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Anticorrosion Pigments and Derived Coating Systems on Their Basis

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ABSTRACT

The paper deals with a possibility of replacing the toxic anti–corrosion pigments based on lead and chromium salts with the ecologically harmless pigments of at least equal anticorrosion efficiency. A series of anticorrosion pigments reflecting the anticorrosion efficiencies as shown in primers was obtained. The highest efficiencies of the corrosion inhibitors were shown by a zinc ferrite based pigment and a barium calcium phosphosilicate based pigment. The hitherto usual lead and chromium pigments showed an inferior efficiency.

1 INTRODUCTION

1.1 General

Today's coating formulations have to fulfil a number of properties for applicability in modern systems. With primers, the most significant property is resistance to corrosion. Thus, primer formulations always contain appropriate anticorrosion agents (such as anticorrosion pigments or corrosion inhibitors). Further, the substrate must be protected via the so-called 'barrier effect', which involves close bonding between the binders and fillers used in the formulation. In this way, lead can be embodied in a painting formulation, providing the metal substrate with efficient anticorrosion protection.

Nevertheless, efficiency of the coating is not the only criterion for the selection and prospective development of individual types of coating compositions. Requirements for environmental-friendliness are steadily

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rising for both coating compositions and in their production and application. Particularly harmful toxicity can arise from the use of certain anticorrosion pigments and organic solvents. Typical compounds with toxic effects include lead-based pigments such as red lead, lead suboxide and lead powder alone; the group of toxic pigments also includes zinc yellow, the application of which in coating formulations is to be prohibited in the near future.[1]

With respect to this, water-dilutable coating compositions, characterized by a comparatively high dry-matter content, and also coating powders, appear to be potentially useful materials.

1.2 Protective effects of coatings

The coating-compound layers protect the metal substrates essentially via four basic mechanisms based on: (a) the 'barrier effect', (b) the inhibition effect, (c) the electrochemical effect, and (d) the adhesion effect. It has been found that the barrier mechanism alone does not provide the metal surface concerned with long-time anticorrosion protection. Nevertheless, the barrier-protection mechanism combined with the inhibition and adhesion protection systems results in a remarkably increased duration of the protective-coating function.

The barrier mechanism is based on preventing contact of electrolytes with the metal surface to be protected, i.e. it results from the imperviousness of the coating to water. There has not yet been found a binder which is completely watertight. This necessitates, therefore, the metal substrate being subjected to a precoating treatment process to remove all water-soluble substances. When such a process is not carried out, water which diffuses through the coating layer dissolves the salts deposited at the surface, resulting in blistering and loss of adhesion. The protection efficiency achievable through the barrier mechanism depends primarily on the coat thickness. With an increase in layer thickness the porosity falls, which results in increased anticorrosion protection.

It is not practicable to increase the coat thickness above a certain level, with respect to both economic reasons and reduced protection function. At high thickness values internal stresses appear, resulting in coat/surface adhesion losses and inferior physicomechanical resistance properties.

The corrosion processes occurring at the surface of steel under the coating layer require both oxygen and water for their development. Of the pigments which exhibit only the barrier effect (i.e. which remain chemically intact in the system concerned), the most broadly used ones are micronized talc with a flake structure, micronized mica with a chip structure, aluminium flakes, iron-containing mica, and glass flakes.

The use of the barrier pigments in the coats is not universal. It depends not only on the particle shape, but also on their chemical composition. The barrier protection effect is also involved in coating compositions which do not contain any plate pigments and any inhibition-inducing pigments. In such compositions the protective function is proportional to the adhesiveness of the coats concerned. The adhesion power of a coat to the metal surface to be protected results from the ability of the molecules concerned to form hydrogen bonds between the metal surface and the binder; the surface of most metals is covered with an oxide film, the oxides being able to bind the polar polymer groups.

The inhibition mechanism in the coating layer is secured, in most cases, by the effects of anticorrosion pigments. To a minor extent, the coating compositions additionally contain organic corrosion inhibitors, which also act via the inhibition mechanism. The problems of replacing the most common anticorrosion pigments such as red lead, lead suboxide and zinc yellow have not yet been fully resolved.

Of the nontoxic anticorrosion pigments, the most important are:

—zinc phosphate ($Zn_3(PO_4)_2 . 2H_2O$)
—calcium and zinc molybdate
—calcium and zinc ferrite
—aluminium triphosphate
—aluminium polytriphosphate
—zinc aminosalicylate
—calcium salicylate
—barium metaborate
—silicate anion/calcium cation-based ion exchange pigment.

