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Influence of Paper Surface Compounds on Corrosion of Printing Machines

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Abstract:

This paper deals with investigation of corrosion processes on construction steel in contact with aqueous solutions of surface coatings of high gloss and standard uncoated papers for sheet-fed printing. During the period of four months, changes in the mass of steel specimens were measured (loss of material), as well as changes in pH values and conductivity of the examined solutions. Formation of corrosion products on the surface was identified by changes of spectrophotometric reemission in the visible portion of the steel spectrum and by FT-IR spectral recordings. In addition, the electrochemical potentiodynamic measurements were carried out with the direct current and the method of linear polarization and Tafel's extrapolation, by which the corrosion parameters were determined: corrosion potential, corrosion current density, polarization resistance cathodic and anodic inclination of Tafel's lines, as well as the corrosion rate.

The results show that the dynamics of the corrosion in printing machines is directly influenced by the type of the paper used for printing. This investigation gave an insight into dynamics and mechanisms of corrosion under conditions close to those in printing production, thus facilitating better understanding of the entire process.

Keywords:

Corrosion, Steel, Paper Coatings, FT-IR, Linear Polarization, Tafel's Extrapolation

1. Introduction

Metallic corrosion is a pervasive phenomenon, which can be noticed in contact of metal with the aggressive environment, but can also be caused by other reasons - pitting, stress corrosion, cavity corrosion, roaming currents etc. Very often corrosion is combined with erosion, thus multiplying undesirable effects. Not all metals are equally affected by corrosion, however, iron and its alloys (mostly steel) - as dominant materials in many areas - are to a great extent subject to deterioration caused by corrosion.

According to the type of the process, diverse methods of protection have been developed, like anticorrosive primer layers, corrosion inhibitors, cathodic protection etc. They, solely or in combination with other methods, more or less prevent corrosive dissolution of metals, or can - at least - decrease the rate of corrosion.

Printing industry is not an exemption to this. Metallic parts of printing machines and other equipment are - due to the requirements of the production process - exposed to different aggressive liquids and solutions, which can cause material destruction on the solid/liquid interface. Most significant case, however, is influence of the solutions of surface coatings to the metallic parts of offset printing machines. It is, therefore, necessary to consider different aspects and examine influence of solutions of paper surface compounds on metallic corrosion in printing technology - including chemical, electrochemical and mechanical investigations.

In addition to its primary function, fountain solution has a number of secondary, although not less important roles in the printing system. Along with other ingredients, most of commercial solutions contain inhibitors with the aim of preventing corrosion. However, under dynamic conditions of the printing process, surface coating of the paper is entering the solution, particles being either released from the surface, or dissolved in contact with the solution. Although intended to cover non-printing areas of the printing plate, it is distributed from the offset cylinder to other machine parts, where it can remain deposited.

Although in a very short time, fountain solution is therefore polluted by dissolved particles, thus having the composition and characteristics changed. This can reflect to the quality of printing, but, if deposited, can gradually cause deterioration of ball bearings, metallic rollers and other movable machine elements.

2. Theoretical background

Corrosion is spontaneous transformation of metals into its compounds, resulting in unintentional degradation, wear and loss of material. Corrosion effects can be identified by different methods, emerging from the nature of the process and characteristics of the products involved. A corrosion process can be, qualitatively and quantitatively, determined by a number of different gravimetric, volumetric, spectrometric and electrochemical methods.

Due to the structure of the crystal lattice, smooth and even surface of steel has high degree of specular reflection in the visible portion of the electromagnetic spectrum (380-700 nm). By formation of corrosion products, which are - as a rule of a rough granular structure - incoming light is scattered and the specular reflectance is gradually decreased (*Laćan-Šuprina 1976*). In compounds formed as corrosion products, iron is, together with other elements or ions (oxygen, hydrogen, hydroxyl group, etc…) bound with chemical links of different energy level and, accordingly, their spectral emissions in the visible spectrum will be different.

Atoms in molecules are not static, but in the state of permanent vibrations. Each molecule is characterized by a specific mode and frequency of vibrations, depending on the atomic mass and strength of links among them. Wavelengths of molecular vibrations are positioned in the infrared portion of the EM spectrum (2,5-45 mm or 4000-220 cm^{-1}). Molecules can absorb radiation energy from this part of the spectrum and transform it into the vibration energy, if the frequency of radiation corresponds to the vibration frequency within the molecule. By comparing the incoming and outcoming electromagnetic radiation through the IR spectrum, absorption spectrum of the corrosive product can be obtained. Furthermore, by comparing absorption spectra with those of known standards, presence of certain molecules in the corrosion product can be determined and mechanism of their formation explained (*Zorović 1972 , Van der Maas 1970*).

