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Investigation of Different Types of Black Oxide-Forming Materials on Appearance Quality

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ABSTRACT

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In black oxide generation methods, selecting an alkaline compound capable of generating magnetite under suitable temperature conditions not only improves the protective quality of the resulting oxide but also prevents the loss of energy and raw materials. In this paper, the effects of various commonly used compounds, along with some additional additives, on specific methods were investigated. The optimal conditions for black oxide formation were identified as the appropriate composition ratio, a fixed temperature of 150°C, and a duration of 5 to 8 minutes, depending on the type of parts. In this study, ferrous sulfate was used to recover and improve the properties of the depleted solution, thereby reducing the consumption of solution and alkaline materials. The composition and temperature conditions identified in this study can be applied to carbon steel parts with different levels of carbon contents, including low, medium, and high carbon steel, which are commonly used in industry.



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1. INTRODUCTION

The method of creating surface black oxide can be traced back to the German two-bath process, which is believed to have originated in 1900. Its single-bath variant, representing the modern form, has been in use since 1930 (Farrell, 2002).

There is compatibility between basic nitrate compounds and other substitutes like chromium nitrate and aluminum nitrate, which have their respective effects (Phadnis, 2013). The conversion processes in this coating

method lead to the formation of a specific iron oxide known as ferrous black oxide or magnetite (Mahmoudi et al., 2015).

This oxide possesses unique properties that are highly valuable in various industries, including medicine (Phadnis, 2013, Marks, 1994, Chertok et al., 2008, Yavuz et al., 2006, Soeya et al., 2002). One of the most common applications involves reinforcing steel or rebar. If not properly protected, oxidation of the steel within concrete increases the volume of the steel, leading to significant

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structural damage such as severe cracks. This damage reduces the adhesion between the brittle steel and the concrete, compromising structural integrity ([Roghianian and Banthia, 2019](#), [Berrocal et al., 2013](#)).

In addition to corrosion protection, it is important that the coating does not interfere with the steel's intended applications. For example, steel used for construction should not be too polished to maintain its adherence to concrete. The microscopic holes in steel treated with this method maintain proper adhesion. Unlike plating, this method is cost-effective for high-volume production of large steel parts, such as reinforcing steel ([Phadnis, 2013](#), [Barbier and Rusanov, 2001](#)). Upon using a variety of compounds, the coverage can increase from approximately 0.5 microns in conventional methods to about 20 microns in autoclave methods ([Arab and Rahimi, 2009](#)). Completed methods also enable this coating process to be applied to all types of steel, cast iron, and even stainless steel parts ([Barbier and Rusanov, 2001](#), [Arab and Rahimi, 2009](#)).

One of the key advantages of this coating is that it prevents steel dissolution in molten metals. As a result, this ceramic coating is especially useful in processes like high-pressure casting, where the melting of pre-melted metals is involved, and where iron impurities are added to reduce the affinity of the melt for iron ([Barbier and Rusanov, 2001](#), [Luo, 2013](#)). In cases where machining exposes parts of the surface, the black oxide coating reduces the corrosion rate in these uncovered areas. However, this reduction is limited to a certain extent ([Lu et al., 1995](#)). Additionally, if a steel part with black oxide is bent, the ceramic coating remains adhered to the surface at the bending point, continuing to provide protection ([Burleigh, et al. 2007](#)). Reinforcing steel bars are an example of steel that undergoes significant geometric deformation from the time of manufacturing until their applications in concrete. In such cases, using protective coatings like epoxies is impractical, as these coatings often fail to provide adequate chemical and physical protection, leading to more severe corrosion and damage ([Berrocal et al., 2013](#)). The method of generating black oxide is highly adaptable, allowing for modifications such as the application of electricity to reduce chemical consumption and lower the temperature ([Burleigh et al., 2007](#)). Addition of specific compounds like aluminum or chromium nitrate can significantly enhance the protection of the sample ([Phadnis, 2013](#)).

Another critical factor affecting the formation of a suitable oxide layer is the pH of the alkaline solution ([Li et al., 1998](#)). Higher pH levels typically result in better outcomes ([Melendres et al., 1992](#)). In various magnetite production methods, thermal and electrical approaches use common alkaline and nitrate compounds such as sodium hydroxide, sodium nitrate, sodium nitrite, and potassium hydroxide ([Phadnis, 2013](#), [Arab and Rahimi, 2009](#)), and sometimes other materials like iron chloride ([Laurent et al., 2008](#), [Herranz, et al., 2014](#), [Kim, et al.,](#)

[2001](#)), aluminum nitrate ([Phadnis, 2013](#)), ferrous sulfate, and hydrazine or ammonia-based compounds ([Zhu et al., 2008](#), [Jero et al., 2024](#)).

