Functional Single-Cell Trivalent Chromium Electroplating Method

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This presentation will introduce and explain a completely new technology which successfully replaces hexavalent chromium compounds used in electroplating with a hazard-free, trivalent chromium-based method. More specifically, the technology relates to the hexavalent-free bath and plating method to achieve crystalline, thick, wear resistant functional chromium plating.

The functional coatings industries have recently taken an approach which suggests that only replacement alternatives to chromium metal, such as tungsten carbide, will compete with traditional hexavalent-chromium. The presentation will show that problems associated with electroplating with hexavalent chromium can be addressed without the necessity of using chromium "alternatives".

Historical and widely known developmental difficulties of trivalent chromium are eliminated; the Process addresses stability of electrolyte, anode issues, and is a single-chamber procedure. Significantly, unlike trivalent-based systems used presently, coating thicknesses of more than 250µm (10000µin.) can be readily achieved. Characteristics including hardness, abrasion resistance, and rate of deposition meet or exceed those achieved by hexavalent compounds.

Supportive and conclusive tests, performed by separate and independent laboratories according to the Federal "QQ-C-320IIB" specifications, will be made available during the Conference.

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SCIENTIFIC BACKROUND

The technology offered herein is based on the use of a particular ligand, which when complexed with ions of Chromium III, results in high stability of the resultant electrolyte within a wide range of temperature during plating as well as during periods of non-use or storage. Also, the present technology is based upon the findings that the use of a particular anode, of special ratio to cathode, in combination with the use of mentioned ligand, results in chromium electrodeposits of exceptional quality from the Cr3+ complexed electrolyte, preventing the formation of hexavalent chromium. Said technologies enable the plating process to occur in a single tank compartment.

The anodes used are of platinized titanium. A proprietary buffer utilized as part of the electrolyte broadens the range of the current density of chromium plating to 20 - 50 A/dm^2 (1 - 3 A/in^2) with the temperature range of 30 -50°C (85 -125°F) and pH range of 1.0 -2.5. The speed of plating depending on conditions is 1 - 3μm/min. (40 - 120μin/min.).

After thermal treatment the chromium deposit exhibits hardness in the range of 1100-1200 HV. This unusually high hardness is due to the presence of carbon in the deposit, with FES data indicating 0.2% chrome carbide present in the coating lattice.

PRESENTLY AVAILABLE PRODUCTS: PROBLEMS AND CONDITIONS

Electro plated chromium has been in commercial use for over 75 years. Used as a wear resistant coating on parts such as gun bores, piston rings, and hydraulic piston/cylinder sets; and as a decorative coating in automotive, surgical, and home appliance industries it is usually deposited via an electrolyte containing chromium in the hexavalent chemical state; in this form, chromium (Cr+6) is a known carcinogen and has been targeted for significant use reduction in the United States and most industrialized nations.

The chromium electroplating industry therefore is affected by both general public awareness and governmental (OSHA, EPA, DEP, etc) scrutiny. Growing concerns have resulted in regulations such as the end-of-life vehicle directive in the European Union which prohibits the use of traditionally plated parts in automobiles sold in the EU. Most recently, in February 2006 the United States

Congress approved legislation reducing employee exposure to hexavalent chromium by one order of magnitude: from 52 micrograms/cubic meter to 5, per eight hour weighted daily average per employee. This legislation will have dramatic financial impact on all chromium electroplaters both in the U.S. and abroad, requiring large capital investments for compliance with the new standard.

Due to the unique characteristics of chromium as a functional and decorative coating, it has retained widespread use in major industrial market segments. Other coatings have been utilized as, or developed as intended replacements for chromium. While some of them have found limited acceptance, the fact remains that none of them reproduce the full range of desirable characteristics of chromium such as hardness, lubricity, anti-galling properties, and both molecular adhesive and cohesive strengths.

Due to difficulties encountered during the development of various trivalent chromium plating technologies, the industry found itself best served using differing approaches to what became separate and distinct market categories: functional and decorative. Ideally, the desirable characteristics of chromium would be produced using a single, simple to control trivalent -based electrolyte suitable for both decorative and functional applications. This paper recognizes the broad amount of research devoted to such a product, however it is well known that no such technology has to date been successfully created. Presently-offered trivalent chromium systems have not found widespread use for a variety of reasons including instability, expense, and difficulty of control. The technology being presented solves these problems, due to the stability, ease-of-use, and inexpensive implementation of a process easily adaptable to both functional and decorative chromium market applications.

A large market remains for industries which desire to continue to use chromium as their coating of choice. However, until successful development of the herein-described technology, no method has been invented which is capable of electro or chemical deposition of chromium metal via a harmless chromium-containing electrolyte.

PROPERTIES AND CHARACTERISTICS

The Technology herein described is unique in its ability to serve, in many cases, as a "drop-in" replacement for existing single-cell, chromium-based electrolyte systems. Equipment typically used in both functional and decorative methods will be incorporated into systems using the described electrolyte. Naturally, this technology does not serve as remediation for hexavalent chromium already present in the system or building to be converted; nonetheless, this new technology neither utilizes nor creates hexavalent chromium in the electrolyte once use has ensued. Hexavalent electrolytes, if currently in use, must be removed in order to correctly utilize this technology. Wet bed air scrubber devices are not presently required by Federal regulation for use with trivalent plating systems; our research team does not anticipate or expect users to endure expenses associated with such air purification systems. The current traditional systems can be utilized as a part of this technology (the tank material, air equipment and material of anodes can be used as the tank for preparation of metals prior to plating).

The electrolyte replenishments consisting of the chromium salt and ligand are easily calculated based on A-hr. Additions can be made via manual or automated methods.

Operating parameters including temperature, current density, and pH values have broad ranges, and are dependent upon the requirements of the coating being produced.

A variety of coatings can be easily engineered, depending on the requirements of the final product, to ensure the qualities the industry is looking for – wear resistance, corrosion protection, ductility, and other desirable metallurgical properties. In addition, this simple to use method can be utilized as a replacement for hexavalent chromium in a broad range of decorative applications.

Structure

Historical and widely known developmental difficulties with trivalent chromium technologies are largely due to the non-crystalline (amorphous) structure of deposits achieved, which in turn leads to limited thickness, poor adhesion, low hardness, no corrosion or wear resistance and therefore an undesirable coating. The technology presented here has eliminated all of the above mentioned difficulties by delivering a crystalline body-centered, cubic structure chromium metal deposit with columnar build-up (typical for metallic, electrodeposited chromium), ensuring thicknesses in excess of 250 μm (10000μin) with properties including hardness, adhesion, corrosion and wear resistance meeting or exceeding those achieved by conventional chromium technologies. (See slide)

QQ-C-320II: PROPERTY CHARACTERISTICS (See slide)

SUMMARY

The chemistry of the technology offered here is safe and economical compared to traditional chromium electroplating methods. Chromium sulfate, a major component of this technology is much more economical than chromium trioxide; the ligand is the fraction of the cost of Chromium sulfate.
Factors listed below are expected to reduce operating and capital costs by 20-70% depending on existing facility equipment and standards:

- Absence of wet-bed scrubber systems
- Elimination of air and water treatment systems required by hexavalent use
- Energy savings resulting from efficiency of the bath
- Raw material, and make up, chemical expenses.
- Exceptional savings due to applicability as a “drop-in” replacement in both functional and decorative installations.

