Developing New Surface Engineering Processes

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Surface engineering processes, whether for hard or soft, thick, or thin films should be designed to achieve minimal environmental impact and maximum sustainability which meets the needs of the present without sacrificing the future. Use of energy, material, labor, and emissions metrics to compare options during the development cycle is imperative. In order to maximize consideration of possible options computational (in-silico) tools can be employed which also hasten development and minimize waste generation. In this paper experiences in the implementation of such practices, from an industrial research perspective, will be described.

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There is considerable activity in a field defining itself as 'green' chemistry. In the field of surface engineering, particularly as applied to metal finishing, our research group has employed environmental metrics and computational chemistry, part of the panoply of technologies available within 'green' chemistry for some time. Applying the results of environmental metric calculations at every step of the development cycle not only aids in minimizing environmental impact but also in anticipating market interest. Computational chemistry not only minimizes the exposure of personnel to potentially hazardous chemicals and decreases waste generation but also allows a more effective screening of candidate solutions during the development of new processes.

Environmental Metrics:

It is a characteristic of environmental metrics that the lower the value of a metric the more environmentally effective is the process. Thus the metrics are typically ratios constructed by having a numerator that is the 'negative' impact of the process, and a denominator that is the output of the process. Table one enumerates some commonly proposed metrics.

It may be convenient to categorize the metrics based upon literature review^{1,2,3,4} into three categories: *Conservation* metrics that emphasize energy, material impact, and water usage are useful. It is common to use *pollutant production or emission* metrics that describe jeopardy to human health and ecotoxicity. We believe that at least two *productivity* metrics for labor and replacement frequency are important. The fewer labor hours used, then the fewer miles traveled by commuters, the less energy consumed, and the less impact there is to the environment. The less frequently a part is replaced/resurfaced within the life cycle of the structure where it functions the less impact there is to the environment. The metrics in table one are ones that we have seen in the literature as well as ones we feel are important in our industry.

Denominators for the metrics may vary. In surface engineering at a development level 'per unit' denominators such as surface area, or mass of part are easy to employ. At the production level such denominators may be difficult to provide and the more inclusive and usually very closely monitored process cost or net sales value may serve as a denominator. Value added (sales price less cost of raw materials) has also been proposed as a denominator.

Numerators vary in complexity. Material intensity may have a numerator that is the difference between material consumed and useful product. Water consumption and energy are simple mass/energy balances common to chemical processing. Sludge generated can often be derived from waste treatment facilities. Landfill data is generally obtainable from accounting. More complex are pollutant production metric numerators that can include total kg CO₂ equivalent as a greenhouse gas metric, C_2H_4 equivalent as a photochemical ozone creation metric, SO₂ equivalent as an acidification metric, and phosphate equivalent as an eutrophication metric. Ecotoxicity and human health metrics that have been proposed rely upon (Yi*Mi) where Yi is the effect of an emission and Mi is the mass of an emission. The calculations of the Yi vary between the two metrics and can be a bit complex⁶ utilizing bioaccumulation⁵ factors in concert with LC₅₀, EC₅₀, PEL, and TLV's for the materials used in the process. Recently Internet tools have begun to be available for helping estimate bioaccumulation and related factors⁶. For

¹ AICheE, "CWRT Industry Technology Alliances, Collaborative Projects, Focus Area: Sustainable Development, Development of Baseline Metrics", http://www.aiche.org/cwrt

² "Bridges to Sustainability – Product Level Metrics", http://brigestos.org/product_detail.htm

³ James J. Kay, "Ecosystems, Science and Sustainability", www.ecologistics.com/nesh/scisust.html

⁴ Rebecca L. Lankey and Paul T. Anastas, "Advancing Sustainability Through Green Chemistry and Engineering", ACS Publication, 2002.

⁵ Bioaccumulation is the process by which the chemical concentration in an aquatic organism achieves a level that exceeds that in the water, as a result of chemical uptake through all possible routes of exposure.