While black oxide coatings have historically been used in military applications for their anti-glare and corrosion-resistant properties, their use today extends to a wide range of industries. In the automotive sector, black oxide is applied to components such as gears, pistons, and fasteners for added corrosion protection and improved lubricity ([Farrell, 2002](#); [Barbier & Rusanov, 2001](#)). Tooling and machinery manufacturers use black oxide to reduce light reflection and improve wear resistance on cutting tools and dies ([Mahmoudi et al., 2015](#)). In the woodworking and furniture industries, black oxide-coated screws are preferred in products like MDF and furniture joinery for both aesthetic and functional reasons ([Phadnis, 2013](#)). The coating is also useful in construction, especially for reinforcing bars and structural fasteners, where both adhesion to concrete and protection during storage are essential ([Roghianian & Banthia, 2019](#); [Berrocal et al., 2013](#)). Its cost-effectiveness, ease of application, and adaptability make black oxide coating a practical solution across diverse commercial and industrial applications.

The aim of this study is to investigate the effectiveness of various commonly used and supplementary additives in alkaline black oxide solutions, with a focus on improving the visual appearance and protective performance of black oxide coatings on different grades of carbon steel. Unlike previous studies that often focused solely on corrosion resistance or specific solution compositions, this work introduces a comparative analysis of multiple chemical additives—including ferrous sulfate, aluminum nitrate, iron chloride, and hydrazine-based compounds—under controlled temperature and time conditions. The novelty of this research lies in its emphasis on appearance quality as a key performance metric, along with the restoration of depleted solutions using ferrous sulfate, which offers both economic and environmental benefits. This approach enables the optimization of black oxide coating processes for industrial applications where both functional and aesthetic qualities are essential.

2. Materials and Methods

2.1. Sample Cleaning

The process can be divided into three stages: sample cleaning, use of a suitable blackening solution at a controlled temperature, and sample quality evaluation. In industrial settings, a fourth stage—final finishing—is typically applied, often using organic compounds such as oil. For this project, two types of steel, i.e., high-carbon and low-carbon, commonly used in the manufacturing of screws and fasteners, were selected. The cleaning step involves acid washing, followed by thorough rinsing with water to ensure that no acid remains on the surface. During the peeling phase, sulfuric acid was used to create

a more uneven corrosion surface. The cleaning process follows these steps: the sample is first placed in a low-temperature alkaline solution, then it is immersed in a 10% hydrochloric acid solution, and finally it is put a 10% sulfuric acid solution, with a washing step between each stage. To prevent severe corrosion, an inhibitor was used, the type of which was determined based on the duration the sample was in the acid. Once removed from the acid, the sample was rinsed thoroughly to ensure that all acid residues were completely washed off.

2.2. Blackening Solution and Temperature

Based on the estimated conditions for magnetite formation, six different methods were designed to evaluate the effects of various parameters. Distilled water was used as the solvent in all compositions; hence, it will not be repeated in the description of the solutions.

- 1. Sodium Hydroxide (200g NaOH) - Sodium Nitrite (50g NaNO₂) - Sodium Nitrate (50g NaNO₃):** Samples were tested at two temperatures of 130°C and 150°C in a solution where the boiling point was slightly above 150°C. The temperature was held constant at 130°C or 150°C using various methods, such as increasing the solvent amount to maintain the boiling point. Samples were then immersed in the solution for 5 to 8 minutes, depending on their types, to achieve the darkest black oxide color. At 150°C, some samples were immersed for up to 16 minutes to examine the effect of prolonged immersion. Of note, in some cases, the blackness of the oxide diminished with extended exposure.
- 2. Potassium Hydroxide - Sodium Nitrite - Sodium Nitrate:** The effect of these compounds on the alkaline solution was tested under the same conditions, with boiling point variations due to different solution compositions.
- 3. Aluminum Nitrate in Alkaline Sodium Hydroxide Base:** The solution was tested to observe any differences in oxide formation.
- 4. Iron (III) Chloride Hexahydrate (<5g) in Alkaline Solution:** This was investigated for its effect on black oxide formation.
- 5. Ferrous Sulfate Addition:** The role of adding ferrous sulfate to the alkaline solution was studied.
- 6. Hydrazine-Dependent Compounds in Alkaline Solution:** The effect of hydrazine compounds on the black oxide process was evaluated.

