A Review of Functional and Decorative Black Oxide Coatings

By Robert Farrell, Hubbard-Hall

Black oxide is the conversion of a base metal material to an oxide of that base metal material. A prime example would be Fe3O4, which is black iron oxide, otherwise known as magnetite; another is a CuO, or copper monoxide. It occurs when the chemicals react with a base material to form an oxide of the base's primary constituent. In the case of stainless steel, not only does it form oxides, but it also forms sulfides of the base materials that tend to be black as well.

Black oxide is the conversion of a base metal material to an oxide of that base metal material. A prime example would be Fe3O4, which is black iron oxide, otherwise known as magnetite; another is a CuO, or copper monoxide. It occurs when the chemicals react with a base material to form an oxide of the base's primary constituent. In the case of stainless steel, not only does it form oxides, but it also forms sulfides of the base materials that tend to be black as well.

Generally, the term 'black oxide' has taken on a bigger definition in that almost any inorganic black produced on a metal substrate could be referred to as a black oxide coating. That might not necessarily be absolutely true; it could be a deposit, and — in the case of room temperature black oxide — it is putting down an immersion copper and then subsequently forming either selenides or tellurides, which tend to be black compounds on the surface. Some other metals that also could be blackened include zinc, pewter, or aluminum.

One of the most commonly asked questions in regards to black oxide is the thickness of the coating. Generally speaking, we refer to it as not affecting the tolerance of the part; in other words, the coatings are so thin that they really don't affect the tolerance of the part. For hot black oxide on steel, the Fe3O4 type coatings thickness is anywhere from 0.4 to 2.4 microns, and that relates to about 0.00016 to 0.00096 inches; it's a very thin coating.

Black oxide is used as a functional or decorative coating. A functional black oxide coating is one that's produced to give a characteristic to the base material; it could be used to enhance the corrosion protection of the base material, or it could be for optical purposes to affect or alter the absorptivity and the reflectivity of the part. Black oxides are also used for anti-galling purposes to modify the friction of meshing parts. Decorative applications are more for aesthetic appeal or for the presentation of the part at point-of-sale. For example, black oxide conversion coating on steel has been used in the firearms industry for a very long time, and it's used for a functional purpose to enhance both the abrasion resistance and the corrosion resistance of the firearm, but it's also used for decorative purposes particularly in commemorative type firearms.

Let's take a look at some common questions that have been asked regarding functional or decorative black oxide coatings:

For decorative hot black oxide, if I start with a shiny steel part, will the blackened part have a shine as well? What about a dull steel part?

When you look at hot black oxide, they're not all created equal. It really comes down to the substrate as well. For instance, on steel, the black oxide will typically take on the same level of gloss or polish as the substrate; it doesn't have a dulling effect. It doesn't really enhance the brightness, but the black may appear brighter — of a higher luster — than the bare material that is polished. In the case of the hot black oxide and steel, it takes on the degree of luster that the base material has. If the part is matte to start with, the black oxide will be matte; if the part is a high-gloss, the black oxide will be high-gloss.

For black on copper or black on brass, the black oxide produced always tends to be dull. A unique thing about the black on brass and copper is what is called the 'nap' that is present on it; when the part comes out of the blackening solution and is rinsed, it almost looks like it has a velvet appearance. If you rub it, that nap lays down, and the part will be dull. On substrates that are dull — or for oxides that produce a dull black —if you want a glossy finish, you'll have to rely on a subsequent topcoat.

When compared with a blackened steel part, why does a blackened stainless- steel part for decorative hot black oxide possess more of a dull, matte finish?

That's very similar to the black on copper; it's the nature of the black itself. Black on stainless steel is a combination of oxides and sulfides of the alloying constituents of the particular stainless steel that's being blackened. Although oxides — as in the case of steel — might take on the luster of the substrate and could be bright, the black finish on SS tends to be duller because of the presence of the sulfides mixed with the oxides. The stainless-steel black will always be duller — or take on a duller appearance — than the base material.

For decorative room temperature black oxide, if I start with a shiny steel part, will the blackened part have a shine as well? What about a dull steel part?