⁶ http://www.pbtprofiler.net/

productivity metrics the labor metric numerator is simply person hours, but the replacements while in service or product durability numerator should be a reciprocal or a difference, such as years of anticipated service divided by years between anticipated replacements, desired neutral salt spray (NSS) or corrosion cycles requirement divided by average expected survival, or the difference between device lifetime and component lifetime. For example a shaft for a machine which has an expected service life of twenty years with annual resurfacing of the shaft would have a numerator of 20 using the ratio method or 19 using the difference method while a proposed new surfacing technique that would only require five resurfacings in twenty years would have a numerator of 5 (ratio method) or 16 (difference method). A coating used as part of a unit subjected to functional corrosion cycling tests where the unit has a minimum corrosion cycle requirement of 60 cycles and achieves 120 cycles would have a numerator of 0.5 by ratio.

In order to compare metrics data it is convenient to normalize. When comparing processes the same method for calculating the metric should be used for each process and then the lowest metric in a particular category becomes one and the others in that category are multiples.

A recent survey⁷ of American plating shops conducted by the National Center for Manufacturing Sciences (NCMS) for the Environmental Protection Agency (EPA) has benchmarked many surface engineering processes using metrics with a denominator of revenue. In table two a summary of their study is presented as it relates to the processes that had the greatest response from recipients.

Data such as these can be used to provide direction for future research in metal finishing. It is not unreasonable to suggest that inventions that decrease the high value metrics will achieve interest if not automatic commercial success. As researchers work toward reducing a high metric, they must not greatly increase the other metrics. Minimizing water while greatly increasing energy use may not be a wise course of action.

Our research group has seen success with environmentally targeted technologies such as noncyanide alkaline and acid zinc to replace cyanide zinc, trivalent chrome based passivation to replace hexavalent chrome based passivation, and high alloy zinc nickel as a coating to extend service life of components. Systems which minimize human exposure during hard chromium plating have had commercial success as well as electroless nickel (EN) palletized electrodialysis systems⁸. These latter systems improve productivity and conservation metrics by extending bath life, produce more consistent product quality, increase bath loading, avoid process interruption for new make ups, improve energy efficiency, and decrease sludge.

In fact we had also developed seemingly 'simpler' EN systems, such as selective precipitation of orthophosphite⁹ and others had developed sodium and sulfate free (nickel hypophosphite) systems. The simpler systems have not enjoyed the same market success as has electrodialysis and a review of the metrics of the various processes provides insight into why this may be the case. By examining environmental metrics it appears that neither selective precipitation nor the nickel hypophosphite process favorably impacted toxic dispersion even when attempts were made to recycle the orthophosphite salts that were produced. The lead, cadmium, nickel and other undesirable chemicals in the sludge remained a problem for transportation and for the recycler. As well, other environmental metrics did not benefit significantly from alternative methods¹⁰.

Trivalent passivation was patented for the first time in 1951¹¹. This process eliminated hexavalent chromium but it did not commercially succeed until the late 70's and early 80's when clear or blue

⁷ "Benchmarking Metal Finishing", NCMS Report 0076RE00, June 2000, Ann Arbor, MI.

⁸ G. Orgill et al., "Development of Electroless Nickel Bath Life Extension – the EDEN System", Trans. IMF, 2001, **79**(5), 87.

⁹ C.V. Bishop et al., US Patent 5,221,328.

¹⁰ Craig V. Bishop "Surface Engineering, a Green Technology" presented 2002 IMF AGM

¹¹ D.M. Johnson, US Patent 2,559,878.

trivalent based passivates were introduced^{12,13,14}. The European End of Life Vehicle (ELV) requirement for hexavalent chrome removal will come into effect in 2007. An array of trivalent alternatives is now available (figure 1): Inorganic based trivalent passivates without cobalt. Inorganic based trivalent chrome passivates with cobalt. Organic trivalent chrome salt passivates with cobalt. Which should be used? Already trivalent based passivates which use peroxide or other potent oxidizers are being eschewed due to their non-inadvertent introduction of hexavalent chromium into the passivation layer. In some cases the choice of substrate (zinc or Zn/M alloy) may direct the decision. In all cases it is likely that examination of the various impacts of the differing trivalent passivate processes in terms of environmental metrics will provide insight into what processes will enjoy the greatest commercial success.

