Compound-Layer Blackening of Steel at Room Temperatures

By Z. Zhongcheng*

Compound layer blackening of steel at room temperature was studied, including a two-step parkerizing and blackening sequence. The steel was first parkerized and then blackened in a solution containing copper (II) and selenous acid, with both solutions operated at room temperature. A compound layer formed on the surface of the steel sample which exhibited a black color, with good adhesion and corrosion resistance.

Blackening technology for iron and steel is widely used in metal finishing industry. There are two general types of blackening for iron and steel: hot blackening and room temperature blackening (or cold blackening).[1] Hot blackening can be done from generic mixtures of caustic soda, sodium nitrite / nitrate, wetting agents and stabilizers or from proprietary mixtures. The result of the process is a dark black iron oxide finish with both good durability and corrosion resistance.

The hot blackening process however, uses toxic chemicals and operates at about 140°C (284°F) for 45 min. Working at temperatures well above the boiling point of water leads to major problems, particularly when replacement water is introduced. Hot blackening is a polluting, energy consuming and time consuming process.

In order to reduce the hazards of hot blackening, and to save energy, proprietary cold blackening solutions have been developed.[2] They are operated at room temperature, and are based on different chemistries, so they are substantially less hazardous. Further, room temperature blackening processes are simple and safe to operate. They are becoming more and more attractive. On the other hand, room temperature blackening is not a true black oxide process. Rather it involves the application of a copper-selenium compound. This compound is not always an acceptable substitute for black oxide, as it does not look as durable as the one obtained with a hot blackening process. In the past decade, considerable research work has been done to improve the adhesion properties of the black surface layer. Most studies have been focused on the composition of the room temperature blackening solutions.[3] In our work, a compound layer was formed on the iron and steel substrate surfaces. It consisted of a phosphate coating and a blackening coating, formed separately in a two-step operation.

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Experimental

Solution formulations

The solutions used in the surface treatment process cycle were made up as follows:

Degreasing solution:
Commercially available metal detergent powder in a 20 wt% aqueous solution.

Derusting solution:
20 wt% sulfuric acid solution.

Room temperature parkerizing solution:
7.88 mL/L phosphoric acid, 23.3 g/L sodium dihydrogen phosphate, 0.53 g/L trimeric sodium phosphate, 0.5 g/L citric acid, 0.67 g/L ammonium molybdate and 0.002 g/L thiourea. The pH of the solution was about 2.5.

Room temperature blackening solution:
3 g/L SeO_2, 1 g/L Na_3PO_4, 1.5 g/L $NiCl_2 \cdot 6H_2O$, 2 g/L $CuSO_4 \cdot 5H_2O$, 1 mL/L acetic acid (36%), 2 mL/L H_3PO_4 and 12 g/L sodium citrate.

Experimental steps

The steel sample, with dimensions of 50 × 30 × 1 mm (~2.0 × 1.2 × 0.04 in.), was immersed in the degreasing solution for 20 min at about 95°C (203°F) to remove oils and greases. If the sample surface was not clean enough, the cleaning time was extended. Ordinary tap water was used to wash and rinse the degreased sample. This was followed by the derusting treatment. The sample was then parkerized in the room temperature parkerizing solution for 30 min at 30°C (86°F) to form the phosphate coating, the first coating layer. After rinsing again, the sample was blackened in the room temperature blackening solution for about 8 min to produce a black surface coating. Finally, the sample was rinsed, dried and sealed with lubricant oil.

Nuts & Bolts:
What This Paper Means to You

Operating at high solution temperatures, steel blackening processes are not the most pleasant things to be around. This paper discusses a room temperature alternative, a two-step parkerizing and blackening sequence. The result is a black copper-selenide, with good adhesion and corrosion resistance.

Results & discussion

The finished sample, without lubricant oil sealing, has a black compound layer on the surface. With this surface coating, adhesion was clearly improved. The table (ar right) compares the two processes. Adhesion was determined by rubbing the surface with filter paper 200 times and observing it to see if the layer was destroyed. Corrosion resistance was determined by a spot test, in which a drop of 0.1 mol/L copper sulfate solution was applied to the sample surface and the time to a notable coating color change was recorded. It can be seen that the adhesion of the single-layer cold blackening coating was poorer than that of the compound layer coating, but the corrosion resistance remained unchanged.

It is well known that parkerized coatings have strong adhesion. Thus, this type of coating is durable. Unfortunately, the color of a parkerized coating is grey, which is not suitable for the decorative finishing of metals. The cold blackening process produces a black copper selenium compound on the surface with good color but the adhesion is poor. The combination of the two processes produces a compound layer, which not only has improved adhesion but also has good color.

In the first step of coating formation, *i.e.*, the parkerizing process, the main chemical reaction is:

$$4Fe + 4NaH_2PO_4 + 3O_2 \rightarrow 2FePO_4 + Fe_2O_3 + 2NaH_2PO_4 + 3H_2O.$$

The products in the above reaction form the parkerized coating. It is important to note that the formation of this coating involves a chemical reaction with sample and not a precipitate on it. Therefore the coating thus formed is durable. In the table, the corrosion resistance of the general cold blackened layer and the compound layer are identical. This is because the top layers obtained by the two methods are nearly identical.

These results show that it is possible to form a black copper selenide (CuSe) coating on a phosphate coating. This is important to the formation of the compound layer coating. Generally speaking, the cold blackening process is suitable for many base materials. We have found good results on steel, cast iron, stainless steel and brass. Black coatings were formed on all these substrates. There are primarily two mechanisms proposed for the cold blackening of iron and steel with the copper-selenium system. One is that an oxidation-reduction reaction takes place between the iron and selenous acid, producing Fe^{+2} and Se^{-2}:[4]

$$3Fe + SeO_3^{-2} + 6H^+ \rightarrow 3Fe^{+2} + Se^{-2} + 3H_2O$$

Next, Cu^{+2} adjacent to the sample surface reacts with Se^{-2} to form a black precipitate of CuSe:

$$Cu^{+2} + Se^{-2} \rightarrow CuSe\downarrow\text{(black)}.$$

The second mechanism involves two steps.[5] In the first, Cu^{+2} reacts with Fe for replacement, and then the copper formed on the surface is oxidized by selenous acid, forming a black copper selenide. Our experimental results do not support the latter, because the replacement reaction does not occur on the phosphatized coating. Therefore the first mechanism is more reliable in describing the blackening of iron and steel. The mechanism of blackening on the phosphatized surface is therefore not clear.

Table
Adhesion & Corrosion Resistance of the Two Processes

Coating	Adhesion	Corrosion Resistance (min)
Cold blackening (single layer)	Poor	3
Cold Parkerizing (single layer)	Good	6
Compound layer	Good	3

Conclusions

It is possible to blacken a phosphatized iron or steel surface in a cold blackening solution based on the copper-selenium system. By this process, a black compound layer with improved adhesion is formed. Two main steps, parkerizing and blackening, are all done at room temperature. This is an energy saving process. Our results also show that it is not first necessary to deposit copper on the surface to promote the formation of the black coating.

References

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