A Performance Evaluation of Traditional and Green Surface Finishes for Zinc Die Castings
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Introduction
Zinc die castings are an outstanding choice for countless decorative and functional applications. Due to its unique physical and mechanical properties zinc can be cast into virtually limitless shapes and sizes ranging from simple toy cars to complex connector housings. Zinc has many attributes for die cast parts: high ductility; high impact strength and dimensional stability; resistance to corrosion and wear; electric and electromagnetic characteristics and excellent lubricating properties. Zinc also can be die cast at moderate temperatures thus providing significant energy and processing savings over other metals and engineering alloys. Zinc also accepts a broad assortment of finishes, from chemical conversion treatments to electroplating to sprayed and baked polymers. When a finish is properly selected and applied to die cast zinc, almost any desired aesthetic characteristic and coating durability can be achieved. Zinc castings can be made to look like solid gold, weathered brass, stainless steel, and even leather. The majority of zinc die cast applications are not exposed to corrosive environments and the aesthetic requirements of the part defines which finish should be used, which in many cases means no finish at all.

For applications where the service environment is aggressive, such as marine hardware, external automotive parts, and items for use outdoors at industrial sites, corrosive attack can result in white rust, black staining, or, in some cases, flaking and peeling of the finish due to corrosion of the underlying zinc. For such severe environments the manufacturer should select corrosion resistant finishes.

Traditional finishes including solvent-based painting, electroplating and hexavalent chromium conversion coatings have been providing reliable performance for decades. With a global trend towards environmentally friendly materials, a series of new, innovative electrophoretic surface finishes using “best practice” green technology have been developed. These finishes include simulated metallic looks and real metallic finishes reformulated to be free of cadmium or lead and without chromium plating topcoats.

The Studies
To assist end users and parts manufacturers in selecting the optimum finish for a given application the International Zinc Association (IZA) commissioned a study to evaluate the performance of 39 different surface finishes – 20 commonly used traditional finishes and 19 new “green” finishes that employ reduced or zero volatile organic compounds (VOC).
Data was compiled from two studies: the first – conducted in 2006 – covered traditional finishes, while the other – conducted in 2012 – analyzed the new green finishes. For comparison purposes the 2012 study was designed on the basis of the earlier study, which focussed on two performance criteria – the ability of a finish to protect the underlying zinc against corrosion; and the ability of the finish to maintain its initial aesthetic properties in corrosive conditions. In addition, the 2012 study ensured that the new finishes used best practice green technology and were in compliance with the EU Restriction of Hazardous Substances (RoHS) regulations.

Test Procedures
The 2006 study was performed by the Corrosion and Materials Research Institute (CAMRI) in Newark, Delaware, USA. The tested casting was a complex shaped “bolt boss plate” that incorporated flat and curved surfaces, rounded and sharp edges, holes of various diameter-to-depth ratio, and inside and outside corners. For the purpose of providing a challenging test to the finisher the shape of the tested specimen was designed to maximize failure of the coating. These test panels were drilled and tapped, and stainless steel screws were added after finishing but before test exposure. An “X” was scribed through the finish, to expose the underlying zinc.

After evaluating three corrosion tests, including the B-117 salt spray and ASTM G-85 cyclic fog test, CAMRI decided to use a test developed by DuPont in the 1980s to evaluate finishes for industrial fasteners. During the test, finished die cast specimens were exposed to a constant 100% relative humidity at 50°C (122°F) with weekly misting of the panels with a solution of 1% sodium chloride and 1% sodium sulfate. The 20 panels were exposed for six months, with detailed interim evaluations after the first and third months.

