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Research Article

SYNTHESIS, CHARACTERIZATION AND EVALUATION OF COBALT BASED GREEN COLORED PIGMENT AS ECO-FRIENDLY ALTERNATIVE

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ABSTRACT

The present work describes the synthesis of environment friendly green colored inorganic pigment, from cobalt oxide with zinc oxide. These pigments have been synthesized by the incorporation of cobalt admixtures in zinc oxide in varying amounts. They are of special interest as they provide an alternative to replace toxic chromates in anticorrosive coating formulations. Their intense green color, hues, lower cobalt content, and thermal stability also provides additional advantages. Synthetic chemistry of such pigments is based on the non-stoichiometric interaction of the crystal lattices of both zinc oxide (ZnO) and cobalt oxide (CoO). Various pigments were prepared using various stoichiometric ratios of cobalt and zinc oxide. The prepared pigments were incorporated in the epoxy matrix and tested for their anticorrosive performance and found satisfactory in comparison to the chromium (III) based pigment having toxicity and environmental constrains.

Keywords: Cobalt oxide Zinc oxide, Green pigment, Anticorrosive coatings.

1. INTRODUCTION

Pigments are an integral part of the coating system and offer many properties *i.e.* color obliterating power and mechanical properties. Anticorrosive pigments are very useful ingredients in protective coating formulations [1, 2]. Chromates are one of the most frequently used anticorrosive pigments in the anticorrosive coatings [3, 4]. However, the toxicity of the chromates restricts their use, and coating technologists are always in search of low-cost green alternatives to replace them [5, 6]. Inorganic pigments have greater commercial importance in this regard and offer an obvious advantage in terms of their obliterating power and high-temperature stability as compared with their organic counterparts [7, 8].

Nowadays the use of pigments is increasing as in the case of glasses, glazes, ceramics and there are no alternatives to inorganic pigments for coloring [9]. High-quality pigments are of utmost importance in the paint industry and are used extensively. Many important properties of the pigments such as hiding power, tinting strength are greatly affected by particle size and distribution [10, 11]. Pigments with high tinting strength and hiding power are favored as the surface gets obliterated with a thinner coat. Thus, the coloring properties (*e.g.,* color, tinting strength and hiding power) of the pigment are important in determining the cost of painting [12, 13]. They are vital ingredients in protective coatings because of their better coloring properties such as hiding power, covering power in combination with their complete inertness in the film former [14]. Green inorganic pigments have aroused great interest recently in many applications such as ceramics, inks, coatings, rubber, glass, etc. [15, 16]. These inorganic green pigments are mostly based on Chromium/Chromate based materials and provide excellent properties in terms of colour, chemical resistance, and anti-corrosive performance. Chromates as a pigment are cost-effective but present a significant threat to humans and the environment because of their toxicity [17, 18]. Zinc oxide is widely used in many industrial applications due to its excellent property profile including color, particle size, hiding power and binder compatibility [19]. Zinc oxide owing to its wurtzite structure has an intense green color and can be suitable for use as medium-temperature pigments [17, 20]. Literature suggests some cobalt-based pigments as an eco-friendly alternative. They may be substituted as an alternative to the toxic chromates but their evaluation in high-performance binders like epoxy can only suggest their suitability in the field of protective coatings [21-24].

The present work describes the synthesis of an environmentally friendly green inorganic pigment having comparable properties to chromium oxide-based green pigment. These pigments synthesized by solid-state interaction between cobalt oxide and zinc oxide. The effect of stoichiometric substitution of cobalt oxide on the synthesized pigment is also studied. The anticorrosive performance of them is evaluated in high-performance epoxy binder, as well as other properties of this eco-friendly pigment, are also compared.

2. EXPERIMENTAL

2.1. Materials

CoO and ZnO were purchased from S.D. Fine Chemicals. liquid binder, epoxy resin Epotec YD 128 and amine curing agent Epotec TH-7320 were supplied by Aditya Birla Chemicals. Other raw materials *e.g.* solvents, additives used in paint formulations and were supplied by different companies.

2.2. Pigment Preparation

Solid solutions in different stoichiometric compositions of $Zn_{1-x}Co_xO$ (x = 0.02, 0.04, 0.06, 0.08, 0.1) were synthesized by a solid-state reaction, using precursor oxides ZnO, CoO. CaF_2 was added 2% by weight as a modifier. The stoichiometric quantities of the raw materials were weighed and then mixed thoroughly in mortar pastel. The resultant powders were taken in alumina crucibles and calcined at 1100°C for 1 hour in an electric furnace at the rate of 10°C/min. The samples were cooled down to room temperature. The above-obtained pigments were then grounded in mortar pastle thoroughly to break the clusters and homogenize the particle size. It was then sieved, resulting in a fine powder of cobalt green pigment.