In our laboratories at this time totally non-chromium passivation processes are being developed. We are presently wrestling with ways to decrease the energy metric in one of the processes that, in all other metric categories, matches or exceeds both thick and thin film trivalent chromium passivates. To achieve metric values we merely rely upon the operating temperature of the process and assume that equivalent masses of parts are each heated to the operating temperature of the processing bath since energy is proportional to the product of mass, heat capacity of the parts, and temperature difference. In table three a simple comparison is made for various non-hexavalent processes based solely upon energy metric. This simple calculation points out why consideration of more than one metric may be critical in developing a greener process. Compromises with cobalt introduction and NSS are necessary if lower operating temperatures with zinc are required. If cobalt is to be avoided and lower energy requirements sought then specific alloys of zinc iron and zinc nickel must be used and their environmental metrics also considered. This discussion has avoided incorporating the post treatments that are becoming common with non hexavalent passivation of zinc and zinc alloys. To properly evaluate a process using environmental metrics we should include all dissimilar processes including recommended sealers, top coats, curing cycles, etc. While the process may be complex the environmental metrics simplify comparison. In general, the use of environmental metrics will involve some compromises in deciding upon process and sequence.

Zinc alloy plating has also had a long history and only relatively recent widespread acceptance. Electroplating has counter-intuitive and poorly understood abilities to produce 'anomalous' alloys (where the more noble metal is not deposited as quickly as the less noble metal) and alloy mixtures with crystallite phases that are at non-equilibrium states compared to pyrometallurgical alloys. Many alloys, especially zinc nickel has both behaviors¹⁵. Electrodeposits in general may exhibit 'preferred orientation' crystal structure when examined by X-ray diffraction. Such preferred orientation suggests anisotropic material properties exist. For an alloy of 5% nickel careful examination by XRD or TEM may find small amounts of gamma phase alloy that only exists in pyrometallurgical alloys at nickel concentrations above 12%. In a similar way above 12% nickel an electrodeposit may have significant amounts of zinc phase crystallites. Additives affect the degree of preferred orientation. Taken as a whole these properties allow corrosion resistance from gamma phase to be varied and combined with zinc phase material properties. The resulting 'high' alloy has achieved very high acceptance as a coating, especially in Europe.

Why?

The productivity metric of replacement frequency is vastly reduced when high alloy zinc nickel is used rather than its half brother of low to mid alloy, or its cousins zinc iron, zinc cobalt and zinc. Predicted product life of high alloy zinc nickel plated parts, based upon NSS and a variety of cyclic tests,

¹² Bishop, Foley, Frank, US Patent 4,171,231.

¹³ Guhde et al., US Patent 4,263,059.

¹⁴ Such as Huvar, US Patent 4,349,392; Crotty, US Patent 4,578,122; and Klos, US Patent 5,368,655.

¹⁵ Silomon et al., "Werkstoffliche Betrachtung von galvanischen Zink- und Zinklegierungsüberzügen und deren Nachbehandlungen", Galvanotechnik, **91** (2000), 2932.

typically is 3 to 8 times those of zinc, zinc iron, zinc cobalt or low to mid alloy zinc nickel¹⁶. In some cases the high alloy is a cost effective alternative to organic coatings even with hydrogen relief requirements.

To understand the importance of replacement frequency and lower cost alternatives please visit the NACE web site "The Cost of Corrosion"¹⁷. There is a recent report, over 700 pages long, describing some of the value of what the surface engineering community does. Table four lists the impact of corrosion from a variety of studies reviewed by NACE. The studies indicate corrosion costs to average 3.1% of gross domestic product (GDP) with little change over the past quarter century although cleaner air has reduced corrosion in some sectors, such as infrastructure¹⁸. For the US this was ~\$276 billion in 1998. Metal finishing helps contain the costs. The NACE study estimates the cost of corrosion protection by metal coating to be ~\$1.4 billion dollars and by corrosion resistant special purpose organic coatings to be ~\$2.3 billion of which automotive was ~\$1.3 billion. The NACE study estimated that state-of-the-art technologies could save \$70-\$80 billion. Processes that can extend a part's lifetime by factors of three or more, such as high alloy zinc nickel, and/or reduce such costs have an excellent chance of commercial success.