2.3. Sample Quality Evaluation

In this research, the visual appearance of industrial samples was a priority. Detailed evaluation and explanation were omitted for samples that did not achieve

a dark black color. However, some samples, such as those produced with aluminum nitrate, showed higher resistance to acid corrosion. However, since they did not exhibit the desired appearance, they were not further investigated. Industrial samples, such as those made from Ck45 and St37 steel (Table 1), showed varying results based on the duration of immersion in the solution. Prolonged immersion could sometimes decrease the coating quality in terms of appearance and corrosion resistance. Generally, the best appearance quality was achieved by immersing samples in the solution for 5 to 8 minutes. Finally, two St37 steel sheets that demonstrated the best appearance quality in a sodium hydroxide-based solution at 150°C were subjected to polarization tests using a 3.5% NaCl brine solution.

3. Results and Discussion

3.1. Effect of Different Temperatures and Durations in Alkaline Compounds Containing Sodium Hydroxide

Samples treated at 150°C exhibited a noticeably better surface appearance and a darker black color than those treated at 130°C. This darker color typically indicates a complete and more uniform layer of magnetite (Fe₃O₄), which is known for its corrosion-resistant properties (Phadnis, 2013; Zhu et al., 2008). In contrast, dull or reddish hues can signal the presence of less protective oxides like hematite (Fe₂O₃). To better understand the performance of the coatings, polarization tests were conducted in a 3.5% NaCl solution. As shown in Figure 1, the uncoated steel sample (Base) had a corrosion potential of around -0.72 V.

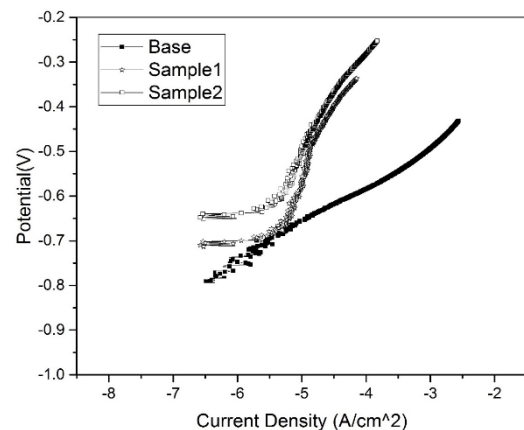


Figure 1. Anodic branch polarization curve in a 3.5% NaCl solution (Base), compared with samples held in a sodium hydroxide-based solution at 150°C for 8 minutes (Sample 1) and 16 minutes (Sample 2). The black oxide coating shifts the corrosion potential to more positive values and decreases the current densities in the anodic branch.

Table 1. Nominal composition of St37 and Ck45 steels based on EN 10025 and EN 10083-1 standards, respectively

Steel Grade	C%	Si%	Mn%	P%	S%	Cr%	Mo%	Ni%
St37	≤0.17	-	≤1.40	≤0.045	≤0.045	-	-	-
Ck45	0.42-0.50	≤0.4	0.50-0.80	≤0.035	≤0.035	≤0.40	≤0.1	≤0.40

In contrast, the coated samples shifted to more positive values of approximately -0.63 V (8 minutes) and -0.61 V (16 minutes) for Samples 1 and 2, respectively. This shift indicates that the coated samples are less prone to corrosion. In addition, both Samples 1 and 2 showed were characterized by lower current densities in the anodic region, suggesting that the black oxide coating slowed down the corrosion reactions.

These results confirm that treatment at 150°C , especially for 8 to 16 minutes, provides both a better-looking and more protective surface.

3.2. Results for Potassium Hydroxide Alkaline Compounds

The black oxide formed on low-carbon parts using potassium hydroxide was insufficient, hence unacceptable. On high-carbon steel screws, the results were somewhat more acceptable, but overall, potassium hydroxide proved ineffective and not suitable for this process.

3.3. Aluminum Nitrate Combination Results

Addition of aluminum nitrate reduced the pH by about 1 unit, compared to the pure alkaline solution. Upon re-peeling of the coated samples, the aluminum nitrate-based coating exhibited slightly higher resistance to peeling than other samples. However, due to the lack of a dark black appearance, further investigation of this coating was omitted.