The method of Tafel extrapolation is based on a Butler-Volmer equation (1) which is the fundametal relationship in electrochemical kinetics (*Stupnišek-Lisac 2007*).

$$j = j_{+} - |j_{-}| = j_0 \left\{ \exp\left[\frac{(1-\alpha)zF\eta_e}{RT} \right] - \exp\left[-\frac{\alpha zF\eta_e}{RT} \right] \right\} \quad (1)$$

With Tafel extrapolation of anodic and catodic slopes, conducted for a wider range of potential ($E=E_{cor} \pm 250mV$), is posible to determine a corrosion potential (E_{cor}) and a corrosion current density (j_{cor}). Corrosion potentials, Tafel constants (β_a and β_c) and polarization resistance can be determined from voltammograms obtained by potential-dynamic recordings in different mediumsfrom Butler-Volmer equation (1), Stern and Geary developed equation (2) on which the method of linear polarization is based. With this method corrosion current can be determined if polarization resistance is known.

$$j_{cor} = \frac{\beta_a \beta_c}{2{,}303(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{R_p} \quad (2)$$

where:

j_{cor} - corrosion current density (μA cm^{-2}),

B - Stern-Geary constant, (V).

R_p- polarization resistance

β_a - slope of the anodic Tafel reaction, when plotted on base 10 logarithmic paper in V/decade,

β_c - slope of the cathodic Tafel reaction when plotted on base 10 logarithmic paper in V/decade

Polarization resistance is determined experimentally (for potential close to E_{cor}) with equation (3):

$$R_p = \frac{\Delta E}{\Delta j} \quad (3)$$

The value of current density was obtained by using both methods, Tafel extrapolation and linear polarization. This values were used to calculate the corrosion rate using the formula:

$$CR = K\, j_{cor} \frac{M}{z\rho} \quad (4)$$

where:

CR - corrosion rate (mm yr^{-1})

K - constant from Faraday´s Equation Rate ($3.27\ 10^{-3}$ mm g μA^{-1} cm^{-1} yr^{-1})

j_{cor} - corrosion current density (μA cm^{-2}),

M - the atomic weight of the element (M_{Fe} = 55.845)

z - the number of electrons required to oxidize an atom of the element in the corrosion process (in the observed system is z = 2)

ρ - density in g cm^{-3} (steel ρ = 7.861 g cm^{-3})

3. Experimental

An extensive number of methods have been developed for investigation of corrosion, ranging from mechanical, over chemical to electrochemical investigations. However, most of experimental work in this investigation was intended to determine state of the surface and identify corrosion products by specific experimental methods. The investigation was conducted in two phases. In the first phase of the experiment, steel specimens where immersed in solution, which was, through entire time of the experiment (126 days), exposed to air. Thus, the oxygen from the air was spontaneously absorbed in the system. In the second phase of the investigation, electrochemical experiments were conducted in standard closed electrochemical cell. All experiments were performed under standard laboratory conditions and on room temperature.

3.1 STEEL SPECIMENS

Specimens used in experiment were prepared from carbon steel according to DIN Ust 12 (C_{max} 0,12%, Mn_{max} 0,50%, P_{max} 0,04%, S_{max} 0,04%), measuring 60 x 47 mm. Surface was treated with sand paper T400 and T 800 and then highly polished with the polishing paste. After chemical treatment in dimethyl ketone and 10% sulphuric acid, specimens were washed out, dried and immersed into the electrolyte. It should be noted that this procedure is slightly different than those proscribed by ASTM standard. The use of dimethyl keton is recomanded by the polishing paste manufacturer; In addition, the same procedure was used by Musić (*Musić et al., 1993a and Musić et al. 1993b*).

For electrochemical measurements, steel specimens of diameter 15.5 mm where cutted from the steel plate with hydraulic cutter. Surface of the specimens where treated in same was as in the previous phase of research. Immediately after treatment the electrode was left in contact with air to form a natural oxide layer, it is then placed into a holder and immersed in the solution.