The electrochemical mechanism of steel surface protection is involved in coatings pigmented (filled) with a high content of zinc powder, the zinc particles being spherical shape. The electrochemical action consists in freezing Zn^{2+} ions, which then give the inhibition effects. The protective function due to the electrochemical mechanism is exhibited only by the freshly prepared coatings. The efficiency drops gradually as the pores become filled with the products of the electrochemical zinc reactions. The aged coatings protect only via the barrier effect.

2 EXPERIMENTAL SECTION

The anticorrosion properties were evaluated using model recipes in which an oil binder was used in combination with fillers, anticorrosion pigments, and further coating-composition ingredients. The anticorrosion pigments were added in all the cases in constant amounts, their volume concentration (VPC) being 5% vol. Each anticorrosion pigment was tested in combination with inert pigments and fillers and in combination with zinc white, the VPC of which was also 5% vol.

The coating-composition samples were prepared by a dispersing procedure using an attrition apparatus filled with glass spheres having a diameter of 2 mm. The dispersion time was 30 min, operating at 800 rpm. The coating compositions thus prepared were spread[2] over glass plates, steel sheets, and steel rods having a diameter of 14 mm. The coating films on the glass plates and ground steel sheets were obtained using a special spreading rule. The steel rods were coated using a brush operating in such a way that a constant layer thickness was observed.[3]

With the samples of anticorrosion coatings thus prepared, evaluations were made of the corrosion resistance in a condensation chamber[4] in an SO_2-containing atmosphere at 35°C and relative humidity of nearly 100%. The resistance of films exposed to static liquid effects[5] was also followed, using aqueous 10% NaCl solution as the aggresive medium. The coating films were also evaluated with respect to physicomechanical properties, i.e., their hardness by means of a pendulum device,[6] adhesion,[7] resistance to cupping by means of the Erichsen machine,[8] resistance to impact,[9] and resistance to bending.[10] The time of drying[11] in the coating compositions prepared was determined for stages 1 and 4. The anticorrosion pigments used and discussed are listed in Table 1.

TABLE 1
Properties of the Anticorrosion Pigments Used

Designation	*Pigment used*	*Density* ($g\,cm^{-3}$)	*Oil consumption per 100 g*
I	Ferric oxide with the zinc phosphate-treated surface	4·75	36·3
II	Basic calcium zinc molybdate	3·00	22·9
III	Zinc phosphate	2·90	36·0
IV	Calcium carbonate modified with calcium hydrogen phosphate, zinc phosphate, zinc oxide, and calcium molybdate	2·90	19·9
V	Red lead	9·12	12·1
VI	Lead suboxide	9·70	10·8
VII	Zinc yellow	3·00	39·5
VIII	Barium calcium phosphosilicate	2·97	31·5
IX	Anticorrosion pigment based on zinc ferrite	5·00	21·8

3 RESULTS AND DISCUSSION

The object of the investigation was to evaluate possible replacements for lead-based pigments (red lead, lead suboxide) and chromium-based pigments (zinc yellow) with physiologically harmless, and at the same time highly efficient, anticorrosion counterparts. The results indicate a relationship between the corrosion-coating resistance and the type of anticorrosion pigment used. The barrier effect of the filler alone with inert pigments and fillers, compared to the anticorrosion effect of special pigments, may be considered to be negligible. High anticorrosion efficiency of Zn phosphate or zinc ferrite-based pigment was observed. Comparable results were obtained on using usual pigments such as red lead, lead suboxide, or zinc yellow and the ferric oxide–zinc phosphate type of pigment.

To improve the anticorrosion coating properties, zinc oxide was used as an ingredient affecting favourably the pH value of the aqueous coating extract.[12] It was found that the pH value of the aqueous coating-film extract

TABLE 2
Corrision Resistance in SO_2 Chamber

Anticorrosion pigment	*Number of cycles*			
	28 Cycles	*56 Cycles*	*84 Cycles*	*112 Cycles*
Without any anti-corrosion pigment	3	4	5	5
I	0	1	2	3
I/ZnO	0	0	1	2
II	0	2	3	4
II/ZnO	0	1	3	3
III	0	0	1	1
III/ZnO	0	0	0	1
IV	1	2	3	3
IV/ZnO	1	1	2	3
V	0	1	1	2
VI	0	1	1	2
VII	0	0	1	2
VIII	0	1	1	2
VIII/ZnO	0	0	1	1
IX	0	0	0	1
IX/ZnO	0	0	0	1

Values 0–5 denote the severeness of corrosion-attack for mild steel: 0 = sheets without corrosion traces; 5 = sheets completely corroded.

obtained from thickened linseed oil varied within the range 3·5–4·5, which is the region in which intense corrosion of steel occurs. Zinc oxide binds low-molecular-mass organic acids always present in oils, thus shifting the pH to a comparatively high value, which is beneficial from an anticorrosion point of view. The data in Table 2 indicate that the added ZnO influences the inhibition effect with almost all the anticorrosion pigments used.

