

Conversion Coating Science and Technology -Is It Still Evolving, or Is It Stuck?

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Overview. Chromate conversion coatings (CCCs) are used to increase the corrosion resistance and paintability of aluminum alloys (1,2). For most of their 90-year recorded history, the evolution of CCCs on aluminum has been characterized by technologically significant innovations, which were prompted by the need to improve either coating performance or processing.

It can be argued that conversion coating technology has been in a developmental rut for the past 15 years. Chromate use in surface finishing faces regulatory extinction because of chromate toxicity (3). R&D investment in chromate conversion processing has been small outside of reducing the Cr profile in bath formulations and development of engineering controls to reduce worker exposure and environmental release. On the other hand, significant R&D investment has been made in Cr-free conversion coating technology. Many diverse approaches have been explored (4-7). Have any crossed the commercialization threshold and showed sustained profitability? Certainly none have the extreme versatility of CCCs.

The Edisonian approach that has characterized much of the Cr-free development effort has received strident criticism since no broadly applicable Cr-free alternatives have emerged despite 15+ years of research (8). There is no doubt that the Cr-replacement problem is difficult scientifically, but in an attempt to more properly direct coating technology development, the U.S. DoD has commissioned several large research activities aimed "reverse engineering" chromate corrosion protection, including CCCs. These activities have also been criticized as not being "forward-looking". The success of the DoD investment experiment will depend on how well chromate corrosion protection has been diagnosed, and how well these principles can be applied using environmentally acceptable chemistries.

The Past. Chromate conversion coating evolution has been characterized by considerable innovation. A selected list of these developments illustrating this innovation is presented as follows:

- (1910 - 1920) Conversion coating in alkaline carbonate-chromate solutions was developed for Al alloys, which were emerging as important lightweight structural materials (9).
- (1934) Dichromate sealing of hydrothermally grown polycrystalline Al oxide coatings was developed (10). Corrosion resistance in mildly aggressive aqueous environments was noted.
- (1940s) Acid chromate-phosphate-fluoride formulations arose (11). These chemistries produced thin amorphous coatings with excellent corrosion resistance. Coatings formed in a matter of minutes during immersion or during spray at ambient temperatures.
- (1940s) World War II. The demand for corrosion protection of various metal parts in military systems used in tropical and marine climates during the war stimulated widespread use and increased experience with chromate metal finishing.
- (1950) Acid chromate-fluoride formulations, in which

dichromate was the primary film forming agent, came into widespread use in the late 1940s and early 1950s. (12,13).

- (1950s) Self-healing was recognized as a component of chromate coating protection in acidic chromate-fluoride formulations of the 1950s (14).
- (1970) Perhaps the last significant development in CCC chemistry was the use of accelerants (15). The predominant accelerant in commercial formulations was ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$.
- (1992) Coating formulations for reducing of cracking due to drying were patented.

The present. As a result of past innovations CCC technology is exceptionally versatile; coatings may be applied by immersion, spray, or rolling. Coatings may be applied to a wide range of aluminum alloys and other metals. Coating technology is robust, mature, trusted, and inexpensive. Nonetheless, chromate is a potent human carcinogen, and its use is accompanied by intense scrutiny from both the public and private sectors. As a result, this technology is becoming increasingly costly to use, and identification and implementation of replacement technologies is a high priority.

The future. Several general classes of approaches and chemistries have been explored as CCC replacements (4-7). These include sol-gel and sol-gel-like processes involving chemistries based on Al, Si, Ti, Zr. Precipitated coatings have been formed from Ce, Mn, Co, Li, and Al chemistries. Novel techniques and materials such as silane coupling agents and conductive polymer coatings are also receiving attention. Currently there is no frontrunner technology poised to broadly replace of CCCs. In the absence of revolutionary advances in structural alloy corrosion resistance or surface engineering, CCC replacement will not occur until its performance, ease of application and low cost is exceeded.

- 1) T. Biestek, J. Weber, Electrolytic and Chemical Conversion Coatings, Portcullis Press Limited-Redhill, Surrey UK, (1976).
- 2) S. Wernick, R. Pinner, P.G. Sheasby, p. 220 in The Surface Treatment and Finishing of Aluminum and Its Alloys, 5th ed., Vol. 1, ASM Int., Metals Park, OH (1987).
- 3) P. O. O'Brien, A. Kortenkamp, *Trans. Met. Chem.*, **20**, 636 (1995)
- 4) B. W. R. Hinton, *Metal Finish.*, Sept., 55 (1991) and Oct., 15 (1991).
- 5) M. W. Kendig, R.G. Buchheit, p. 1 in *Surface Conversion for Aluminum and Ferrous Alloys for Corrosion Resistance*, NACE, Houston, TX (2000).
- 6) R. L. Twite, G. P. Bierwagen, *Prog. in Org. Coatings*, 33, 91 (1998).
- 7) S. M. Cohen, *Corrosion*, 51, 71 (1995).
- 8) U.S. Air Force Blue Ribbon Advisory Panel Report (1995).
- 9) O. Bauer, O. Vogel, *Ger. Pat. Spec.* 423 758 (1923).
- 10) J. D. Edwards, U.S. Patent No. 1 946 151 (1934).
- 11) J. Spruance, U.S. Patent No. 2 438 887 (1945).
- 12) W. Marchand, *Electroplat. and Metal Finish.*, **14**, 439 (1961).
- 13) S. Spring, K. Woods, *Metal Finish.*, **79**, 49 (1981).
- 14) G.W. Ostrander, *Plating* **38**, 1033 (1951).
- 15) N.J. Newhard, *Metal Finish.*, p. 69, July (1972).
- 16) L.J. Bailin, Kostinko, U.S. Patent 5 123 978 (1992).