In our labs and in others around the world there is a competition to find a better sacrificial, heat and corrosion resistant alloy than high alloy zinc nickel. We must also report that this difficult child continues to provide surprises. Colleagues in the UK have produced an interesting high nickel zinc alloy that is much more bendable than the high alloy process of the past decade. This new process is currently in alpha test trials being applied to tubing prior to bending.

There are many examples of projects where environmental metrics have been or are playing a role: In development of non-cyanide zincates, in developing process control software, in testing ionic liquid electrolytes, and in attempting to develop in line or at line process analytical methods.

'Green' technology can be practiced at many levels including the laboratory level. Rather than do test after test and generate waste after waste can we do our experiments using computer models?

Computational Chemistry:

In order to develop a new process, our industry has tended to rely upon empirical methodologies. In 1979, while on a mountaineering trip to the Mexican volcano Orizaba, this paper's authors began to consider improvement of electroplating additives using methods similar to those being developed in pharmacology¹⁹. One author (Chuck McFarland) has an interest in mathematics and had been working with finite element and finite difference analyses of primary and secondary current distributions in Hull cells and similar testing devices²⁰. As a student, the other author (Craig Bishop) had worked for Mike Wartell²¹, a physical chemist who was interested in moving quantum mechanics programs from large mainframe computers to the emerging desktop machines of the seventies. He had Craig program simple Hückel molecular orbital calculations using clever algorithms from the Soviet $Union^{22}$.

After our trip we attempted to examine structurally dissimilar additives that appear to function ('brighten' or 'level') in a plating solution in a similar manner. Examining the computationally derived properties of such molecules, using what was available at that time, did not reveal any unique properties that could be used to help direct synthesis of new molecules. But, as the 1980's progressed, hardware and

 ¹⁶ Paul Wynn, "Zinc Nickel Electroplating in the New Millennium" AES SUR/FIN 2001, Nashville, TN.
 ¹⁷ "Corrosion Cost and Preventive Strategies in the United States", FHWA-RD-01-XXX, Sept. 30, 2001, http://www.corrosioncost.com/home.html

¹⁸ Desmond Makepeace, "So you want to stop it rusting! Zinc coatings and their performance", Materials Processing Initiative Workshop, Midlands Engineering Centre, Birmingham, UK, Mar., 2001.

 ¹⁹ W.G. Richards, "Quantum Pharmacology", Butterworths, London and Boston, 1977.
 ²⁰ C.W. McFarland, AESF 68th Sur/Fin Conference, 1981, Boston, MA and AESF 69th Sur/Fin Conference, 1982, San Francisco, CA.

²¹ Currently Chancellor/ Professor of Chemistry at Indiana Purdue Fort Wayne University.

²² V.N. Faddeeva, "Computational Method of Linear Algebra", translated by Curtis D. Benster, Dover Publications, NY, NY, 1959.

software kept advancing (which, of course, they continue to do), and increasingly powerful programs became available (e.g., the public domain, semi-empirical computational chemistry program known as MOPAC²³). There were very good predictions of conformational and thermodynamic properties of molecules that consisted of atoms not having d orbital properties. Craig's aerospace projects had involved thermodynamic modeling which would predict equilibria amongst many species²⁴. In order to make these predictions reliable, free energies and entropies of formation must be available. With many electroplating salts and additives such data was scarce, particularly in solution. By the start of the nineties, computational methods had now improved the situation.

Using derived data from molecular models in a thermodynamic multiple equilibrium model we were able to successfully predict concentrations in mixtures of silanes in mixed alcohol solvents where trans-esterification occurs. The predictions were verified by ²⁹Si and ¹³C NMR spectra. We also used computer models to test imaginary silanes for bonding efficacy and hydrophobicity by simply comparing the geometry of the imaginary siloxanes (hydrolyzed silane), in aqueous solution, to the predicted geometry of the siloxanes we knew had the necessary bonding and hydrophobicity²⁵. When we converged upon a silane that looked promising it was synthesized and tested and found to meet the bonding and water repulsion characteristics we had been trying to match²⁶. It was our first success at *in silico*' development.

