

Investigation of the Efficiency of Film Forming Amines for System Component Corrosion Protection by the Inhibition of the Electrocatalytic Reaction of *N,N*-diethyl-*p*-phenylene-diamine with Chloropentaaminocobalt(III) Complex

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ABSTRACT

The application of film forming amines (FFAs) as an effective protection against general and selective corrosion phenomena has been proven as a successful water chemistry improvement method for water-steam cycles of pressurized water reactors (PWRs). Since 2011 Framatome GmbH (formerly AREVA GmbH) has performed ten FFA applications worldwide as a regular complement to the applied secondary side water chemistry treatment with the main goal of establishing a hydrophobic and protective film on all inner surfaces of the water-steam cycle which are exposed to corrosion attack.

So far well-known practices have been applied to evaluate the effectiveness of the film formation on metal and metal oxide layers, for example hydrophobicity testing and contact angle measurements. Electrochemical methods have been investigated with respect to their applicability to provide additional information on the homogeneity of FFA films on metal and metal oxide surfaces and thus their ability as corrosion inhibitors.

This paper describes a method to determine qualitatively the completeness and homogeneity of the film formation on FFA pretreated corrosion specimens by the inhibition of the electrocatalytic reaction of a *N,N*-dialkylated *p*-phenylenediamine with chloropentaaminocobalt(III).

NOMENCLATURE

Co(III)	cobalt(III)
FFA	film forming amine
<i>K</i>	equilibrium constant
DEPPD	<i>N,N</i> -diethyl- <i>p</i> -phenylenediamine
NPP	nuclear power plant
Ox	oxidizing agent
PPD	<i>p</i> -phenylenediamine
PWR	pressurized water reactor
QDI	quinonediiimine
Red	reducing agent
SQDI	semiquinonediiimine

INTRODUCTION

In 2010 Framatome GmbH (formerly AREVA GmbH) qualified an innovative protection technology for the water-steam circuit of PWRs using FFAs. This technology has been applied by Framatome GmbH since 2011 at NPPs as a regular complement to the applied secondary side water chemistry treatment to reach the following objectives [1,2]:

- Reduction of the deposit load of steam generators caused by corrosion product transport;
- Minimization of degradation effects of steam generator component materials;
- Optimization of lay-up strategies for long-term outages;
- Reduction of hydrazine use during the outage (wet lay-up of the steam generators).

The main goal of a controlled and time-limited injection of FFAs into the water-steam cycle is the formation of a hydrophobic protective film on all secondary side inner surfaces exposed to corrosion attack during all phases of plant operation.

The effectiveness, especially the hydrophobicity, of the film formation may be evaluated directly or indirectly by the following measures [3]:

- Water droplet testing on the plant components to determine the degree of the repellence;
- Contact angle measurements;

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- Electrochemical measurements, e.g. open circuit potential or electrochemical impedance spectroscopy [4].

Figure 1 shows an evaluation of film effectiveness by laboratory testing of corrosion strip coupons (contact angle measurement), and an application example in a NPP (visual inspection, repellency testing) is shown in Figure 2 [5].

Due to the physico-chemical properties of fatty amines, FFAs can create a hydrophobic surface which is able to decrease the corrosion rate by decreasing the mass transfer between the surface and the bulk solution and by stabilizing the protective oxide layer (for instance hematite or magnetite).

As of research and development investigations, Framatome GmbH was looking for alternative test methods to confirm the film integrity after application of the film forming technology in the water-steam cycles of NPPs. In pilot experiments with corrosion strip coupons it could be

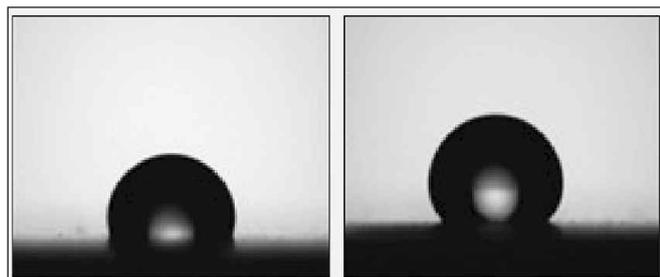


Figure 1: Contact angle measurement on stainless steel (ASTM A 240, alloy 410) corrosion strip coupons: untreated (left) and FFA-treated (right) samples [5].