The 2012 study was conducted by Finishing.com Inc. and performance testing was done by Corrosion Test Laboratories, Inc. (CTL). CTL used the same test used previously by CAMRI. The casting selected for this test was approximately 200 mm long x 52 mm wide (8” x 2”) with a smooth, flat “A surface” which was an ideal challenge for the application of coatings with today’s popular metallic looks. If the finishes were poorly done, blisters, pits, variations in color and smoothness, and other defects would be quickly evident. Like in the 2006 test, an “X” was scribed through the finish of most test specimens to expose the underlying zinc. However, where two samples of the same finish were available one was left unscribed to better evaluate the aesthetics of the finish after exposure to the corrosive environment. Given the commercial importance of electrophoretic coatings, samples were obtained from two different coaters.

To put the test in perspective relative to actual field exposure, the original DuPont studies found that a three month test in the laboratory equated in nature and severity to about one year of actual exposure at a severely corrosive chlorofluorocarbons plant site on the U.S. Gulf Coast, or three to five years at inland chemical plant sites.
A. Green Finishes tested in 2012 included:

1. Antique bronze electroplating
   This finish is achieved by copper electroplating followed by blackening; relieving; and clear coating. It provides a smooth warm finish. Die castings with this finish resemble more expensive metals, and also have an aesthetic standard against which synthetic “metal look” finishes could be judged. Antique bronze electroplating is a popular finish for kitchen and bathroom faucets, light fixtures and other builder hardware.

2. Single component clear coat on raw casting
   Parts were wiped with xylene to remove any oils, dipped and, after a minimum one hour drying, re-dipped. This finish was selected to learn what could be achieved with the very simplest of finishes.

3. Single component clear coat on steel wool buffed casting
   Same coating as sample 2, but on a steel wool polished casting. The casting had a moderately bright finish at the initiation of the test which could be a fine “clean” finish for some applications where this is not the primary decorative surface.

4. Trivalent chromate and silicate-based organo-mineral topcoat
   The samples were alkaline-cleaned, acid activated, chromated and top-coated. EU RoHS standards prohibit older hexavalent chrome conversion coatings. This finish can be considered as an engineering finish or pretreatment.

5. Electrochemical hard coating process
   This process includes a proprietary electrochemical hard coating of 0.13 to 0.18mm (.005 to 0.007”); 35 minutes plating time, with no bead blasting or post treatments. The hard coating is an engineering finish rather than a decorative finish.

6. Black electrophoretic coating (sample A)
   Applied in an immersion tank similar to electroplated coatings, but without the use of chromium. The electricity alters the paint molecules, causing them to deposit onto the die casting as an electrically resistive, insulating coating. This diverts the electrical power to any uncoated area, insuring 100 percent coverage, and results in a coating that is highly corrosion resistant despite being very thin (approximately 10 microns, or about 1/6 of typical powder coating thicknesses). This is an environmentally friendly polyurethane cathodic e-coating.

7. Clear electrophoretic coating with stainless steel effect post dye (sample A)
   See 6

8. Clear electrophoretic coating with brass effect post dye (sample A)
   See 6

9. Clear Electrophoretic Coating with Bronze Effect Post Dye (sample A)
   See 6

10. Electroless nickel plating
    This finish is comprised of 7 microns (.0003”) copper cyanide, 7 microns (.0003”) acid copper, 7 microns (.0003”) sulfamate nickel and 7 microns (.0003”) mid-phos electroless nickel. It has been a staple of the metal finisher’s toolkit for decades for its bright, wear resistant, and highly corrosion resistant appearance; with a lead-free formulation now being available.

11. Tin-nickel alloy plating
    This is a bright nickel chromium-free electroplated finish, achieved by bright nickel electroplating, followed by a flash of tin-nickel plating.

12. Black nickel plating
    This finish achieves a ‘smoke look’ without the customary chromium plating by employing a black nickel flash after bright nickel plating. This is currently a much sought-after finish for automotive components, display racks and other applications.

13. Clear electrophoretic coating with gold post dye (sample B)
    These are polyurethane-based E-coatings of 4 – 14
micron (0.00015-0.0006") thickness on alkaline-cleaned die-castings with no phosphate pre-treatment. A gold-effect post-dye was applied. Since the goal of the study was to determine both corrosion resistance and preservation of aesthetics, electrophoretic coatings of several different colors were tested (see below 15-17).

