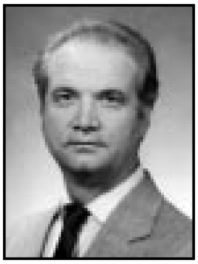
Advice & Counsel



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Training "Colombo"—Part VI

Dear Advice & Counsel,
I need some information on the high-temperature black oxide process in a hurry! Our parts are not meeting salt spray requirements. They don't look right and I really don't know enough about the process. Please help.

Signed,
Red

Dear Red,
We can use the answer to your needs as Part VI of our series on troubleshooting metal finishing processes.

Black is a widely used color in the electrolytic or chemical processes of metal coloring and, with the exception of the phosphate coatings, is the predominant conversion coating for iron and steel. It can be produced by multiple processes with the aqueous alkali-nitrate solution, the most frequently used. Colors range from matte gray to glossy jet-black.

Black oxide coatings have a fair amount of corrosion resistance that is closely tied to the quality of oil applied after the oxide coating is formed. Black oxide coatings aid in lubrication because the coating reduces the coefficient of friction of the metal surface. They are, therefore, well suited for moving parts that cannot tolerate the dimensional buildup of a more corrosion-resistant finish. The black finish minimizes light reflection. This property makes the black finish a preferable finish for optical electrical and photographic equipment and for the military's production of defense systems and weaponry. Black finishes also increase the heat absorption of a metal and reduce its heat reflection properties.

Bare (oil-free) black oxide coatings are not recommended on parts going into long-term storage. If long-term storage is required, a protective preservative fluid is recommended or a desiccated package may be used. A supplementary water displacing preservative coating such as MIL-C 16173, grade 3 can also be applied.

Table 1

	Parts/Weight
Solution 1, 125-135 °C (257-275 °F)	
Caustic Soda	75
Disodium Phosphate	16.5
Sodium Nitrate	5
Solution 2, 130-138 °C (266-280 °F)	
Caustic Soda	60
Sodium Nitrate	40
Solution 3, 145-160 °C (293-320 °F)	
Caustic Soda	60
Disodium Phosphate	10
Trisodium Phosphate	14
Sodium Nitrite	3

Black Oxide Coatings—Overview

While there are numerous methods of producing oxide coatings on ferrous substrates, the most common method employs sodium hydroxide and oxidizers, such as sodium nitrate, plus chlorates, peroxides, permanganates, dichromates and other proprietary oxidizers, to produce a black oxide finish on steel. This process has advantages over the other methods, such as more consistent coating performance, low-temperature application, successful application on a wide variety of alloys and ease of process control.

When ferrous parts are immersed in this solution, the iron on the surface is converted to iron oxide. While common iron oxide (Fe_2O_3) is known as rust and is reddish brown, the black oxide solution produces an alternate form of iron oxide [Fe_3O_4, more correctly written as $Fe(FeO_2)_2$], which has a color similar to charcoal. Any carbon particles and other nonferrous alloying elements are not converted by the solution, and may be left behind to form an adherent powder or off-color coatings if the solution is not capable of removing them. The corrosion resistance of black oxide coatings are low, with low-carbon steel yielding the highest level of protection. If black oxide coatings will be exposed to weathering and salt spray, additional measures need to be taken to improve corrosion resistance. A protective coating of oil, lacquer or wax may be required.

The purpose of applying black oxide coatings that will retain an oil film is to increase the anti-chafing and anti-friction properties of carbon and low-alloy steel parts, particularly those that are involved in sliding or bearing surfaces.

Black oxide coating thicknesses range from 0.00006 to 0.0001 in. Thicker coatings are possible with longer immersion times, but run the risk of producing a loose film and poor corrosion resistance. Dimensional changes are minimal (<0.00001 in.).

While low-temperature black oxidizing processes are commercially available, the high-temperature process remains in general use because of its overall performance advantages.

Coating Mechanism

Black oxide is a conversion coating process. Such coatings are produced through chemical reaction with the metallic surface of the part to be coated. Ferrous substrates react with nitrates in a hot alkaline-water mixture to form a ferri-ferro-oxide [$Fe(FeO_2)_2$]. While the most common oxidation product of iron is ferric oxide (commonly referred to as "rust"), which is reddish brown, ferri-ferro-oxide is near-black in color and is slightly porous, and serves as a fair corrosion resistive barrier when the porosity in the oxide is impregnated with oil. Proprietary chemical formulations contain a variety of additional oxidizers to enhance and quicken the chemical reaction.