Figure 2: Water droplet testing during visual inspection in the condenser of a NPP during an outage following time-limited FFA application [5].

shown that redox reactions on bare metal surfaces can be inhibited by hydrophobic coatings consisting of fatty amines.

In general, certain homogeneous redox reactions ($\text{Ox}_2 + \text{Red}_1 \rightarrow \text{Red}_2 + \text{Ox}_1$) are accelerated at the surface of a metal (heterogeneous catalysis). They are schematically depicted in Figure 3.

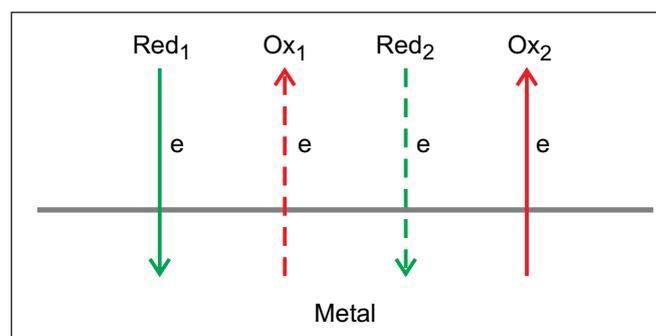


Figure 3: Schematic representation of general electrocatalysis, regarding Ox and Red.

The "new" method described in the present paper is based on the well-known electrocatalytic acceleration of the homogeneous redox oxidation of *p*-phenylenediamine (PPD) by a Co(III) complex [6].

Both the homogeneous and heterogeneous oxidation of PPDs have been investigated under kinetic, mechanistic, and thermodynamic aspects. The homogeneous redox reactions are enhanced at the surface of several metals, particularly silver, gold, and platinum, because the electron exchange between the metal and the reactants occurs more easily than the direct electron transfer from the reducing agent to the oxidant [6].

The first oxidation product of a *p*-phenylenediamine is the stable radical cation, *N,N*-dialkyl-*p*-semiquinonediamine (SQDI⁺). As this radical absorbs strongly in the visible, the course of the reaction can easily be followed spectrophotometrically [7].

The completely oxidized form, *p*-quinonediimine (QDI⁺), undergoes deamination in acidic as well as in alkaline solution, resulting in the formation of a *p*-quinone-monoimine. The redox behavior of PPD in aqueous solution is shown in Figure 4 [8].

A good model reaction for such investigations is the noble-metal catalyzed oxidation of *N,N*-dialkyl-*p*-phenylenediamine by $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ (Ox) in aqueous solution at a pH between 4 and 8. The homogeneous redox reaction is very slow, whereas the catalyzed reaction can be quite fast. Both the homogeneous and the

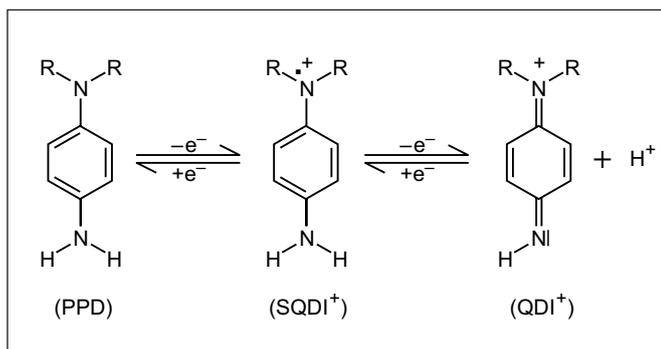
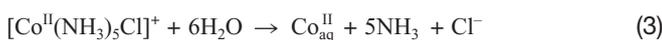
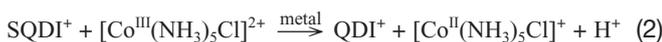


Figure 4: Reaction scheme of the general redox behavior of *p*-phenylenediamines in aqueous solution.

heterogeneous reactions, Eqs. (1) and (2), occur irreversibly because the reduced cobalt(II) complex rapidly loses ammonia and the resulting $\text{Co}^{\text{II}}_{\text{aq}}$ ion is a very weak reducing agent, Eq. (3) [9].