3.2 SOLUTIONS

For the investigation three solutions where used:

Solution (S1) – distilled water

Solution (S2) – is a solution of surface compounds of a gloss coated sheet-fed printing paper 120 gm^{-2} produced by Euro Art

Solution (S3) – is a solution of surface compounds from uncoated paper for sheet-fed printing 80 gm^{-2}, produced by Tauro

The solutions S2 and S3 were prepared with strips of standard gloss coated and uncoated sheet-fed printing paper (dim. 460 x 60 mm), 10 of which have been immersed into 500 ml of distilled water for 15 seconds. In such a short time merely primary penetration occurs, therefore only surface compounds from the paper can dissolve. In this way, real process of paper/solution interaction can be simulated.

Solutions were prepared with distilled water manufactured by INA-Maziva Zagreb d.d which adhere to ISO 9001, ISO14001 and OHSAS 18001 norms.

According to the data obtained from the vendor, papers used in this investigation are among the most represented on the regional market for sheet-fed printing.

3.3 METHODS

All solutions prepared for this investigation had volume of 350 ml. Values of electrical conductivity and pH were measured by standard instrumental methods.

Spectral reflectance from the surface of steel was measured in the visible portion of the spectrum (380-700 nm) by X-Rite spectrophotometer Swatch Book and furthermore processed by Colour shop 6.2 software. Before each measurement, spectrophotometer was calibrated on the white standard according to manufacturer's specifications. Spectrophotometric measurements of the steel surface were done before, as well as after 7, 14 and 28 days, while FT-IR spectrometry of corrosion products was performed, using Perkin-Elmer spectrometer, 1720-x after total of 126 days.

Corrosion products were pressed for this purpose and recorded by technique of pure KBr pastilles at room temperature. Steel specimens were taken from the electrolyte before measurement, dried in the air, without removing corrosion products.

For investigation the electrochemical measurements were carried out with the direct current methods of linear polarization and Tafel's extrapolation. The measurements also were conducted with potentiostat/galvanostat Versa STAT 3 manufactured by Matek-EG&G Princeton Applied Research. Obtained measurements were processed with VersaStudio software.

All tests were conducted in a standard sealed electrochemical cell with auxiliary electrode made of pressed carbon and saturated calomel reference electrode (SCE) which was, with luggin capillary, brought near the working electrode. All potential values in this study were measured and will be shown in relation to the value of the reference electrode. The surface of the sample is sealed in the holder of the working electrode with a teflon ring so that the area of exactly 1 cm^{-2} of the sample is exposed to the solution.

Before measurement of linear polarization and potentiodynamic polarization the working electrode was left immersed for some time in the solution system, in order to establish an open circuit potential (E_{ocp}). Depending on the solution that time were in the range 30-240 min. Measurement started when the value of open circuit potential (E_{ocp}) is stabilized within ± 2 mV bias for longer than 5 min.

In determining the polarization resistance by linear polarization, the potential varied in range of -20mV to +20 mV from the value of open circuit potential (E_{ocp}). Tafel's extrapolation is implemented in a wide range of potential values, in range of -200 mV to +200 mV of the value of open circuit potential (E_{ocp}). The potential value was increased by 0.5 mV each 2 seconds, thus, the scan rate in potential was 0.25 mV s^{-1}

4. Results and discussion

The phenomenon of corrosion is present in the processes of graphic reproduction; however, it has never been a great concern in discussions and research. Nevertheless, an *ad hoc* poll showed that 8 out of 10 printers can indicate, or at least are aware of the effect of corrosion in printing processes, some of them experiencing problems on printing machines.

Corrosion in the process of printing can be caused by a number of different reasons. They seem to be more evident with the use of ecological inks and fountain solutions.

Results obtained by the experimental methods applied in this investigation can elucidate the rate of corrosion and mechanisms of formation of corrosion products in the examined systems.

Steel specimens - besides iron - include also traces of other elements with different redox potentials. Therefore, when immersed into solution, micro galvanic cells appear, which are actually causing dissolution of metal and its corrosion. It is clear that the course and rate of corrosion, as well as products emerging, are related to the composition of solution. Elementary iron from the steel transits into Fe^{++} ions. They, in further secondary and tertiary reactions form oxides and hydroxides of different composition and crystal structure.