The production of experimental data has also not abated over the years. Here, too, computer power can be utilized for the compilation of, and the efficient searching of, databases of laboratory measurements. We have found the NIST Standard Reference Database 46²⁷ (NIST Critically Selected Stability Constants of Metal Complexes) to be usefully comprehensive (almost 90,000 stability constants, acidity constants, enthalpies, and entropies). Combining NIST Database 46 information with a "Gibbs energy minimizer" algorithm like that present in Outokumpu's HSC Chemistry program (http://www.outokumpu.com/hsc), we can ask (and answer) fundamental questions. In table five are listed the predicted species and concentrations for simple, additive free, electrolytes of typical acid and alkaline zincs. The highlighted free metal ion concentrations are related to electrodeposition potentials via the Nernst equation. The enormously different free zinc ion concentrations found in acid zincs and alkaline zincs have more than a little to do with the metal plating efficiencies exhibited by these two types of solutions.

Table five is a static listing of the concentrations of chemical species in just two formulations. Current programs allow us to obtain more dynamic views of "what if" situations. Suppose, for example, we are studying zinc nickel alloy plating, and have a complicated mixture containing a compound known (from the NIST Database) to bind more strongly to nickel than to zinc. Figure 2 shows us that the free nickel ion, present in greater concentration than the zinc before the complexing compound is added, rapidly declines to a concentration two orders of magnitude less than that of zinc (the zinc ion concentration itself is unaffected). Such an outcome undoubtedly is related to the alloy composition which is plated out. Modern graphics software further enables us to visualize the effects of varying several parameters at the same time.

For that matter, we need not confine ourselves to atomic and molecular calculations. There is a lot of effort being given to the modeling of the properties of materials, and the amount of our work in this area is increasing. Phase diagrams, stress-strain relationships, adhesion factors, and electrocrystallization mechanisms are examples of things which interest us. ASM International (The Materials Information

²³ The latest version of MOPAC, developed by J.J.P. Stewart and distributed by Schrödinger, can be found at http://www.psgvb.com/Products/mopac.html

²⁴ One program from that period was StanJan, http://blue.caltech.edu/tcc/stanjan.html

²⁵ John Palladino, US Patent 5,073,456.

²⁶ Craig V. Bishop, US Patent 6,215,011.

²⁷ NIST Critically Selected Stability Constants of Metal Complexes: Version 6.0, http://www.nist.gov/srd/nist46.htm

Society; http://www.asm-intl.org/) and The Minerals, Metals & Materials Society (TMS; http://www.tms.org/) are examples of professional organizations which are sources of further information. For instance, the 2002 TMS Annual Meeting featured a conference titled "Computational Modeling of Materials, Minerals, and Metals". Fundamental issues such as predicting or even understanding anomalous co-deposition remain to be solved. A model that could predict corrosion behavior of co-deposited species is needed. And, an understanding of the material relationship of preferred orientation in electrodeposits and anisotropic behavior remains elusive.

The pace of better programs becoming available^{28,29} and expectations increasing is undiminished. Ab initio computations may now be performed on PC's. We may not discuss all the projects that currently employ computational development methods but we can demonstrate the need for such methods. With empirical methods test chemicals would be ordered or synthesized and plating tests (e.g., with the Hull cell) run. When some success is achieved, patents are filed and the new process is taken to the field. The process iterates upon itself until commercial viability is achieved. Empirical methods tend to stop development after commercial success. Other ideas that might have been tried had they been in the testing queue prior to the success may be 'shelved' or abandoned. Today the development cycle must include much attention to environmental concerns and as many environmental metrics as possible should be minimized if commercial success is likely. The matrix now becomes too large in many cases. There are over 1400 materials that are known to bind zinc or nicke l^{26} and perhaps 70-300 additives that reliably and favorably affect electrodeposition appearance. In solution each of these species may create three or more ions and in many cases complex ions can arise. A typical alloy bath will have nearly two to three times as many species as single-metal solutions and the free zinc and alloying metal ions may be 3-6 orders of magnitude less in concentration. By preparing models of systems that have successful additives a pattern may be obtained of free metal concentration vs. additive (as shown before in figure 2) or salt in the presence of additive. Screening new additives becomes a problem of obtaining thermodynamic data and matching patterns.