It's much less frequent to see room temperature black oxides used for decorative purposes. They might be used to enhance the salability of the part — which could be conceived as decorative — but they are rarely used. Instead, they are used more for functional purposes. Room temperature blacks being really selenides of copper or copper telluride; if someone is using a tellurium-based room- temperature chemistry tend to be dull deposits anyway. They will dull the part, and the black will be duller than the substrate material; it could be enhanced with a topcoat, but they do naturally tend to be duller type finishes. A dull part will remain dull after blackening.

For function use, if I black oxide a steel part, what kind of corrosion protection can I expect from the black oxide coating? What about a blackened stainless steel part?

With black on steel, the oxide coating —the magnetic magnetite Fe_3O_4 coating— will give a certain degree of corrosion protection, particularly if it were to be sealed with an inorganic mil-spec specified seal. Mil-C-13924D for black oxide on steel and had originally

recommended chromic acid dip afterward. The black oxide — particularly with chromic acid after it —will give up to two hours of salt spray resistance (ASTM B117) without a supplemental topcoat. There is so much variability in the corrosion resistance of a given part; it's alloy dependent, hardness dependent, micro structure-dependent, but more importantly, the biggest contributor is the subsequent topcoat that is put on it. Black oxide on steel tends to be somewhere between nanoporous and microporous and is simplistically stated, a coating that acts as a sponge and will bond and absorb subsequent topcoats to a much greater extent than the bare substrate itself.

With black oxide on a steel part — with a given topcoat — it could give twice the salt spray resistance than the substrate with the same top coat, but without the black oxide. If you were to put water displacing corrosion preventive —which is probably the most common type corrosion inhibitor— on a black oxide, you might get 80 hours on the black oxide, where you'd only get 40 hours on the bare steel substrate itself. For steel, you do get a little bit of corrosion resistance from the oxide coating, but much more due to its ability to absorb the topcoat. Stainless steel black — being a blend or a mixture of oxides and sulfides —does not impart any corrosion protection enhancement to the part. In other words, if you were to salt spray the stainless steel part unblackened, you'd get the same result if you were to salt spray it with a black coating on it. Due to the fact that sulfur is present in the coating, you may actually see that you get slightly less corrosion protection with the black on it. Being a microporous or a nanoporous type coating, the stainless steel black will also absorb a topcoat to a greater extent. With stainless steel, it depends on the corrosion resistance of the stainless itself, which is ordinary very high — particularly if it is passivated—or passive before the black. If you want to enhance the corrosion protection above and beyond what you'd ordinarily get with stainless steel, you could use water displacing or a water-soluble oil to do that.

For functional hot black oxide, what temperature range is the functional black oxide coating on a steel part stable?

My experience is if you have black oxide on a steel part and it's not sealed — it's just the oxide, it's been rinsed, no chromate seal and no corrosion inhibitor top coat — and you were to put that in an oven, it should hold up to 700°F before you see any type of discoloration or mottling. When I talk to customers, and they ask that question, I say you could probably go up to 700°F, but after 700°F, you're going to start to see some oxidation occurring that may be a conversion back to more of red rust and maybe spots.

For functional, what is the thickness of the black oxide coating on a steel part? What about a blackened stainless steel part?

The hot black on steel is between 0.4 and 2.4 microns, and that is very dependent on a couple of parameters: the temperature that the bath is boiling, which typically is 285° F and will give you a slightly thicker coating. Probably the biggest contributing factor of the thickness is the dwell time; typical black oxide applications in a job shop is going to go 10 to 15 minutes; if it's a bearing manufacturer and they really want to optimize the coating thickness of the black up to a point before you start getting diminishing returns on your dwell time, I've seen them go 30 to 60 minutes, and that's where you get those thicker

coatings. With stainless steel, the problem you are running into is the thickness of the black oxide coating if you go too long is detrimental; you actually get a coating that exfoliates at sharp angles on the part. If you have a 90° bend on a stamped part and you go too long in the black, you could actually see a loss of adherence in that area. Unlike hot black oxide, where longer is better for coating thickness, it doesn't hold true with stainless steel black. I would imagine if it were to be cross-sectionally looked at, the stainless steel black would probably be down closer to the low end of the coating thickness of hot black oxide on steel, which would be about 0.4 to maybe 0.6 microns.