During the process of corrosion, ions in secondary and tertiary reactions are bound to ferrous ions or are exchanged with ions of different conductivity. Therefore, conductivity cannot remain the same as in the initial state. Electrical conductivity of aqueous solution of paper surface compounds of gloss coated paper (S2) in the observed time is decreasing in the first 30 days and then increasing until 60th day. pH in this case is decreasing from initial value (9,92) to almost neutral. On the contrary, aqueous solution paper surface compounds of uncoated paper (S3) shows linear decreasing of electrical conductivity, while measured pH values are continuously growing during the corrosion process, i.e. solution is becoming more alkaline. After that, further significant changes cannot be noticed. This proves that steel has been exposed to different corrosive environments, which resulted in diverse state of the surface (and corrosion products.

Corrosion of the carbon steel in distilled water is thoroughly investigated, and available in literature (*Music et al., 1993a; and Music et al. 1993b*). Therefore, this system is used as a referent system for the experiments in this paper, and the corrosion parameters for different systems where compared with the results of corrosion parameters for system with distilled water.

Corrosion products emerging on the surface of steel are of rough, granular structure and have - as a rule - larger volume. Since they are falling from the surface, mass of steel is consequently decreasing. By means of precise balance, rate of corrosion can be determined gravimetrically. Results of change in mass as a function of time are shown on Fig. 1.

Contrary to previous expectations, specimen exposed to the aqueous solution of surface coating of gloss coated paper, showed increase of mass in the first 35 days.

By measuring the values of the electric conductivity of solutions as a function of time, dynamic changes of the concentration of dissociated ions were indirectly examined (Fig. 2). pH values measured are indicating influence of the ratio of H^+ and OH^- ions on the corrosion reaction (Fig. 3).

Before the beginning of the corrosion process, even and polished surface of steel has rather high degree of reflection (0.55), equally in the entire visible portion of the spectrum. However, smallest traces of corrosion products on the surface will disperse the incoming light, so generally, total reflectance will be lower. This can be seen for all specimens regardless of the solution in which they were immersed (Fig. 4 - 6).

Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after exposure to solution S1 is shown in figure 4. The values of the spectral reflectance decrease uniformly through the entire visible spectrum. Also, this decrease in the value of the spectral reflectance is proportional to the length of exposure to the solution (Fig. 4).

Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after exposure to solution S2 is shown in figure 5. It can be seen that after 7 days of exposure, the value of spectral reflectance decreased more in blue part of the visible spectrum (i.e., 400-500 nm) then in the rest of the visible spectrum. This difference in spectral reflectance is proportional to the length of the exposure to the solution (Fig. 5.).

Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after exposure to solution S3 is shown in figure 6. After 7 days corrosion products formed on steel in the solution of paper surface compounds absorbed radiation almost equally along the entire portion of the visible spectrum. In the next period, compounds created on the surface of steel are decreasing spectral reflectance in the blue part of the visible spectrum. After 14 days no obvious changes in reflectance have been indicated; therefore, it can be assumed that the formed corrosion products are of the same crystal structure (Fig. 6).

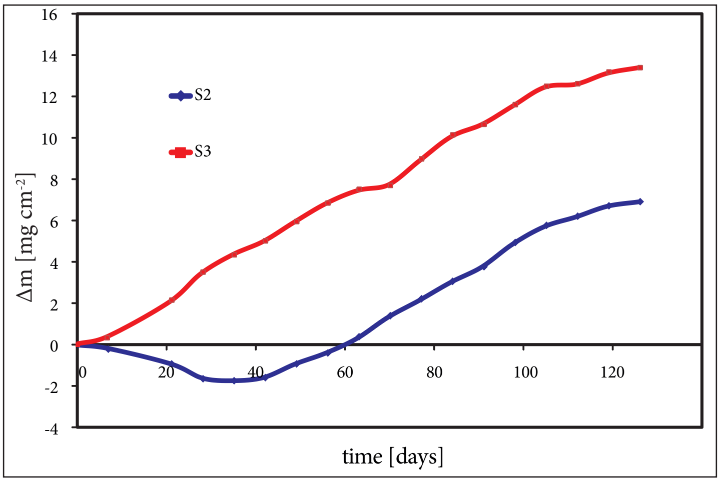

Figure 1. Loss of the material (Δm) of steel specimens in solutions S2 and S3 depending on the duration of the corrosion process