Nevertheless, the need for experimental verification of theoretical calculations will stay with us for at least the near future. Even here, though, the use of computers has made laboratory work much easier and more productive. The statistical design of experiments enables one to achieve the happy combination of obtaining a maximum amount of understanding from a minimum number of experiments. Often, a formulation researcher can show that a truly optimum combination of ingredients has been found. Or designed experiments can lead to the best set of desired material properties. Using "design of experiments" as a search phrase in the Internet Google search engine (http://www.google.com/) readily leads one to useful references and software packages.

It may be that a person has generated lots of experimental data over time, or that techniques which tend to produce much data (analytical spectroscopy comes to mind) are being used. Here, too, powerful computer methods are available. Chemometrics (the application of statistical and mathematical methods to chemical data) allows one to ferret out valuable information from seemingly unmanageable masses of numbers. An example is our ongoing interest in deriving the concentrations of many dissolved chemical species from a few spectra (ideally, just one spectrum). We have most often utilized the PLS (Partial Least Squares) algorithm, but a good many other techniques are "out there". The Homepage of Chemometrics (http://www.acc.umu.se/~tnkjtg/chemometrics/) is a good academic site to visit for learning more.

²⁸ Charles W. McFarland, "Small Business Chemist Meets the Cray", Ohio Supercomputer Center Visions, Issue **5.4**, Fall 1992.

²⁹ PC program examples: HSC Chemistry © Outokumpu Research; Gaussian © Gaussian, Inc.

Conclusions:

Employing environmental metrics at nearly every stage of the development cycle can help assure 'green' products and likely economic success. As an alternative to empirical development methods for new electroplating solutions, computational chemistry may enable more comprehensive testing of candidate molecules with diminished impact upon the health of workers and the environment.

Table 1 Typical environmental conservation, pollution and productivity metrics.						
CWRT Alliances ¹ "Eco-Efficiency Metrics"	"Bridges" Process Economic Program Library Metrics	"Bridges" CEP, July 2002	NCMS Benchmarking Metal Finishing	Proposed productivity metrics		
Material intensity	Material intensity	Material intensity	Electricity usage Total energy used	Labor used		
Energy intensity	Energy intensity	Energy intensity	Water generated	Replacements while in service		
Toxics dispersion, human health risk, greenhouse gas, photochemical ozone creation, acidification, eutrophication	Toxics dispersion Pollutants dispersion Greenhouse gas	Toxic emissions Pollutant emissions	Organic chemical emissions Sludge generated Sludge land-disposed			
Material recyclability	Water consumption	Water consumption				
Use of renewable						
Product durability						
Service intensity						

Table 2 Summary data from "Benchmarking Metal Finishing". The processes are those that had the greatest number of respondents. Red indicates the process with the highest value for a particular metric. The bottom two rows may not have statistically significant variation between processes as do sludge values under anodizing. Data in parentheses are normalized values.

	Zinc	Nickel	Decorative Cr	EN	Anodizing	Hard Cr
Water (gal/\$ sale)	4.79 (24)	1.99 (10)	2.27 (11.35)	1.42 (7.1)	1.96 (9.8)	0.20(1)
Sludge generation (lb/\$ sale)	0.0542 (9) 0.0164 (rack) (2.7)	0.0164 (2.7)	0.00658 (1.1)	0.00824 (1.4)	-0.01548 (2.5) statistical aberration	0.00601 (1)
Sludge land-disposed (lb/\$ sale)	0.0245 (16.3)	0.0015 (1)	0.00530 (3.5)	0.0113 (7.5)	-0.0186 (12.4)	0.0021 (1.4)
Electricity (kWh/\$ sale)	0.51 (3.4)	0.45 (3)	0.46 (3.1)	0.15 (1)	0.49 (3.3)	0.54 (3.6)
Energy use (BTU/\$ sale)	6,306 (4.9)	6,967 (5.4)	7,115 (5.5)	1,300 (1)	4,020 (3.1)	4,649 (3.6)
Organic emissions (lb/\$ sale)	0.00269 (4.6)	0.00153 (2.6)	0.00206 (3.5)	0.00155 (2.6)	0.00059 (1)	0.00193 (3.3)