Coating compositions containing various anticorrosion pigments were also tested, in addition to an SO_2 atmosphere, in an NaCl-containing medium. The samples tested were exposed continuously to aqueous 10% NaCl and evaluated after one, two, three, four, and five months exposures. Table 3 shows the various anticorrosion performance values for individual pigment types. Results were in a similar order to the SO_2 atmosphere tests (Table 2).

The anticorrosion test results indicate that there are differences among individual anticorrosion-pigment types, the relative efficiency being such that it cannot be generally understood, since each pigment behaves in the composition in close relation to the binder used in the respective

TABLE 3

Corrosion Resistance in Exposure to an Aqueous 10% NaCl Solution

Anticorrosion pigment	*Degree of corrosion after exposure for*				
	1 Month	*2 Months*	*3 Months*	*4 Months*	*5 Months*
Without any anticorrosion pigment	1	3	4	5	5
I	0	2	2	3	3
I/ZnO	0	1	2	2	3
II	0	3	3	4	5
II/ZnO	0	2	3	5	5
III	0	1	2	2	3
III/ZnO	0	1	1	2	2
IV	1	1	2	3	4
IV/ZnO	0	1	1	2	3
V	0	1	1	2	3
VI	0	1	2	3	3
VII	0	0	1	3	3
VIII	0	1	2	3	3
VIII/ZnO	0	1	2	3	3
IX	0	1	2	2	2
IX/ZnO	0	1	1	2	2

Values 0–5 denote the severeness of corrosion-attack for mild steel: 0 = sheets without corrosion traces; 5 = sheets completely corroded.

TABLE 4

Physicomechanical Properties of the Coating Compositions containing Individual Anticorrosion Pigments

Anticorrosion pigment	*Hardness (%)*	*Adhesion (degrees)*	*Cupping (mm)*	*Bending (mm)*	*Impact (cm)*		*Drying (h)*	
					Face side	*Back side*	*Deg. 2*	*Deg. 4*
Without any anti-corrosion pigment	10·4	1	9·1	4	80	100	24	48
I	10·8	1	9·3	4	75	100	24	48
I/ZnO	10·7	1	8·3	4	80	100	24	48
II	10·1	1	9·0	4	75	100	24	48
II/ZnO	12·4	1	9·0	4	80	100	24	48
III	9·4	1	9·3	4	80	100	24	48
III/ZnO	11·7	1	9·0	4	75	100	24	48
IV	10·0	1	9·2	4	75	100	24	48
IV/ZnO	11·4	1	9·0	4	75	100	24	48
V	13·7	1	9·3	4	80	100	24	48
VI	12·5	1	9·0	4	80	100	24	48
VII	11·3	1	9·3	4	75	100	24	48
VIII	10·7	1	8·9	4	75	100	24	48
VIII/ZnO	10·2	1	9·1	4	75	100	24	48
IX	10·3	1	9·0	4	80	100	24	48
IX/ZnO	11·2	1	9·3	4	80	100	24	48

composition. Thus a pigment showing high efficiency in an oil binder is not necessarily effective in water-dilutable coating compositions, and vice versa.

With respect to the physicomechanical properties of the coating composition, these properties were not affected by the anticorrosion pigments used. Properties such as hardness, adhesion, and resistance to cupping, impact, and bend are affected primarily by the binder used and do not depend on the anticorrosion pigment added. Table 4 shows some physicomechanical properties of samples containing various pigments.

4 CONCLUSIONS

The results on the anticorrosion performance of individual anticorrosion pigments usable in oil-based coating compositions show the favourable effect of the addition of zinc oxide, which appears to be due to adjustment of the pH of the system. Addition of Zn raised the corrosion resistance, and had no adverse effect on the physicomechanical coating properties tested. The physicomechanical coating properties were not substantially affected by the type of anticorrosion pigment used.

Of the anticorrosion pigments shown in Table 1, their corrosion-resistance efficiencies were in the order: IX > III > VIII > VII = V = VI > I > IV > II (cf. Tables 2 and 3).

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