by their failure.

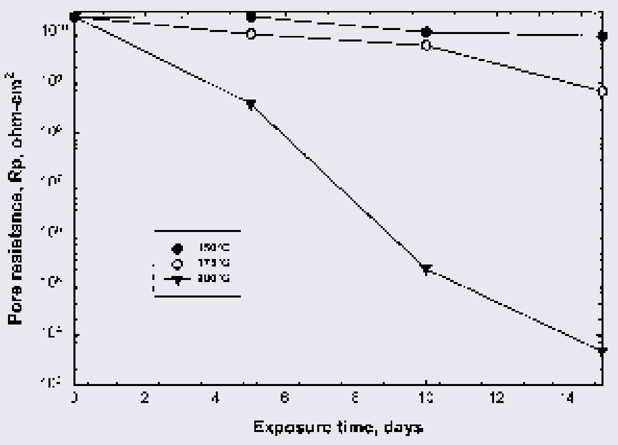

Figure 6—Changes in Rp for 150°-, 175°-, and 200°C-autoclaved coating steel panels as a function of exposures up to 15 days.

Interfaces Between Coating and Steel

To visualize the microstructure at the interfaces between the coating and steel before and after exposure for 15 days at 150°, 175°, and 200°C, the cross section of coated steel panels was inspected using SEM coupled

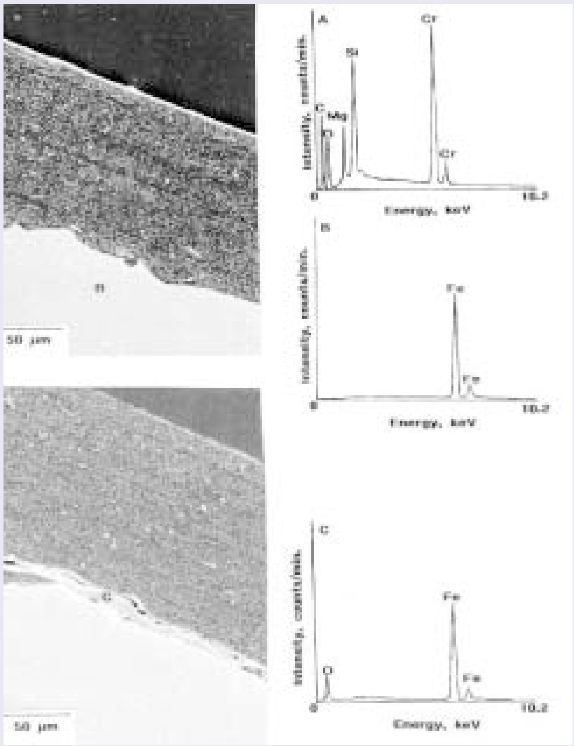

Figure 7—SEM-EDX examinations for the cross-sectional regions of 150°C-15-day-autoclaved (top) and 175°C-15-day-autoclaved (bottom) coating/steel joints.

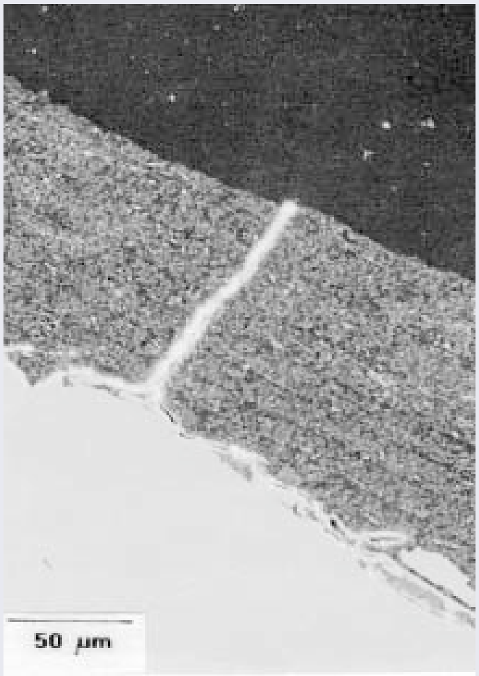

Figure 8—SEM image of the cross sectional area of a 200°C-15-day-autoclaved coating/steel joint.

