# Historical processes of chemical blackening of steel and their corrosion resistance

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*This study focuses on the evaluation of historical acid blackening of steel in terms of their applicability to historical objects, such as tin-soldered multi-barrelled firearms, where the alkaline bath blackening method cannot be used. The acid blackening method was also compared with the alkaline hot bath blackening method used nowadays, both on the conversion layer itself and in combination with a preservative agent. The procedures were tested on low carbon steel samples and fragments of damaged historic steel barrels. The quality of the surface treatment was evaluated both in terms of visual appearance and corrosion resistance. The corrosion properties were evaluated both by a condensation chamber test and by electrochemical methods such as polarization resistance measurements or electrochemical impedance spectroscopy.*

## INTRODUCTION

Surface treatment of iron objects by blackening or browning has been known since the end of the 16th century and can therefore be described as a historical surface treatment used mainly for firearms, where it fulfilled both a protective (preservative) and decorative function. From a chemical point of view, the principle of blackening or browning is the formation of an inorganic ferric oxide layer with good adhesion to the metal surface and its subsequent preservation with drying oil. What means and natural substances were used in past centuries to create a black or chocolate brown layer of iron oxide can be found in professional literature [1]. It was usually a cold solution that was applied to the surface of the metal several times. It is the technology (the method of application) that makes the old method of blackening fundamentally different from the modern method of blackening, which is carried out by hot immersion at a temperature of approx. 130 °C in a melt containing nitrate, nitrite and caustic soda. The immersion bath technology, which has the trade name Brunigal, is faster and simpler, but cannot be applied to multi-barrelled weapons where the barrel bundles are soldered with soft tin solder. For the acid blackening tests, the formula AZ40 from Adamovské strojírny (Adamov Machine Works) was chosen. This process has been used in the past at Adamovské strojírny as a surface finish, e.g. on printing machine components or on fuel dispensers at petrol stations. The aim of the study was to evaluate the quality of both surface treatment procedures for their use in the conservation-restoration of historical weapons [2–4].

### *Materials and sample preparation*

For the test of the application of acid blackening methods, cuttings of damaged historical steel gun barrels were used, a total of 3 pieces (Fig. 1). The dimensions of the samples were different, namely the length of 136-240 mm and an outer diameter of 18-26 mm. The barrels were circular or hexagonal in outer diameter.


Fig. 1. Firearms barrel fragments before blackening

A sample was taken from each barrel in order to prepare a metallographic sample for the purpose of examining the material microstructure. The microstructure of the samples was similar, in all cases being low carbon steel with the ferritic structure visible in Fig. 2. Table 1 summarizes the results of the surface XRF analysis of the material, where the content of other elements besides iron was detected. This content was only up to 0.5 wt.% and is more likely to be surface contamination than alloying element in the material. Analysis was performed by handheld Olympus Innov-X Delta XRF spectrometer with beam focusing to an area of 9 $mm^2$ and a total spectral loading time of 1 min.

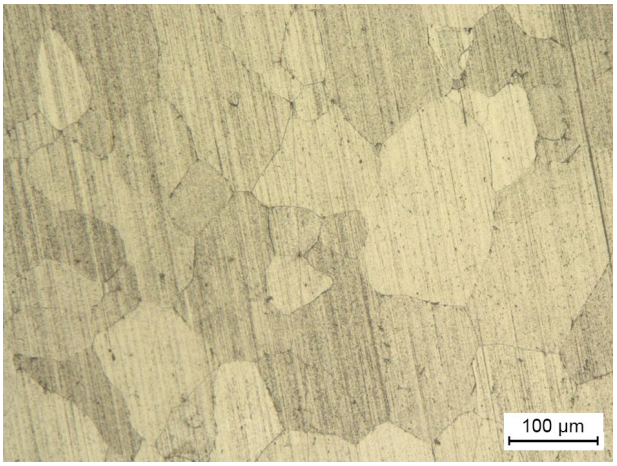


Fig. 2. Microstructure of steel in the barrel sample (500× magnification)

