Final Progress Report of Major Research Project

Entitled

Design Modelling and simulation of stirred ball mill and ultrasound assisted dispersion of nanopigments for utilization in formulations of coatings, printing ink, pharmaceuticals and cosmetics

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1. Introduction

Pigments are inorganic or organic particulate materials which are insoluble in polymeric binders and physically and chemically unaffected by the vehicle in which they are incorporated. Pigments selectively absorb certain wavelengths of visible light and reflect the rest of the wavelengths, which results in color appearance. The manufacture of paint constitutes dispersion of particulate pigments in polymeric binder in presence of additives and solvents using suitable dispersion machineries where a sufficient shear stress is imparted to separate the pigment aggregates in the presence of a dispersion stabilizer. The dispersion of pigment in polymeric binder in presence of additives and solvents is one of the most expensive steps in manufacture of paint. High performance pigment production can be accomplished by effectively controlling shape, particle size or surface of the pigment. Successful grinding requires both effective particle capture and sufficient impact intensity with optimum energy utilization. Generally, the influencing parameters for breaking up the agglomerates in a dispersion process can be divided into the properties of the dispersed particles, the formulation of the homogenous phase and the stress mechanisms, stress intensity and stress frequency of the dispersing machine itself. Different dispersion machineries such as kneader mill, bead mill, stirred ball mill etc utilize combinations of different stress mechanisms for breaking of agglomerates. Consequently, every dispersing machine has its own specific dispersing behavior [1]. Stirred ball mill has simple construction; high size reduction rate and low wear contamination by which it can produce fine and super fine material very effectively [2]. Owing to their high efficiency stirred ball mills have replaced traditional system.

Conventionally particle size reduction and dispersion is being achieved by grinding in equipments such as Ball Mill, Bead Mill using grinding media of specific size, geometry and composition [3-4]. In surface coating/ink formulation dispersion is most expensive component so it is always advantageous to achieve the highest color strength and shade matching at lowest possible amount of pigment. Correct pigment dispersion technology and optimum mill base formulation facilitates better color strength, brightness and stability of final coating formulations. Dispersering and wet grinding techniques for preparation of ready tints have advantages over the direct paint manufacture in terms of utilization of best processing technology, faster production and reduced inventory of pigment concentrates.
Current commercial challenge often faced by the surface coating industry is to keep these pigments in the stable dispersed form with ultimate achievement of colour strength (e.g.

jertness in case of carbon black) The commercially available pigments are dispersed into the polymeric vehicle/suitable medium by cascading and attrition In these process, high shear rate homogenization is used to redisperse the pigment agglomerates. However the breaking of agglomerates requires high energy inputs when high shear rate homogenizers and grinding process is being used to achieve segregation of particles and dispersion of particles. Cavitation is one of the ideal options to achieve the segregation of particles and their stabilized dispersion. Large aggregation of particles are being fragmented into the smaller particles by use of continuous mechanical shearing action and micro jets, attrition effect and knife effect by continuous implosion of ultrasound waves. The use of ultrasound power in grinding and making stable dispersions has numerous of advantages such as it is the most viable technique for highly energetic grinding materials it does not affect thermal behavior of materials, requires shortest processing period there is minimum consideration. These advantages permit use of high intensity ultrasounds for the preparation of variety of commercial materials in which particle size of major concern such as catalytic materials, ceramic, pharmaceutical sol, color concentrate. [5-7]. In recent times, the potential use of ultrasound in leather, textiles, and chemical process industries with the aim to increase the process efficiency, reduce process time, and improve product quality as an advanced manufacturing technique are being studied [7] Our earlier studies demonstrated that ultrasound helps to improve the coloristic properties of coating such as color strength and purity. In cavitation based dispersion, formation of intense turbulence coupled with strong liquid circulation currents can enhance mass transfer rates and generate a very fine and stable dispersion [8] Hence it can be said that physical and chemical effects of ultrasound helps in the intensification of the dispersion process though micro-jets, micro-mixing and high shearing as well as extreme adiabatic temperature and pressure conditions. Thus in the present work, we have proposed the use of ultrasonic irradiation as source of energy to intensify the process of dispersion which is expected to give beneficial effects via simultaneous action of shearing and compression.

2. Brief Objectives of the Project

a) To explore the practical issues associated with energy optimization and pigment dispersibility in ultrasound assisted dispersion of nanopigments in stirred ball mill.

b) To investigate the effects of primary and secondary mechanochemical processes on degree of dispersion.

c) The experimental outcomes will be analyzed and a vigorous mathematical modeling and simulation will be performed to optimize the operating conditions for minimum energy utilization for to achieve maximum tinctorial strength.

3. Methodology

Design and Fabrication of stirred ball mill

A cost effective stirred ball mill will be fabricated for paint dispersion purpose. Effects of several parameters such as radial distribution of beads, axial distribution of beads as a function of agitator type and speed on tinctorial strength, purity of colour, colour difference, gloss, impact resistance, mar resistance, adhesion, hardness, and scratch resistance of film will be studied by dispersing suitable formulations development in the developed mill.

4. Work done (Phase wise) and Results achieved:

Phase I: a) Literature Survey:

A rigorous literature have been referred (still continues) in the form research papers and reference books for studying various aspescts of pigment dispersion including methodologies, mechanism, energy requirements, design of equipments, respective cost of operation and modeling of dispersion techniques. For generating a bank of information in the form of high impact referred journal libraries of institutes like IIT Bombay, IIT Kanpur, IISc Bangalore, UICT Mumbai, NIT Warangal, North Maharashtra University Jalgaon etc have been referred. List of research papers generated as a part of literature survey have been enclosed (Appendix I).

b) Design and Fabrication of stirred ball mill.

Amalgamations of ball mill and bead mill is performed in a simple, novel Impeller Assisted Circulation Mill using circular disc and cross shaped stationary impellers. Mill base calculations and let down additions were worked out successfully for ball mill, bead mill and Impeller Assisted Circulation Mill for green glossy paint, yellow chrome glossy paint, white flat paint, white undercoat paint and white undercoat base yellow tinter and to obtain formulations that met the requirements of finer dispersion at the lowest material cost and to verify the feasibility of new design.

The prototype stirred ball mill was designed, fabricated in the institute workshop with following dimensions.

Sr. No	Specification	Details
1	Mill diameter	115mm X 116mm (Inside diameter X height)
2	Mill Capacity	1.33 L (suspension)

3	Motor power	1.5 Hp
4	Motor Speed	400 rpm
5	Electric Supply	230 V, Single Phase, 50 Hz

Stirred Ball Mill

Ultra Sonicator

Phase II: Experimental runs:

Preliminary experiments in batch mode have been completed to study the effect of ultrasound assisted cavitation on dispersibility of various organic and aqueous based pigment formulations. Blue and green pigments were selected to make the water and organic solvent based pigment concentrate in presence of surfactant.

Formulations of Phthalocyanine Blue and Green water based and THF based Dispersions for Preliminary runs
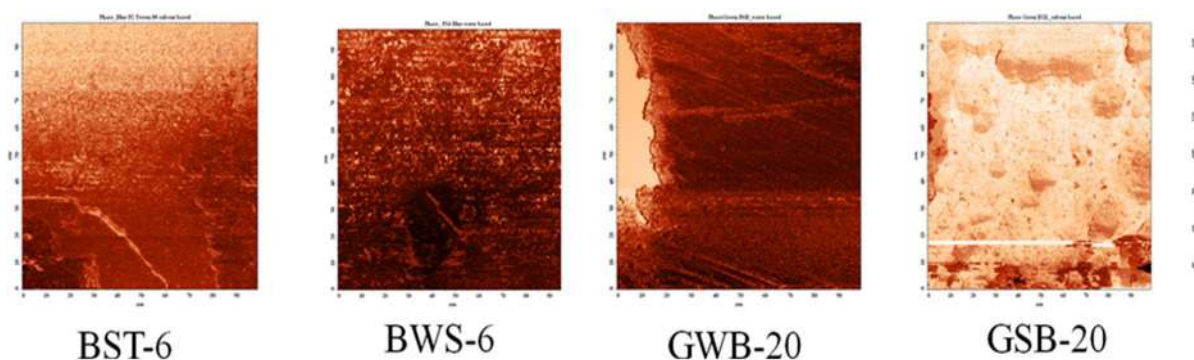
Formulation-1

Tint base	Ingredients	Weight (%)
	Pigment (Blue/ Green)*	5.156
	Surfactant (Tween 80/ SLS/ BYK)*	1.031
	Oleic acid*	0.578
	Iso propyl alcohol*	10.3

Water based	THF	10.3
	Water	72.2
Organic solvent based	THF	82.5
Total		**100**
* Common ingredients for both water based and THF based Tints		

Operating parameters for Preliminary experimental runs of formulation 1)

Pigment	Ultrasound Probe Size (mm)	Surfactant	Phase
Blue	6	Tween 80	Aqueous and Solvent
	10	Sodium Lauryl sulphate	
	20	BYK-192	
Green	6	Tween 80	
	10	Sodium Lauryl sulphate	
	20	BYK-192	

Preliminary experiments on fabricated stirred ball mill have also been carried out with following formulation

2) Formulation Green Glossy Paint for experimental runs for prototype stirred ball mill

Sr. No.	Ingredients	Weight in %
1	Phalocyanine Blue	1.0
2	Hansa yellow G	10.0
3	Ferrite yellow	3.5
4	Lond oil alkyd(70% solid)	59.9
5	Mineral turpentine oil	20.6
6	Dipentene	3.0
7	Methyl ethyl ketoxime	0.1
8	Cobalt octoate	0.4
9	Calcium octoate	1.5
	Total	**100**
Solids by volume = 50.3, Sp. gravity = 0.97, % pigment volume concentration (PVC) = 25.5		

The fineness and stability of colloidal dispersion was monitored by AFM analysis, SEM analysis and particle size distribution while colour matching spectral analysis (K/S analysis) was undertaken to determine the variation in colour strength.

