PREPARATION OF ZINC VANADATE NANO-PIGMENT AND PROPERTIES TESTING

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Abstract - We report here a simplistic and cost effective method for the synthesis of zinc vanadate Nano-pigment. Nowadays elimination of lead and chromate based pigments and substitution of molybdate and phosphate based pigments are having new demands in coating industries. The preparation of zinc vanadate Nano-pigment was done, characterized and evaluated for its pigmentary properties. The synthesis of zinc vanadate Nano-pigments was carried out by co-precipitation method by using two different zinc salts and ammonium meta-vanadate. The successful formation of zinc vanadate Nano-pigment was confirmed through various characterization techniques like UV-vis spectroscopy, FESEM, XRD and FTIR etc.

Index Terms - Co-Precipitation Method, Cost Effective, Pigmentary Properties, Zinc Vanadate Nano-Pigments.

I. INTRODUCTION

Corrosion-resistant metals (1) are by nature passive (more noble) and can cause severe galvanic corrosion of active (less noble) materials. Coatings are used to (2) protect, seal or colour the solid surface. For this purpose, various(3) pigment plays an important role introducing different properties in the coatings. Nowadays Nano-pigments are being used, increasing the functionality and properties of coatings. Due to hazardous nature, (4) the lead and chromate based pigments are excluded in the coating industries replacing it by phosphate and molybdate pigments. Zinc vanadate can be used as a good substitution over chromate pigments in coatings. Zinc vanadate Nano-pigments (5)can be synthesized by controlled co-precipitation method using zinc acetate as precursor and ammonium meta-vanadate as the precipitant in comparison with synthesis of zinc vanadate by zinc sulphate and ammonium meta-vanadate.

II. EXPERIMENTAL

A. Raw Materials

In this study zinc acetate with 99.9% purity is obtained from Loba Chemi.,(Mumbai), zinc sulphate and zinc phosphate were obtained from Kemhasol, ammonium meta-vanadate from HiMedia,(Mumbai). Ethanol is obtained from MEARCK. The raw materials taken were of analytical grade so the analysis of the raw materials were not performed.

B. Synthesis of zinc vanadate Nano-pigment

Zinc vanadate was synthesized, characterized and evaluated. The Nano sized zinc vanadate pigment was synthesized by controlled co-precipitation reaction using zinc acetate as precursor and ammonium meta-vanadate as the precipitant in comparison with synthesis of zinc vanadate by zinc sulphate and ammonium meta-vanadate.

12 mL of a 0.1 M aqueous solution of $ZnSO_4$ was mixed with 28 mL of a 0.1 M aqueous solution of NH_4VO_3 in a beaker with stirring for 5 minutes.Then, the mixture was heated at 70 ^{0}C for 1 h on a water bath.The precipitate was collected and washed several times with water and ethanol followed by drying at 60 ^{0}C for 6 h. Then calcined for 6 h at 500 ^{0}C.

$ZnSO_4 + NH_4VO_3 \rightarrow Zn_3V_2O_7 (OH)_2 (H_2O)_2 \rightarrow Zn_3V_2O_8$

Figure 1. Reaction of zinc sulphate and ammonium meta-vanadate.

0.1 M aqueous solution of Zinc acetate was added dropwise to 0.1 M aqueous solution of NH_4VO_3 in a beaker at room temperature. Mixture was stirred and heated at 80^{0}C for 45 min on a hot plate. The orange precipitate was filtered, washed with ethanol and water followed by drying in an oven at 60 ^{0}C for 12 h.Then calcined for 1 h at 600 ^{0}C.

$Zn(CH_3 COO)_2.2H_2O + NH_4VO_3 \rightarrow ZnV_2O_6$

Figure 2. Reaction of zinc acetate and ammonium meta-vanadate.

In this preparation, the experimental setup as shown in the figure no.1 consists of a 500ml 3-neck round bottom flask placed in water for constant heating. Dropping funnel is attached to one neck of the 3-neck flask and a water condenser to another neck of the 3 neck flask. Thermometer pocket is attached to the remaining neck of the 3-neck flask. The assembly is fixed firmly with the help of clamps and stand. Magnetic needle is placed inside the 3 neck flask to facilitate stirring. The inlet of the water condenser is supplied with water from motor and the outlet is kept in the bucket for continuous water circulation.

