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POC-3507; No. of Pages 7

ARTICLE IN PRESS

Progress in Organic Coatings xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

High performance anti-corrosive powder coatings based on phosphate pigments containing poly(o-aminophenol)

M.A. Abd El-Ghaffar[a,*], N.A. Abdel-Wahab[a], M.A. Sanad[a], M.W. Sabaa[b]

[a] Polymers and Pigments Department, National Research Centre, Cairo, Egypt
[b] Chemistry Department, Cairo University, Egypt

ARTICLE INFO

Article history:
Received 6 January 2013
Received in revised form
18 September 2014
Accepted 27 September 2014
Available online xxx

Keywords:
Powder coatings
Corrosion inhibitors
Conducting polymers
Phosphate pigments
Poly(o-aminophenol)

ABSTRACT

Great progress has been devoted recently in the applications of conducting polymers and their composites in corrosion protection of metals by coatings. The ultimate goal of this study is to formulate anti-corrosive hybrid epoxy/polyester and polyester powder coating composites based on phosphate pigments containing poly-o-aminophenol for corrosion protection of steel. The formulations were prepared in two steps. The first step involved *In situ* emulsion polymerization of o-aminophenol in presence of some phosphate pigments (mainly zinc phosphate, Ca phosphate and Ca–Zn phosphates) via chemical oxidation process using ammonium peroxydisulphate. The second step involved the formulation of the various ingredients of the powder coating composites using hybrid epoxy/polyester and polyester as binders with various doses of phosphate pigments and other inorganic pigments and fillers. The prepared powder coating composites were applied on a cold rolled steel panels and were investigated for physico-mechanical properties and evaluated for their corrosion protection properties via salt spray chamber for 1000 h. The obtained results showed high performance anti-corrosive powder coatings formulations for steel protection.

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1. Introduction

Organic coatings are widely used to protect metals against corrosion. It has been estimated that 85% of metal structures exposed to different corrosive media are painted [1,2]. At US $2.2 trillion, the annual cost of corrosion worldwide is over 3% of the world's Gross Domestic Product (GDP). Yet, governments and industries pay little attention to corrosion except in high-risk areas like aircraft and pipelines. Now is the time for corrosion professionals to join together to educate industry, governments, and the public.

Development of protective coatings, free of lead or chromate pigments and containing only safe materials had been enhanced due to the environmental regulations implemented by governmental agencies.

Hence, in recent decades, the surface finishing industry had undergone fundamental changes with respect to the development and promotion of environmentally friendly pigments for primer formulations [3–10]. Phosphate pigments are considered highly effective, safe corrosion inhibitors in various coating applications and safer alternatives for the toxic chromate and lead pigments [11]. This compound had a level of toxicity 50 times lower than chromates [12]. Fillers may also improve film performance, alter its gloss and improve corrosive resistance, as well as increasing the bulk of the paint film. Most paints include small percentages of other additives to improve paint application and appearance. So we can use zinc phosphate as a dual functional pigment due to the presence of zinc ions, that ions may act to form soaps, as well as the phosphate group. Zinc phosphate is also compatible with, and performs well in, a number media including alkyds, chlorinated rubber, epoxy esters and polyurethanes when added to these resins, zinc phosphate improves both the drying property and the adhesion of paint film to substrate. The recent developments in the area of corrosion inhibitors involve the use of non toxic, environmentally acceptable polymers. In an earlier study carried out by our group, polyanilines were synthesized and evaluated as corrosion inhibitors. The results obtained showed aniline polymers as excellent non toxic, corrosion inhibitors for steel protection [13,14]. The fundamental material in paint is the binder – usually called 'resin'. This is usually a liquid which flows out and then dries to form a hard film. In the case of powder coatings, the resin flows when heated – changing from its solid state.

One of the most important classes of thermosetting polymers Epoxy resins are considered and find extensive use in various fields, including structural adhesives, coatings and matrix for

* Corresponding author. Tel.: +20 2 01227901129; fax: +20 2 33355146.
E-mail address: mghaffar50@yahoo.com (M.A. Abd El-Ghaffar).

http://dx.doi.org/10.1016/j.porgcoat.2014.09.021
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Please cite this article in press as: M.A. Abd El-Ghaffar, et al., High performance anti-corrosive powder coatings based on phosphate pigments containing poly(o-aminophenol), Prog. Org. Coat. (2014), http://dx.doi.org/10.1016/j.porgcoat.2014.09.021

high performance composite materials. There is a general trend to improve the conversion rate of thermosetting polymers by increasing the curing temperature, which unfortunately, usually tends to increase the crosslink density and thus leads to a brittle polymer. This is the reason why the toughening of the epoxy resins has been a subject of extensive study during the last years [15–20].

Powder coatings are solvent-free paints applied to metal and other conductive surfaces. They made up of raw materials, similar to other coatings, but without any organic solvents. As a result there is no volatile release of organic compounds (VOCs) into the atmosphere during application. Also, as no solvent is required with powder, there is a reduction of fire risk during storage and handling and also less waste compared to liquid coatings.

Epoxy resin powders exhibit good chemical resistance to solvents, acids and alkaline liquids. A predominant disadvantage of epoxy resin powders is their chalking and yellowing tendency when exposed to UV light. Chalking does mean loss in esthetics, but not in anti-corrosive benefits. Today, epoxy powder coatings nearly exclusively serve in the functional domain, e.g. in the electrical and electronic industry, for automotive parts, fittings, reinforced iron, pipe coatings, etc.