Color strength analysis

A) Formulation-1

	Water Based								
Color	Probe 1 (6mm)			Probe (10mm)			Probe(20mm)		
	WT-6	**WS-6**	**WB-6**	**WT-10**	**WS-10**	**WB-10**	**WT-20**	**WS-20**	**WB-20**
Blue	65.41	68.88	75.25	9.24	69.08	67.06	50.22	71.67	63.37
Green	82.77	87.02	91.34	35.02	49.17	9.007	55.05	99.86	68.71
	Solvent Based								

Color	Probe 1 (6mm)			Probe (10mm)			Probe(20mm)		
	ST-6	SS-6	SB-6	ST-10	SS-10	SB-10	ST-20	SS-20	SB-20
Blue	93.02	**100**	93.37	76.77	82.75	73.44	66.80	69.21	71.82
Green	78.67	88.34	56.09	61.9	**100**	20.10	25.73	57.98	77.72

B) Formulation 2
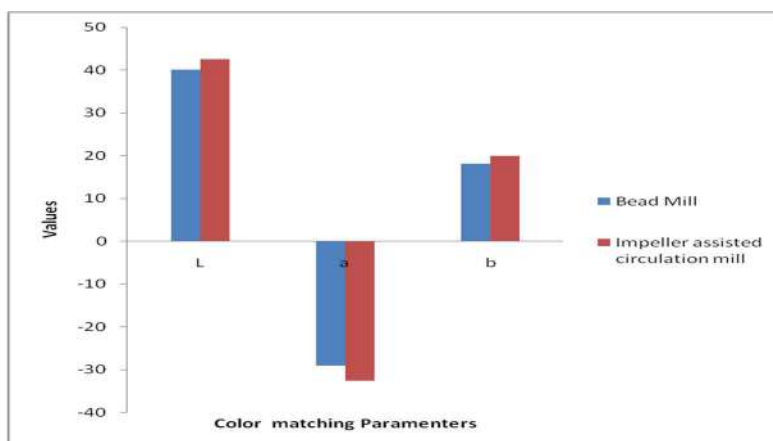
AFM analysis for formulation 1

BST-6   BWS-6   GWB-20   GSB-20

SEM analysis for Formulation 2
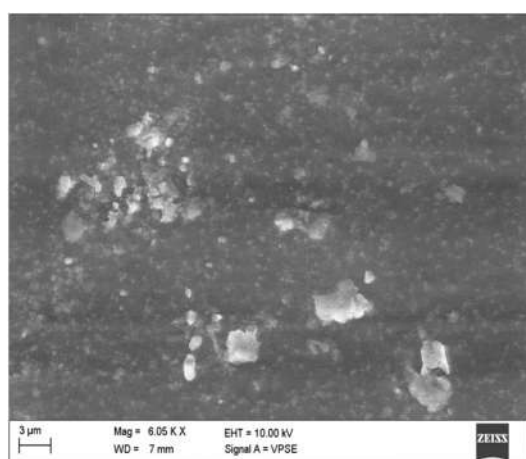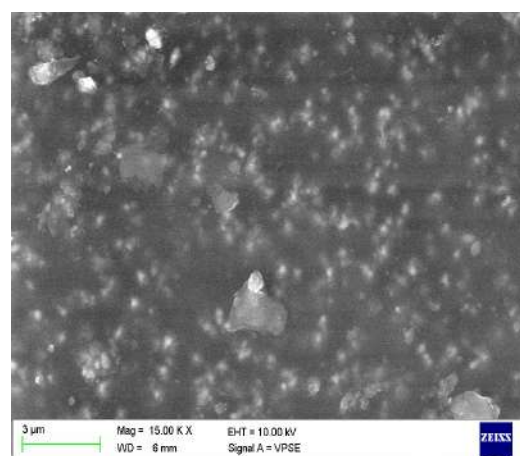
(2 hrs)   (4 hrs)
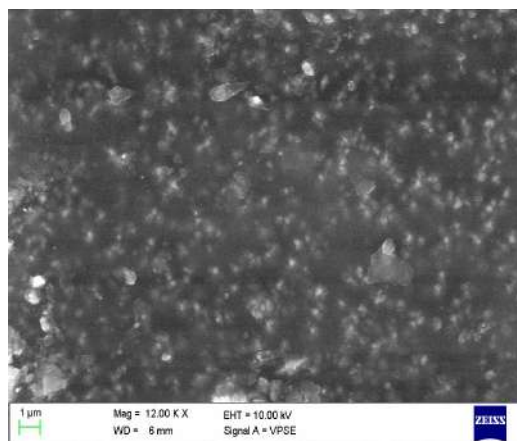
(6hrs)

Particle Size Distribution results Formulation 1:

Pigment	Particle size distribution	Average particle size in nm	Particle size distribution	Average particle size in nm
Probe tip (mm)	6		20	
Blue Pigment	78-825	451	68-531	299
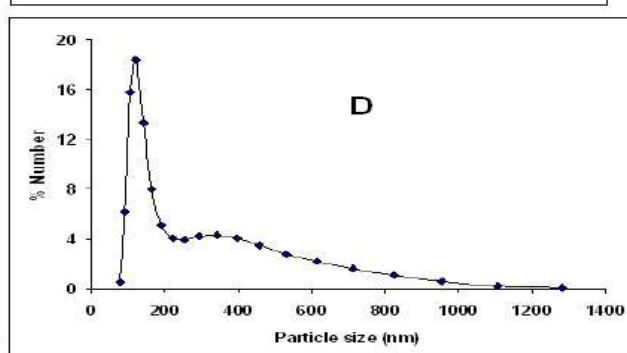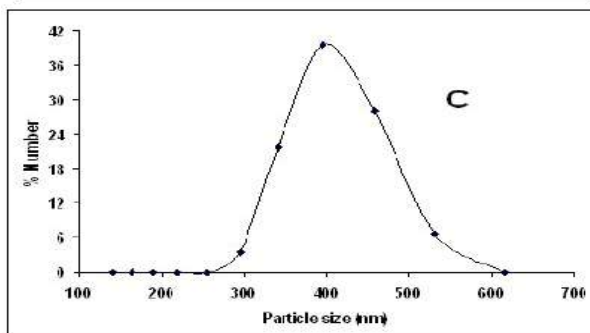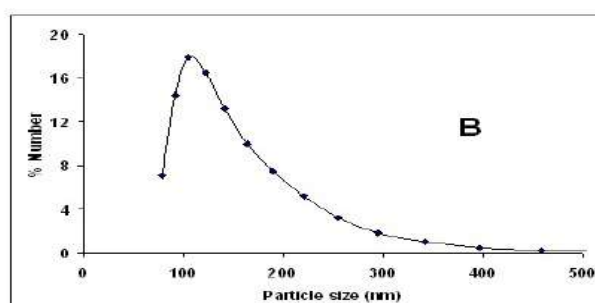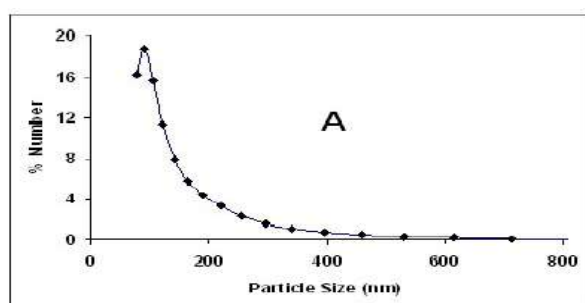
Particle size distribution of blue pigment (organic) when a) 6 mm probe tip b) 20 mm probe tip was used and particle size distribution of Green pigment (organic) when c) 6 mm probe tip and d) 20 mm probe tip was used in water solvent.

Comparison of energy required achieving complete dispersion by high speed dispersion mill and high intensity ultrasound was investigated. Correlation was established with dispersion quality parameters and energy consumption, quantity of surfactant.