As already mentioned, electrocatalysis occurs because the electron is more easily transferred from PPD via a metal to the oxidizing agent than through the solution. The rate of this electrocatalytic reaction can be decreased by auto-inhibition if a product of the reaction forms a protective layer on the surface and thus the active surface is decreased. If a layer which can hinder the electron transfer is present on the metal surface before starting the reaction, the electrocatalytic reaction does not take place. This effect was taken as the basis for the testing of the efficiency of film forming amines as corrosion inhibitors.

EXPERIMENTAL

The DEPPD · H_2SO_4 adduct (*pro analysi*) and the cobalt(III) complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (98 %) were obtained from Aldrich. 100 mL stock solutions of 1 mM DEPPD and 1 mM Co(III) were prepared immediately before use with argon saturated millipore water; the pH was adjusted by adding ammonia or a highly diluted phosphate buffer.

Phosphate buffer solutions were prepared according to Sørensen from $\text{Na}_2\text{H}(\text{PO}_4)$ and $\text{KH}_2(\text{PO}_4)$ purchased from Merck. A pH of 6.5 was chosen for the test solutions in order to suppress possible general corrosion of the blank metal specimens and to avoid desorption of the FFA film on coated specimens.

Coating of Corrosion Strip Coupons with Film Forming Amines

The corrosion specimens were degreased using wet chemical methods. After this pre-treatment the specimens were fixed on a special specimen holder and put into the upper part of a high-pressure reactor for film formation in the steam phase.

The FFA was diluted in 300 mL millipore water, the pH adjusted with ethanolamine, and the autoclave was closed and degassed with argon for approximately half an hour. The coating temperature was 120 °C, and the exposure time 2 hours.

Electrocatalytic Experiments

The stainless steel specimens (uncoated and coated with FFA) were inserted into two different rolled edge glasses (inner diameter 27 mm) with snap lids and fixed with plastic coated metal clips, plugged through a centered hole (diameter 1 mm) in the snap lid. A third rolled edge glass was used as a blank sample. A 5 mm cannula was used for the sampling solution and a 2 mm one for pressure compensation due to argon. The reaction solution was prepared by mixing 50 mL of the PPD stock solution, 5 mL buffer solution, and 10 mL of the Co(III) stock solution in a plastic beaker covered with parafilm. 8 mL of the reaction solution were rapidly put into each of the three rolled edge glasses.

Usually the course of the reaction was followed visually, by taking photographs at regular intervals. Spectra were recorded in the visible region between 500 and 600 nm and at a fixed wavelength of 552 nm, corresponding to the maximum absorbance of SQDI⁺. Samples of 2 mL volume were taken with a syringe, measured photometrically, and filled back into the rolled edge glasses.

All photometric measurements were performed with a UV/vis spectrophotometer (Lambda 2, Perkin Elmer) using plastic cuvettes with an optical path length of 1 cm.

RESULTS AND DISCUSSION

As shown in Eqs. (1) and (2) the oxidation of *p*-phenylenediamines follows a two-step mechanism, and as first mentioned by Michaelis a fast synproportionation equilibrium (Eq. (4)) is established [10]:



with the synproportionation constant K_{syn} , expressed in Eq. (5):

$$K_{\text{syn}} = \frac{[\text{SQDI}^+]^2}{[\text{PPD}][\text{QDI}^+][\text{H}^+]} \quad (5)$$

The position of the synproportionation equilibrium (Eq. (4)) depends on the structure of the PPD.

Due to their high reactivity, the concentration of most radicals remains low. Some ion radicals, however, are very stable, even in aqueous solution, e.g. SQDI⁺, which is obtained by the oxidation of the corresponding PPD [7,10].