(seals, top toats, turing cycles are ignored).					
	Blue inorganic CrIII passivate	Iridescent inorganic 'thick' CrIII (no Co) passivate	Blue inorganic Co/ CrIII passivate	Iridescent organic salt 'thick' Co/CrIII passivate	Clear inorganic electrophoresis (non cobalt non chrome passivate)
Substrate	Zn and ZnM	Zn/Fe, Zn/Ni	Zn and ZnM	Zn, Zn/M	Zn, Zn/M
Operating temperature	RT	52-57 °C	RT	71-77 °C	82-93 °C
NSS FWR	~24-72 hrs	~120-400 hrs	~72-96 hrs	~72-120 hrs	~72-120 hrs
Replacement metric (96 hrs minimum)	1.33-4	0.24-0.8	1-1.33	0.8-1.33	0.8-1.33
Heat energy required / mass of parts	0	~26 mCp	0	~46 mCp	~59 mCp

 Table 3 Rough estimate of heating energy needed by various non hexavalent zinc And zinc alloy passivation methods (seals, top coats, curing cycles are ignored).

 Table 4 NACE¹⁶ summary –

 Economic impact of corrosion from several reports.

Country	Year	Estimated Cost (\$MM)	% GDP	Author or Organization	
USA	1949	\$5,500	2.1%	Uhlig	
UK	1970	\$1,365	3.5%	Hoar	
Japan	1974	\$9,200	1.8%	Okamoto	
USA	1975	\$70,000	4.2%	Battelle/NBS	
Australia	1982	\$2,000	1.5%	Cherry & Skerry	
Kuwait	1987	\$1,000	5.2%	Al-Karafi et al.	
W. Germany	1967	\$6,000	3.0%	Behrens	
Finland	1965	\$54		Linderborg	
India	1960	\$320		Rajagopalan	
USA	1998	\$257,700	3.1%	NACE	
average			3.1%		

Acid Zinc	Input	Equil.	Alkaline Zinc	Input	Equil.
H2O	4.86E+01	4.86E+01	H2O	5.15E+01	5.17E+01
BO2(-a)		3.13E-05	H (+ a)		6.37E-15
B(OH)3(a)	4.85E-01	2.34E-01	HZnO2(-a)		3.77E-03
B(OH)4(-a)		1.57E-05	Na(+a)		1.48E+00
Cl(-a)		3.00E+00	NaOH(a)	2.50E+00	1.02E+00
H (+ a)		6.23E-06	OH(-a)		1.18E+00
HBO2(a)		8.34E-07	Zn(+2a)		9.99E-18
H3BO3(a)		2.51E-01	ZnO(a)		2.15E-07
H2BO3(-a)		2.49E-06	ZnO2(-2a)		9.98E-02
HCl(a)		3.65E-06	Zn(OH)2(a)	1.53E-01	2.20E-05
K(+a)		2.85E+00	Zn(OH)4(-2a)		4.86E-02
KCl(a)	2.88E+00	2.49E-02	Zn(OH)3(-a)		8.22E-04
KOH(a)	2.00E-04	1.21E-04	ZnOH(+a)		1.69E-11
OH(-a)		1.13E-09			
Zn(+2a)		2.40E-02			
ZnCl2(a)	5.35E-01	3.83E-01			
ZnCl(+a)		1.14E-01			
ZnCl3(-a)		1.42E-02			
Zn(OH)2(a)		4.90E-08			
Zn2(OH)(+3a)		2.07E-07			
ZnOH(+a)		3.91E-05			

 Table 5 Predicted species and concentrations (moles/liter) using the HSC program for additive free acid

 KCl and alkaline zinc electrolytes (a=aqueous species).



Figure 1 Fracture studies of non-annealed trivalent chrome based passivates on zinc and zinc alloy obtained using field emission SEM. Clockwise from upper left, 'thick' film organic (TFO) CrIII and Co on Zn, CrIII black on ZnFe (room temp.), 'thick' film inorganic (TFI) CrIII on ZnFe, *ibid.* on ZnNi, TFO CrIII and Co on ZnNi, *ibid.* on ZnFe. Unless noted process temperatures of ~60°C.



Figure 2 Predicted variation in zinc and nickel ion concentration as a function of one complexer in a three complex alkaline Zn/Ni system.