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ACRYLIC ACID AND TRANSITION METAL DERIVED NOVEL WATER SOLUBLE PIGMENT

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ABSTRACT

We intend to synthesis water soluble pigment which is finely divided complex structured substance, usually a stable solid added to produce a stable surface coating which gives opacity, colour, control of flow during application, influence on the courses of weathering after exposure to different environment; using first order transition metal and acrylic acid. Properties of synthesized pigment were examined using magnetism, gravimetry, infrared spectroscopy and thermo-gravimetric analysis. Also, their properties were examined with respect to particle size distribution, surface area and oil absorption. The complexes synthesized were found to be useful in industrial paint.

Key words: *Acrylic acid complex, Water Soluble Pigment, Infrared Spectra, XRD.*

INTRODUCTION

Pigment, which is the integral part of colour media, paint or ink, is both organic as well as inorganic. Conventionally inorganic pigments, which are insoluble in water or organic solvents, are dispersed with sufficient binding agent [1]. The general requirement in the good quality pigment is fine particle size, excellent binding power, homogeneity in the paste form, good texture, excellent wetablity, high tinting strength etc as well as good storage properties along with cost effectiveness.

An important variable determining the properties of pigments is particle size and particle size distribution. Pigments manufacturing processes are designed to afford the particle size and particle size distribution that provides the best compromise of properties for that pigment. In the process of drying the pigment, the particles generally aggregate. The coating manufacturer must disperse these dry pigment aggregates in such a way as to achieve a stable dispersion where most, if not all, of the pigment is present as individual particles. An excellent treatise on the chemistry, properties, and uses of pigments is available [2-5].

Pigments are divided into four broad classes; white, colour, inert, and functional. The ideal white pigments, after dispersion would absorb no visible light and thus gives white colouration. Scattering of light increases rapidly with respect to refractive index of pigment particles and binder.

In large only natural pigments are used which are inorganic in nature and thus limited in processability and colour range. On the other hand Organic pigments, normally azo, pthalocyanine, anthraquinone, indigoids etc, have environmental difficulties and limited uses.

Pigment synthesis is a multi step tedious process. There have been numerous attempts to develop an effective system to synthesis of the pigment [6-7].

The present works comprises the feasibility to synthesize pigment in economical and convenient way. For better environmental adaptability synthesis of organic acid complex with first order transition metal has been carried out. The synthesized series of complex were evaluated in terms of pigment as its ultimate use.

MATERIALS AND METHODS

Acrylic acid was purchased from Merck, Germany and was used as such. Metal nitrates of transition series procured from Chiti chem., Baroda, India. All other chemicals used in this process were of laboratory grade.

Synthesis of Metal Complex

Acrylic acid (2.2 mole), metal nitrates (1 mole) and 100 ml of alcohol as solvent were taken in 250 ml of three necked round bottom flask equipped with nitrogen inlet, thermometer pocket and downward water condenser. The reaction mixture was heated at a rate of 2-3 ^{0}C per minute till reflux and maintained for 250 minute to complete the reaction. Acid value was checked periodically by siphoning the sample. The mixture was refluxed till the acid value reached its minimum, ensuring that maximum amount of acrylic acid had reacted with metal nitrate. After attaining the minimum acid value mixture was further stirred for 10 minutes and was allowed to cool to room temperature. Non-solvent, water was added to the mixture with high-speed stirring to get the fine crystallized product. Crystal thus obtained, was washed thoroughly with water for several times, to remove acrylic acid homopolymer. Fine crystal thus obtained were filtered, dried and examined for its use as a pigment.

Particle Size

For determination of particle size distribution, sedimentation methods were adopted. This method comprises of separation of complex into number of fraction by the use of centrifuge.

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Specific Gravity

Determination of the specific gravity was carried out by the method suggested by British standards.

Tinting Strength

Tinting strength of colored pigment is measured by milling the sample of pigment and standard white paste of a 1:10, 1:20. A similar paste of standard pigment with a standard white paste was prepared [8]. Colour of both the paste were observed.