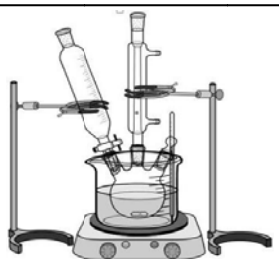


Figure 3. Experimental setup

III. RESULT AND TESTINGS

A. Analysis of pigmentary properties.

Analysis of pigmentary properties of zinc vanadate Nano-pigment were performed. The oil absorption, bulk density and hiding power was found to be 32.25g/ml, 5g/ml, 2.5m^2/kg. It is observed that the pigmentary properties of both zinc vanadate Nano-pigment by zinc sulphate and zinc acetate is almost same. The surface area was 21.5m^2/kg.

C. Analysis of zinc vanadate Nano-pigment by zinc sulphate

Study of synthesis of zinc vanadate pigment was done at different temperature, time, rate of stirring for different molar ratio. At 60^{0}C for 0.1M concentration, zinc vanadate Nano-pigment was prepared at stirring rate of 300 rpm for 60 min and the % yield observed was 61.05%. Similarly, for 80 min and 100 min, the rate of stirring was kept at 500 rpm and 700 rpm and the % yield observed was 61.91% and 63.41% respectively.

At 70^{0}C for 0.1M concentration, zinc vanadate Nano pigment was prepared at stirring rate of 900 rpm for 60 min and the % yield observed was 62.76%. Similarly, for 80 min and 100 min, the rate of stirring was kept at 1100 rpm and 1300 rpm and the % yield observed was 63.83% and 64.48% respectively.

At 90^{0}C for 0.1M concentration, Zinc vanadate Nano pigment was prepared at stirring rate of 1400 rpm for 60 min and the % yield observed was 63.41%. Similarly, for 80 min and 100 min, the rate of stirring was kept at 1500 rpm and 1600 rpm and the % yield observed was 64.05% and 64.91% respectively.

For 0.2M concentration at 10 mins of constant addition of zinc sulphate, zinc vanadate Nano pigment was prepared at 70^{0}C at the stirring rate of 1000 rpm for 60 min and the % yield observed was 62.76%. Similarly, for 80 min and 100 min, the rate of stirring was kept at 1200 rpm and 1400 rpm and the % yield was observed as 63.41% and 63.94%.

B. Analysis of zinc vanadate Nano-pigment by zinc acetate

Study of synthesis of zinc vanadate pigment was done at different temperature, time, rate of stirring for different molar ratio. At 80^{0}C for 0.1M concentration of 30 mins of constant addition of zinc acetate, zinc vanadate Nano-pigment was prepared at stirring rate of 1000 rpm was kept for 45 min and the % yield was observed as 58.89%. Similarly, for 65 min and 85 min, the rate of stirring was kept 1200 rpm and 1400 rpm and the % yield was observed as 61.27% and 62.22% respectively.

At 80^{0}C for 0.2M concentration for 30 mins of constant addition of zinc acetate, zinc vanadate Nano-pigment was prepared at stirring rate of 1000 rpm and the % yield observed was 60.98%. Similarly, for 65 min and 85 min at 90^{0}C and 100^{0}C respectively, the rate of stirring was kept at 1200 rpm and 1400 rpm so the % yield was observed as 61.33% and 62.82% respectively.

C. XRD

In XRD test of pigment by zinc sulphate is shown in Figure 4 by the reference code 00-023-0757, $ZnV_2O_6$is formed with the purity score of 83. The size of the nanoparticles obtained were estimated to be 71.88 nmusing Debye-Scherrer Equation, which may indicate a high surface area, and surface area to volume ratio of the Nano-crystals. Similarly, XRD test of pigment by zinc acetate clearly indicates the formation of monoclinic phase of $Zn_2V_2O_7$(JCPDS No.00-03780251). Particle size of 82-89 nm is formed with high purity.