2.3. Paint Formulation

For the paint formulation, epoxy resin was used as the binder. The resin was first stirred at 800 rpm in a dispermat mixer (BYK Gardener, Germany). To this, the toluene and xylene were gradually added along with wetting and dispersing agent at the same speed. The resultant mixture was then allowed to stir for at 1000-1200 rpm for 5-10 min. The pigment was then added into the mixture and stirring was continued for another 15 min. The extent of dispersion was checked using Hegman gauge. A stoichiometric amount of hardener was finally added to the above mixture and all components were mixed with a spatula. Paint formulations were thus prepared with different pigment loading for each experiment *i.e.* different mole percent of cobalt oxide. The coatings were then applied using air spray gun on mild steel panels and tested for their performance.

2.4. Pigment Analysis

The properties of the pigments were determined using standard test methods including specific gravity (ASTM D 153-54, 1981), oil absorption (DIN EN ISO 787, 1980) concentration (pH value) (DIN EN ISO 787, 1995), bleed test (ASTM D 279-02), chemical resistance (ASTM D 2794-93, 1980).

2.5. Film Properties

All the coated panels were tested according to standard test methods for testing of coatings including drying time (ASTM D 1640- 83, 1981), dry paint film thickness (ASTM D 1186-81, 1974), adhesion by tape test (ASTM D 3359-74, 1979), (impact resistance) (ASTM D 2794-73, 1979). The anticorrosive performance of the coatings was evaluated using the salt spray method (ASTM B-117).

2.6. Characterization

The crystallinity and the phase purity of $Zn_{1-x}Co_xO$ particles were examined through X-ray diffraction patterns recorded by using Bruker D8 ADVANCE diffractometer using Cu Kα radiation (λ=1.5406 Å, 40 kV, 40 mA). The diffraction patterns were analyzed and matched by DIFFRACT.EVA with Bruker software using ICDD database.The morphologies and particle size of the synthesized powders were observed by Field Emission Scanning Electron Microscopy (FESEM) (Hitachi F-4800, Japan). The CIE-L*a*b* chromatic coordinates were measured using Color Spectrophotometer (Premier Colourscan., Mumbai).

3. RESULTS AND DISCUSSION

3.1. Colour Analysis

The effects of the increasing amount of cobalt oxide on colouring properties of the ZnO.CoO pigments were investigated. Color co-ordinates of the produced pigments are tabulated in Table1. The pigments show lightness value *L** ranging from 42-52, color coordinates with low *a** and high *b** (+ve) values. Increasing the content of cobalt oxide in the combination, results in a shift of color hue from dark green to black-green. Pigment containing 10 mol % CoO shows excellent hue of the green color. From the appearance, it is clear that, as the cobalt content increased, the color intensity also increased. From L*, a*, b* values it is observed that synthesized green pigment has chroma a* value better than chromium oxide green pigment.

Table 1: Color value of Zn 1-x CoxO at different mol ratios

Composition	L*	a*	b*
Cr_2O_3	53.255	-10.268	9.784
x = 0.02	52.643	-22.802	7.79
x = 0.04	47.293	-19.16	5.905
x = 0.06	48.719	-19.582	6.484
x = 0.08	45.264	-16.18	4.892
x = 0.10	42.108	-12.701	3.671

Table 2 shows the tinting values of pigment. It can be seen that $Zn_{1-x}Co_xO$ green pigment has lower tinting strength as compared to Cr_2O_3. Chromium oxide has darker shade as compared to synthesized pigment. Chromium oxide pigment has b* value towards yellow shade while pigment-containing cobalt oxide and zinc oxide having bluish undertones. There is not much difference in the a* value between synthesized pigment and chromium oxide green pigment. They both have a green hue.

Table 2: Tint tone values for Zn 1-x CoxO

Composition	L*	a*	b*
Cr_2O_3	60.476	1.010	9.784
x = 0.02	84.265	-9.653	7.79
x = 0.04	80.351	-9.519	5.905
x = 0.06	76.688	-12.324	6.484
x = 0.08	76.443	-10.669	4.892
x = 0.10	76.543	-9.406	3.671

Physical properties of synthesized pigment and chromium oxide pigment were evaluated using standard test methods. In table S1, S2, S3, S4 and S5 indicate varying mole percent of cobalt oxide 2, 4, 6, 8, 10 respectively. From Table 3 it is observed that the above-prepared pigments have oil absorption values in medium range. There is variation in oil absorption values as the fraction of cobalt oxide varies. With an increase in the proportion of cobalt oxide in the mixture, oil absorption decreases until pigments have 8 mole percent of cobalt oxide.