To cause the chemical reaction to proceed requires a significant amount of energy. The typical reaction temperature range is 240-305 °F (116-152 °C). Typical reaction time is 15-30 min.

Preparation for Black Oxide Coating

Cleaning and acid pickling to remove surface grease/oil and oxides is an important step in preparing a ferrous surface for black oxide coating. The cleaning normally involves a soak cleaner followed by acid pickling. After cleaning, the metal is immersed in the black oxide process solution.

The Black Oxide Process

The intensity of black oxide color is dependent upon the time of immersion and the solution temperatures. Immersion for 15-30 min in a solution operating between 240-305 °F (116-152 °C) is common with single-solution treatments.

One method of improving both the corrosion and abrasion resistance of the parts is to use the same blackening solution as a two-stage process, operating the first treatment at 211-220 °F (100-115 °C), and the second treatment at 247-256 °F (118-123 °C). Other frequently used methods to improve corrosion and abrasion resistance are the two- or three-stage blackening processes that use solutions of different composition and increased operating temperatures.

In one alternate two-stage process, the parts are immersed in the initial solution that is boiling at temperatures from 280-293 °F for a period of 15 min. After this first immersion, the parts are immediately immersed in a second blackening solution. This solution is also boiling at a temperature of 310-315 °F. The immersion time in the final solution is 15-20 min. An exception is with carburized parts, for which the solution temperature should not exceed 300 °F.

Table 1 shows a typical sequence for a three-stage process (obtained from Ref. #1 and covered by German Patent 704.400):

This process has been reported to produce coatings with twice the corrosion resistance and approximately four times the abrasion resistance of coatings obtained by a single-stage blackening process.

Table 2 is a typical processing sequence for MIL-C-13924C Class 1. Alternate processing sequences per other specifications can also be performed (see Table 3).

Following cleaning and rinsing, a water film break test is conducted. Water breaks indicate poor cleaning and a need to re-process the parts through the cleaning cycle. The parts are then blown dry with compressed air prior to immersion in the black oxide to avoid splattering from the hot caustic.

After the black oxide process, parts are thoroughly drained and rinsed in stagnant warm water (140-190 °F), followed by minimum five-min running cold-water rinse and finally a hot-water rinse (160-190 °F) for another minimum of five min. An optional addition of two percent potassium dichromate may be added to this rinse.

Following air drying of the parts, quality control tests are performed. Upon passing these tests, parts may be baked within four hr of the black oxide application. The parts are baked for 2-4 hr at 302 °F. The final step in the process will be the application of an anticorrosive oil.

Next month in “Training Colombo—Part VII,” we’ll continue this discussion, and focus on oil quality issues, post-coating processing and part handling. P&SF

Table 2

Process	Tank Contents	Time, min	Temperature, °F
Vapor Degrease	100% trichloroethylene	3-5	180
Hot wWater Rinse		1	160
Blow Dry			
Black Oxide	112 oz/gal	6-75	180-295
Hot Water Rinse		1-2	180
Cold Water Rinse		1-2	AMBIENT
Neutralize	$Na_2Cr_2O_7$, 0.06 oz/gal	0.5-1	150
Blow Dry			
Inspect			
Oil	1-2		AMBIENT

Table 3

Process	Tank Contents	Time, min	Temperature, °F
Vapor Degrease	Trichloroethylene	5	180
Alkaline Cleaning	Proprietary	10-20	180-200
Cold Water Rinse		1	AMBIENT
Hot Water Rinse		2	140-190
Blow Dry			
Black Oxide	Proprietary	45-60	285-290
Hot Water Rinse		1	140-190
Cold Water Rinse		5-6	AMBIENT
Neutralize	$Na_2Cr_2O_7$,0.06 oz/gal	5-6	160-190
Blow Dry			
Inspect			
Test			
Bake		2-4 hr	302±5 °F
Oil		1-2	AMBIENT

References

1. W. Wiederholt, *The Chemical Treatment of Metals*, Robert Draper Ltd., Teddington, England (1965).
2. D. Fishlock, “Black Finishes for Metals,” *Met. Fin.*, Sept. 1963, p. 56.
3. L.F. Spencer, “Conversion Coatings,” *Met. Fin.*, April 1960, p. 62.