3.4. Iron Chloride Combination Results

In the case of iron chloride, the sample exhibited little difference from the freshly peeled steel, indicating that no effective protection occurred, and corrosion may have even increased due to the presence of chloride ions. With the addition of ferric chloride, color of the solution changed from milky to black, and the magnetite solution lost its magnetizing ability. Moreover, the pH of the solution decreased.

3.5. Ferrous Sulfate Addition Results

Adding ferrous sulfate to blackening solutions that had lost effectiveness, especially those containing iron chloride, helped restore their ability to produce a proper black oxide coating. This is likely due to ferrous sulfate reintroducing Fe^{2+} ions, which are essential for forming magnetite. Without enough Fe^{2+} , the solution may instead form other iron oxides that do not offer the same level of protection or color quality.

The rejuvenated solution produced a darker and more uniform coating, as seen in Figure 3(c). This not only improved appearance but also offered a practical advantage by extending the life of the blackening solution. Instead of discarding and replacing spent solutions, ferrous sulfate can help refresh them, reducing both cost and environmental impact. From a processing standpoint, this makes the solution more stable and efficient over time.

3.6. Results of Adding Hydrazine-Dependent Compounds Like Ammonia

Addition of hydrazine-dependent compounds, such as ammonia, decreased the pH of the solution due to the amphoteric nature of ammonia, acting as an acid in the alkaline environment. As expected, the reduced pH weakened the reaction in the magnetite solution, preventing the formation of black oxide on the part surface. Amphoteric compounds, such as ammonia, reduce the effectiveness of the black oxide solution and should be replaced with alkaline compounds to maintain the solution strength.

3.7. Characteristics of the Final Piece

Due to the microscopic cavities in the black oxide coating, the surface remains rough, which is advantageous for applications such as reinforcing rebars where the surface should not be polished. The black oxide coating formed in this study naturally contains a degree of porosity, which is common for this type of surface treatment. These microscopic pores develop during the growth of magnetite (Fe_3O_4) crystals, especially at elevated temperatures, whose structure depends on some factors namely solution composition and immersion time (Phadnis, 2013; Zhu et al., 2008). While porosity might seem like a drawback in some protective coatings, it can actually be helpful in applications where surface roughness improves performance—for example, in reinforcing bars where better adhesion to concrete is needed, or in fasteners where some grip is advantageous (Mahmoudi et al., 2015). However, in case the porosity is too high, corrosion resistance is reduced by allowing moisture or chemicals to reach the steel underneath. In our tests, coatings created under optimal conditions (150°C , 5–8 minutes) had a fine, even texture that balanced appearance with moderate protection. In real-world applications, manufacturers often apply oil or other sealants to fill these pores and boost the coating's resistance to corrosion (Farrell, 2002). In addition to protection, the aesthetic appearance of steel parts is also significant in many fields of industry. For instance, in the woodworking industry, black oxide coatings are commonly utilized in manufacturing the screws used in MDF boards for both protective and aesthetic reasons. Figure 2 presents a comparison of an uncoated steel screw and one with a black oxide coating. Figure 3 demonstrates other examples of parts with a visually appealing black oxide finish created in this study. Given the growing demands for steel protection in construction, the black oxide method can be considered an economical and efficient option. This method can also be applied in scenarios where lower-quality coatings such as those used for storage or in cases where plating is unnecessary, are required. The black oxide process is easy to perform with a variety of heating methods and energy sources. Moreover, the long lifespan of the black oxide baths

makes this method cost-effective, with older solutions sometimes producing even better results.

3.8. Context with Recent Developments in Black Oxide Coating

Although this study primarily focuses on the conventional hot alkaline blackening method, it is worth mentioning that research in this field has continued to evolve in recent years. For instance, a review by [Manoj et al. \(2021\)](#) highlights advances in black oxide coatings across various metals—including aluminum, copper, and magnesium—and discusses how these coatings remain

relevant in both traditional and emerging applications. Their work reinforces the idea that black oxide coatings are still widely used and technically valuable across multiple industries. In another recent study, [Eckl et al. \(2019\)](#) proposed a nitrite-free, electrochemical approach to blackening steel. While this method differs from the thermal technique used in our work, it reflects a growing interest in safer and more environmentally friendly alternatives. Including these references helps position this study within a broader landscape of surface treatment technologies.