Table 3: Physical Properties of Pigments

Material	Cr_2O_3	S1	S2	S3	S4	S5
Oil Absorption	10	20	19.20	17.67	21.5	10.98
pH	6	10	10	10.5	10.5	11
Bleeding Test	None	None	None	None	None	None
Chemical Resistance	5	5	5	5	5	5
Specific Gravity	3.25	3.05	2.98	2.853	2.82	2.80

Table 4: Physico-mechanical properties of paint films (5% Pigment Loading)

Test Methods	CoO- 2%	CoO- 4%	CoO- 6%	CoO- 8%	CoO- 10%	Cr_2O_3
DFT (μm)	50-60	50-60	50-60	50-60	50-60	50-60
Drying Time (hr)	5-6	5-6	5-6	5-6	5-6	5-6
Adhesion	Gt2	Gt1	Gt0	Gt0	Gt0	Gt0
Flexibility	Pass	Pass	Pass	Pass	Pass	Pass
Impact Resistance(in.lb)	Pass	Pass	Pass	Pass	Pass	Pass

The bleeding test of the pigments was carried out to check their stability in variety of solvents with high solvency. Solvents used for the bleed test were xylene, toluene and butanol. The exposure of pigments to various acidic and alkaline media showed their high stability and resistance to these chemicals. The pigments showed excellent colour retention and colour hue after exposure to severe alkaline and acidic conditions. Specific gravity values of the pigments were in medium range, which are helpful in preventing there settling thus increasing the storage stability of the coatings.

Physico-mechanical properties of paint films: The epoxy-based paint was formulated with 5, 10 and 15 wt% of pigment. 1-5 stands for different mol percent of cobalt oxide in synthesized pigment 2, 4, 6, 8, 10 respectively. The properties of the pigments are compared with chromium oxide pigment. Table 4, 5 and 6 shows the properties of various formulated coatings. It is seen that pigment-containing less mol percentage of cobalt oxide exhibits poor adhesion where remaining paints show good adhesion as well asgood flexibility. Chromium oxide has better impact resistance as compared to synthesized pigments. Paint containing less amount of cobalt oxide in pigment shows poor flexibility and low impact resistance where pigment-containing 10 mol percent of cobalt oxide shows similar flexibility, adhesion and impact resistance as chromium oxide. All paints show similar properties as chromium oxide. They have excellent adhesion, high impact resistance and flexibility.

3.2. Salt spray testing (ASTM B-117)

All coated Panels were exposed to continuous deposition of 5% NaCl solution at 35ºC. Panels were examined for 500 hrs. From Fig. 1, it is observed that the pigment-containing 2 mol percentage of cobalt oxide shows poor corrosion resistance in all three groups containing 5, 10 and 15 percentages of pigment concentrations in paint formulation. As the cobalt content in paint increased it gives better anti-corrosion properties. The paint which contains 5 wt % of pigment shows good corrosion resistance but as the percentage of pigment in the paint were increased up to 15% it shows excellent anticorrosive properties as compare to chromium oxide pigment.

Table 5: Physico-mechanical properties of paint films (10% Pigment Loading)

Test Methods	CoO- 2%	CoO- 4%	CoO- 6%	CoO- 8%	CoO- 10%	Cr_2O_3
DFT (µm)	50-60	50-60	50-60	50-60	50-60	50-60
Drying Time (hr)	5-6	5-6	5-6	5-6	5-6	5-6
Adhesion	Gt1	Gt0	Gt0	Gt0	Gt0	Gt0
Flexibility	Fail	Fail	Pass	Pass	Pass	Pass
Impact Resistance(in.lb)	Pass	Pass	Pass	Pass	Pass	Pass

Table 6: Physico-mechanical properties of paint films (15% Pigment Loading)

Test Methods	CoO- 2%	CoO- 4%	CoO- 6%	CoO- 8%	CoO- 10%	Cr_2O_3
DFT (µm)	50-60	50-60	50-60	50-60	50-60	50-60
Drying Time (hr)	5-6	5-6	5-6	5-6	5-6	5-6
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Flexibility	Pass	Pass	Pass	Pass	Pass	Pass
Impact Resistance(in.lb)	Pass	Pass	Pass	Pass	Pass	Pass