Oil Absorption

It is the amount of the break free linseed oil required by 100 gms of pigment to form a stiff putty paste. This property is evaluated by adding break free linseed oil from a burette to accurately weighed pigment on a glass plate and incorporating oil into the pigment after addition of each drop by rubbing up with spatula. This test is completed when the pigment, to produced stiff putty paste absorbs no more oil. Oil absorption is calculated as

$$\% \text{ oil absorption} = \frac{Grams\ \ of\ \ oil}{Grams\ \ of\ \ Pigment} x\ 100$$

Structural Analysis

Magnetic effect (μeff) of complex was calculated in the 4 amp. field of current. Magnetic acceptability of the compound can be determined from the following equation:

$$\mu g = \frac{K.V + \beta.w}{W}$$

where, W = weight of the compound
w = Apparent change of the weight
β = Tube constant

Structural analysis was also carried out using gravimetric analysis in which accurately weighed compound was taken into silica crucible. It was then kept into the muffle furnace for complex combustion for 3 hr. The metal complex was combusted and converted into the metal oxide.

$$M(Ac)_2 \longrightarrow M_2O_3$$

From the above formula we can calculate the metal content within the complex. The result derived after calculating the metal content is tabulated in the Table 4.

RESULT AND DISCUSSION

For a complex to be used as a pigment were examined by means of different parameter, such as: particle size, specific gravity, surface area, tinting strength and oil absorption.

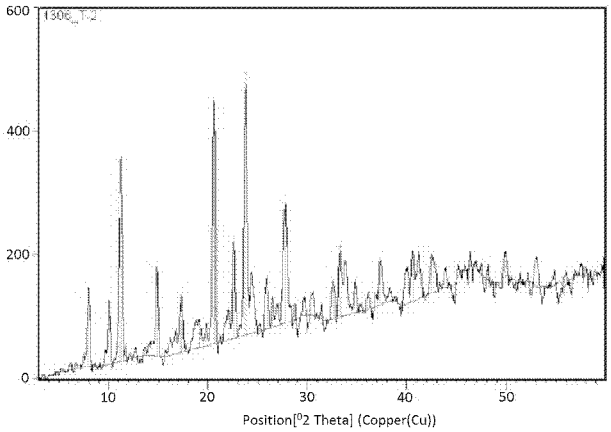
Particle Size

The representative histogram of $Cu(Aa)_2$ complex is displayed in Figure 1. A critical examination of the method has been made by J. Breford [9], which was applied to determine the particle size distribution of complex. According to histogram the range of particle size distribution is 0.5-5μm, which is of acceptable grade for complex to be used as pigment from the point of view of particle size distribution. The particle size distribution of the pigments synthesized is tabulated in Table 1.

Table 1 Particle Size distribution of $Cu(Ac)_2$

Particle Size (mm)	Sedimentation Centrifugation (rω /min.)			
	250	500	1000	2000
4.0	5.80	-	-	-
3.0	-	2.70	-	-
2.0	-	-	9.30	-
1.0	-	-	-	37.00
0.5	-	-	-	147.00

Figure - 1 (particle size distribution histogram)



Specific Gravity

Results obtained for specific gravity of pigment are tabulated in Table 2.

Table 2 Specific gravity of pigment

Pigment	Specific Gravity
$Cu(Ac)_2$	2.8
$Co(Ac)_2$	2.4
$Ni(Ac)_2$	2.1

Surface Area

The surface area of the pigment is related to the average particle size of the complex. An approximate figure for the surface area can be calculated from the equation that has been derived by Brunear [10].

Surface Area (mt^2/gm) = σ/ρd

ρ= Specific gravity of pigment, ρ=2.8

D= Volume/ Surface mean diameter d = 0.25μm

σ = a factor applicable to the spherical particle, with irregular the expression therefore gives and approximate figure.

Surface area of the synthesized Cu-complex is 0.857mt^2/gm. The surface area of the commercially available pigment ranges from 0.7-1.5mt^2/gm.

Tinting Strength

Tinting is defined as a process of producing color by mixing a color material, dye or a pigment with white pigment or paint. The coloring power of given pigment is called tinting strength.