The total concentration of $\overline{\text{PPD}}$, is given by the sum of the concentration of the unprotonated [PPD], the protonated [PPDH⁺], and the doubly protonated [PPDH₂²⁺]; see Eq. (6):

$$[\overline{\text{PPD}}] = [\text{PPD}] + [\text{PPDH}^+] + [\text{PPDH}_2^{2+}] \quad (6)$$

With $K_{\text{PPD}} = [\text{PPDH}^+]/[\text{PPD}][\text{H}^+]$ and $K_{\text{PPDH}} = [\text{PPDH}_2^{2+}]/[\text{PPDH}^+][\text{H}^+]$, the synproportionation constant K_{syn} can be expressed by Eq. (7):

$$K_{\text{syn}} = \frac{[\text{SQDI}^+]^2}{[\overline{\text{PPD}}][\text{QDI}^+]} \frac{(1 + K_{\text{PPD}}[\text{H}^+])(1 + K_{\text{PPDH}}[\text{H}^+])}{[\text{H}^+]} \quad (7)$$

Influence of pH

Regarding the influence of the pH, at $\text{pH} > (\text{p}K_{\text{PPDH}} + 1)$ the term $K_{\text{PPDH}}[\text{H}^+]$ is small compared to 1 and the equilibrium constant K_{syn} is formulated according to Eq. (8) [11–13]:

$$K_{\text{syn}} = \frac{[\text{SQDI}^+]^2}{[\overline{\text{PPD}}][\text{QDI}^+]} \frac{(1 + K_{\text{PPD}}[\text{H}^+])}{[\text{H}^+]} \quad (8)$$

At a $\text{pH} > (\text{p}K_{\text{PPD}} + 1)$ the term $K_{\text{PPD}}[\text{H}^+]$ also becomes small and K_{syn} can be expressed by Eq. (9):

$$K_{\text{syn}} = \frac{[\text{SQDI}^+]^2}{[\overline{\text{PPD}}][\text{QDI}^+]} \frac{1}{[\text{H}^+]} \quad (9)$$

At a pH between $(\text{p}K_{\text{PPDH}} + 1)$ and $(\text{p}K_{\text{PPD}} - 1)$ the term $K_{\text{PPD}}[\text{H}^+]$ is much higher than 1. Therefore in Eq. (8) the proton concentration can be neglected and the term given in the equation is valid. In this pH-region the synproportionation constant is almost independent of the pH, as given in Eq. (10):

$$K_{\text{syn}} = \frac{[\text{SQDI}^+]^2}{[\overline{\text{PPD}}][\text{QDI}^+]} K_{\text{PPD}} \quad (10)$$

The position of the equilibrium and thus the value of the synproportionation constant depends particularly on the values of the protonation constants, which are different for each of the various PPD derivates. The pH-dependence of the values of the synproportionation constant of DEPPD is shown in Figure 5.

By means of the Eqs. (11) and (12)

$$[\text{PPD}]_0 = [\overline{\text{PPD}}] + [\text{SQDI}^+] + [\text{QDI}^+] \quad (11)$$

$$[\text{Ox}]_0 = [\text{SQDI}^+] + 2[\text{QDI}^+] \quad (12)$$

the equilibrium concentration of SQDI⁺ can be calculated for any pH, not taking into account possible side reactions like deamination. Ox is an oxidant which accepts one electron. Within the framework of the investigations it could be shown that the DEPPD derivate is the best choice for the electrocatalytic experiments with FFA-treated and -untreated corrosion specimens. Figure 6 shows the dependence of SQDI⁺ on the pH for equivalent initial concentrations of *N,N*-diethyl-*p*-phenylenediamine and the oxidizing agent ($[\text{PPD}]_0$ and $[\text{Ox}]_0$).

