Black Oxide Treatment of Fasteners

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Black oxide coatings have been used for many years to protect fasteners (Fig. 1) and many other parts manufactured from a variety of metal types (Fig. 2). These coatings are commonly used on products for the automotive, appliance, machine tool industries as well as where formed products are employed (Fig. 3), because this type of coating is both adherent and attractive. Advantages of black oxide coatings for manufacturers include:

- Corrosion Resistance
- Anti-Galling
- Pre-treatment for Paint
- Dimensional Stability
- Decorative Finish
- Reduced Conductivity
- Improved Lubricity
- Reduced Glare

Black oxide coatings are formed by a chemical reaction between the metal surface and oxygen. The surface layer formed consists of magnetite (Fe_3O_4), a form of iron oxide, which is black in color and tightly adherent to the metal surface. By contrast, rust is a red oxide of iron called hematite (Fe_2O_3), which easily flakes off a metal surface and as such is highly undesirable. While some black oxide type coatings can be applied at room temperature, most are applied at elevated temperature in the presence of an oxidizing agent in the form of a gas or an aqueous solution including molten salt baths.

A unique aspect of black oxide coatings is due to the fact that it is a chemical conversion process, parts such as springs and other shapes can be coated and subsequently formed without concern of chipping, cracking, or flaking of the surface layer (Fig. 2). Black oxide coatings are quite often used where there is a tight tolerance requiring a minimal change in surface dimensions, typically around 0.013 mm (0.0005”). Steels that benefit from this type of coatings include low and medium carbon steels, alloy steels, stainless steels and tool steels. Certain nonferrous materials such as brass and aluminum can also be treated.

The decorative black color serves many purposes in addition to providing a strong adhesion between the coating and the substrate. It has good lubrication characteristics and will not peel away from the surface under moderate loading. It improves anti-galling properties, decreases the coefficient of (sliding) friction and improves abrasion resistance. In addition, since the process does not involve hydrogen as part of the chemical process, there is no possibility of hydrogen embrittlement.

Additional advantages to black oxide coatings are an anti-glare surface and that they can be exposed to a temperature up to 900˚ F (482˚ C) before their color begins to change. Black oxide coated parts can be welded and no harmful fumes are produced.

One of the misnomers about black oxide coatings, however, is that they significantly improve corrosion resistance. While slight improvements have been reported, parts in corrosive environments will not generally be protected. To improve their corrosion resistance, rust preventative oil (or wax) can be used after the black oxide coating has been applied.

The first steps in the process of applying black oxide coatings are cleaning, rinsing, and thoroughly drying of the parts surface, ensuring the best possible adherence. If rust or scale is a present, additional steps such as acid pickling or alkaline de-scaling should be done and then the surface may need to be neutralized in preparation for oxidizing. Prior to the black oxide process, removal of all other types of coatings is necessary. The resulting oxide layer will have inconsistent thickness, and will vary in color and/or flake off if attempted over dirty or parts plated in coatings such as zinc, nickel, chromium, cadmium plating or phosphates.

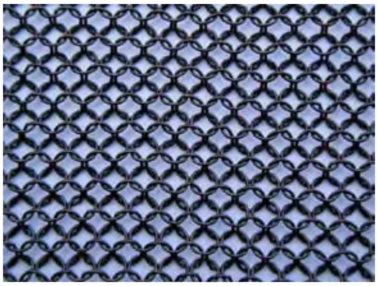
When considering use of a black oxide coating, the design engineer must evaluate the material to be coated, the application (end-use) environment and length of time the protection will be required, post oxidation finishing operations and storage conditions prior to use (humidity, temperature, etc.)

A variety of black oxide coating chemicals can be used. One such family of product is shown in Tables 1 and 2.

Figure 1
Black Oxide Coating on Fasteners

(Photograph Courtesy of Cleveland Black Oxide)

Figure 2
Black Oxide Coating Ring Mesh



(Photograph Courtesy of Cleveland Black Oxide)

Figure 3
Black Oxide Coating Products Made From Wire

(Photograph Courtesy of Cleveland Black Oxide)

Table No. 1 Black Oxide Coatings for Ferrous Metals

Form	For Use On	Product Name	Description
Powder	Steel	Pentrate® Ultra	Black oxide used for the deepest black finish on steel. Produces a uniform black oxide finish with no rub off or dimensional change. Low drag out reduces operating costs. Contains rectifiers to remove non-ferrous contamination. This premium black oxide product has incorporated inhibitors for the control of colloidal iron build up in the operating bath. Pentrate Ultra meets or exceeds all government specifications, including MIL-DTL-13924D for Class 1 black oxide coatings.
Liquid	Steel	Pentrate® Ultra Liquid	Liquid version of Pentrate Ultra.
Powder	Stainless Steel, Cast and Malleable Iron	PX®-5	A black oxide with a unique balance of alkali and oxidizers that operates at 121 - 127°C (250° -260°F). Meets the requirements of MIL-DTL-13924D for Class 4 black oxide coatings.
Liquid	Stainless Steel, Cast and Malleable Iron	PX®-5-L	Liquid version of PX-5.
Liquid	Steel, Cast or Malleable Iron (Not for use on Stainless Steel)	Kwik-Blak® LT	A room temperature black oxide process that saves energy and time. Produces a deep black finish when used at 10-15% by volume. Bath can be filtered for extended service life.
Liquid	Steel	Pentrate® Touch Up	Used to repair scratches or imperfections on previously blackened steel parts.