Following achievements from work carried out in the project:

a) **Patent:** 01 patent filled as detailed below

    Title: Design of Impeller assisted circulation milling for finer dispersion

    Application No.: 1844/MUM/2012

    Ref. No.: E-11/138/2012-MUM

    Date of filing: 27/06/2012

b) **Conferences**

Sr. No.	Name of Conference	International/National	Date and Venue	Title of Paper/Poster presented
1.	9th International Symposium on Surface Protective Coatings (SSPC 2011 India)	International	7-9 Dec. 2011 Banglore, India	Surfactant assisted ultrasound dispersion of phthalocyanine pigments in water borne and solvent thinnable systems: Modeling and Simulation studies
3.	Nanomaterials Industrial Polymer and Eco-friendly Coatings Prespective and Challenges (NIPEC-2012)	National	18 Feb. 2012 SOCS and UDCT, North Maharashtra University, Jalgaon.	"Surfactant mediated synthesis and ultrasound dispersion of nano Iron Oxide Pigment"
4.	8th Coating Science International 2012	International	25 - 29 June 2012 Noordwijck, The Netherlands	"Mathematical modeling of microbead and high speed dispersion and evaluation of dispersion stabilization mechanism"
6.	10th International Symposium On Surface Protective Coatings, SSPC India 2013 (SSPC-2013), (2nd **Best poster paper awarded**).	International	Feb. 15-16, 2013 Mumbai	"Phase selective synthesis of bismuth vanadate (BiVO4) nanopigment using surfactant assisted impinging solution spray process and their application as high performance pigment in paint"
7.	Nano India 2013	National	19-20, February 2013, Thiruvananthapuram, India	"Polymorph selective synthesis of CaCO3 nanoparticles using impinging solution spray process and their utilization for preparation of PBSA/ CaCO3

				Latex Composites"
8.	5th Asian Conference on Colloid and Interface Science [ACCIS-2013]	International	Department of Chemistry, University of North Bengal, Darjeeling, West Bengal, India, 20-23 November 2013.	"Synthesis of copper phthalocyanine blue nanopigment comparative evaluation of fusion, solvent and microwave technique"

Summary of the findings:

Amalgamations of ball mill and bead mill is performed in a simple, novel Impeller Assisted Circulation Mill using circular disc and cross shaped stationary impellers. Mill base calculations and let down additions were worked out successfully for finer dispersion of green glossy paint, yellow chrome glossy paint, white flat paint, white undercoat paint and white undercoat base yellow tinter to verify the feasibility of new design. Comparison of energy required achieving complete dispersion by newly fabricated ball mill and high intensity ultrasound was investigated.

Correlation was established with dispersion quality parameters and energy consumption, quantity of surfactant.

Contribution to the society:

Dispersion of pigment concentrates is an important processing step in the formulations of paints and coatings. Current commercial challenge often faced by the surface coating industry is to keep these pigments in the stable dispersed form with ultimate achievement of colour strength. We demonstrated that newly fabricated ball mill and ultrasound helps to improve the coloristic properties of coating such as color strength and purity and will be beneficial for optimizing the operating conditions for minimum energy utilization for to achieve maximum tinctorial strength for many paint surface coating industries.

Ph.D. enrolled/produced out of the project:

Yes, Co-investigator Mr. Nilesh P. Badgujar and Project Fellow Mr. Yogesh E. Bhoge have enrolled for Ph. D.

Details are as follow:

Name of Enrolled Candidate	Mr. Nilesh P. Badgujar	Mr. Yogesh Eknath Bhoge
Post	Co-Investigator	Project Fellow
University	North Maharashtra university,	North Maharashtra university, Jalgaon

	Jalgaon (M. S.) India	(M. S.) India
Faculty	Engineering and Technology	Science
Subject	Chemical Engineering	Chemistry
Title	Physicochemical characterization, process Engineering and Mathematical Modelling of Pigmented Dispersion for Utilization in Formulation of caotings	"Synthesis and crystal design of high performance pigments for development of special effect coatings"
Registration No.	NMU/11/Ph. D/Chem. Engg./28/2011, Dated 23/02/2011	NMU/11/Ph.D./Chem/277/2012, Dated: 20/01/2012

No. of publications out of the project:
Published: 02, Communicated: 00 (Reprints are enclosed)

1. N P Badgujar, Y E Bhoge, T D Deshpande, Bharat Apparao Bhanvase, Parag Gogate, Shirish H Sonawane, Ravindra D Kulkarni, "Ultrasound assisted organic pigment dispersion: advantages of ultrasound method over conventional method", *Pigment and Resin Technology*, Vol. 44, Issue 4, pp. 214-223, (2015) [IF: 0.79].

2. Y. E. Bhoge, V. J. Patil, T. D. Deshpande, U. D. Patil and R. D. Kulkarni, "Synthesis of Mica Doped Calcium Carbonate Filler for Partial Replacement of TiO_2 in Decorative Paint", *International Journal of Engineering Trends and Technology*, pp. 279-282, (2016) [IF: 1.79]

Pigment & Resin Technology

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Ultrasound assisted organic pigment dispersion: advantages of ultrasound method over conventional method

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Abstract

Purpose – The present work aims to deal with ultrasound-assisted organic pigment (phthalocyanine blue and green) dispersion and its comparison with the conventional approach.

Design/methodology/approach – Ultrasound is expected to give beneficial results based on the strong shear forces generated by cavitational effects. The dispersion quality for preparation using an ultrasound-based method has been compared with dispersion obtained using high-speed dispersion mill. Effects of different operating parameters such as probe diameter and use of surfactants on the physical properties of dispersion and the colour strength have been investigated. Calculations for the energy requirement for two approaches have also been presented.

Findings – The use of sodium dodecyl sulphate and Tween 80 surfactants shows better performance in terms of the colour properties of dispersion prepared in water and organic solvent, respectively. Ultrasound gives better dispersion quality as compared to the conventional approach.

Originality/value – The present work presents a new approach of ultrasound-assisted dispersion of phthalocyanine blue and green pigments. Understanding into the effect of surfactants and type of solvent also presents new important design-related information.

Keywords Dispersions, Ultrasonic frequencies, Surfactants

Paper type Research paper

Introduction

Dispersion of pigment concentrates is an important processing step in the formulations of paints and coatings (Smith, 2002). A narrow range of particle-size distribution in the final product achieved due to the efficient pigment dispersion process facilitates improved colour strength, brightness and stability (Wennerstrum *et al.*, 2002). Superior dispersion of nanomaterials can be achieved using different surfactants (Vaisman *et al.*, 2006; Zheng *et al.*, 2003; Hwang *et al.*, 2008) and a range of aqueous/organic solvents have also been explored as dispersion media (Giordani *et al.*, 2006; Cheng *et al.*, 2008; Bergin *et al.*, 2009). Water- and organic solvent-based dispersion can be used in coatings that can be applied to most substrates, including metal, plastic, wood and glass surfaces. The current commercial challenge often faced by the surface coating industry is stability of the pigment dispersion. The conventional approach for dispersion of commercially available pigments into suitable medium is based on the use of high-speed homogeniser. In this approach, high shear mixer is used to redisperse the pigment agglomerates but the use of high shear homogenising mixer requires higher energy input to break tightly bound aggregates (Suslick *et al.*, 1996; Raman *et al.*, 2011; Huang and Terentjev, 2012; Perez-Maqueda *et al.*, 2005). To break the aggregates of the particles, the supplied energy must be greater than the binding energy of the aggregates. An alternative approach for obtaining a uniform dispersion can be based on the use of sonochemical reactors, which work on the principle of cavitation.

Cavitation is caused by passing high-frequency sound waves above 20 kHz through liquid media. When ultrasound passes

through the liquid media, molecules are pulled apart in the rarefaction cycle to create cavities which then pass through different stages of growth and size oscillations before collapsing violently generating various physical and chemical effects (Bhanvase *et al.*, 2011, 2012a, 2012b; Prasad *et al.*, 2010; Pinjari and Pandit, 2010, 2011). The extreme transient conditions generated in the vicinity and within the collapsing cavitational bubbles can bring about the size reduction of the material to nanoscale (Patel *et al.*, 2013; Deosarkar *et al.*, 2013). The strong shear force generated during the cavity collapse can also effectively disperse the pigments, and the effects are dependent on several factors such as nature of the solvent including the physicochemical properties, number of cavitation events, operating temperature and pressure, as well as the ultrasound parameters such as intensity, frequency and irradiation time. The use of ultrasound in the formulation of stable dispersion has many advantages, and this approach can be a viable technique for the preparation of small, uniform-size particles of colloidal materials. Further, the use of ultrasound does not alter the thermal behaviour of materials and dispersion can be achieved in lower processing time (Raman *et al.*, 2011; Huang and Terentjev, 2012; Perez-Maqueda *et al.*, 2005; Bhanvase *et al.*, 2011, 2012a, 2012b; Patel *et al.*, 2013; Deosarkar *et al.*, 2013; Suslick *et al.*, 1987; Raman and Abbas, 2008; Patil and Pandit, 2007).