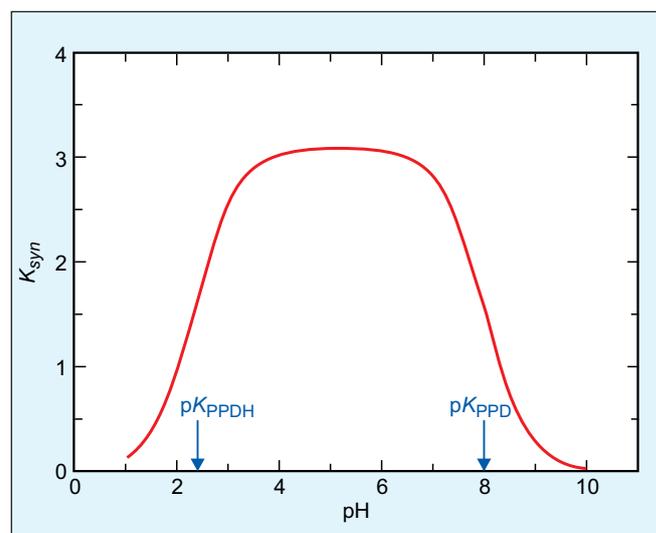


Figure 5: Dependence of the synproportionation constant K_{syn} of *N,N*-diethyl-*p*-semiquinonediimine on the pH.

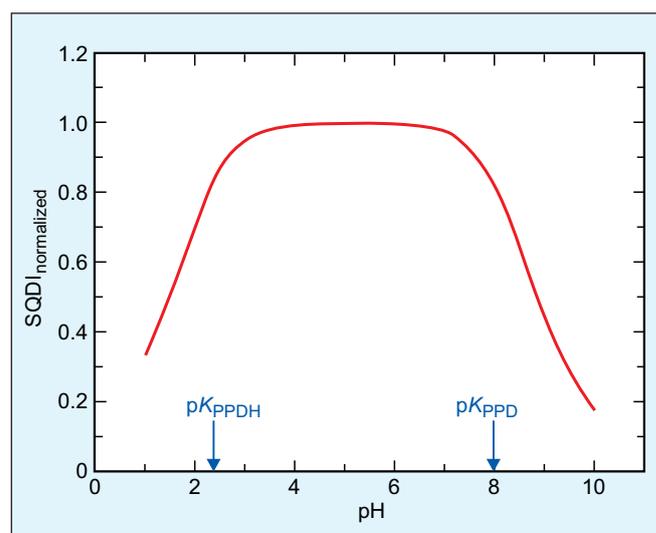


Figure 6: Dependence of the maximum concentration of *N,N*-diethyl-*p*-semiquinonediimine on the pH, normalized for the pH range from 4 to 7.

Inhibition of the Electrocatalytic Reaction of *N,N*-diethyl-*p*-phenylenediamine and Chloropentaminecobalt(III) Complex by Filming Amines

Immediately after preparation of the reaction solution containing *N,N*-diethyl-*p*-phenylenediamine, chloropentaminecobalt(III) complex, and buffer solution or ammonia, the course of the electrocatalytic process was followed visually by regularly taking photographs. The results at the start of the reaction are shown in Figure 7 and after a reaction time of 2, 5, 7, and 14 minutes in Figure 8 to Figure 11, respectively. The light rose color that can be observed after 7 minutes in the pure sample (no catalyst, no inhibitor) and the sample containing the FFA-coated metal specimen is caused by residual atmospheric oxygen.

As could be shown, a possible catalyst, completely covered by a filming amine, inhibits the electrocatalysis (middle position, red clip) and the results are equivalent to the homogeneous reaction (right). If the uncoated metal specimen is inserted into the reaction solution (left, green clip),

the oxidation of DEPPD due to the Co(III) complex is catalyzed and is therefore faster. Thus the SQDI⁺ formation catalyzed by a blank metal surface is the fastest reaction (most intensely colored).



Figure 9:
Course of the formation of SQDI in homogeneous solution (uncoated metal specimen, FFA-treated metal specimen, and reference) 5 minutes after start of the reaction.

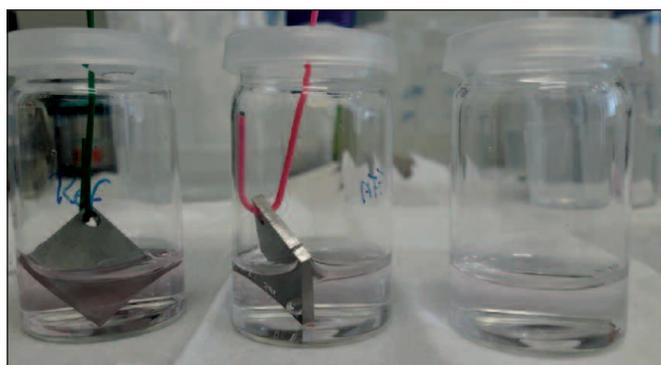


Figure 7:
Course of the formation of SQDI in homogeneous solution (uncoated metal specimen, FFA-treated metal specimen, and reference) after start of the reaction.