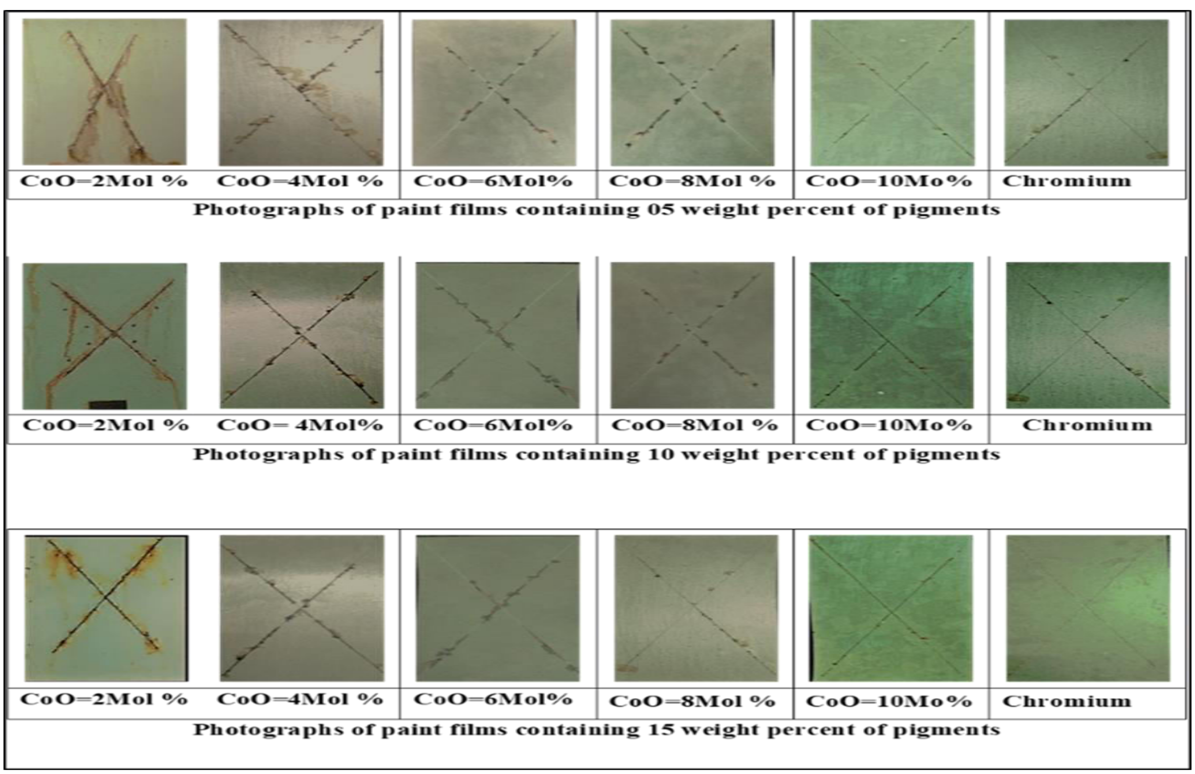

Fig. 1: Salt Spray Test of formulated coatings

3.3. XRD Analysis
The XRD diffractograms of pigments containing varying amounts of CoO are shown in Fig. 2. The stronger peak of the samples indicates higher crystallinity. The XRD diffractograms of S1 to S5 show that in all the pigments, the basic structure of ZnO remains intact. The main peaks of ZnO are in the region 2θ 36–36.5 no shifting to higher 2θ value or lower 2θ value is observed by the addition of CoO. Increasing the cobalt oxide percentage in thepigments does not have any effect on the structure.