Tab. 1 Primer systems specification

| Number of sample | Content of element (w.%) | | | | | |
|---|---|---|---|---|---|---|
| | Fe | P | Si | Cu | Mn | Ni |
| 1 | 99.0 | – | 0.3 | 0.2 | 0.4 | – |
| 2 | 99.4 | 0.3 | 0.1 | – | – | 0.2 |
| 3 | 99.8 | 0.1 | 0.1 | – | – | |

### *Cold acid blackening in the bath of Adamovské strojírny*

The cold blackening was carried out according to the formula of Adamovské strojírny AZ40. Prior to the blackening bath application, the surface of barrels 1–3 was brushed with a steel brush and then degreased with acetone and re-polished with precipitated chalk. Then, the surface was pickled in HCl (1:1 solution of conc. acid and water) and neutralized in 10% $Na_2CO_3$. This was followed by the application of the blackening solution in long strokes using a polyurethane sponge a total of 4 times at intervals of 24 hours.

The chemical composition of the bath is as follows:

- 20 g $HgCl_2$
- 20 g $CuSO_4$
- 10 g $FeSO_4$
- 65 g ethanol

all in 1 litre of demineralized water

After the first layer was applied, the surface turned green (Fig. 3), which further changed to orange rust by the formation of iron hydroxide-oxides (Fig. 4). Next, the samples were placed in a climate chamber with 100% RH where they were left at 60 °C for 12 h. Surface rust was mechanically removed with a steel brush, followed by boiling the layers in demineralized water for 30 min. After boiling and drying, the surface of the barrel samples was polished with a fine cloth and preserved with Konkor 101 oil (Fig. 5), which was sprayed and spread on the surface.

Fig. 3. Appearance of the barrel samples after application of the first layer of the cold blackening solution


Fig. 4. Appearance of the barrel samples after application of the fourth layer of the cold blackening solution


Fig. 5. Final appearance of the blackened barrel samples after final preservation

### *Corrosion testing in condensation chamber*

For corrosion testing, sets of samples were prepared for both acid blackened steel and alkaline blackened steel. As samples, low carbon steel tubes (outer diameter 30 mm, length approx. 160 mm, steel grade 11) were used, which were blackened by the Adamovské strojírny bath formula using the same procedure as for the gun barrels mentioned above, but without final preservation with Konkor 101 oil. The second set of samples was alkaline blackened at Adamovské strojírny by immersion in Brünn Rekord (solution based on NaOH and $NaNO_2$) according to DIN 50938. The blackening was carried out in 2 steps at temperatures of 138/140 and 144/148 °C for 15 minutes [5].

Ready samples of blackened steel were subsequently subjected to a corrosion test in a condensation chamber according to ČSN 03 8131 at the Military Research Institute in Brno. The test was carried out for 14 days at a temperature of (35 ± 2) °C. The evaluation was based on a visual assessment of the extent of corrosion attack on the sample surface.

While only 10 corrosion spots were found on one sample in the case of alkaline blackened samples, the extent of corrosion on 10% of the area was evaluated in the case of acid blackened samples. The Fig. 6 clearly shows that the surface layer is not as compact as in the samples blackened industrially in an alkaline bath (Fig. 7).

a) b)

Fig. 6. Samples of acid blackening before (a) and after corrosion testing (b)

a) b)

Fig. 7. Samples of alkaline blackening before (a) and after corrosion testing (b)


Fig. 8. Appearance of blackened samples (1 – blank, 2 – acid blackening, 3 – acid blackening with preservation, 4 – alkaline blackening, 5 – alkaline blackening with preservation)