If I process steel parts through a room temperature black oxide, what kind of corrosion protection can I expect from the functional black oxide coating? What about a room temperature blackened stainless steel part?

When it comes to room temperature, black oxide on steel — because it is a copper selenide type or a copper telluride type of coating — tends to be very prone to corrosion. If you are blackening a steel part in room temperature black oxide, you come out of your water rinse after black, and you could get flash rusting starting to occur before you get to your subsequent topcoat. Room temperature black oxide on steel is never used without a subsequent topcoat; it offers no corrosion protection whatsoever, and it probably detracts from the corrosion resistance of the base material. You always have to use a topcoat with room temperature black oxide; it's just the nature of the coating itself not being a true oxide, but more of an immersion coating of copper that's subsequently black.

For stainless steel black, it probably offers no corrosion protection whatsoever; there is a room temperature black for stainless steel, but it's rarely used. It is a selenium copper-based material, and it works well on small parts like fasteners; it probably distracts slightly from the corrosion protection offered by the base stainless steel alloy itself, but if you're looking for color-coding, you are looking just to have a black part or to cut down on the reflectivity it has its application.

For fasteners, as an example, it doesn't distract so much from the corrosion protection that it instantaneously rusts; again, it is better to topcoat it with something to give it a little bit more protection. The trouble with room temperature black on stainless steel is that, if you go to larger substrates, it is difficult to get a consistent black across the entire surface area of the substrate without getting a smutty finish or a black sooty type rub off. Black sooty type rubs off with room temperature black on steel, and stainless steel is probably one of the biggest problems encountered in a production situation that customers complain about. Tune in the concentration, and tune the dwell time to try to lessen the chance of producing that sooty type coating.

Functional room temperature black oxide, what temperature range is the black oxide coating on the steel part stable?

If you were to take a room temperature black oxide coated steel part and rinse it and thoroughly dry it, so there's no corrosion occurring whatsoever on the part before putting it in an oven, it would be stable may be up to 250°F. But with room temperature black oxide, you never put it on a part that would be subjected to high temperatures above 100°F; you would go to hot black oxide for that particular type of application. Being a selenide type coating — and with selenium having multiple oxidation states or valence states — you could get some unusual things happening. It's rare that you would ever subject a room temperature black oxide part to a temperature above 100°F, but I suspect if the test was done under controlled situations, you might be able to get to 250°F.

For functional room temperature black oxide, what is the thickness of the black oxide coating on a steel part? What about a blackened stainless steel part?

In all the years the 44 some odd years I've been in this industry, no one has actually asked me to cross-section and measure the oxide thickness of room temperature black oxide, but I would suspect that it's at the low end of what hot black on steel would be. You are probably looking at 0.4 microns in that range. Thickness is typically looked at for tolerance; of course, with black oxide, tolerance of the part rarely does come into play; on very rare occasions, it does. If you know that a micron affects the part from a tolerance standpoint, of course, then you have to consider it, but generally speaking, for the types of parts that are black oxide coated, tolerances are not that tight. If coating thickness is important, then it would normally be important because you are looking for enhanced abrasion resistance or enhanced anti-galling friction characteristics due to the fact that this micro sponge oxide coating will absorb the subsequent topcoat or a lubricant. It then becomes important to try to get a thicker coating, and you could do that with hot black oxide.

Of course, it tends to plateau off and becomes self-limiting when you get up over an hour or 90 minutes, and it probably flat lines. On room temperature black, if you try to go longer to get a thicker coating, you will get smut or black rub off, which is objectionable. You don't really look at room temperature black oxide for abrasion resistance because one of the characteristics of room temperature black is that it is much softer and less abrasion resistant than hot black oxide. You could take a room temperature black oxide part and rub it with a pencil eraser and remove the coating in a short period. You could rub hot black oxide for a much longer time before you get any type of removal of the black occurring.

Thickness never really seems to come into play with room temperature black oxides, whether they're on stainless steel, steel, copper brass, aluminum, or zinc. It's just not a variable or a characteristic that's important.