There have been some earlier reports related to the use of ultrasound for pigment dispersion, and recently, Hielscher (2013) has provided a good overview of the applications of ultrasound in the area of paints and coatings. Some of the earlier works related to use of sonication for dispersion and stabilisation of pigments include the work of Cheng *et al.* (2010a) and Bergin *et al.* (2008). The quality of dispersion is dependent on the sonication conditions including sonicator types, sonication times (generally reported range is 2 to 30 min) and probe diameter. In addition, the solvent properties also affect the dispersion process, and the effects have been generally analysed on the basis of solubility parameters such as Hildebrandt or Hansen parameters (Cheng *et al.*, 2008; Bergin *et al.*, 2008; Cheng *et al.*, 2010a; Cheng *et al.*, 2010b; Usrey *et al.*, 2009; Detriche *et al.*, 2008) or surface energy (Bergin *et al.*, 2008). Scale-up of ultrasonic reactors has been a problem over the years, but the recent advances into new efficient designs such as flow cells, designs based on longitudinal horns or multiple transducers and continuous processing have made some applications possible at commercial-scale installations (Kumar *et al.*, 2007; Gogate *et al.*, 2003, 2011; Gogate, 2008). Englert *et al.* (2012) reported the scaling up of a process for achieving dispersion of nanoparticles in epoxy resin using ultrasound-assisted continuous flow operation.

An analysis of the literature reveals that there has not been much work regarding the establishment of the dependency of quality of dispersion on the probe diameter which plays an important role in deciding the physical effects of cavitation. The effect of the presence of surfactants which can alter the stability of the prepared dispersions in combination of ultrasound has not been studied in details. A comparison of the energy requirements for the ultrasound-assisted approach and conventional milling processes is also lacking. The present work deals with the use of ultrasonic irradiation for the dispersion of organic pigment evaluating the effect of probe diameter and addition of different surfactants. Two commercially important organic pigments (phthalocyanine blue and green) have been considered for the dispersion study in different organic solvents. Energy consumption analysis has also been attempted to establish the efficacy as compared to the conventional approach.

Experimental

Materials

Pigments such as phthalocyanine blue ($CuC_{32}H_{16}N_8$, specific gravity: 1.6-1.8, oil absorption value of 43 per cent) and phthalocyanine green ($C_{32}H_{16}Cl_8N_8$, specific gravity: 1.4-1.45, oil absorption value of 36 ± 6 per cent) were procured from Sudarshan Chemicals, Pune. Tween 80 (polyoxyethylene sorbitan monooleate, density of 1.07 g/cm^3 at 25°C) was procured from Loba Chemie, Mumbai. Oleic acid (analytical grade, density 0.895 g/cm^3) was procured from Merck Specialties Pvt. Ltd., Mumbai. *Sodium dodecyl sulphate* (SDS, $C_{12}H_{25}SO_4Na$, density of 1.01 g/cm^3) was procured from S. D. Fine Chemicals Pvt. Ltd., Mumbai. Distilled water was used as a medium for the preparation of water-based dispersion. BYK 192 acrylic polymeric surfactant was obtained as a gift sample from BYK Chemie (pH 5-9, density of 1.05 g/cm^3 at 20°C). Organic solvents such as isopropyl alcohol (density of 0.786 g/cm^3) and tetrahydrofuran (density of 0.889 g/cm^3) were obtained from S.D. Fine Chemicals Pvt. Ltd., Mumbai, and Merck Specialties Pvt. Ltd., Mumbai, respectively. All chemicals were used as received from the supplier.

Pigment dispersion using conventional high-speed homogeniser and ultrasound

The dispersion of pigment in organic solvents- and water-based systems has been investigated using an ultrasound-assisted approach based on the use of ultrasonic horn (diameters 6, 10 and 20 mm) operating at a constant frequency of 22 kHz and the rated output power of ultrasonic horn was 750 W (Crometech Model, Taiwan). The actual power input could be controlled by varying the amplitude. In the present work, an ultrasonic horn was operated at 50 per cent amplitude giving supplied power of 375 W. Experiments were carried out to understand the effect of probe diameter on the extent of deagglomeration and the colour strength. The effect of probe diameter was investigated using different diameters as 6, 10 and 20 mm diameter and the treatment time was fixed at 30 min. For establishing the efficacy of the ultrasound-based approach, conventional approach was also used for preparation of water- and organic solvent-based dispersions using a high-speed dispersion mill (0.125 HP, 8,000 RPM 230 V, Make REMI Mumbai, India).

Formulation of blue and green pigment dispersions

The formulations of phthalocyanine blue and green (water- and organic solvents-based dispersions) were prepared as per the compositions reported in Table I. Three different surfactants, SDS, Tween 80 and BYK 192, were selected for the water- and organic solvent-based dispersion (Usrey *et al.*, 2009). Based on hydrophilic–lipophilic balance values, the selection of surfactant type and quantity was decided. SDS

Table I Formulations of phthalocyanine blue and green water-based and THF-based dispersions

Serial no.	Ingredients	Waterborne pigment concentrate	Organic solvent-based pigment concentrate
1	Pigment (blue/green)*	5.2	5.2
2	Surfactant (Tween-80/sodium lauryl sulphate/BYK-192)*	1.0	1.0
3	Oleic acid*	0.6	0.6
4	Isopropyl alcohol*	10.3	10.3
5	Tetrahydrofuron	10.33**	82.5
6	Water	72.2	–

Notes: *Common ingredients for both water-based and organic solvent-based pigment concentrate; **small quantity of THF is used in water-based pigment concentrate as pigment is hydrophobic

surfactant was used mainly in the water-based formulation, while Tween 80 was used mainly in the organic-based formulations. Other ingredients such as oleic acid, isopropyl alcohol were common ingredients in both the water- and organic solvent-based system. At room temperature, organic pigments such as phthalocyanine blue and phthalocyanine green (5 weight% loading) were dispersed in the presence of different surfactants (Tween 80/SDS/BYK) in a 250-ml beaker. In a typical formulation, 1 g surfactant (Tween 80/SDS/BYK), 0.578 g oleic acid, 10.3 g of isopropyl alcohol, 10.3 g of tetrahydrofuran (THF) and 72.2 ml of water was mixed in the case of water-based system; 82.5 gm of THF was added instead of a mixture of THF (10.3 g) and water (72.2 ml) for the case of organic solvent-based dispersion (all the other components were mixed in same ratio).

Characterisation

Atomic force microscopy (AFM) measurements were performed using an AFM Explorer microscope (ThermoMicroscopes, USA) at room temperature, in a non-contact mode with Si cantilevers of a 1,650-00 type (ThermoMicroscopes) with a nominal tip radius of 10 nm and resonant frequency of about 220 kHz. Colour strength (K/S) of the pigment was measured using the standard reset method for colour and strength of the pigments (ASTM D387-00) which measures the K/S values using a reflectance spectrophotometer based on the Kubelka Munk equation. The size distribution and average particle size of phthalocyanine blue pigment were obtained using an optical microscope (Olympus CX21). Particle-size distribution analysis of phthalocyanine green pigments was carried out by Photon Correlation Spectroscopy (PCS, 3,000 HAS, analyser, Malvern) with images being acquired at a magnification of 40 ×.

Results and discussion

Comparison of microscopic images of dispersion prepared using high-speed dispersion mill and ultrasound-based method

Pigment dispersions prepared using high-speed dispersion mill as the conventional approach were compared with those prepared using ultrasound (10- and 20-mm–diameter probe) based on the microscopic colour images of phthalocyanine blue pigment dispersion as shown in Figure 1. Comparison of the images depicted in Figure 1(a-f) reveals that the high-speed dispersion mill shows maximum agglomeration as compared to the ultrasound-assisted dispersion for both 10- and 20-mm-diameter probe. It is also observed that

Figure 1 Microscopic images at 40 × magnification of the ultrasound-assisted dispersed blue pigment in the water-based system using
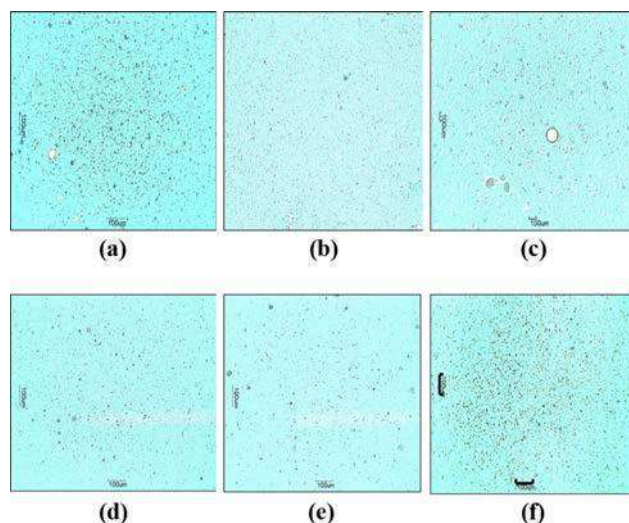
Notes: (a) 10-mm probe; (b) 20-mm probe ; (c) the high-speed dispersion mill along with SDS surfactant and in organic solvent-based system using; (d) 10-mm probe; (e) 20-mm probe; (f) the high-speed dispersion mill along with Tween 80 surfactant