with EDX. The top portion of *Figure* 7 is an SEM micrograph of a cross sectional area of a 150°C coating panel, in which two distinctive regions of the cross section are highlighted. The EDX spectrum taken from the area denoted as site "A" in the top layer had two intensive lines originating from Cr and Si elements, and three moderate lines belonging to C, O, and Mg elements. Since the C and some O elements are assignable to the phenolic polymer coating, the three other elements together with the remaining O may be attributed to the chemical constituents of the inorganic fillers added as corrosion-inhibiting pigments to the coatings. Also, the SEM image revealed that the overall structure of the coating consists of multiple layers being assembled by repeated coating processes. The EDX spectrum at site "B" in the bottom layer had only Fe-related peaks, revealing the underlying steel. There was no distinctive feature in the microstructure of the critical interfacial regions between the coating and steel of exposed specimens, compared with unexposed ones (not shown). The SEM image (*Figure* 7, bottom) of the 175°C coating panel was different; specifically, a new layer denoted as site "C," appeared at the coating/steel interfacial contact zone. The EDX of this newly formed layer showed a strong Fe signal and a weak O peak, suggesting that iron oxide compounds as the corrosion products from the underlying steel had formed during exposure at this temperature. Thus, although no destruction of the coating layer was observed from the SEM image, a possible interpretation for the formation of such internal iron oxides is that the coating layer allowed the corrosive brine to permeate through its layer with the thickness of ~138 µm. This finding strongly supported our previous information on the uptake and absorption of a certain amount of brine by the exposed coatings. *Figure* 8 shows the profile of the cross-sectional area of the 200°C coating panel. The SEM image revealed the development of a crack in the coating layer, which was brought about from internal stresses generated by an excessive growth of iron oxides as the corrosion products of steel. The propagation of the crack through the brittle coating seemed to be straightforward. However, there is no evidence as to whether such brittleness is inherent in the "as-received" coating or whether it arises from oxidative degradation of the coatings, or from both. Nevertheless, although elevated temperature was thought to be one of the factors affecting the increase in the rate of ion transportation because of an increased pressure, we believe that the extended oxidation of the coatings allows a corrosive brine to permeate through them, promoting the internal growth of iron oxides which cause the development of stress-cracks in the film. In the worst case, the formation of a massive amount of iron oxides led to the delamination of the coating from the steel surfaces in conjunction with creating a growing number of blisters.

CONCLUSION

Integrating all the data obtained from the combination of these modern analytical techniques gave us a comprehensive understanding of the hydrothermal degradation pathways of resole-type phenolic polymer coatings. The 15-day-autoclave exposure tests for the coatings deposited on the carbon steel demonstrated that they suffer hydrothermal oxidation in a low pH (~1.6), geothermal brine at temperatures > 150°C. The oxidative degradation pathway of phenolic polymer took place through three-step oxidation routes: first, the bridging methylene linkages in the network polymer structure were preferentially oxidized to form benzlhydrol-type linkages in the oxidation-inductive stage; second, further oxidation led to the substitution of the benzlhydrol linkages for the benzophenone-type linkages; and third, incorporating more oxygen into the oxidized polymer caused the breakage of C–C–C linkages in the benzophenone derivative, thereby forming salicylic acid as the ultimate oxidative degradation products of phenolic polymer. The kinetics of such a methylene → benzlhydrol → benzophenone → salicylic acid transition depended mainly on the hydrothermal temperature; at > 175°C, this transition was completed in a short-term exposure period. The introduction of the salicylic acid derivative at the end of the main oxidation route was detrimental to the function of the coatings as corrosion-preventing barriers for the underlying steel, thereby enhancing the magnitude of susceptibility to moisture, increasing the rate of brine absorption, and heightening ionic conductivity. The uptake of brine by the highly oxidized coatings led to the creation of an iron oxide layer as the corrosion product of the underlying steel at the critical interfacial zone between the coating and steel. Further, the excessive growth of the interfacial oxide layer promoted wedging activity, which put tremendous stress on the interfacial coating side, thereby resulting in the generation of internal stress-induced cracks in the coating film. In the worst case, the brine penetrating through the cracks caused the delamination of coating from the steel surfaces in conjunction with a growing number of blisters. Nevertheless, the upper limit of a useful temperature of this polymer for use as corrosion-preventing interior coatings on heat exchanger tubes seems to be around 150°C.

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