## Corrosion testing by electrochemical methods

### *Preparation of blackened samples*

The steel sheet samples were made of low carbon steel grade 11 of 5 × 5 cm size, which were blasted with glass beads (size 200-300 μm). One set of samples was blackened in acid solution according to AZ40 from Adamovské strojírny, half of which was preserved with Konkor 101 oil. The second set of samples was blackened with Brünn Rekord alkaline bath under hot conditions on an automated line at Adamovské strojírny with a final preservation with Emulsin 5382. To evaluate the effect of the preservative, it was removed from half of the samples by repeated immersion in petroleum spirit prior to measurement. The appearance of the blackened samples is shown in Fig. 8. For comparison, blank steel sheet samples were prepared. They were treated only by blasting or preserved with Konkor 101 oil.

### *Morphology survey of the blackening layers*

The structure of the oxide layers of blackening on steel samples was evaluated under the scanning electron microscope Tescan Mira 3. Fragments of the samples were taken from the blackened sheets, which were embedded in resin and prepared as metallographic samples. In Figures 9 and 10, the surface layer of the blackened samples can be observed. The images show elemental maps where oxygen is shown in yellow to highlight the oxide layer. In the case of the acid-blackened sample, the oxide layer was very thin, up to 1 μm, and thus has only an aesthetic function. Although a solution containing chlorides was used during the acid blackening process, their presence was not detected on the surface of the sample in section. In the alkaline blackened sample, the average thickness of the iron oxide layer was 5 μm, being was therefore thicker.

### *Measurement of polarization resistance of the blackened layers*

In order to compare the corrosion resistance of the surface, measurements of their polarization resistance were made using linear polarization. A contact cell in a classical three-electrode setup with an argent chloride reference electrode and a platinum counter electrode was used for the measurements (Fig. 11). The exposed area on the working electrode was circular with a diameter of 35 mm, corresponding to an area of 9.6 $cm^2$. Drinking water (with chloride concentration of 48,6 mg $dm^{-3}$) was used as the electrolyte. A Metrohm Autolab PGSTAT204 potentiostat equipped with an FRA32 impedance module was used for the measurements. The measured data were evaluated using Nova 2.1.7 software.

First, the open-circuit potential ($E_{OCP}$) was recorded for 30 min, which is shown in Fig. 12 and 13. The polarization resistance ($R_p$) of the samples was then measured using the linear polarization method to evaluate the protective function of both the blackening layer and then also in combination with the preservative agent [7].

It can be seen from the graphs that in the case of samples without final preservation, there is initially a sign of a protective function in the case of alkaline blackening before the oxide layer is disturbed by chlorides in the electrolyte. The blank and acid blackened sample then

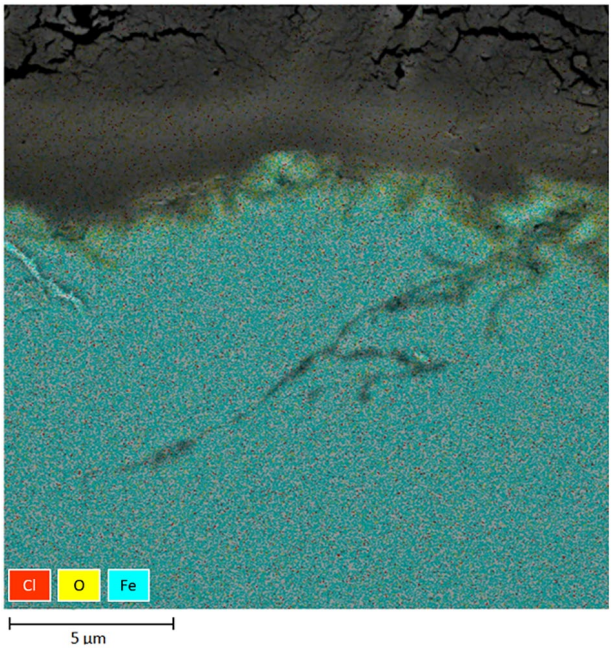


Fig. 9. Surface of acid-blackened sample (15 000× magnification)