ultrasound-assisted dispersion using 20-mm probe gives the best colour strength due to finer dispersion as compared to the 10-mm-diameter probe in both water- and organic solvent-based system. An image of colour shade prepared by the 20-mm probe shows lesser agglomeration of the particles, while images of colour shade prepared by the 10-mm probe show the presence of coarser particles. The above results clearly indicate that the 20-mm probe is more efficient in breaking the agglomeration of pigment particles. Generation of fine dispersion in the presence of ultrasound is attributed to the physical effects of cavitation, namely, intense micro-scale turbulence and acoustic streaming (Vichare et al., 2001; Tuziuti et al., 2005; Gogate, 2008; Chen et al., 2010; Moholkar et al., 2000). Use of the high-speed dispersion mill does not provide intense mixing at micro scale and hence it results into agglomeration of pigments. Also, in the case of the 20-mm-diameter probe, increased extent of cavitation and liquid circulation velocity (Vichare et al., 2001) gives higher breakage of agglomerates as compared to the 10-mm probe,

resulting in fine dispersion. It is also established that higher energy delivery through a smaller area of the tip (in the case of 10-mm probe) gives some fraction of particles with smaller size and remaining particles lie in the large particle size range giving uneven dispersion of particles. In the case of the 20-mm probe, the particles are obtained in narrow range as compared to the 10-mm probe because of increased liquid circulation velocity (Vichare *et al.*, 2001) giving uniform and finer dispersion of pigment. The effect of probe diameter should not be generalized, as any continuous increase in probe diameter may cause a decrease in the efficiency as a result of increasing probe weight and overloading of piezoelectric and electric power source. Also, with an increase in the probe diameter after a certain value, it is expected that ultrasonic wave reflection in the direction perpendicular to the probe axis increases and a decrease in the extent of cavitation occurs. Due to these reasons, it is recommended that the probe diameter should be less than a quarter of the probe length (Mcculloch, 2008).

Particle-size analysis of organic pigment dispersion: effect of the probe diameter

Figure 2 represents the particle-size distribution of phthalocyanine blue pigment obtained from the experiments based on the use of 6- and 20-mm probe tip in the case of the ultrasound-assisted approach with SDS as a surfactant in the water-based system. Further, it was also observed that 6- and 10-mm-diameter probe gives comparable results (data for 10 mm not shown to avoid repetition and give clarity in

Figure 2 Particle-size distribution of blue pigment (organic) along with SDS surfactant in the water-based system
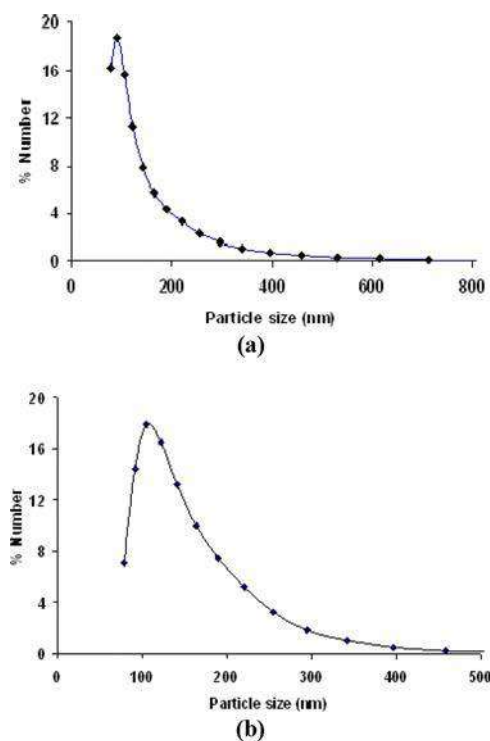

Notes: (a) 6-mm-diameter probe;
(b) 20-mm-diameter probe

representation), which can be attributed to the fact that the wave intensity produced by these probes with 6- and 10-mm diameter is near about similar. From Figure 2(a), it is observed that the 6-mm probe shows the particle-size distribution in the range of 78-825 nm with average particle size as 451 nm, while the blue pigment dispersion prepared using the 20-mm probe shows narrow particle-size distribution over the range of 68-531 nm with average particle size as 299 nm (Figure 2(b)). Particle-size analysis clearly indicates that the narrow range of distribution is obtained using the 20-mm probe. It is attributed to increased cavitational activity and hence increased liquid circulation velocity due to the increase in probe diameter from 6 to 20 mm (Vichare *et al.*, 2001) resulting in uniform and fine dispersion. Due to higher active cavitational volume, it is expected that there will be higher breakage of agglomerates in the case of the 20-mm probe as compared to the 6-mm probe, which results in a narrower particle-size distribution. It should be noted that larger diameter till an optimum value (Mcculloch, 2008) will be more preferred where narrow overall size distribution is required with lower average size of the dispersion.

AFM analysis of organic pigment dispersion: effect of probe diameter and surfactant

Figure 3(a-d) shows the representative AFM images of the four best batches obtained in the present work for the comparison purpose. Figure 3(a) represents the AFM image of blue pigment dispersion prepared using Tween 80 surfactant using 20-mm ultrasonic probe for the organic solvent-based system. Figure 3(b) represents the AFM image of water-based blue pigment dispersion using an SDS surfactant in the presence of the 20-mm ultrasonic probe. Figure 3(c) shows an AFM image of organic solvent-based blue pigment dispersion using BYK-192 surfactant using 20-mm ultrasonic probe. Figure 3(d) shows the three-dimensional image of the water-based blue pigment dispersion obtained using the 20-mm ultrasonic probe. From Figure 3, it is observed that the dispersion prepared by the 20-mm probe in the aqueous system in the presence of SDS surfactant shows the best dispersion characteristics as depicted in Figure 3(b and d). On the other hand, Figure 3(c) shows the least dispersion when blue pigment dispersion was prepared in the presence BYK surfactant using organic solvent-based system with the 20-mm probe. The use of the 20-mm probe size and SDS surfactant showed better dispersion as compared to other surfactants. The exact order of effective dispersion in these systems (dispersion of blue pigment prepared by ultrasound assisted approach using the 20-mm probe) is as follows: water-based system in the presence of SDS surfactant > organic solvent-based system in the presence of Tween 80 surfactant > water-based system in the presence of BYK-192 surfactant. It is also established that dispersion prepared using the 20-mm probe shows a more regular pattern of distribution of particles because of increased cavitational activity (Vichare *et al.*, 2001) for the case of larger diameter of the probe as reported in the Figure 3(b). It is also found that the use of SDS surfactant showed uniform and fine particles in dispersion prepared using the 20-mm probe in the water-based system (Figure 3(b)). It is also observed that Tween 80

Figure 3 (a) Two-dimensional AFM image of blue pigment dispersion prepared in Tween 80 surfactant organic solvent-based system using the 20-mm probe; (b) Two-dimensional AFM image water-based blue pigment dispersion using SDS surfactant and the 20-mm-diameter probe; (c) Two-dimensional image of green pigment dispersion prepared by BYK surfactant – organic solvent based-system under the 20-mm-diameter probe; (d) Three-dimensional image of the water-based blue pigment dispersion using SDS surfactant and the 20-mm-diameterprobe
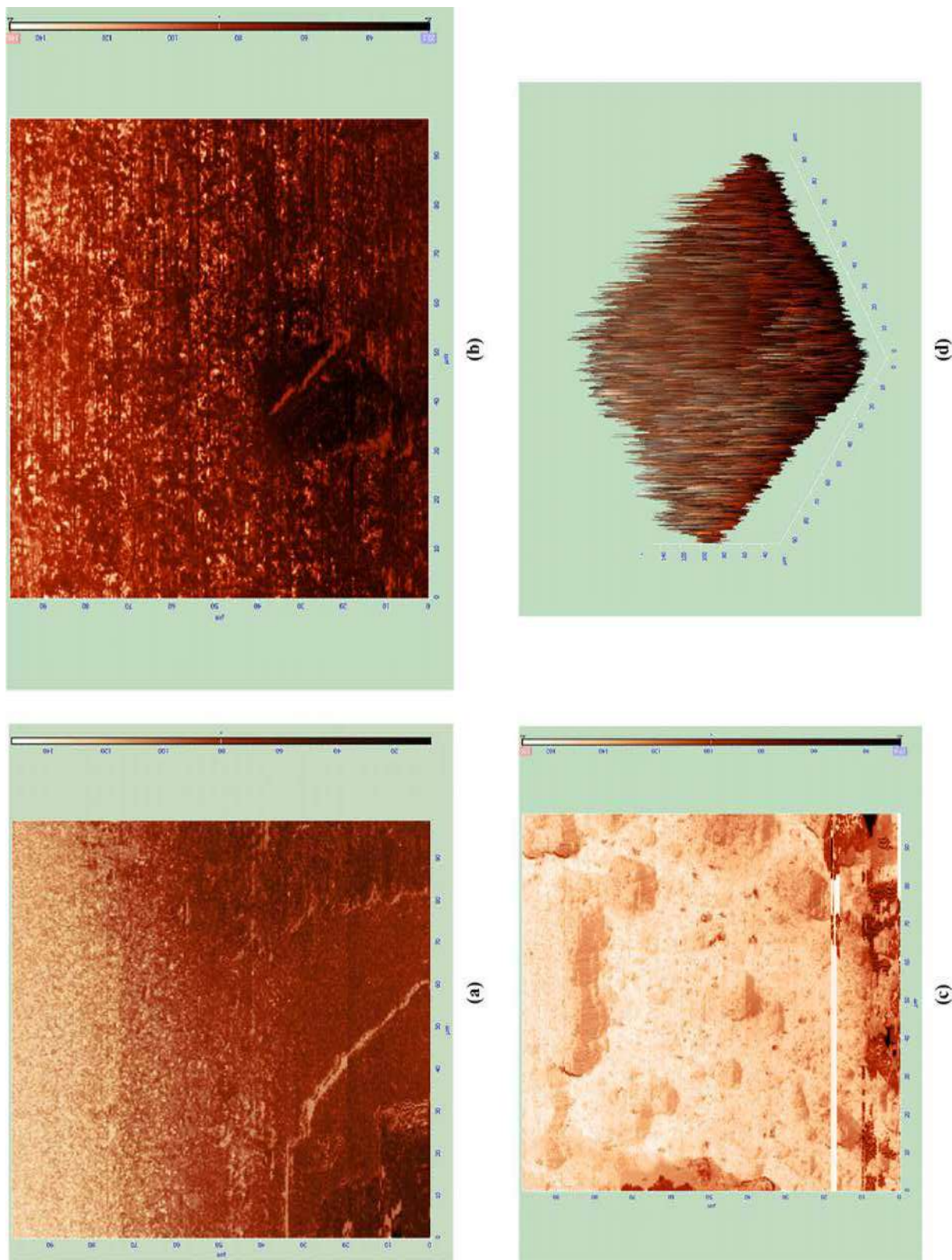
surfactant shows good dispersion of organic pigments with the use of the 20-mm probe in the organic solvent-based system with some degree of agglomeration.

