Metal Antik conservation coatings on iron specimens

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The surface treatment of historical iron artefacts involves application of right conservation coating to the material to prevent further corrosion deterioration. Among common conservation agent of iron belong tannate coating, which is considerably preferred with the desired black appearance of the surface. In this work the new potentional conservation agent Metal Antik was studied. The change of this possible surface treatment was evaluated over time. The comparison between long-term exposed samples (15 years), short-term exposed samples (1.5 year) and fresh cured samples was done by spectrocolorimetry measurement. This was also compared to standard samples prepared with tannate coating. Surface analysis for all types of samples was done by μ-Raman spectroscopy. Results proved that effect of time changes the surface of coatings. It was demonstrated by colour change of surface and by formation of areas with local corrosion. Another study of Metal Antik in order to improve corrosion resistance is open.

INTRODUCTION

With few exceptions, all metals are subject to corrosion by electrochemical reaction of the metal with its environment. The corrosion effects in the case of artistic or historical artefacts can be seen as positive, e.g., forming a patina considered as aesthetically pleasant. However, in most cases, corrosion causes metal deterioration [1]. Especially historical objects made of iron alloys exposed to atmosphere require complex protection due to exposing them at outdoor or indoor conditions.

Tannins based on saccharide and gallic acid are commonly used for the protection of historical iron artefacts forming tannate coatings. Concerning the efficiency of tannate coatings there is a controversy due to low stability in humid environments. Some new potential alternatives appeared (decanoate etc.) among them a new commercial agent Metal Antik (MA). MA is a decorative two components organically modified zinc-silicate paint commonly used as anticorrosion agent for materials from steel and cast iron exposed at outdoor atmosphere with corrosivity category C2-C5 [2]. The paint consists of inorganic bin-der, organic solvents and zinc pigment with the curing in the air with atmospheric humidity. The paints simulate genuine colour of the ferrous smithery products and contributes to conservation of the historical objects [3].

The research aim of this work is to compare treated iron samples with MA paint and exposed at long term atmospheric conditions to tannate treated specimens. The results could help to gain information about changes in MA paint over time.

EXPERIMENTAL

Samples Preparation

Corroded mild steel sheets with dimension of 7 × 5.5 cm had been used as a substrate after exposure at atmospheric environment. On surface the typical layer of corrosion products was formed. At first, corroded samples were mechanically cleaned by emery paper (Parkside) with grain size 400. Small particles of rust were wiped out with cotton tampon. Subsequently, free of non-adherent rust samples were degreased with detergent (Aktigal), then rinsed with deionized water and dried out by hot-air fan 2 mins from both sides.

MA paint was applied with brush in following steps:

- Metal E with dilution 30 vol.% of thinner
- Metal E with dilution 10 vol. % of thinner
- Metal Antik layer
- Metal Antik layer