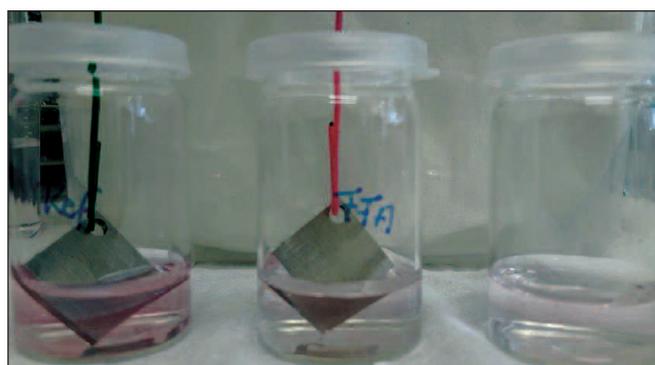


Figure 10:
Course of the formation of SQDI in homogeneous solution (uncoated metal specimen, FFA-treated metal specimen, and reference) 7 minutes after start of the reaction.



Figure 8:
Course of the formation of SQDI in homogeneous solution (uncoated metal specimen, FFA-treated metal specimen, and reference) 2 minutes after start of the reaction.



Figure 11:
Course of the formation of SQDI in homogeneous solution (uncoated metal specimen, FFA-treated metal specimen, and reference) 14 minutes after start of the reaction.

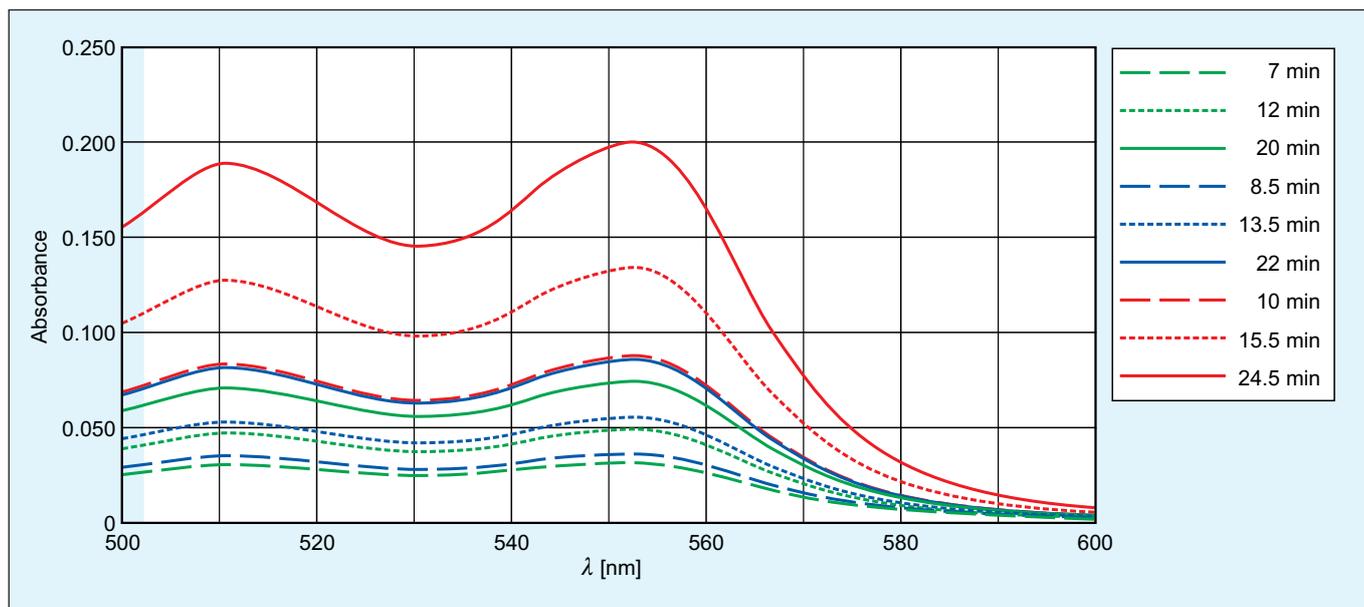


Figure 12:

Time-resolved spectra (reaction of DEPPD and Co(III)).

