Proceedings of the 2006 IASME/WSEAS International Conference on Energy & Environmental Systems, Chalkida, Greece, May 8-10, 2006 (pp11-14)

NEW ENVIRONMENTALLY FRIENDLY METHODS AND MATERIALS IN SURFACE TREATMENT

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Abstract: - This work presents an overview of our research work to develop environmentally friendly methods in different chemical processes (mainly surface treatment). Chrom-free methods in different chemical processes (mainly surface treatment – anticorrosion protection of metal alloys like aluminium and/ or magnesium, metallization of plastics, anticorrosive treatment of tin plate etc) have been developed. A new class of materials, the conductive polymers and in particular the polypyrroles (Ppy) have been used for these methods. Applications of Ppy are presented, referring to corrosion protection of Al and Mg alloys and metallizing of plastics (ABS and glass-reinforced epoxy polymers).

Key-Words: - Chromium; conductive polymers; polypyrrole ; corrosion- protection; etching; metallization;

1 Introduction

In recent years intrinsically conductive polymers (henceforth ICPs) have attracted much attention as advanced materials and have led to the development of novel and diversified applications. ICPs have a number of interesting features that make their application in industry particularly attractive. The most interesting property of ICPs is the high, almost metallic electrical conductivity. In advance, ICPs can be deposited even in complex topographies and possess sufficient mechanical properties within copolymers. They have low density and good flexibility and they are often redox reactive. Finally, ICPs belong to a small class of materials changing their properties by reversible intercalation processes. Thus, various technological applications of these novel polymeric materials have been proposed in the field of light emitting diodes (LED), rechargeable batteries, gas sensors, micro/nano devices, electrochromic displays, corrosion protection, metallization of insulators, antistatic coatings, shielding of electromagnetic interference, printed circuit technology, for radar avoidance coatings etc.

This class of polymer is completely different from “conducting polymers” which are merely a physical mixture of a non-conductive polymer with a conducting material such as a metal or carbon powder distributed throughout the material [1]. ‘Conventional’ –non conductive polymers have all four electrons of carbon used up in covalent bonds, while in ICPs the chemical bonding leads to one unpaired electron (the π-electron) per carbon atom [2]. π-bonding, in which the carbon orbitals are in the sp^2p_z configuration. A electronic delocalization provides a way for charge mobility along the backbone of the polymer chain.

In advance, the concept of doping is the unique, central and underlying theme, which distinguishes conducting polymers from all other types of polymers [1]. During doping process, an organic polymer (typically in the range of 10^{-10} to 10^{-5} S/cm) is converted to a polymer, which is in the “metallic” conducting regime (~1 to 10^4 S/cm) (Table 1 & 2 specific electrical conductivities). The controlled addition of known, usually small (<10%) non-stoichiometric quantities of chemical species result in dramatic changes in many polymers’ properties. Doping is reversible to produce the original polymers with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counteranions which stabilize the doped state, may be carried out chemically or electrochemically.

Table 1: specific electrical conductivities of various conventional polymers.

Conventional polymers (insulators)	Electrical conductivity (S/cm)
Polyethylene (PE)	10^{-15}
Cellulosic	$10^{-12} – 10^{-16}$
Polytetrafluoroethyleneo	10^{-18}
Polystyrene (PS)	$10^{-17} – 10^{-19}$
Polyester	$10^{-15} – 10^{-16}$

Table 2: specific electrical conductivities of various conductive polymers

Intrinsically conductive polymers	Electrical conductivity (S/cm)
Polyacetylene (PA)	200 – 1000
Poly-p-phenylene (PPP)	500
Polythiophene (PT)	10 – 100
Polyaniline (PANI)	5
Polypyrrole (PPY)	$100 – 10^3$

2 Problem Formulation

Chromium compounds are involved in many metal surface processes (Al and Mg alloys,Tinplate industry etc).

The use and disposal of chromium compounds give rise to a complex environmental and public health protection problem. These compounds received much regulatory attention because of their toxicity (most of these compounds are confirmed or suspected human carcinogens) and there is the tendency their use to be completely banded in the future from all the industrial sectors where contaminated effluents can be produced.