14. Black electrophoretic coating (sample B)
   See 13

15. White electrophoretic coating (sample B)
   See 13

16. Blue electrophoretic coating (sample B)
   See 13

17. Blue electrophoretic coating plus polyurethane top-coating (sample B)
   See 13

18. Oil-rubbed bronze electrophoretic coating (sample B)
   See 13

19. Oil-rubbed bronze electrophoretic, polyurethane topcoating (sample B)
   See 13

B. Traditional Finishes tested in 2006 included:

A. Zinc Black
   This is a process in which a relatively thick black phosphate film is imparted to the casting to protect against humidity and moderately corrosive atmospheres. This finish is not usually proposed as a stand-alone corrosion barrier, but rather is a paint pre-treatment. Unlike the smooth, dense blacking that is used widely on steel guns and tools, the blacking on zinc is dull and somewhat powdery in consistency. Zinc blacking by itself did not offer significant protection in this test, and was largely dissolved or washed off by the periodic wetting of the panels with mixed salt solution.

B. Copper-Tin-Zinc Electroplate
   This is a proprietary process that forms a dull, silvery finish on the zinc. In these tests it offered fair protection to the zinc, but the finish itself developed an unsightly, sometimes black, splotchy appearance. The overall thickness of the finish in this case was about 25 microns (1 mil).

C./E. Chromate Conversion Coatings
   These are chemical immersion treatments which produce a thin protective film on the zinc surface. They are intended primarily to protect parts during storage or in mild (e.g. indoor) environments or, like the zinc black, to provide an optimum surface for adhesion of subsequent paint or other organic finishes. Conversion coatings are sometimes followed by a sealer or lacquer to enhance their performance and extend the range of their applicability. In these tests it was observed that the hexavalent chromate conversion coatings, with or without a sealer, performed much better than did trivalent chrome or “clear” chromate finishes.

D. Sprayed & Baked Liquid Coatings
   This includes a broad spectrum of different chemistries, including epoxies, polyesters, phenolics and urethanes, just to mention a few. The test matrix included low friction fluoropolymer coatings not primarily intended for protecting against corrosion. The coatings were applied approximately 25 to 50 microns (1-2 mils) thick, and provided only moderate protection. Some also tended to discolor or become generally unsightly during the test. There are many thicker industrial sprayed and baked organic coatings on the market that would have performed better in this test.

F. Mechanical Plating
   This name is somewhat misleading, as this general category of finishes involves placing the parts in a drum with the desired mixtures of metal powders and a chemical “activator” and tumbling the parts until the desired thickness of coating builds on the part by mechanical plus chemical action. It is possible in this way to coat with an “alloy” of almost any desired metals, including zinc + tin, zinc + cobalt, zinc + iron and zinc + nickel. Zinc is almost always included because it responds especially well to the mechanical/chemical bonding process. This process has a distinct advantage over electroplating in that materials can be applied very uniformly on all surfaces, including on inside corners. The use of different metal combinations offers different aesthetics (colorations). This process was originally developed with zinc alone – a process usually applied to steel parts and called “mechanical galvanizing”. The zinc + tin alloy was tested with a coating thickness of approximately 50 microns (2 mils), including a topcoat with trivalent chrome and clear sealer.