Effect of the probe diameter and surfactant type on the viscosities of dispersion

For processing stable colloidal dispersions, two main features of surfactants, namely, adsorption at interface and self-accumulation into supramolecular structures, are very important. The adsorption of surfactants on the inorganic and organic surfaces generally depends on the chemical characteristics of particles, surfactant molecules and solvent. The effect of the probe diameter and surfactant type on the viscosities of dispersion prepared in organic solvent and water has been depicted in Table II. It is found that the dispersion of organic pigments prepared in the organic solvent-based system shows higher viscosity (ranging from 46.5 to 479 cps) in the presence of different types of surfactants and ultrasound. It is attributed to the higher viscosity of organic solvent compared with water, which is further enhanced by the addition of pigments in the organic solvent. Water-based dispersion shows the viscosity ranging from 0.74 to 70 cps in the presence of different types of surfactants and ultrasound which is less than the organic solvent-based pigment dispersion.

SDS surfactant was found to be effective in combination with ultrasound in the case of the 10-mm probe in the water-based system giving the minimum viscosity as 0.74 cps. It is attributed to the formation of more homogeneous pigment dispersion in the aqueous medium. In the case of organic solvent-based pigment dispersions, with an increase in the ultrasound probe diameter, the viscosity values are found to decrease, indicating more homogeneous pigment dispersion. In the case of Tween 80 and SDS surfactants in the organic solvent-based system, the viscosities were found to be reduced from 375.0 to 114.8 and 416.3 to 73.66 cps, respectively. The observed decrease in the viscosity can again be attributed to higher cavitational activity (Vichare *et al.*, 2001) at larger size of the ultrasound probe. For the BYK 192 and Tween 80 surfactants, the viscosities of organic solvent-based dispersion are 46.50 and 114.8 cps at 20-mm ultrasound probe diameter, respectively, which can be attributed to the formation of more homogeneous pigment dispersion using BYK 192 surfactant as compared to Tween 80 surfactant.

Variation in the colour strength

For the enhancement in the colour strength, uniform distribution of pigment particles is required, which is dependent on the ultrasound probe diameter, as well as the presence of surfactant. Due to increasing intensity of ultrasound, there is no effect on the surface charge, but there is a reduction in the pigment particle size due to the effects of cavitation. The reduction in the size is also dependent on the addition of suitable surfactant and the combined effect is helpful for the uniform distribution of the pigment particles in the suspension. The role of surfactants is attributed to the pigment wetting that is achieved when suitable surfactants and solvents adhere to exposed pigment surfaces. Surfactants sustain pigment particle separation by maintaining a minimum safe distance between two pigment particles of about approximately 5 nm. If the distance between pigment particles is less than the minimum safe distance, attractive forces will bring particles together, forming flocculates. Flocculation leads to noticeable changes in the pigment properties such as colour strength, gloss and viscosity. Thus, the overall enhancement in the colour strength is attributed to the combined effect of surfactant and ultrasonic irradiation. The variations in colour strength of prepared dispersion using different diameter probes and surfactant type are represented in Figure 4(a and b). As evident from the Figure 4(a and b), it is found that water-based dispersion show highest colour strength in the case of dispersion obtained in the presence of SDS surfactant. It is also found that an increase in the diameter of the probe does not show any appreciable change in the colour strength, when SDS surfactant was used in the water-based system. On the contrary, BYK-192 shows clear effect of the diameter of the probe on colour strength. It is found that an increase in the diameter of the probe results in a reduction in the colour strength in the presence of BYK-192 surfactant. The observed results can be attributed to a reduction in the coverage of particles by BYK-192 surfactant due to an increase in the probe size resulting in reduction in the final colour strength [Figure 4(a)]. In the case of organic solvent-based system [Figure 4(b)], use of higher probe diameter during the dispersion results in a decrease in the colour strength. This might be due to degradation of organic compounds in the presence of larger size probes which gives higher cavitational intensity. It is also interesting to note that, all surfactants show better colour strength in the organic solvent-based system. Tween 80 and BYK surfactant shows almost the same performance.
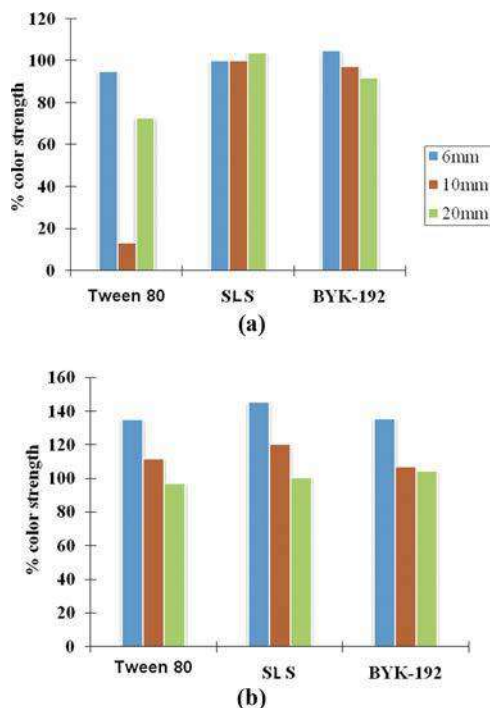
Prediction of deagglomeration using probability analysis

Paint properties such as colour strength and viscosity changes significantly with the degree of deagglomeration. Therefore, the colour strength (K/S) can be considered as representative of the extent of dispersion of the agglomerates under active dispersion volume (as per first-order kinetic model). The

Table II Effect of surfactant and the diameter of the probe on the viscosities of the pigment concentrate

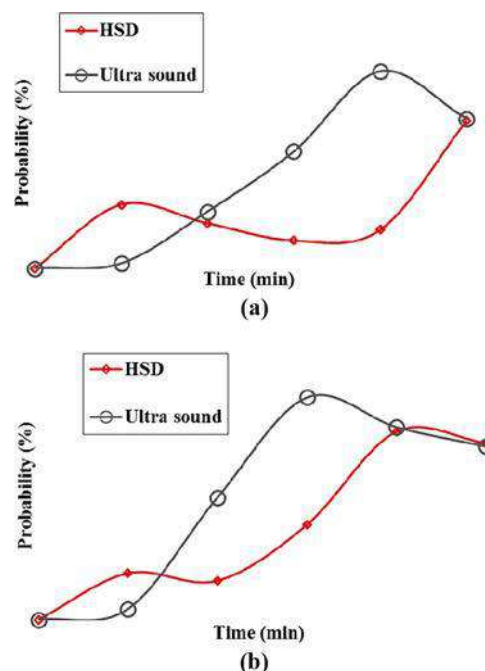| Colour	Probe (6 mm)			Probe (10 mm)			Probe (20 mm)		
	Tween 80	SDS	BYK-192	Tween 80	SDS	BYK-192	Tween 80	SDS	BYK-192
Viscosity values (cps) water-based									
Blue	9.6	7.06	1.302	4.09	0.74	9.11	69.94	63.43	2.79
Viscosity values (cps) organic solvent-based									
Blue	375.0	416.8	479.3	129.3	171.9	145.3	114.8	73.66	46.50

Figure 4 Effect of the surfactant type, ultrasound and diameter of the probe on colour strength of green pigment

Notes: (a) Water-based system; (b) organic solvent-based system

Figure 5 Probability predictions of ultrasound and high-speed disperser vs time in minute

colour strength values (K/S) obtained for different dispersions using different diameter of probe for each surfactant have been reported in Table III. The morphology of pigment dispersion for four best batches has been depicted in Figures 5(a and b). It is observed that the degree of dispersion is the maximum in the case of blue pigment dispersion, prepared using Tween 80 surfactant and ultrasound (6-mm-diameter probe) for the organic solvent-based system, showing a K/S value of 2.395. Organic solvent-based green pigment dispersion prepared with the use of BYK surfactant under the 20-mm probe shows the least dispersion with a K/S value of 1.916 and approximate average particle size of 4.5 μm. The probability of dispersion for the various formulations shows that organic solvent-based

green pigment dispersion with the use of BYK surfactant shows the lowest extent of deagglomeration, while organic solvent-based blue pigment dispersion using Tween 80 surfactant under 6-mm-diameter probe resulted in maximum dispersion.