3 Problem Solution

The following environmentally friendly methods are discussed:

1. Application of conductive polymers in corrosion-protection of aluminium alloys (patented method) – replacing of chromatizing. An innovative formula, where polypyrrole based coating could be easily formed on the aluminium surface, has been developed (aqueous system, pyrrole monomer, fluorometal acids, zinc oxide). These conversion coatings show advanced corrosion resistance [5][6][7][8][9][10].

2. Application of conductive polymers in corrosion protection of magnesium alloys -replacing of chromatizing. For the corrosion inhibition of Mg alloys (AZ31) a thin polyacrylic – polypyrrole film, has been developed. The optimized synthesis conditions achieved 70% reduction of corrosion rate with respect to uncoated specimens [11][12].

3. Use of polypyrrole powder as a pigment in conventional anticorrosive coatings (primers) – replacing of zinc chromate pigments. Chemically produced polypyrrole was used after having been grinded and added as pigment in conventional binders like alkyd resins. It was proved that polypyrrole has satisfactory inhibitive properties in a corrosive milieu of sodium chloride [13].

4. Metallization of plastics using polypyrrole coatings - replacing of sulfuric-chromate acid etching solution - direct copper plating without palladium deposition. ABS (acrylonitrile butadiene styrene) specimens were coated *in situ* with polypyrrole. The conventional etching bath, hot sulfuric-chromate acid was not necessary. The Ppy coating was enough conductive for further copper plating [14]. The use of non-toxic chemicals with no etching, no rinsing, and therefore no effluent, makes our methods environmentally friendly.

This technology offers an attractive alternative to the classical methodology that is summarized in the following figure (Table 3 & 4). Advantages of this novel method over the "conventional" one are : no use of precious and hazardous materials, much less steps, environmentally friendly method, ease of processing etc.

Table 3: Conventional method for metallizing non-conductive substrates

Conventional Industrial Method
▪ Degreasing
▪ Polymer etching (chrome-sulfuric acid)
▪ Rinsing
▪ Immersion in $PdCl_2$ – solution
▪ Surface activation / reduction of Pd^{2+} in $SnCl_2$ solution
▪ Electroless Copper or Nickel plating
▪ Degreasing (10%H_2SO_4)
▪ Rinsing
▪ Electrodeposition of Copper
▪ Further process

Table 4: alternative method for metallizing non-conductive substrates based on ICPs

Alternative Method
▪ Polymer etching with $(NH_4)_2S_2O_8$
▪ *In situ* Ppy chemical deposition
▪ Rinsing (water)
▪ Drying
▪ Electrodeposition of Copper

· Further process

A similar methodology has been developed for the metallization of PCBs (Printed Circuit Boards). In this process Ppy is deposited by chemical polymerization, provided on the surface of a glass fiber reinforced epoxy resin (insulating) composite. Thus, through hole plating can be achieved by copper electrodeposition. This method provides promising advantages and is already in industrial use in USA and Europe replacing the graphite through hole technique

5. Application of conductive polymers in galvanoforrming.Galvanoforming is an advanced manufacturing process based on the electrodeposition of a metal (24-carat gold) onto a substructure (duplicated prepared master die i.e. type IV dental stone), after which, the substructure is removed, leaving the electrodeposite as a three-dimensional, stable, homogeneous metal structure. Our research work is being carried out in cooperation with a German company and focuses on facilitating and accelerating the gold deposition by applying on type IV dental stone (gypsum product) a conductive polymer (Ppy)

6. A new chrome-free passivation method of tinplate used in the canning industry - alternative to the traditional cathodic dichromate procedure (CDC). A coating has been developed that is a combination of an acrylic copolymer with an active pigment based on fluorozirconic acid. Results of experiments were encouraging [15][16][17].

4 Conclusion

Environmentally friendly methods in different chemical processes (mainly metal surface treatment-surface modification) have been developed in laboratory scale. The problem of chromium compounds can be tackled using innovative materials like conductive polymers of pyrroles.