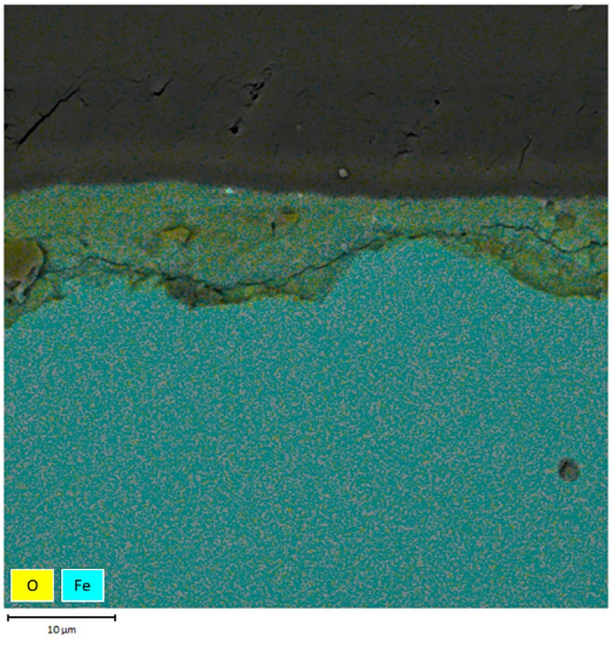


Fig. 10. Surface of alkaline-blackened sample (5 000× magnification)

exhibit similar behaviour showing active corrosion. In the case of samples preserved with Konkor 101 oil, the trend was again similar. On the other hand, the industrial alkaline blackened sample which was preserved with Emulsin 5382 showed a higher corrosion resistance.

Polarization measurements were made within ± 20 mV of the $E_{OCP}$ after 30 min of stabilization, and the polarization rate was 0.1 mV $s^{-1}$. From the resulting curves, the polarization resistance was calculated using linear regression, the values of which are summarized in Table 2. The measurements were repeated 3 times.

The polarization resistance values show that the oxide layer has no significant protective character and depends on the thickness of the layer. In the case of alkaline blackened samples, the resistance was slightly higher than that of acid blackened samples. The $R_p$ values for the samples preserved with Konkor 101 were highly variable, which was probably due to the inconsistent thickness of the preservative layer during sample preparation. In the case of the alkaline blackened samples, the values showed greater consistency and also the greatest surface protection.

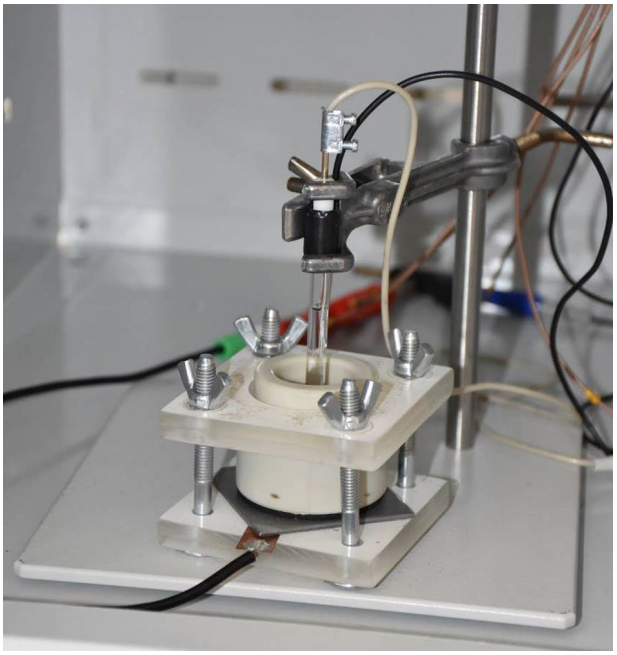

Fig. 11. Contact cell for electrochemical measurement

Tab. 2 $R_p$ values of the samples

| Sample | $R_p$ (Ω cm$^{-2}$) |
|---|---|
| Blank | 7.6-22.7 |
| Acid blackening | 4.2-9.0 |
| Alkaline blackening | 24.7-26.7 |
| Blank + Konkor 101 | 2.2-215.2 |
| Acid blackening + Konkor 101 | 16.1-351.2 |
| Alkaline blackening + Emulsin 5382 | 184.4-409.4 |