Tinting strength of the pigment can be calculated by the following formula:

$$\% \text{ Tinting Strength} = \frac{Weight\ of\ Standard\ Pigment}{Weight\ of\ Sample\ Pigment} x\ 100$$

The results are recorded in Table 3. Tinting strength of the synthesized pigment is very low and ranges from 20.2-26.1%.

Table 3 Tinting strength of the pigment

Pigment	% Tinting Strength
$Cu(Ac)_2$	20.2
$Co(Ac)_2$	23.7
$Ni(Ac)_2$	26.1

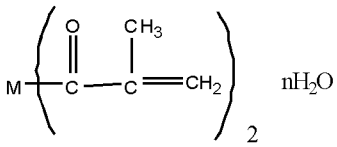
Oil Absorption

It is very significant property of the pigment while formulating the paints. If oil absorption value is very high it will absorbed maximum amount of the oil during the formulation and will change the Pigment Volume Concentration (PVC) and chalking of the paint takes place.

The oil absorption value of the above synthesized water based pigment is very low and it ranges from 7-13%.

Structural Analysis

The metal complex has the general formula given below:



Where n=2, M=Cu, Co, Ni.

In order to have additional information regarding the structure of the complex, it was examined by magnetic properties, identification of functional groups by Infrared Spectroscopy and thermal stability and percentage of the metal within the complex were calculated from TGA.

Calculated magnetic effect with the help of anticipated molecular model was very near to the ideal effect. Ideally, the Copper containing complex has magnetic field effect 1.73 B.M [11].

Another, possible way to confirm the proposed structure of complex is to evaluate the metal content within the complex by gravimetric analysis.

Table 4 Percentage metal loaded on complex

Pigment	% Metal Content (Theoretical)	% Metal Content (Practically)
$Cu(Ac)_2$	37	36.71
$Co(Ac)_2$	37	37.92
$Ni(Ac)_2$	37	39.02

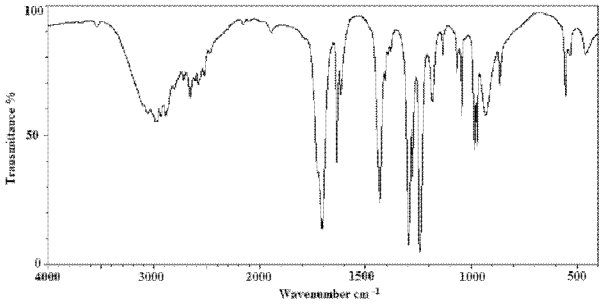
Infrared Spectroscopy

Infrared Spectroscopy determined the functional groups within the complex. Figure 2 indicates the representative IR of Ni- based pigment.

The band at 1700 cm^{-1} in the spectra is assigned to the metal ligand, centered by two ether-based groups. The band at low frequency 550 cm^{-1} is attributed to the metal within the complex [12]. The strong band around the 2925 cm^{-1} indicates the presence of C=C group within the complex. Stretching band around the 1210 cm^{-1} indicates the presence of ether linkage. The strong absorption at 450 cm^{-1} indicates the presence of water molecule attached cordially with the complex.

Key band, which assists the identification of attachment of carbonyl group with the metal in the plane deformation, shows absorption at 1415 cm^{-1} [13].

Figure – 2 (indicates the representative IR of Ni- based pigment)



Thermo gravimetric analysis

Initial decomposition of the complex (10%) occurs at 200^{0}C which is responsible for the dissociation of the water molecule from the complex, which was cordially, linked with the metal within the complex.

More than 50% of the weight loss of the pigment occurs at 240^{0}C which is attributed to the decomposition of the entire organic content present within the complex.

Residual matter does not get affected upto 875^{0}C. Around 39% of the residual material is not decomposable confirming the amount of transition metal within it.

CONCLUSION

The complex synthesized by above mentioned process can be used as a pigment for the industrial paint. Comparing to the properties with the commercially available pigments, Oil absorption value of the synthesized pigment is very low, particle size distribution is very narrow as desired in pigment having good dispersing power and it has very good thermal stability. The only drawback with the above-synthesized pigment is it has very low tinting strength.

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