References:

[1] A. G. MacDiarmid, "*Synthetic metals*": a novel role for organic polymers – Nobel Prize 2000 Lecture, Current Applied Physics 1, 2001, pp. 269 – 279.

[2] A. J. Heeger, Semiconducting and metallic polymers: the fourth generation of polymeric materials, *Synthetic Metals*, Vol 125, 2002, pp.23 – 42.

[3] D. R. Askeland, *The science and engineering of materials*, ed. Chapman and Hall, 1990.

[4] G. Inzelt, M. Pineri, J. W. Schultze, M. A. Vorotyntsev, Electron and proton conducting polymers: recent developments and prospects, *Electrochimica Acta*, 2000, Vol. 45, pp. 2403 – 2421.

[5] G. Appel G., A. Yfantis, W. Goepel, D. Schmeisser, "Highly conductive polypyrrole films on non-conductive substrates", *Synthetic Metals* 83, (1996), 197-200

[6] A.Yfantis, G. Appel, D. Schmeisser, D. Yfantis "Polypyrrole doped with Fluoro-metal complexes: Thermal stability and structural properties", *Synthetic Metals*, 106 (1999), p. 187-195

[7] A.D.Yfantis, D.Schmeisser, D.K.Yfantis, L.Kompotiatis, "Polypyrrole based conversion coatings for aluminium alloys", *J. ATB Metallurgie*, Vol. XXXX Nr 3-4 2000/Vol.XXXXI, Nr 1-2 2001, pp.527-532

[8] A.D.Yfantis Dissertation, "Development and Characterisation of Corrosion Resistant Layers of Conducting Polymers on Aluminium Alloys" Technische Universitaet Cottbus, Germany, 2000

[9] A.D.Yfantis, D.Schmeisser, *Greek Patent no. 1003763, 18.01.2002* "chemical deposition method of composite conductive polymer on aluminium alloys surfaces."

[10] A. D. Yfantis, D. K. Yfantis, L. Kompotiatis, Filiform corrosion of powder coated aluminium extrusions- the effect of mechanical surface pretreatment, *J. ATB Metallurgie*, vol. XXXVII. No 2-3-4, p.295-298, 199

[11] N. Ahmad N., A.G.MacDiarmid "Inhibition of corrosion of steels with the exploitation of conducting polymers", *Synthetic Metals*, 78 pp. 103 - 110 (1996)

[12] A.Yfantis, I.Paloumpa, D.Schmeisser and D.Yfantis " Novel corrosion –resistant films for Mg alloys" *Surface and Coatings Technology*, Vol.151-152 (2002) pp.400-404

[13] D.K.Yfantis, D.K. Tsiniarakis, S Labrakopoulos, A. D. Yfantis, D.Schmeisser "Conductive polymers of polypyrrole as pigment in organic coatings –Application in aluminium alloys ",*18th Panhellenic Conference of Chemistry* ,Proceedings ,p.78-81 ,(in greek), Piraeus, 2001, Greece

[14] A.Anagnostaki, D.K.Yfantis, S.Labrakopoulos, A.Yfantis, " Application of conductive polymers in metallization of insulators ", *5th*

Panhellenic Conference of polymers ELEP – 2001 Abstracts (in greek), ITE, Heraklion Crete – Greece 2001

[15] D.Yfantis, A. Yfantis, B. Tzalas, D. Schmeisser "A New Chrome -Free Passivation Method of Tinplate Used in the Canning Industry", *Corrosion (NACE)* Vol.56, No.7 p.700-708, July, 2000

[16] D. K. Yfantis, I. Anoussis, A. D. Yfantis, and D. Scordas, "Internal Corrosion of Tin Cans containing Tomato Paste /TomatoJuice - Determination of Fe, Sn and Cr by AAS and INAA" in *Molecular Properties and Chemistry of Biological Systems*, p.221-225, edizioni dell'orso, Italy, 1995

[17] D. K. Yfantis, N. Karakasidis, "The assessments of some types of anticorrosion used for tomato paste tin cans -" *Pitture e Vernici Europe N. 10*, p. 13-21, 1995