Green: Only in homogeneous solution after 7, 12, and 20 minutes.

Blue: In the presence of a metal specimen coated with FFA (after 8.5, 13.5, and 22 minutes).

Red: In the presence of a blank (uncoated) metal specimen (after 10, 15.5, and 24.5 minutes).

In Figure 12 the corresponding time-resolved spectra (600–500 nm) are shown. The green spectra show the course of the absorbance for the homogeneous reaction solution after 7, 12, and 20 minutes. If a metal covered with a filming amine is present in the reaction solution (blue spectra, taken after 8.5, 13.5, and 22 minutes after start of the reaction), the results are similar to the spectra of the homogeneous reaction. If a blank metal surface catalyzes the oxidation of DEPPD (red spectra after 10, 15.5, and 24.5 minutes), the maximum absorbance is nearly three times higher compared to the homogeneous reaction.

The corresponding absorbance-time curves of the rate of SQDI⁺ formation at A_{550} are displayed in Figure 13.

The increase in absorbance is highest for the reaction in the presence of the catalyst, the uncoated metal specimen. The increase in absorbance in the presence of the FFA-coated metal coupon is nearly equal to the course of the homogeneous reaction, confirming that the surface is completely covered by a filming amine without any defective areas. If the film formation is incomplete, the increase in absorbance will be higher.

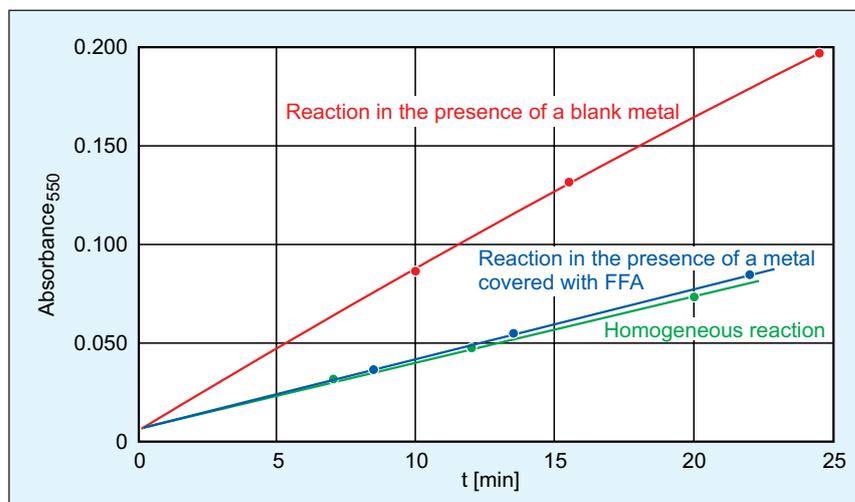


Figure 13:

Temporal change in the absorbance at a fixed wavelength of 550 nm caused by the formation of SQDI.

With regard to further scientific investigations, the experimental set-up needs to be optimized; in particular, the oxygen enrichment during the sampling should be taken into account.

To summarize, it could be shown by means of the different reaction times in the three experiments that the partial or complete deactivation of the catalytically active metal surface can quantitatively be determined by the adsorption of suitable inhibitors.

CONCLUSIONS

The application of film forming amines as an effective protection against general and selective corrosion phenomena has been proven by successful plant applications worldwide. Several scientific methods like contact angle measurement or electrochemical methods are known for the evaluation of the completeness of the film formation on metal and oxide layers.

In general, electrochemical investigations like open circuit potential can only give a qualitative indication of the completeness of the film formation. As could be shown in the present paper, the inhibition of the electrocatalytic reaction of PPD and Co(III) is a promising method for the quantitative determination of the completeness of the film formation of FFA on metal/metal oxide surfaces because the decrease in the reaction rate is directly proportional to the free (uncoated) metal surface.

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