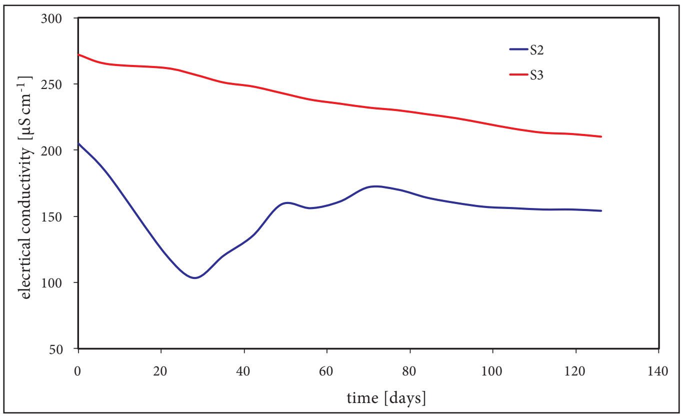

Figure 2. Electrical conductivity of the solutions S2 and S3 depending on the duration of the corrosion process

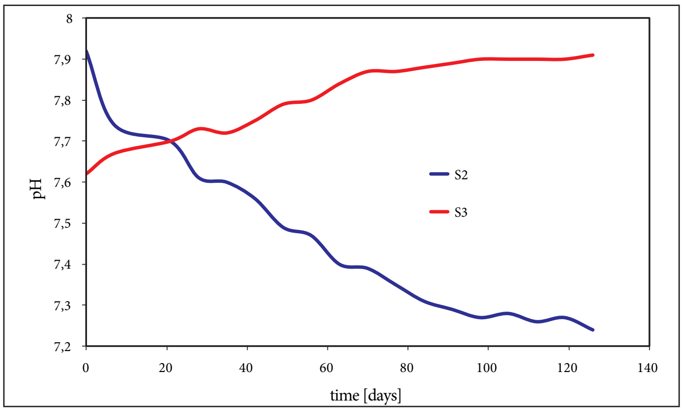

Figure 3. pH value of the solutions S2 and S3 depending on the duration of the corrosion process

FT-IR analysis proved that corrosion products formed in distilled water show that most of the recorded bands indicate presence of lepidocrocite and magnetite, which was also confirmed by measurements in the FAR range. Water solutions of paper surface coatings are, however, giving a composite structure of corrosion products. FT-IR results are showing a composition of lepidocrocite and goethite, as well as a presence of haematite and traces of magnetite (Fig 7).

Most of the bands recorded for distilled water, as well as for normal water indicate high presence of lepidocrocite [γ-FeO(OH)], which is a typical product of under-water corrosion. It can be most clearly identified at 1022, and 743 cm^{-1}. Presence of magnetite [ferrous-ferric oxide (Fe_3O_4)] is detected at 557 cm^{-1} (*Misković 1975*).

Results are confirmed by measurements in FAR range, where bands at 361 and 276 cm^{-1} can be attributed to lepidocrocite, band at 557 cm^{-1} to magnetite, while both crystals share the band at 478 cm^{-1} (Fig. 7). Results obtained for corrosion in distilled water are in accordance with earlier investigations and literature references (*Musić et al 1993a , Musić et al1993b*).

Recordings of FT-IR measurements obtained for corrosion products on steel in aqueous solutions of surface coatings of both papers are indicating a more complex structure. Solution of paper surface compounds of gloss coated paper (S2) (Fig. 7) resulted in a mixture of ghoetite (884 and 795 cm^{-1}) and lepidocrocite (1128 ,1022cm^{-1}), while shoulder of the curve at 366 cm^{-1} can be attributed to lepidocrocite. Solution of paper surface compounds of uncoated paper (S3) (Fig. 7), most of the bands recorded in MID and FAR ranges are corresponding to goethite, only the band at 1022 cm^{-1} and 745 cm^{-1} shows the presence of lepidocrocite, while the FAR band at 560 cm^{-1} indicates the traces of magnetite (*Briston 1998*).

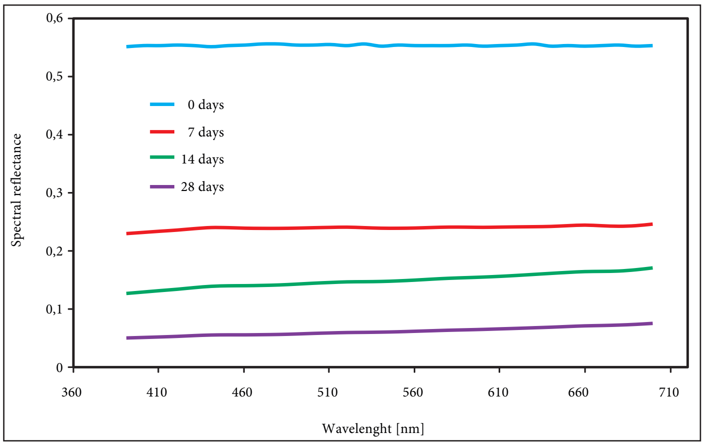

Figure 4. Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after 7, 14 and 28 days of exposure to solution S1