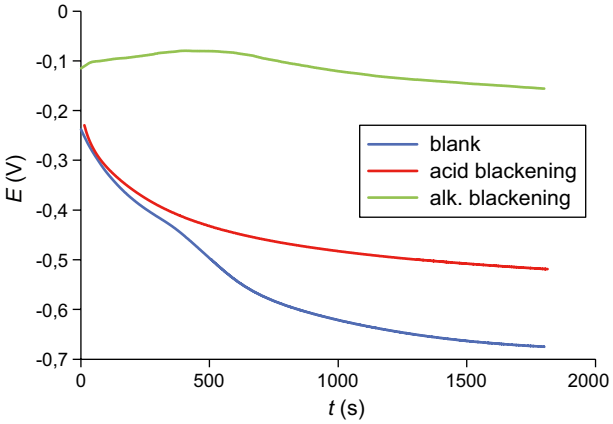


Fig. 12. $E_{OCP}$ in time for samples without preservation

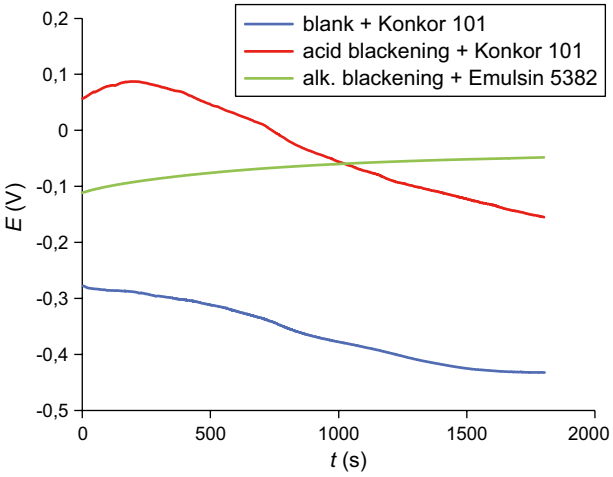


Fig. 13. $E_{OCP}$ over time for samples with preservation

### *Impedance characteristics of blackened layers*

The protective function of the blackened layers was also studied using electrochemical impedance spectroscopy. The measurements were performed in a contact cell like in the case of the previous measurements, the frequency range was set to $10^6$-$10^{-2}$ Hz and the potential amplitude to 10 mV.

Since the iron oxide-based blackening layers are relatively conductive, then based on the evaluation of the Bode diagrams, the equivalent circuit corresponds to the Randels circuit (Fig. 15), where the terms are – electrolyte resistance ($R_s$), polarization resistance ($R_{pol}$) and capacitance of the electrical double layer. However, its layer capacitance behaviour is not ideal, and that is why a constant phase element ($CPE_{dl}$) is used. The CPE is characterized by an admittance Y with an exponent N indicating whether the behaviour of the CPE is close to multiple resistor (N → 0) or capacitor (N → 1). The values for each element of the circuit are summarized in Table 3. The Bode diagrams were similar for all samples, an example for the sample with acid blackening layer is shown in Figure 14. Positive phase shift at higher

frequencies could be caused by lower conductivity of electrolyte or construction of reference electrode which is mentioned by some authors [8,9].