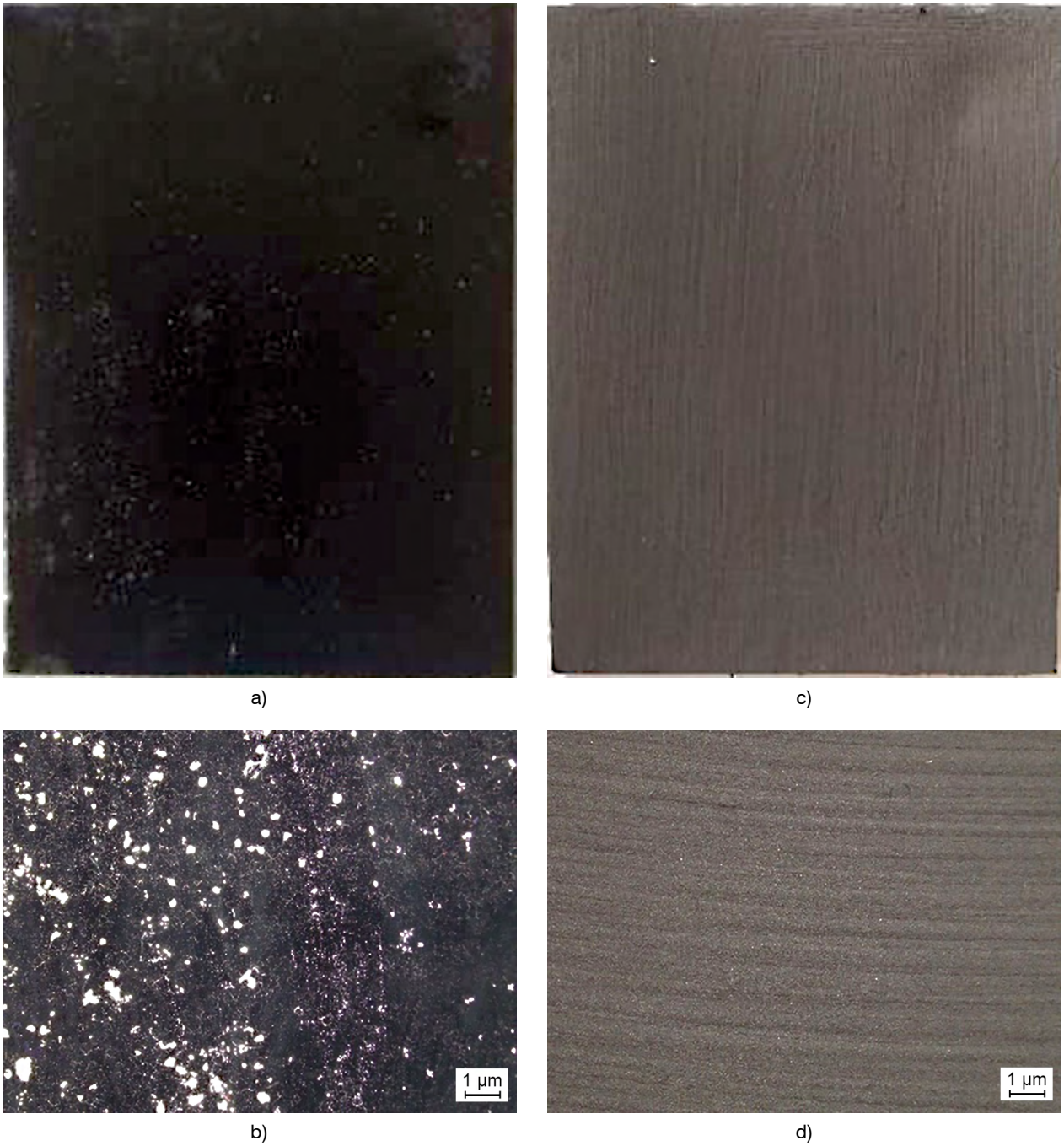
Metal E (Pragolab, Czech Republic) served as a primer. Time interval between individual steps was 12 hours. Samples were cured by influence of atmospheric humidity.

Tannate coating was applied in 4 layers with brush also, each layer was applied after 12 hours of curing at air. It was used 20% solution of tannate, which was made by mixing 200g tannin, 1000ml of deionized water and 75ml of ethanol.

Samples with different surface treatment were exposed at angle around 45° in the climate chamber (Liebisch SKB 400A-TR). Firstly, accelerated corrosion test according to standard [4] was done. The corrosive medium was condensation atmosphere with alternating humidity and air temperature. It was alternated condensation (8 hours) and condewing (16 hours) in total 8 cycles. Subsequently, samples were let in climate chamber year and half.

Long-term exposed samples with MA paint

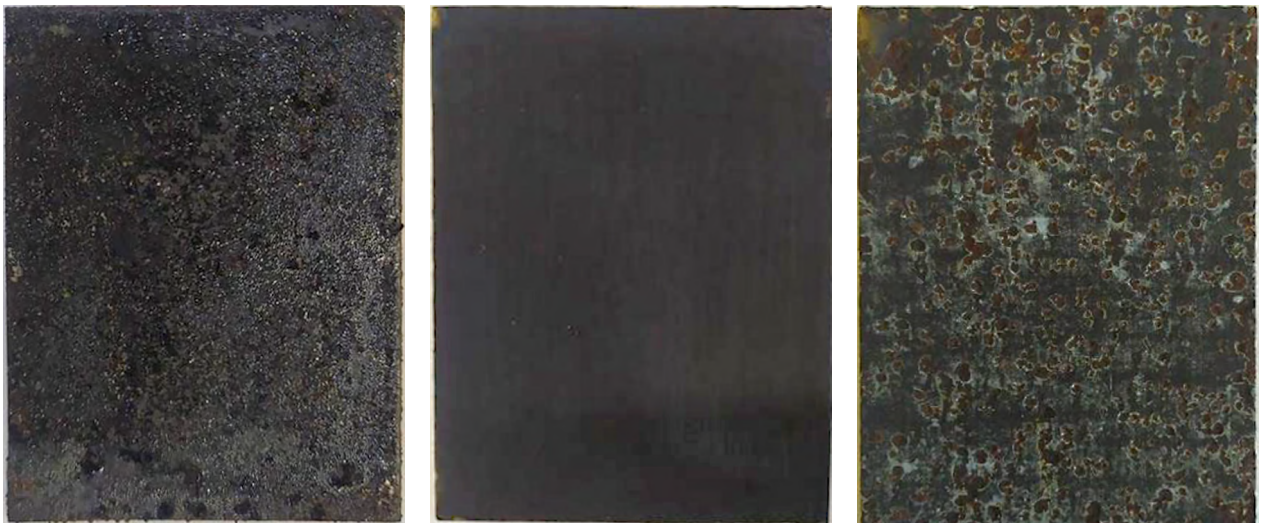
Steel samples were attached to test frame at atmospheric station (Kopisty) with corrosivity category C3 under the angle of 45°. After determined time of exposure (15 years), samples were removed and relocated to laboratory to evaluation changes of surface.