Comparison of the energy efficiency of the ultrasound-assisted method and high-speed dispersion mill

The energy required for the pigment dispersion using the ultrasound-assisted method and high-speed dispersion mill has been estimated as per the procedure described in Appendix (Detriche *et al.*, 2008; Usrey *et al.*, 2009; Cheng *et al.*, 2010a). The energy utilized for the pigment dispersion has been expressed as the total energy required (kJ) per unit weight of the material (g) present in the system. Both the high-speed dispersion mill and ultrasound-assisted process require 30 minutes for the pigment dispersion. The total

Table III K/S values and colour strength (%) for different batches at t = 30 min

Colour	Probe (6 mm)			Probe (10 mm)			Probe (20 mm)		
	Tween-80	SDS	BYK-192	Tween-80	SDS	BYK-192	Tween-80	SDS	BYK-192
Water-based									
Blue	1.533	1.390	1.065	0.499	0.907	1.008	0.791	0.470	0.881
	(94.96)	(100)	(104.88)	(13.42)	(100.28)	(97.35)	(72.91)	(104.04)	(91.99)
Green	0.518	0.421	0.127	0.447	0.322	0.081	0.339	0.627	0.641
	(82.77)	(87.02)	(91.34)	(35.02)	(49.17)	(9.007)	(55.05)	(99.86)	(68.71)
Organic solvent-based									
Blue	2.395	1.253	1.916	1.183	0.913	1.341	1.123	0.784	0.806
	(135.04)	(145.16)	(135.55)	(111.45)	(120.13)	(106.61)	(96.98)	(100.47)	(104.26)
Green	0.477	0.525	0.362	0.434	0.737	0.166	0.172	0.368	0.902
	(78.67)	(88.34)	(56.09)	(61.9)	(100)	(20.10)	(25.73)	(57.98)	(77.72)

energy required per unit mass of formulations in the ultrasound-assisted system with 6-, 10- and 20-mm probes is 8.80, 6.75 and 2.20 (kJ/g), respectively, while the energy required for high-speed dispersion mill is 15.21 kJ/g. Thus, it is clearly established that ultrasound-assisted pigment dispersion is an energy-efficient method in comparison to the high-speed dispersion mill. Energy saving of 13.01 kJ/g was observed when 20-mm-diameter probe is used for pigment dispersion.

Conclusions

The effective application of ultrasound in the dispersion of organic pigments (phthalocyanine blue and green) in water and organic solvents has been demonstrated with beneficial results. Particle-size analysis clearly indicates that small particle size is obtained when ultrasound with a probe diameter of 20 mm is used in the presence of SDS surfactant during the water-based dispersion and particle-size distribution becomes narrower when the larger-diameter ultrasound probe (20 mm) was used with reduced average particle size. The order of effectiveness of the dispersion in these systems is as follows: blue pigment dispersion prepared by an ultrasound-assisted process using a 20-mm probe in an organic solvent-based system in the presence of Tween 80 surfactant > blue pigment dispersion prepared using 20-mmdiameter probe in a water-based system in the presence of SDS surfactant > green pigment dispersion prepared using a 20-mm probe in an organic solvent-based system in the presence of the BYK surfactant. The use of an organic solvent and an increase in the probe diameter resulted in a decrease in the colour strength. It is also interesting to know that all surfactants show better colour strength in the organic solvent-based system. Overall, the present work has reported beneficial results in terms of synthesis of uniform and fine dispersion using a combination of ultrasound and surfactant.

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Appendix A. Calculations for the energy requirements

Energy consumption during sonication using 6-, 10- and 20-mm probe

The total energy consumption during sonication is equal to the electrical energy required to achieve dispersion of pigment in the required time.

Electrical energy delivered during sonication using 6-mm horn (indicated by the power meter) = 21.42 kJ/min.

Electrical energy delivered during sonication using 10-mm horn (indicated by the power meter) = 18.75 kJ/min.

Electrical energy delivered during sonication using 20-mm horn (indicated by the power meter) = 10.71 kJ/min.

Efficiency of horn obtained using calorimetric studies for the 6-mm probe = 34.27 per cent.

Efficiency of horn obtained using calorimetric studies for the 10-mm probe = 30 per cent.

Efficiency of horn obtained using calorimetric studies for the 20-mm probe = 17.13 per cent.

Actual energy delivered by the 6-mm horn during sonication = energy delivery rate × total dispersion time × efficiency of horn = 21.42 × 30 × 34.27/100 = 220.22 kJ.

Actual energy delivered by the 10-mm horn during sonication = energy delivery rate × total dispersion time × efficiency of horn = 18.75 × 30 × 30/100 = 168.75 kJ.

Actual energy delivered by the 20-mm horn during sonication = energy delivery rate × total dispersion time × efficiency of horn = 10.71 × 30 × 17.13/100 = 55.038 kJ.

Quantity of material processed = 25 g.

Net energy supplied per unit weight of the material using the 6-mm probe = actual energy delivered by horn during

sonication/quantity of material processed = 220.22 (kJ)/25 (g) = 8.81 (kJ/g).

Net energy supplied per unit weight of the material using the 10-mm probe = actual energy delivered by horn during sonication/quantity of material processed = 168.75 (kJ)/25 (g) = 6.75 (kJ/g).

Net energy supplied per unit weight of the material using the 20-mm probe = actual energy delivered by horn during sonication/quantity of material processed = 55.038 (kJ)/25 (g) = 2.20 (kJ/g).

Energy delivered during the conventional method

Voltage input to the homogeniser (Model RQ127 A/D, Remi Metals Gujarat Limited, India) = 230 V.

Current measured using a digital multimeter (MECO Model 9A06, MECO Meters Pvt. Ltd., Mumbai, India) = 1.1 A.

Power input to the homogeniser = voltage input × current measured = 230(V) × 1.1(A) = 209.09W.

Time required for completion of dispersion = 30 min.

Net energy delivered during the conventional method = power input × time required

$$= 209.09 \text{ J/s} \times 1800 \text{ Sec.} = 376363.63 \text{ J} = 376.36 \text{ kJ}$$

Energy supplied in the form of heat to maintain the reaction temperature as 70°C = $m.C_{p,mix}$ (Tprocess – TRef) = 25 × 4.0058 × (70 − 30) = 4005.8 J = 4.0058 kJ.

Total energy supplied during conventional method = 380.36 kJ.

Quantity of material processed = 25 g.

Net energy supplied for processing of material using conventional method = net energy delivered during conventional method/quantity of material processed = 380.36 (kJ)/25 (g) = 15.21 (kJ/g).

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Synthesis of Mica Doped Calcium Carbonate Filler for Partial Replacement of Tio$_2$ in Decorative Paint

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Titanium dioxide (TiO$_2$), being a prime pigment has been used essential component in a paint formulation due to its excellent light scattering ability and high refractive index. The growing demand and the increasing cost of TiO$_2$ have driven the attention of paint technologists to search for its alternatives. Many efforts have been made to partial replacement of the TiO$_2$ with fine particle size extenders in paint formulations. In present research work synthesis of mica doped calcium carbonate using co-precipitation method in mixed flow reactor system is achieved. The partial replacement of TiO$_2$ pigment by various percentages of Mica-CaCO$_3$ filler in decorative paint formulations has been made. Paint properties such as hiding power, scrub resistance, gloss, adhesion and weather resistance have been determined to establish the optimum percentage of Mica-CaCO$_3$ pigment in the paint formulation. The optimum percentage of Mica-CaCO$_3$ filler is about 20-30% by weight of TiO$_2$ in paint formulations. The overall paint properties are found to be satisfactory with cost cutting for decorative paints.