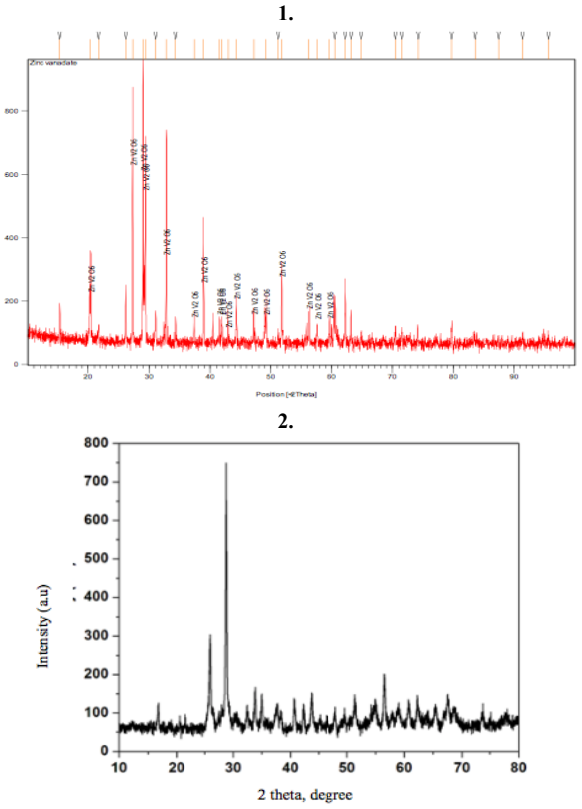
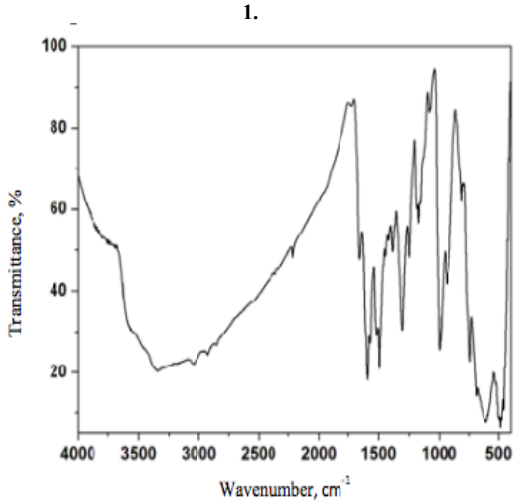


Figure 4. XRD pattern for nano zinc vanadate pigment by 1. zinc sulphate and 2. zinc acetate

D. FTIR

FTIR spectrum is shown in Figure 5. The formation of ZnO phase present in tetrahedron unit of vanadate is characterized by an intense and very broad IR band with poor resolved shoulders at 580, 1400 and 1428 cm^{-1}.

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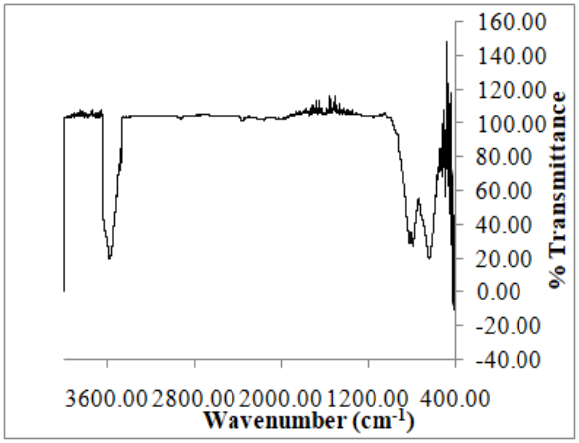
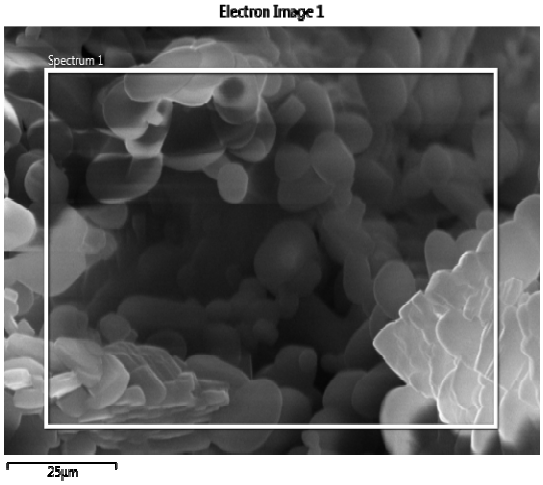