a) c)

b) d)

Fig. 1. Fresh cured samples with surface treatment (a,b); Tannate coating (c,d) MA paint



a) b) c)

Fig. 2. Samples after determined time of exposure with: a) Tannate coating (1.5 year); b) MA paint (1.5 year); c) MA paint (15 years)

Spectrocolorimetry measurement

Using the device spectrocolorimeter (Spectro – guide 45/0 gloss) colour of the surface treatment was measured with CIE coordinates (L^*, a^*, b^*). These parameters represent following: L^* – lightness; a^* – axis green-red; b^* – axis yellow-blue. Spectrocolorimetry measurements were used for comparison change of the surface colour over time.

Raman spectroscopy

Surface of the prepared samples were evaluated by **μ**-Raman spectroscopy (Raman Microscope Thermo Fischer Scientific DXR IMA4476, USA). **μ**-Raman spectra were acquired with an excitation wavelength of 532 nm. The laser power worked at range 0.1-1 mW, in pin-hole mode with exposure time 5 s. Tannate coating (1.5 year), MA paint (1.5 year) and long-term exposed samples with MA paint (15 years) were studied.

RESULTS AND DISCUSSION

Figure 1 shows specimens treated with tannate coating and MA paint after curing. One can see significant visual difference: tannate layer on steel specimens is black, specimens treated with MA paint are represented by greyish colour. At Figure 1a,c are pictures from digital camera, while pictures shown at Figure 1b and d were taken by stereomicroscope (Leica Stereozoom S9).

Figure 2 shows samples exposed to outdoor/indoor atmosphere. All studied samples provide changes on the surface. The changes are visually detectable. Tannate coating (Fig. 2a) and MA paint after 15 years (Fig. 2c) exhibit signs of local corrosion. Change in colour of the surface for MA paint after 1.5 year is noticeable, from greyish to black. Local corrosion on the surface of MA paint after 1.5 year isn't noticeable.

According to **μ**-Raman spectroscopy surface of specimens was investigated. Specific areas for each sample were observed by **μ** -Raman spectrometer. For the sample with tannate coating, after 1.5 year of exposure, it was measured area with red circle shown at Figure 3a. **μ**-Raman spectrum depicted at Figure 3b was acquired.

Tab. 1. Chromaticity of samples from different localities and exposure time

Surface treatment + location	Exposure time (years)	L^* (-)	a^* (-)	b^* (-)
Tannate – Bratislava-lab.	–	2.75	0.10	-0.20
Tannate – Bratislava-lab.	1.5	31.70	3.58	3.73
MA – Bratislava-lab.	–	26.90	0.37	1.67
MA – Bratislava-lab.	1.5	26.21	0.25	0.37
MA – Kopisty	15	36.45	0.51	3.94