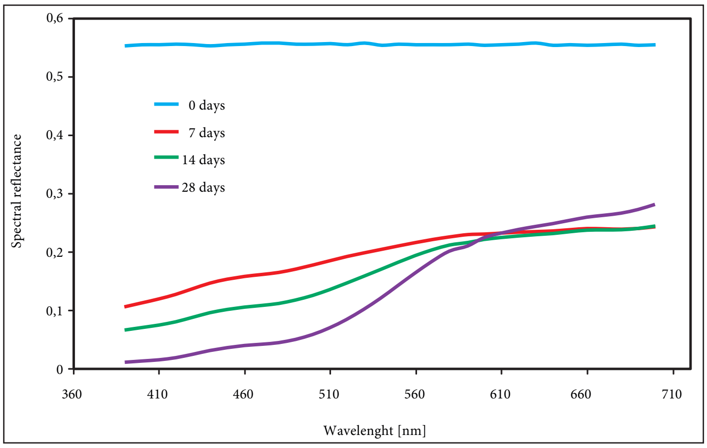

Figure 5. Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after 7, 14 and 28 days of exposure to solution S2

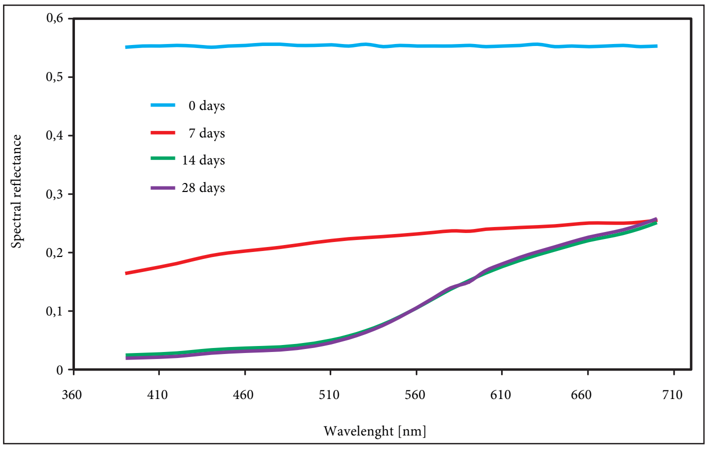

Figure 6. Spectral reflectance from the surface of steel specimens in the visible portion of the spectrum before and after 7, 14 and 28 days of exposure to solution S3