G. Copper-Nickel-Chrome Electroplate
   This has been one of the workhorse finishes for outdoor and corrosive applications for many years. On zinc it begins with a thin layer of cyanide (non-acid) copper flash to protect the zinc against the...
Pollution and greenhouse gases are minimized with zinc die casting:

- Negligible emissions to air, land and water.
- Much smaller energy consumption than comparable alternative mass manufacturing processes.
- No environmentally harmful blanket gases required in processing.
- Any ‘scrap’ product from processing can be recycled.

acidity of subsequent baths. Next comes a thicker layer of acid copper plate, which serves to make the surface more uniform and assures good electrical conductivity. This is followed with one or more layers of nickel, which provides a continuous corrosion resistant barrier. Finally one or more layers of chromium are applied to give the desired shiny “silvery” appearance and to protect the nickel against mechanical forces such as wear and erosion. Electroplating has one disadvantage vs. non-electrical processes in that it is difficult to get plated metal into inside corners and holes. This can be largely overcome by using what are called “conforming” anodes, but these make the process more expensive. A two-nickel layer system commonly referred to by some as “automotive” grade chrome plate, plus a three-nickel-layer version used for more stringent applications and sometimes referred to as “marine” grade, were tested. There was a noticeable improvement in performance with the “marine” vs. the “automotive” grade plating. There was also, with both systems, a noticeable incidence of local failures at inside corners – presumably indicative of thinner plating application at those locations.

H. Epoxy and Polyester Powder Coatings

These polymeric coatings are applied as powders in a dry electrostatic process, and subsequently “fused” in an oven. This process offers environmental and personal hygiene advantages over wet sprayed and baked coatings because there are no solvents to drive off. Because the powder application is usually an electrostatic process, sprayed powder coatings also provide better buildup at edges than do wet-sprayed polymers. On the down side, for this same reason it is difficult to get coating materials into deep recesses and inside corners although this problem was not observed with the sample geometry used for these tests. In fact, no local failures of these coatings
were observed at inside corners, as had been the case with the Cu-Ni-Cr electroplating. In these tests, both the epoxy and the polyester powder coatings did much better than the sprayed liquid coatings. While powder coatings are gaining an excellent reputation as corrosion protecting barriers, it is also true that these powder coatings, at 75-100 microns (3-4 mils) were much thicker than the liquid coatings evaluated in this program.

It is generally accepted that grit-blasting a part gives better coating adhesion and, therefore, better coating performance in aggressive service conditions. The blast finish on some of the epoxy-coated panels produced only about a 25-micron (1 mil) surface profile – and did not enhance performance in these tests as compared to a non-blasted zinc surface. Most coating manufacturers recommend much deeper blast patterns – typically 50 to 75 microns (2-3 mils) for optimum coating performance. Such an aggressive blast, however, may result in warpage and/or a matte coated surface, so should be tested and evaluated on your particular part before specifying heavy blast preparation for a powder coating.

I. Electrophoretic Urethane Coatings
Also known as “e-coats”, the three electrophoretic coatings evaluated here all did exceptionally well. Measuring only about 20-25 microns (0.8-1 mils) in thickness, these finishes defied the rule about thickness being needed for good corrosion protection. One of the finishes tested contained ceramic “nanoparticles” to give added abrasion and wear resistance, and a black color. The nanoparticles did not show any measurable effect on corrosion resistance compared to the regular urethane resin e-coats.

Zinc alloys, as defined by international chemical composition standards, comfortably conform to the requirements of the End of Life Vehicle (ELV), Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) legislation.

Zinc die castings, are premium quality low cost products that are highly resilient to many hostile conditions. They display considerable corrosion and wear resistance resulting in very long and reliable service, frequently measured in decades, and saving resources by not needing to be frequently replaced.
Performance Evaluation

All specimens were tested “as finished” with no heat treatment. The scoring was based on a maximum of 10, with points deducted for observed imperfections. Each specimen was judged against an unexposed specimen with the same surface finish, along with unfinished control parts that had gone through the same test exposure. Each finish was judged on two criteria: corrosion protection and preserving aesthetics. Scores were based on a scale of 0-10 (zero being no better than the unfinished control and ten being visually perfect).