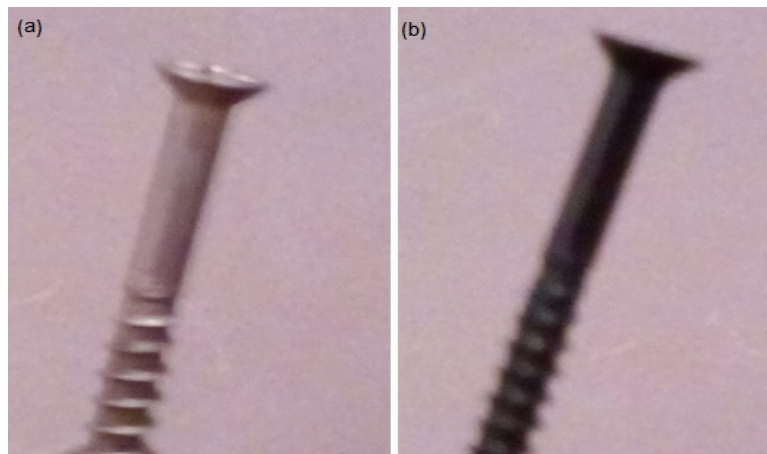


Figure 2. Visual comparison between uncoated and black oxide-coated steel samples: (a) The uncoated steel sample after peeling; (b) A steel sample with a black oxide coating, showing the improved surface appearance.

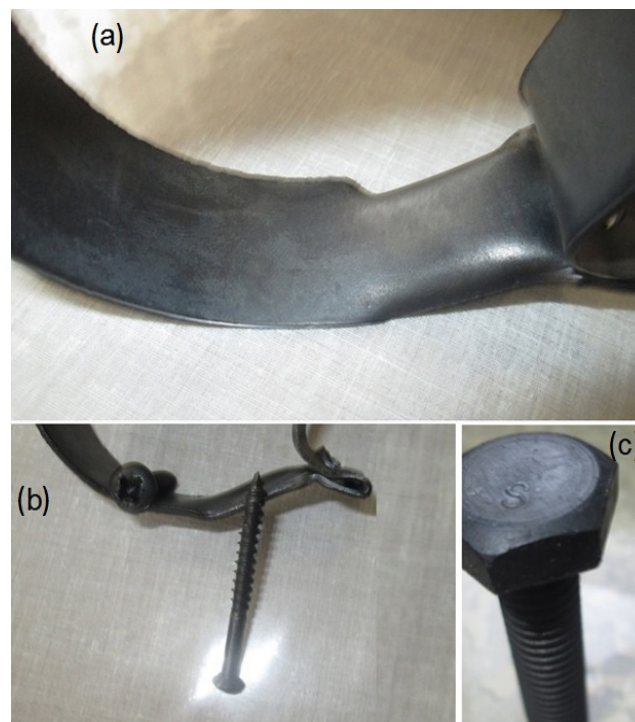


Figure 3. Samples with successfully formed black oxide coatings: (a) The inner surface of a low-carbon steel clamp; (b) Comparison of black oxide samples under different lighting conditions, showing uniformity in blackness; (c) A medium-carbon steel screw treated with a solution rejuvenated by adding ferrous sulfate.

4. Conclusion

This study showed that how you set up the blackening process—including the solution mix, temperature, and immersion time—has a great impact on the final result. Using a sodium hydroxide-based solution at 150°C consistently produced the best-looking black oxide layers with good protective qualities. Treatments lasting 5 to 8 minutes yielded the best results in terms of both surface appearance and corrosion resistance. One of the standout findings was the role of ferrous sulfate. It helped bring spent solutions back to life, allowing them to form black oxide again. This makes the process more cost-effective and environmentally friendly by reducing chemical waste. Nevertheless, additives like potassium hydroxide and ammonia-based compounds did not perform as well and often disrupted the coating process. The electrochemical tests confirmed that the black oxide really functions as a protective layer. The uncoated steel had a corrosion potential of approximately -0.72 V, while the coated samples shifted to -0.63 V and -0.61 V, indicating better resistance to corrosion. The lower current densities in the coated samples also demonstrated that the oxide layer helped slow down corrosion. Overall, this process is not only practical and affordable but also provides clear protective benefits for industrial applications.

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