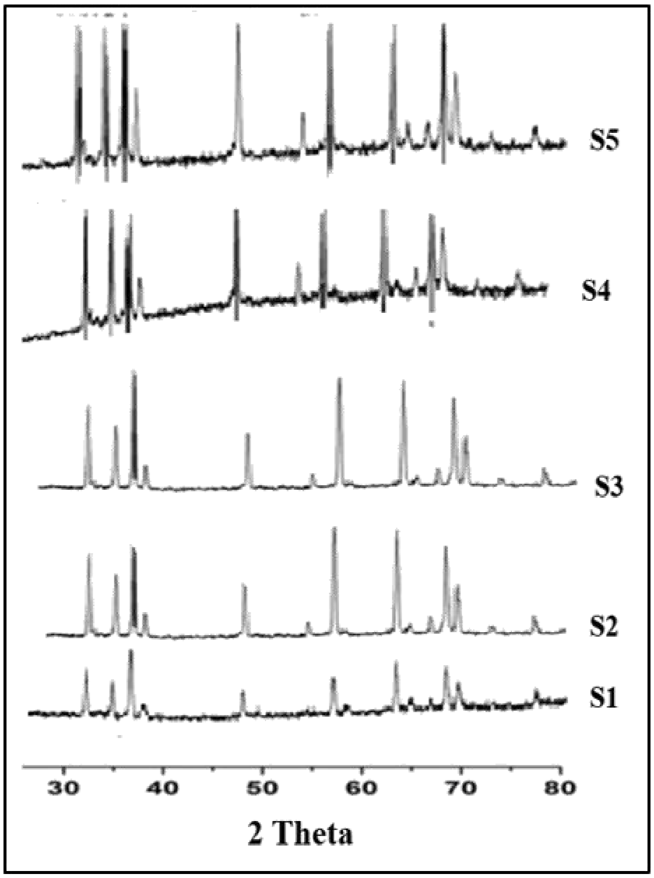

Fig. 2: XRD of pigments

3.4. *SEM Analysis*
The morphology of the pigments is observed by scanning electron microscopy. It is observed from Fig. 3 that the above synthesized pigments are round in shape and the particles have flat morphology. It helps in increasing the packing density of the coating film and reducing the permeability. The reduced permeability of the coating is helpful in increasing the anticorrosive performance. The increase in the amount of cobalt oxide changes the morphology of the particles and particles become flattered and platy. It is observed that the particle size of the pigment increases with an increase in cobalt content.

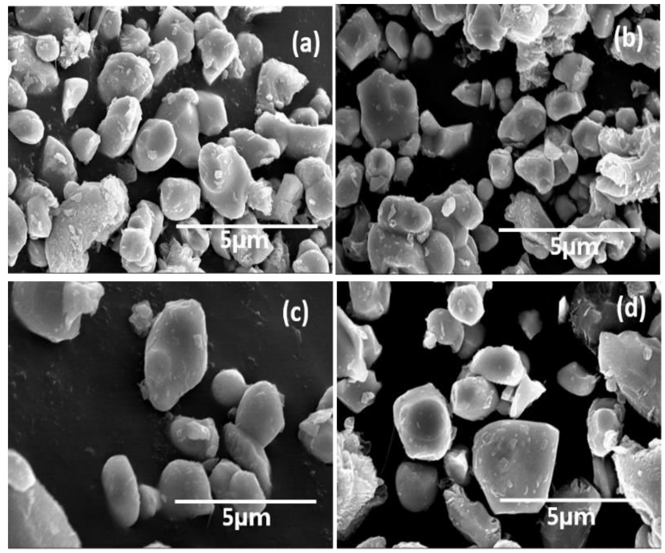

Fig. 3: SEM images of pigments

4. CONCLUSIONS
The solid-solid interaction of zinc oxide and cobalt oxide produces a pigment possessing an intense green color. The prepared pigment powders are highly thermal and chemical resistant and do not contain any toxic metals. Based on the L^*, a^*, b^* values measured of the colour coordinates of the CIE $L^*a^*b^*$ system, a pigment with enough deep green color without any additional grey or black hue was chosen. Pigment with 10 mol% CoO gives a very good hue of the green colour. The variation in color hue is observed with the percentage of cobalt oxide. The lower content causes grey hue in green colour while increasing it results in shifting from dark green hues to black-green hues. Pigment containing Cobalt oxide has no bleeding in the solvent. It remains stable in different solvents such as xylene, toluene and butanol. The synthesized pigment has more oil absorption value than chromium oxide pigment. As the mol percentage of cobalt increases, the oil absorption value increases. Pigment synthesized by cobalt oxide and zinc oxide has less tinting strength. The synthesized pigment gives a bluish tint tone while chromium oxide gives a greenish tint tone. Epoxy-based paint was formulated with different pigment concentrations of newly developed pigment and chromium oxide pigment, took 5 to 6 hours to get through dry, and 7 days for curing. Pigment containing 2 mol percent of cobalt oxide in paint formulation shows less flexibility and poor adhesion. With an

increase inthe percentage of cobalt, flexibility and adhesion were improved. As the amount of pigments in the paint formulations is increased, both physico mechanical, and corrosion prevention properties were improved. It is observed for both 5 % and 10%. Paint formulation as well as those containing 15 % of pigment concentration gives excellent adhesion, high impact resistance and better flexibility. The paint which contains 5 wt % of pigment shows good corrosion resistance but as the percentage of pigment in the paint were increased up to 15% it shows excellent anticorrosive properties as compared to chromium oxide pigment. The combination of cobalt oxide and zinc oxide produced pigments gives equivalent anti-corrosion properties to chromium oxide pigment. The existence of cobalt improves the action of zinc oxide and thus leading to better anticorrosive performance. As the cobalt content in paint increased it gave better anti-corrosion properties. This type of pigment would be a substitute for the greens based on chromium.

5. ACKNOWLEDGEMENTS

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