Green Finishes:
Performance Results

The “CAMRI test” shows that green finishes are able to provide excellent corrosion protection to zinc die castings and to maintain their original aesthetic appearance. The electroless nickel-plated finish performed best, receiving a 10 for corrosion protection and a 9 for visual appearance. The black nickel-plated finish was ranked second, receiving a 9 for both corrosion protection and visual appearance. Other finishes that scored high were the three clear e-coats with post dye, the tin-nickel plated finish and the oil-rubbed bronze e-coat plus polyurethane clear coating. Each of these received an 8.

Parts that performed poorly were removed from the test after 90 days of exposure.

The green finishes were applied to zinc alloy #3. In 2006 two alloys – zinc alloy #3 and #5 - were used for the testing. However, since very little or no difference was reported the 2012 test used solely zinc alloy #3.

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<table>
<thead>
<tr>
<th>No.</th>
<th>Finish</th>
<th>Corrosion Protection</th>
<th>Preserving Aesthetics</th>
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<tbody>
<tr>
<td>1</td>
<td>Tin-nickel alloy plating</td>
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<td>8</td>
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<tr>
<td>2</td>
<td>Electroless nickel plating</td>
<td>10</td>
<td>9</td>
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<tr>
<td>3</td>
<td>Black nickel plating</td>
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<tr>
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<td>Black electrophoretic coating (sample A)</td>
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<tr>
<td>5</td>
<td>Black electrophoretic coating (sample B)</td>
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<td>3</td>
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<td>6</td>
<td>Clear electrophoretic coating with stainless steel effect post dye (sample A)</td>
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<td>7</td>
<td>Clear electrophoretic coating with gold post dye (sample B)</td>
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<td>8</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>Antique bronze electrophoretic coating</td>
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<td>11</td>
<td>Oil-rubbed bronze electrophoretic coating (sample B)</td>
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<td>Oil-rubbed bronze electrophoretic, polyurethane topcoating (sample B)</td>
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<td>White electrophoretic coating (coater B)</td>
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<td>Blue electrophoretic coating (sample B)</td>
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<td>Blue electrophoretic coating plus polyurethane top-coating (sample B)</td>
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<td>Trivalent chromate silicate-based organo-mineral topcoat</td>
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<td>Single component clear coat on raw casting</td>
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<td>18</td>
<td>Single component clear coat on steel wool buffed casting</td>
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<td>19</td>
<td>Electrochemical hard coating process</td>
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The three electrophoretic resin e-coats did all exceptionally well receiving a 9.5 and 9 for corrosion protection and a 10 for visual perfection. The three epoxy and polyester powder coatings also scored well with 9 and 8.5 for corrosion protection and 9 and 8 for preserving aesthetics.

Zinc alloys #3 and #5 were used for testing the traditional finishes. Since very little or no difference was observed in the performance results their performance results are combined in the table at the right.
How to select a finish?

The level of corrosion resistance is the main driver when selecting a surface finish. If a part is used indoors in a dry application, corrosion resistance is not a factor. For indoor parts that are to be frequently wetted in service, such as faucet handles and shower heads, as well as parts to be used outdoor in inland rural areas or non-industrial, non-coastal sites, only moderate corrosion resistance is needed. For constantly wetted parts, hardware for boats and marine facilities, and parts to be used outdoors in industrial applications, a well-performing corrosion resistance is key.

The majority of zinc cast applications are not exposed to corrosive environments and the aesthetic requirements of a diecast part will define the type of finish that is applied.

With the global trend of eliminating lead, mercury, cadmium and hexavalent chromium and the EU RoHS environmental considerations are another important factor. The CAMRI test showed that there is a number of new electrophoretic finishes that provide high corrosion protection and appealing aesthetics including today’s popular metallic looks. These green finishes offer an environmentally friendly alternative to the end user and parts manufacturer.

The charts on the right show the relative performance for the various types of traditional and green finishes. For better corrosion resistance select finish types towards the right of the chart, for better aesthetic retention you may consider all finishes across the top of the charts.
References