Table 2 [1] Black Oxide Coatings for Non-Ferrous Metals

Form	For Use On	Trade Name	Description
Liquid	Copper and Copper Bearing Alloys	Durablack Liquid	A highly concentrated alkaline product used to blacken copper. Operates at 104°C (220°F). Alloys of copper can be blackened when Durablack Pre-Dip L is used.
Liquid	Copper Bearing Alloys	Durablack Pre-Dip L	Conditioning step needed prior to blackening copper bearing alloys in Durablack Liquid. Completely compatible with Durablack Liquid – no rinsing is required between stages.
Powder	Zinc Plate and Zinc Die Castings	Zinol® 1436	A lustrous black conversion coating providing an attractive appearance and excellent corrosion resistance when used in conjunction with a protective seal.
Powder	Silver Solder	Pentrate® EE-2	Used to blend soldered joints with the black oxidized steel surfaces. Operates at 82° – 88°C (180°-190°F)

The final step in the black oxide process is the application of a supplementary coating also referred to as an after-finish. This step will dictate the final appearance as well as improve the functionality of the part. To obtain the best corrosion protection the after-finish is always applied after multiple rinse steps. The most frequently used after-finish is black oxide and oil. In addition to oil, wax or lacquer can also be used, particularly in applications where the part is to be used indoors and where corrosion protection is desired. Black oxide coatings on steel fasteners, for example will not protect them in severe outdoor applications or corrosive environments.

The part geometry and end use applications will usually determine the after-finish that is used. Factors to be considered are the final application of the part, the protection needed and for how long, the environmental conditions (humidity, vapor, temperature) and the desired final finish and appearance. An oil after-finish will generally be glossy while a wax after-finish will be more of a matte finish.

Various testing procedures are used to validate the adherence of the black oxide coatings. The most common is a visual test, which simply involves looking at the component either with the naked eye or under a low power magnification (5 – 50X). The visual test examines whether or not the metal is a uniform shade of black and if all surfaces are covered. In addition the test looks for evidence of pitting, intergranular attack, or etching. It should be noted that although parts will be black in color, pre-existing scratches, tool marks, and other surface defects will be visible after finishing because black oxide does not smooth out or fill in these flaws. The “smut test” is another test performed prior to the application of the after-finish to determine whether or not a black or dark colored powdery residue is present when the part is rubbed by hand. A humidity test per ASTM D2247 (Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity) is another test that can be used when the components in question will be used outdoors.

Black oxide coatings are commonly divided into four (4) distinct classes:

- **Class 1:** Alkaline oxidizing for wrought iron, cast and malleable irons, common carbon, and low alloy steels.
- **Class 2:** Alkaline oxidizing for use on certain corrosion resistant steel alloys tempered at less than 482°C (900°F)
- **Class 3:** Fused salt oxidizing for corrosion resistant steel alloys which are tempered at 482°C (900°F) or higher.
- **Class 4:** Alkaline oxidizing for other corrosion resistant steel alloys.

Bluing

Bluing is a process that is often used as an alternative to black oxide coating and the two techniques are often misunderstood. Bluing is a passivation process as opposed to a chemical conversion process. The purpose of bluing is to provide partial protection of the steel from rust. The process gets its name from the blue-black appearance of the resulting surface finish. Bluing can be achieved by chemical means, dipping hot parts into certain oils and by exposing the steel, for example, to steam or a wet nitrogen atmosphere (after the equipment has been purged of air to less than 1% oxygen) while being heated and held in the temperature range of 260° - 595°C (500° – 1100°F).

Types of bluing can be classified as:

- "Cold" bluing which uses a selenium dioxide based compound that colors steel black (or more often a very dark gray). Difficulties with this form of passivation include applying the product evenly, minimal protection and the fact that this form of bluing is generally best used for small fast repair jobs and touch-ups.
- "Hot" bluing which is performed in either a heat treatment furnace or an alkali salt solution ("traditional caustic black") and is typically performed at an elevated temperature of 135°C to 154°C (275°F to 310 °F). The process results in good rust resistance, which is improved with the use of a protective coating of oil.
- "Rust Bluing" provides the best rust and corrosion resistance as the process continually converts any metal that is capable of rusting into magnetite (Fe3O4). The process involves dipping parts into an acid solution then boiled in (distilled) water and blown dry. Treating with an oiled coating enhances the protection offered by this type of bluing.
- "Fume Bluing" is a process similar to rust bluing whereby acidic vapors are used to produce a uniform rust on the part surface. Exposure times are upwards of 12 hours and the result is an oxide layer similar to that produced by a black oxide treatment.

Final Thoughts

When and where appropriate, black oxide treatments are a simple method to enhance either cosmetic or physical properties of fasteners and wire forms. As with any process, experience will dictate the best combination of techniques for applying and using black oxide coatings.

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