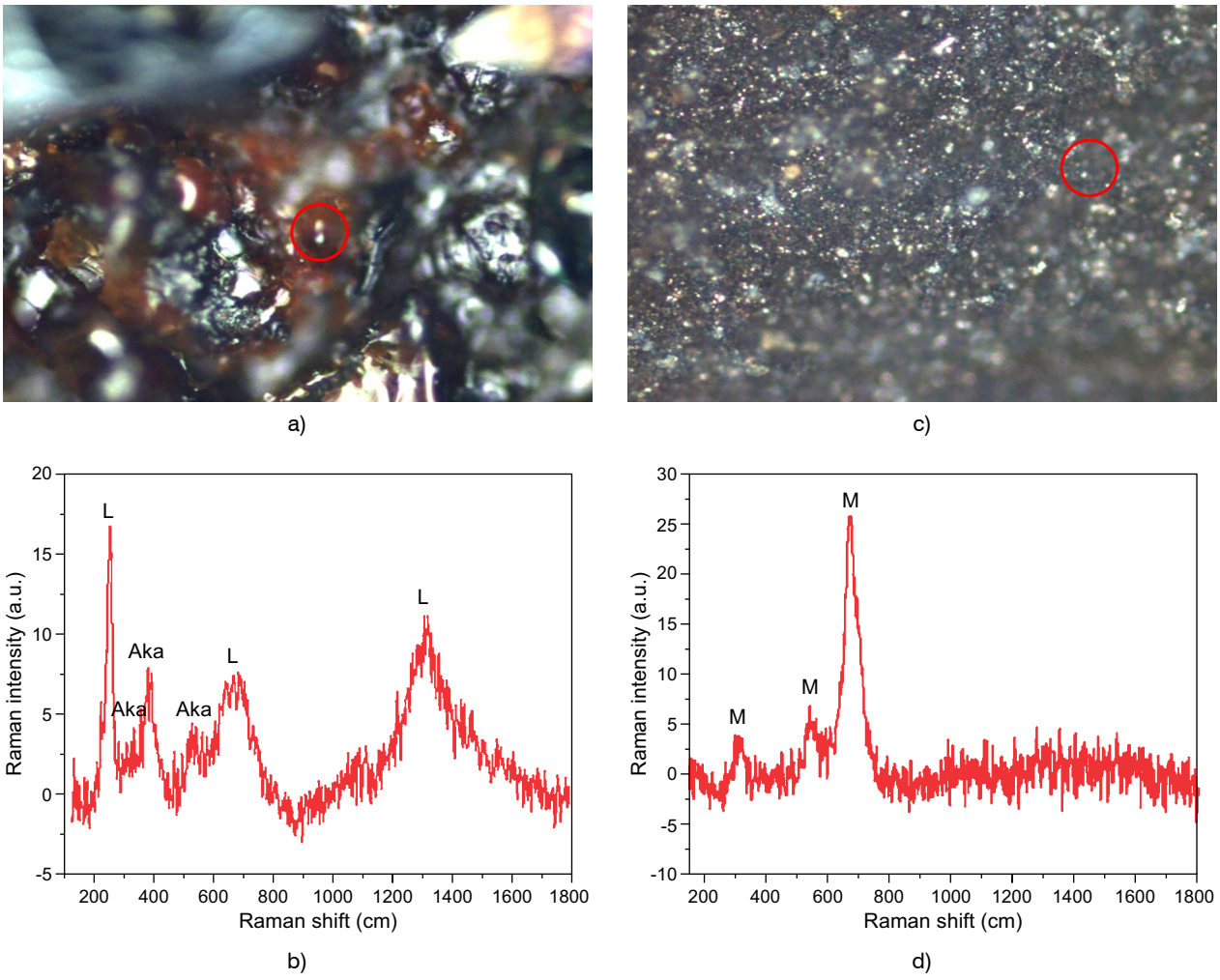


Fig. 3. Raman spectra and areas of measurement for sample after 1.5 year of exposure with: a,b) Tannate coating; c,d) MA paint

This spectrum detected phases L – lepidocrocite (**γ** – FeO(OH)) and Aka – akaganeite (**β** – FeO(OH)). Measurement by **μ**-Raman spectroscopy for the sample with MA paint after 1.5 year of exposure was realized in the area marked with red circle (Fig. 3c). Acquired **μ**-Raman spectrum has revealed the presence of M – magnetite (Fe_3O_4). For the long-term exposed sample areas of measurement are shown at Fig. 4, **μ**-Raman spectra (Fig. 5) were assigned to M in the inner part (band at 670 cm^{-1}) of corrosion products (CPs) in contact with metal. Outer part of CPs is formed by L and Aka [5,6,7]. L and Aka are orange-red CPs of the iron. Magnetite is corresponded to darker layer of CPs, it is usually under red-orange layer of CPs.

Results from spectrocolorimetry measurement in CIE ($L^*a^*b^*$) coordinates for different types of samples with coatings are summarized in Table 1. It was focused on parameter L^* (white/black) and its change over time. This parameter was compared to standard fresh-cured samples. It was found that parameter L^* for exposed sample is higher than parameter for fresh-cured sample. This is evident at both types of surface treatment. It was confirmed a trend of whiting out over time. However, parameter L^* for sample with MA paint exposed only 1.5 year is lower than in 15 years, which means that the surface firstly change colour from greyish to black and consequently starts to white out.