Figure 5. FTIR spectra for zinc vanadate by 1.zinc sulphate and 2.zinc vanadate

E. FESEM

The surface morphology of the synthesized zinc vanadate Nano-pigment was examined and shown in Figure 7. The size of the nanoparticle by zinc sulphate obtained were estimated to be 82nm. Nano-particle by zinc acetate shows the presence of spherical hollow $Zn_2V_2O_7$ nano clusters with good separation, varying in size between 82-89 nm.

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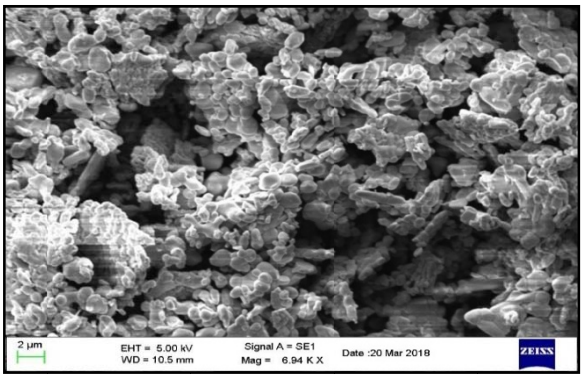
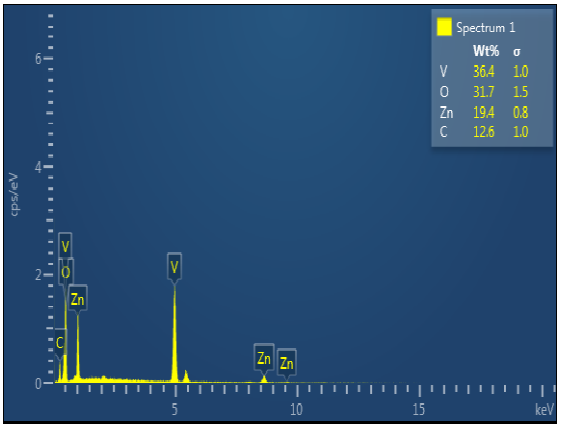


Figure 6. FESEM images of Nano zinc vanadate by 1.zinc sulphate and 2.zinc acetate

F. EDX

Energy Dispersive X-ray (EDXS) in Figure 8 shows atomic percentage of zinc, vanadium and oxygen atoms for the zinc vanadate Nano-pigment by zinc sulphate to be Zn is 19.4wt%, V is 36.4wt%, O is 31.7wt%. The composition of obtained $Zn_2V_2O_7$by zinc acetate was analysed to be Zn is 33.26wt%, V is 33.3wt%, O is 33.44 wt%.

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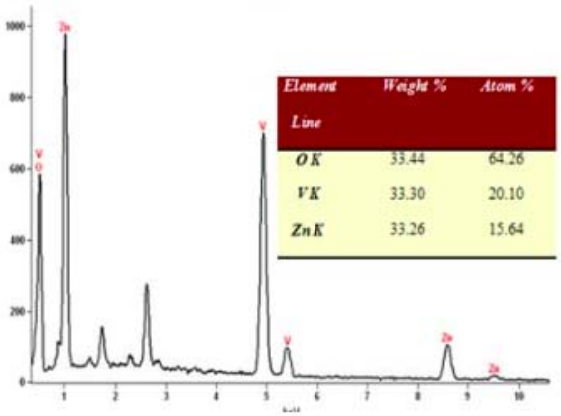