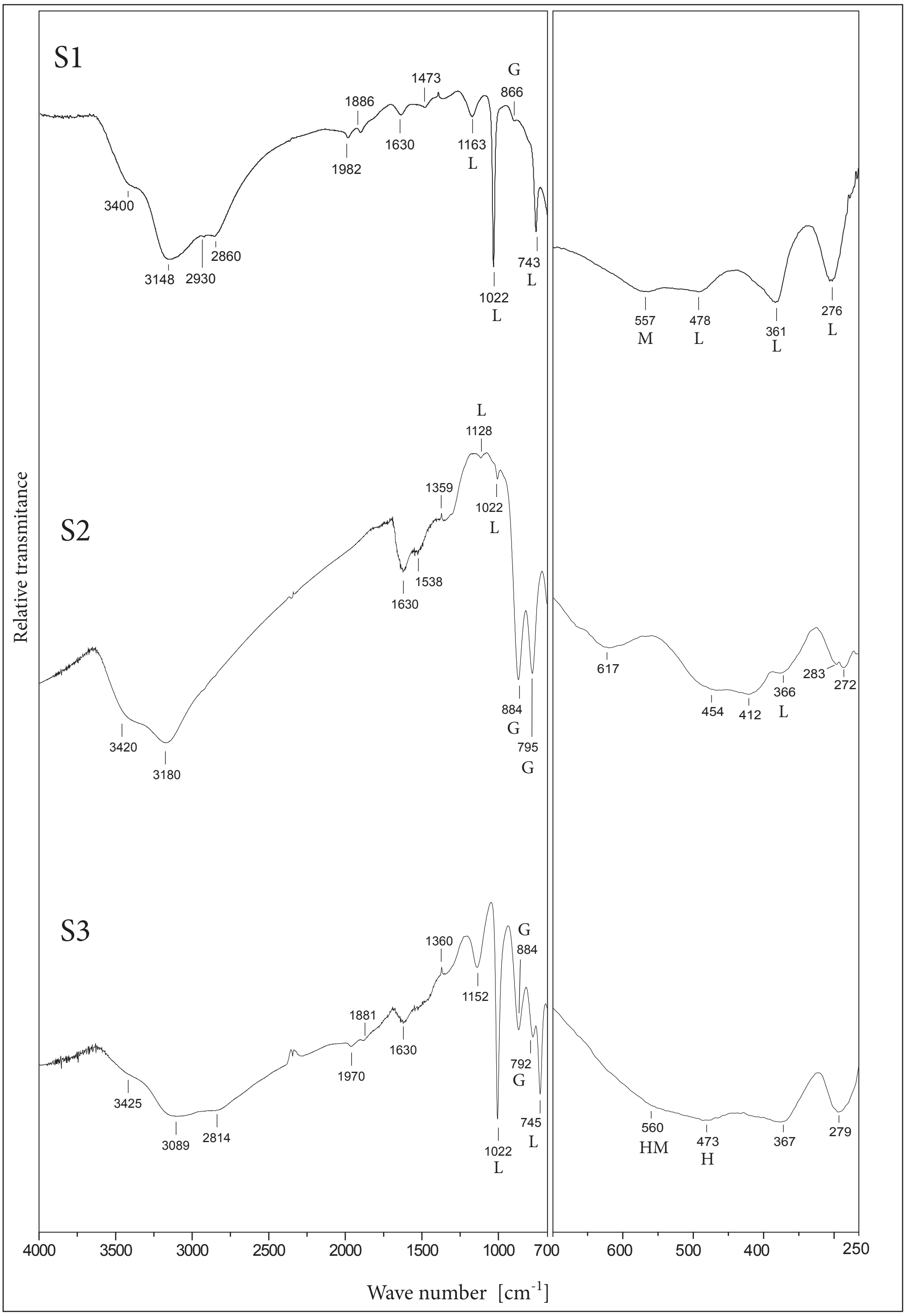

Figure 7. FT-IR spectra of corrosion products of steel specimens in solutions S1, S2 and S3 after 126 days, recorded at the room temperature

Electrochemical potentiodynamic polarization measurements can provide insight into the dynamics of corrosion in a short period of time, and predict the course of corrosion processes in real systems. The tested steel is corroded in solutions whose composition is described in the experimental part. Measurements were carried out by two methods, each of which gave an insight into different segments of the corrosion process. With the method of linear polarization corrosion potential (E_{cor} [mV]), corrosion current density (j_{cor} [μ A cm^{-2}]), polarization resistance (R_p [Ω cm^2]) and finally corrosion rate (CR [mm yr^{-1}]) were determined. With Tafel extrapolation method corrosion potential (E_{cor} [mV]), corrosion current density (j_{cor} [μA cm^{-2}]), corrosion rate (CR [mm yr^{-1}]) and cathode ($-\beta_c$) and anode (β_a) slope were obtained. Since for the observed system has unknown chemical composition of the electrolyte, dynamics of corrosion were evaluated indirectly using the corrosion rate which was calculated from the obtained corrosion parameters.

Figure 8 and the results show that there is a big difference between the measured value of the corrosion potential of the systems. This is due to the soluted ions from a paper surface in solutions S2 and S3. Corrosion current density, from which the corrosion rate is calculated, is inversely proportional to the value of polarization resistance. Therefore, a decrease in polarization resistance leads to an increase in current density. In both aqueous solutions the corrosion rate is higher than in distilled water. However, contrary to predictions derived from the first phase of the investigation, both types of paper used in the investiagion show equal values of corrosion parameters, including the corrosion rate. This phenomenon is explained by absorption of oxygen in the solution for a longer time in the first phase of testing.