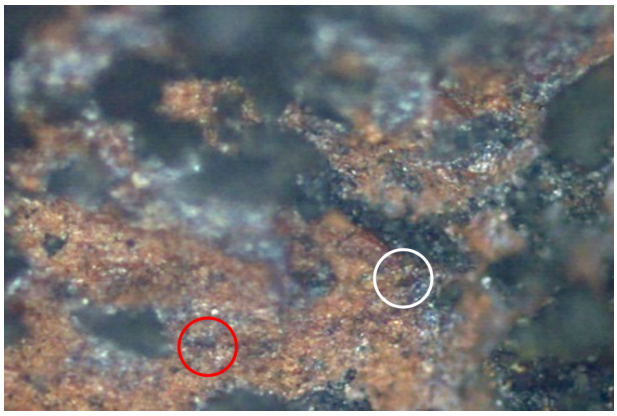


Fig. 4. Sample with marked areas of measurement with MA paint (15years)

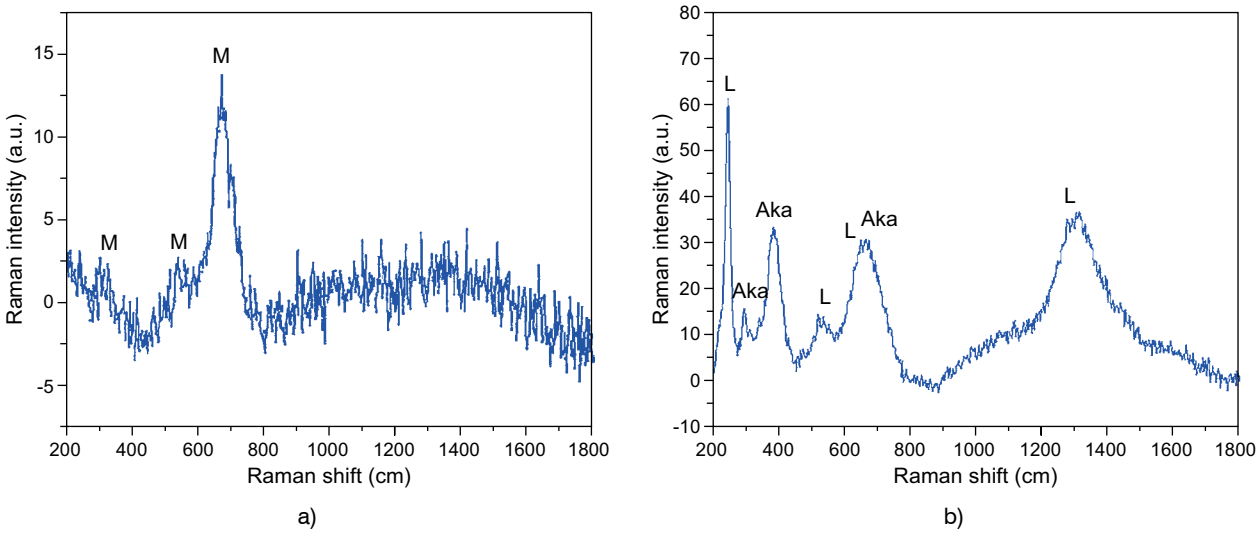


Fig. 5. Raman spectra and areas of measurement for sample after 1.5 year of exposure with: a,b) Tannate coating; c,d) MA paint

The effect of time at MA paint is demonstrated in this work. It's possible to seen that the quality of coating is decreasing over time, especially in the meaning of colour. This is confirmed by spectrocolorimetry measurements shown at Tab. 1. During long-term exposure in outdoor atmosphere, areas with local corrosion starts to occur at the surface. In comparison with short-term exposed samples, where only magnetite had been revealed, long-term exposed samples contained also the oxohydroxides of iron (lepidocrocite and akaganeite). In the future research, attention should be paid to the use of conservative waxes and sprays (Paraloid B72/lanolin). as the final procedure to improve corrosion resistance.

CONCLUSIONS

The surface treatment MA on iron samples was investigated over time. Summary of the work is the finding that exposure to atmospheric conditions worsens the quality of coatings. Colour of coating is becoming more whiter over time and corrosion attack of the surface is significant.

Acknowledgement

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