In the case of coatings with a preservative layer, this has a greater influence on the protective function than the oxide layer on the surface itself and the resulting equivalent circuit model is extended by elements representing the porosity of the preservative layer ($R_{por}$), the capacity of the coating ($CPE_c$) (Fig. 17). In the Bode diagram in Fig. 16, we can observe the appearance of two overlapping peaks in the phase shift versus frequency plot, which indicates the porosity of the preservative layer [10, 11].

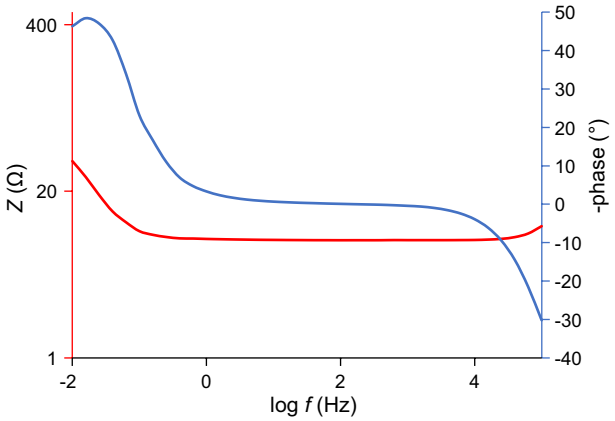


Fig. 14. Bode diagram for acid blackening sample

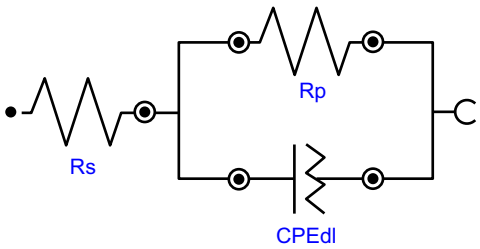


Fig. 15. Equivalent circuit for blackening samples without final preservation

Tab. 3 Values of equivalent circuit elements for samples without preservation

| Sample | $R_p$ (Ω cm$^{-2}$) | $Y_{dl}$ (mS s$^N$) | $N_{dl}$ |
|---|---|---|---|
| Blank | 22.3 | 70 | 0.79 |
| Acid blackening | 6.9 | 381 | 0.94 |
| Alkaline blackening | 32.6 | 46 | 0.7 |

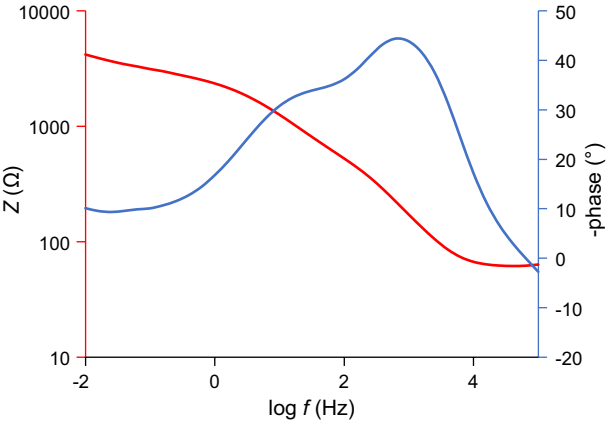


Fig. 16. Bode diagram for alkaline blackened sample preserved by Emulsin 5382

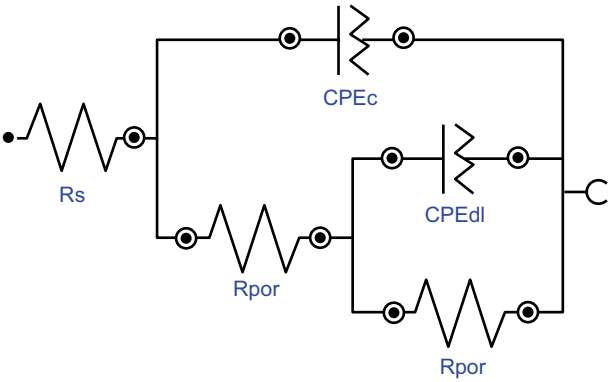


Fig. 17. Equivalent circuit for blackening samples with final preservation

## DISCUSSION

Comparing the samples blackened by acid and alkaline methods, it was found that the layer formed in the alkaline solution is thicker and more compact. Apart from the process used, the fact that it was carried out in an industrial plant under standardised conditions probably had a certain influence. Under laboratory conditions, a compact layer was formed on the sample plates, while on the tubes tested in the condensation chamber the coating was not so homogenous and some defects was noticeable. This is also evident from the results of this particular test, where the surface corrosion activity of the acid blackened samples was higher than that of the alkaline blackened samples.