Figure 7. EDX spectrum of nano-zinc vanadate by 1.zinc sulphate and 2.zinc acetate

G. UV-visible spectroscopy

For Nano-pigment by zinc sulphate the energy band gap value is reflected in the inset of which comes out to be 3.21 eV, that is, less than pure ZnO (3.37 eV). The

band gap energy of $V_2O_5$is 2.3 eV and ZnO is 3.37 eV; when V_2O_5 is doped in ZnO, alloy is formed which causes decrease in band gap. The Nano-pigment by zinc acetate displays an absorption inflection point at around 385 nm, which should be assigned to the absorption feature of $Zn_2V_2O_7$. The direct band gap calculated from diffused reflectance spectra is 3.23 eV, which is higher for Nano zinc vanadate than that for bulk zinc vanadate.

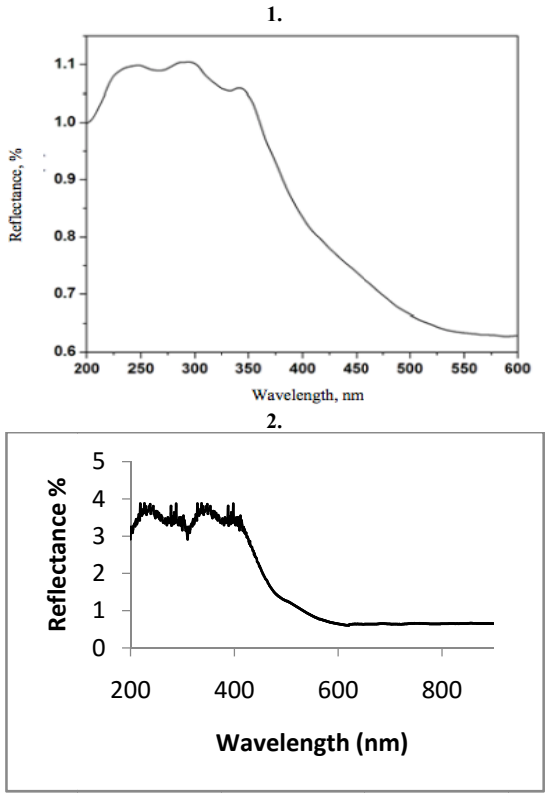


Figure 8. UV-visible diffuse reflectance spectra of zinc vanadate by 1.zinc sulphate and 2.zinc acetate

RESULT AND DISCUSSION

Over the past decade, the shape control of anisotropic Nano- and microcrystals has attracted extensive importance because the morphology, dimensionality and size of materials have great effects on their physical and chemical properties, as well as on their applications in various fields. Due to their fascinating structures leading to enhanced electronic, optical and magnetic properties, which are relevant to such diverse areas as lubrication, chemical sensor, catalysis, cathode materials in batteries, minerals and corrosion inhibitor. Zinc vanadate was synthesized, characterized and evaluated for its performance in coatings. The Nano sized zinc vanadate pigment was synthesized by controlled co-precipitation reaction using zinc acetate as precursor and ammonium meta-vanadate as the precipitant in comparison with synthesis of zinc vanadate by zinc sulphate and ammonium meta-vanadate. Study of synthesis of zinc vanadate pigment was done at different temperature, time, rate of stirring for different molar. The purity score is 83 and the size of the nanoparticles obtained were estimated to be 71.88 nmusing Debye-Scherrer equation, which may indicate a high surface area, and surface area to volume ratio of the Nano-crystals for the zinc vanadate Nano-pigment by zinc sulphate and for zinc vanadate Nano-pigment by zinc acetate, the particle size is 82-89nm of high purity was prepared. The formation of ZnO phase present in tetrahedron unit of vanadate is characterized by an intense and very broad IR band with poor resolved shoulders at 580, 1400 and 1428 cm^{-1} in FTIR spectrum was observed.

CONCLUSION

The synthesis protocol for zinc vanadate pigment by zinc sulphate and by zinc acetate having micro flowers like structure was established by exploiting a facile, cost effective controlled co-precipitation technique.

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