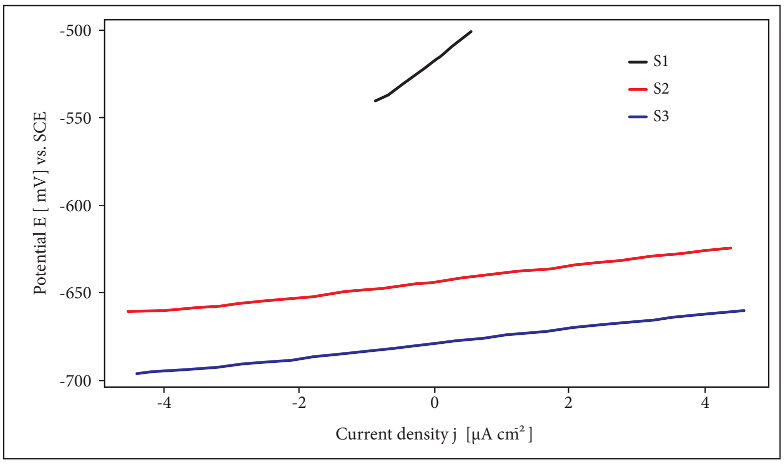

Figure 8. Polarization curves of steel in solutions S1, S2 and S3

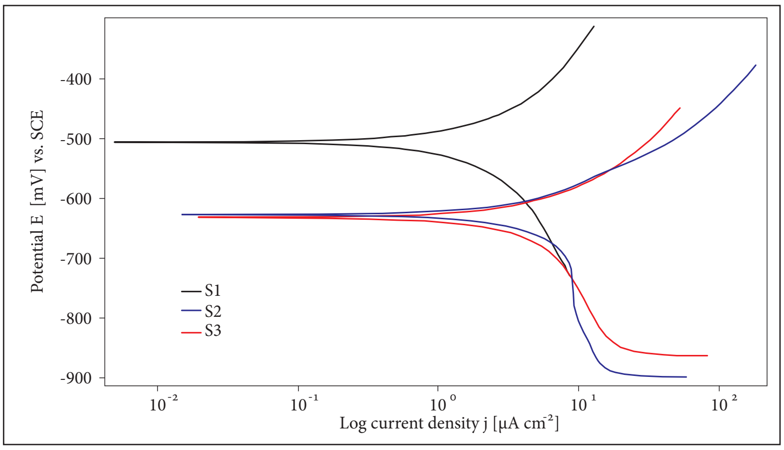

Figure 9. Polarization curves of steel in solutions S1, S2 and S3.

Table 1. Corrosion parameters determined by the method of linear polarization

solution	E_{kor} [mV]	j_{kor} [μA cm^{-2}]	R_p [Ω cm^2]	CR [mm yr^{-1}]
S1	-517	0,732	29670	0,008
S2	-678	5,172	4202	0,060
S3	-643	4,924	4414	0,057

Table 2. Corrosion parameters determined by the method of Tafel extrapolation.

solution	E_{kor} [mV]	$-\beta_k$ [mV/decade]	β_a [mV/decade]	j_{kor} [μA cm^{-2}]	CR [mm yr^{-1}]
S1	-500	323	173	2,206	0,025
S2	-616	261	138	6,516	0,075
S3	-620	283	114	5,313	0,061

Figure 9. shows the potenciodynamic polarization curves, and table 2. gives the values of corrosion parameters of the steel in the observed electrolytes obtained by Tafel's extrapolation method. Corrosion parameters obtained by Tafel's extrapolation of the steel in distilled water showed a significantly higher corrosion rate than that obtained using linear polarization method. The values of corrosion rate in solutions were equal to the values obtained using linear polarization.

6. Conclusion

Spectrophotometric measurements in the visible portion of the spectrum are suitable for detection of corrosion in initial phase only, depending on the dynamics of the process, up to the first 7 days under described laboratory conditions. After that time corrosion products that have emerged are defecting from the surface, therefore, such analysis is not a real indicator of the dynamics and the course of the process. However, in initial phases, formation of corrosion products can be detected on the metal surface, even without analysis of the product in the electrolyte, which usually evaporates in the printing machine. Such a method, although not accurate enough, could be suitable for simple detection of corrosion under production conditions.

Laboratory simulations of real system performed in this investigation gave an insight into corrosion processes for the solutions and papers selected in this study. Since coatings of different chemical compositions are applied in the processing of papers, it can be assumed with great probability that this laboratory simulation of the corrosion rate will have strong correlation with the corrosion rate in real world printing environment.

Depending on the sort of paper, and firstly on the kind of surface compounds, which are transferred in solution by dissolution, the rate of corrosion processes in printing systems is substantially different. From the analysis performed and the results obtained it can be with a high degree of probability stated that the corrosion processes in the systems of graphic reproduction are in direct correlation with the kind of compounds on the paper surface.

In preventing corrosion in the process of printing, it is necessary to control properties of inks and - particularly - papers entering the system, since they can significantly influence the effect of corrosion of printing machine elements.

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