Epoxy/polyester powders, as the name already says, are a blend of epoxy and polyester resins. Featuring better resistance to yellowing and a reduced chalking tendency compared to pure epoxies. These powders are preferably used for decorative purposes, further application fields for hybrids are ceiling elements, lights, metal furniture, shop fittings and shelving, etc.

A disadvantage is the poorer resistance to solvents in comparison with pure epoxy resin powders.

Polyester/TGIC resin powders are used when superior non-chalking and weather-resistant properties are required. Their advantageous mechanical characteristics as impact resistance and good adhesion allow ulterior processing as sawing, drilling or milling. Polyester resins are typically applied to aluminum or steel for outdoor purposes, in particular in the automotive sector, for façade elements, window profiles or high-quality garden and camping furniture. This type of powder is making increasing inroads into the interior decoration market where superior yellowing and chalking resistance is favored. As TGIC is classified a toxic substance, mandatory labeling applies to powder coatings with a TGIC proportion of 0.1%.

Polyester/hydroxy alkylamide powders as an alternative to the above mentioned polyester/TGIC powders, this type of coating was introduced into the market in 1990. Polyester/hydroxy alkylamide powders exhibit excellent weather-resistant and non-chalking characteristics, representing a valid alternative to polyester and polyurethane powder coatings for all outdoor applications.

This study aims to formulate anti-corrosive hybrid epoxy/polyester and polyester powder coating composites based on phosphate pigments modified via in situ emulsion polymeriztion of o-amino phenol for corrosion protection of steel.

2. Experimental

2.1. Materials

Pigments and extenders used included zinc phosphate, calcium phosphate, calcium–zinc phosphate, titanium dioxide (RKB5), carbon black (MB860), iron hydroxide (Yellow 3910), iron oxide (MB370), sodium aluminum sulpho silicate (Blue 5008) and barium sulphate. In addition to the modified phosphate pigments [poly(o-aminophenol zinc phosphate), poly(o-aminophenol calcium phosphate), poly(o-aminophenol calcium–zinc phosphate)]. Ammonium peroxydisulphate initiator. Binders included (Resin + Hardener), Resin [Epoxy resin and Polyester resin], Hardener [XG603-1A (is the salts of poly-carboxylic acid with cyclic amidine) and Primid xl552 (Beta-Hydroxy alkyl amide)]. Additives used included Resiflow PV88 (Wax), Benzoin (Degassing agent), Matting agent (Wax). Materials used were supplied by various Local and International companies.

2.2. Experimental techniques

2.2.1. Preparation of phosphate pigments

Some single and mixed metal phosphate pigments were prepared according to the method reported in a previous study by Abd El-Ghaffar et al. [14]. The prepared phosphate pigments contain one cation e.g. (zinc, or calcium,) or two cations e.g. [(zinc–calcium). The pigments are prepared using the precipitation method by the reaction of divalent water soluble cation salts with phosphoric acid. These pigments are considered as safe and environmentally acceptable pigments, besides being economically feasible. This is in accordance with the international trends in prohibiting the use of hazardous pigments which affect man health or pollute the environment.

The scheme of preparation can be represented as follow:

$$3M(CH_3COO)_2 + 2H_3PO_4 \rightarrow M_3(PO_4)_2 + 6CH_3COOH$$

where M = Ca, or Zn

In case of Zn–Ca phosphate

$$3Zn(CH_3COO)_2 + 3Ca(CH_3COO)_2 + 4H_3PO_4 \rightarrow (Zn{\cdot}Ca)_3(PO_4)_4 + 12CH_3COOH$$

2.2.2. In situ polymerization of (o-aminophenol) in presence of phosphate pigments

(0.1 mol, 10.912 g) of o-aminophenol was dissolved in 60 ml ethanol. 25 g of Ca or Zn or Ca–Zn phosphate pigments was added to o-aminophenol solution with continuous stirring to this mixture (0.1 mol, 22.819 g) ammonium peroxydisulphate is used as initiator was dissolved in 50 ml distilled water and dropwised to o-aminophenol/Ca, or Zn or Ca–Zn phosphate mixture with continuous stirring for 6 h.

The composite was filtered off and the precipitate was washed several times with distilled water, ethanol after that the precipitate was subjected for drying in an electric oven at 110 °C.

The previous steps were repeated using different concentrations of o-aminophenol and ammonium peroxydisulphate [[(0.05 mol, 5.456 g) of o-aminophenol and (0.05 mol, 11.4095g) of ammonium peroxydisulphate] [(0.001 mol, 0.10912 g) of o-aminophenol and (0.001 mol, 0.22819 g) of ammonium peroxydisulphate] in the suitable amount of ethanol and water, after that the composite precipitates were washed several times with distilled water and ethanol and subjected for drying.

The prepared composites of poly(o-aminophenol/phosphate pigments) were introduced in the powder coating formulations (tables) and evaluated as corrosion inhibitors

2.2.3. Preparation of powder coating formulations based on polyester and hybrid epoxy/polyester with modified phosphate pigments

The various ingredients in Tables 7 and 8 were weighed, transferred together to the mixer and stirred for 10 min. The mixture is extruded in the machine to make ships. The ships were ground to powder coating. Steel panels were coated by spraying the powder using electrostatic gun. The powder coating was cured in oven at 200 °C for 10 min.

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