Tab. 4 Values of equivalent circuit elements for samples with preservation

| Sample | $R_p$ (Ω cm$^{-2}$) | $Y_{dl}$ (mS s$^N$) | $N_{dl}$ | $Y_c$ (mS s$^N$) | $N_c$ |
|---|---|---|---|---|---|
| Blank | 723.5 | 0.106 | 0.62 | $1.72 \times 10^{-3}$ | 1 |
| Acid blackening | 258.8 | 0.194 | 0.74 | $0.194 \times 10^{-3}$ | 0.74 |
| Alkaline blackening | 325.4 | 0.078 | 0.526 | $1.33 \times 10^{-3}$ | 0.96 |

A more in-depth study of the protective function of the surface oxide layer was carried out using electroanalytical methods, namely polarization resistance and electrochemical impedance spectroscopy. Here the protective effect of the blackening layer itself as well as the effect of the preservative agent most commonly used on weapons, namely Konkor 101 oil, were compared. The samples preserved industrially in an alkaline bath were left with Emulsin 5382, the exact composition of which could not be determined, but the effect should be similar to Konkor 101. When the equilibrium potential was measured over time, it was found that in the case of alkaline blackening, the oxide layer provides some protection against attack of the metal base due to chloride penetration from the electrolyte (drinking water), especially when combined with the preservation with Emulsin 5382, where a gradual increase to positive potential values was observed (Figures 12 and 13). The polarization resistance of the non-preserved samples was in the order of hundreds of ohms, after preservation it was approximately 10 times higher. However, the values for the samples preserved with Konkor 101 varied considerably, which was probably related to the non-uniformity of the preservative oil layer on the surface. Using the electrochemical impedance technique, equivalent circuits were set up for both non-preserved and preserved samples. If the surface contained only a black oxide layer, the equivalent circuit was then approximated to a Randels circuit, which contains a polarization resistance whose values, in the order of hundreds of ohms, agreed with previous measurements using linear polarization. In the case of blackened surfaces with a layer of preservative, the polarization resistance again increased 10 times, and in the Bode diagram the preservation was indicated by the formation of a broader or two overlapped peaks, which can be expressed by the capacitance (constant phase element) and the pore resistance in the layer.

## CONCLUSION

Chemical blackening of steel, often used as a surface treatment on firearms, fulfils both an aesthetic protective function, increases the protection of steel against abrasion and should also increase the corrosion protection of the surface. However, the blackening process itself requires good surface pre-treatment and precise adherence to the procedure. As the oxide layers are very thin and may contain various cracks, they will not alone provide much corrosion protection to the surface and should always be combined with the preservation of an extra agent (e.g. Konkor 101 oil). It must be emphasised again that blackening procedures applied to historic weapons must be carefully considered on the basis of a comprehensive survey of the artefacts in question. They must be compatible with the original historical techniques of craftsmanship or manufacture, the materials used, the state of deterioration, etc. Although the findings of this study showed a higher corrosion resistance in case of the alkaline hot blackening treatment in the commercial Brünn Record bath, this procedure cannot be recommended for historic percussion or flint guns. This modern product can only be used on modern weapons (i.e. weapons from World War II and younger). In any case, our results also confirm the significant effect of the application of the preservative on the chemically treated surface by blackening, which needs to be considered during the entire surface treatment process.

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