Keywords— *Mica-CaCO$_3$ filler, mixed flow reactor system, co-precipitation method*

I. Introduction

Paints are used to protect the material surfaces against various corrosions along with their decorative purpose. In a dry film, in any case, there are just pigment particles and binder polymer fibers to keep the particles on the surface. As an ensuing, the minerals utilized as a part of the paint formula straightforwardly influence the attributes of the paint. TiO$_2$ is the most significant pigment for whiteness and a core pigment utilized as a part of the paints or coatings. Then again, its high cost advances analysts in paint industry to search for abundant and modest substitutions. In waterborne paints some piece of the pigment is supplanted with filler so that cost of deciding item can be lessened with fillers/extenders. Various minerals are utilized with the point of diminishing the expense and enhancing some physical and mechanical properties of paints [1,2]. The utilization of extenders must be carefully fitted to the formulation design of the paint or coating, as not every extender will work successfully in every system. Filler/extender has an effect on gloss, texture, suspension, tinting strength and viscosity of a paint. Inert pigments, having a low refractive index and being relatively inexpensive, are used as extenders or fillers in paints and allied industries. Fillers are among others barium sulphate, kaolin, calcium carbonate, mica, silicates and silica [3]. The judicious substitution of extender generally produces equivalent hiding, tinting strength, stains, and scrub resistance. The substitution of extenders not only helps to reduce the cost but also helps to improve the properties, such as the flow and rheological movement under stress, gloss, leveling after application, mechanical and impact resistance, hiding, reflectance, and brightness. An extender like high oil absorption calcined clay may replace a part of titanium dioxide that demonstrates true internal hiding and sheen control in flat wall paints. The influence of extenders on the properties of paints has been studied extensively. The incorporation of calcium carbonate and diatomaceous silica, or a blend of micronized talc and dolomite in TiO$_2$ pigmented paints results in good color uniformity, opacity, and washability. Similarly, the addition of finely ground extender to paints produces better dispersion, uniformity, colour, hiding, gloss, and reflectance. The partial substitution of TiO$_2$ by extender barytes in alkyd based coatings exposed outdoors and indoors by measuring properties like scratch hardness, gloss retention, tensile strength, percent elongation, water vapour permeation, and water absorption have been studied [4]. They have showed that paints pigmented solely with 30% PVC titanium dioxide can tolerate its replacement with a barytes extender to the extent of 10% PVC. It was found that properties like adhesion, scratch hardness, and tensile strength are not affected significantly in the case of unweathered alkyd coatings in which TiO$_2$ is partly replaced by zinc oxide, talc, barytes, and china clay to the extent of 30% by weight.

Mica is a complex of hydrous potassium–aluminum silicate minerals which is differ in chemical composition. Mica has a low coefficient of expansion, high dielectric strength, good electrical resistance, a uniform dielectric constant and high capacitance stability; at one time it was one the of best electrical and thermal insulators known. The most important application of mica is pearlescent pigments [5,6], which consist of transparent mica flakes coated on all sides with a thin layer of metal oxide, mostly titanium dioxide. There are variety of methods for doping of TiO$_2$ onto mica flakes, including homogeneous hydrolysis, titration, sol-gel technique, and chemical vapour deposition [7-10]. In present work synthesis of mica doped calcium carbonate achieved through co precipitation method in order to substitute the TiO$_2$

pigment in decorative water based paints. The particle size, morphology, phase and functional group identification was carried out using FESEM, XRD and FTIR analysis respectively. The colour strength of Mica-$CaCO_3$ was accomplished through colour matching spectroscopy. Coatings properties such as hiding power, gloss, scrub resistance, adhesion, pencil hardness and mar resistance were performed as per ASTM and ISO standards.

II. Experimental
II.I Materials
Calcium nitrate tetrahydrate $(Ca(NO_3)_2.4H_2O)$, Tween-80, Sodium carbonate (Na_2CO_3), Propylene Glycol, Ammonia, were purchased from Merck Specialties Pvt. Ltd. Mumbai. TiO_2, Mica, Pine Oil, and Styrene Acrylic Emulsion (46%) were provided by local supplier. Double distilled water was used as a medium for the preparation of Mica-$CaCO_3$ Pigment. The free samples of Antifoam k-35, MIT- 111 and Borchi Gen WS were supplied by K Tech India limited, Thane and OMG Borchers, Germany.

Synthesis of Mica-$CaCO_3$ pigment
The co precipitation process was carried out by using (1M) solutions of Calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$ as precursor and Sodium carbonate (Na_2CO_3) as precipitant in presence of non-ionic surfactant such as Tween-80 were added dropwise over a period of 60 min while at the bottom, suspension of water 100mL and mica 5.05 g with some sort of surfactant was taken. After the completion of addition stirred the suspension for 30 min; decant the supernatant liquid. Wash the precipitate with distilled water and then dry at 60°C. It was characterized on the basis of FTIR, density, oil absorption and tinting strength analysis.

Formulation of Water borne paint
The experiments were carried out with lab dissolver (Dispermat CV3, VMA-Getzmann GmbH) which consists of a milling system and separate instrument control case. The milling system exists as a double wall grinding chamber and a motor for the agitator in the chamber. The essential dispersion parameters can be optimally and independently controlled via the control case. The actual particle size reduction in the grinding chamber of a mill is accomplished by the moving material, which is activated by a high speed and high-energy agitator. The partial replacement with Mica-$CaCO_3$ pigment based decorative paint formulation was prepared as per the compositions reported in Table 1.

Characterizations
The functional group analysis of Mica-$CaCO_3$ was carried by using Shimadzu FTIR–8400 equipped with KBr beam splitter and diffuses reflectance system (DRS).

Table 1 Water based Paint Formulations

Sr. No.	Ingredients	TiO₂ Replace by % of mica-CaCO₃ filler				
		Batch 1	Batch 2 (5 %)	Batch 3 (10%)	Batch 4 (20%)	Batch 5 (40%)
1	Water	20.1	20.1	20.1	20.1	20.1
2	Propylene Glycol	0.8	0.8	0.8	0.8	0.8
3	MIT- 111	0.3	0.3	0.3	0.3	0.3
4	Thickener Solution (3.5%)	0.2	0.2	0.2	0.2	0.2
5	Borchi Gen WS	0.8	0.8	0.8	0.8	0.8
6	Antifoam k-35	0.35	0.35	0.35	0.35	0.35
7	Ammonia sol.	0.15	0.15	0.15	0.15	0.15
8	Thickener Solution (3.5%)	0.1	0.1	0.1	0.1	0.1
9	TiO₂	36.6	34.77	32.94	29.28	21.96
10	Mica-CaCO₃	-	1.83	3.66	7.32	14.64
11	Styrene Acrylic Binder (46%)	37.0	37.0	37.0	37.0	37.0
12	Silicon Oil	0.1	0.1	0.1	0.1	0.1
13	Borchi Gen WS	0.8	0.8	0.8	0.8	0.8
14	Pine Oil	1.6	1.6	1.6	1.6	1.6
15	Propylene Glycol	0.8	0.8	0.8	0.8	0.8
	Total	**100**	**100**	**100**	**100**	**100**

Evaluation of the phase and morphology of Mica-$CaCO_3$ was conducted using D-8 Advance XRD of Brucker, Germany at 40 kV and a current of 30 mA with CuKα radiation (1.54060-1.54439). The assessment color was carried out using color matching spectrophotometer using D65 illuminant. The coatings properties such as Gloss, pencil hardness, adhesion, mar resistance, hiding power, and scrub resistance were carried out using gloss meter, pencil hardness tester (BYK Additive & Instruments, Germany), cross cut adhesion tester, mar resistance tester, P-Fund Cryptometer, and Wet scrub resistance tester respectively as per their ASTM standards.

III. Results & Discussions
Synthesis of Mica-$CaCO_3$ Pigment
The synthesis was carried out using co precipitation process which involves the slow addition of 1M solutions of Calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$ and Sodium carbonate (Na_2CO_3). Fig. 1 shows the characteristic vibrations of alkyl chains in surfactant which is adsorbed on the surface of mica-calcium carbonate. The bands at 2856 and 2926 cm^{-1} observed were ascribed to the symmetric and

asymmetric vibrations of –CH2– and –CH3 groups. The characteristics vibrations for calcite phase at 713 cm^{-1} was observed. The peaks at 1095 and 1026 cm^{-1} are assigned to Si-O stretching motions, and the peak at 913 cm^{-1} is believed to arise from an Al-OH-Al bending. The peak at 699 cm^{-1} is likely the result of Al-O stretching [11]
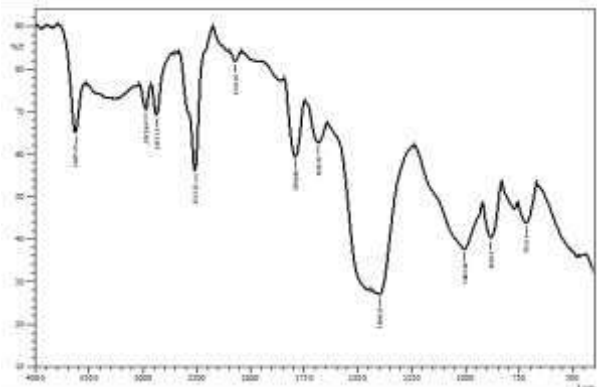

Fig. 1 FTIR of Mica-CaCO$_3$

Coatings properties
Optical Properties: The CIELAB colour system is the most suitable technique for measuring surface colour properties. The primary shading parameters dictated by the CIELAB shading framework are the parameters: L*, which speaks to softness on a size of 0 (dark) to 100 (unadulterated white); a* which is the level of redness if positive or greenness it negative; b* which is the level of yellowness if positive or blueness if negative. Fig.2 shows gradually decrease in whiteness with increase in % loading of Mica-CaCO$_3$. For greater replacement of TiO$_2$ by Mica-CaCO$_3$ color properties deteriorate significantly. This suggests that Mica-CaCO$_3$ can replace sufficiently TiO$_2$ pigments in emulsion paints. The evolution of yellowness index (b*) with increasing replacement of TiO$_2$ by Mica-CaCO$_3$ are shown in Fig.2. Yellowness index decreases gradually with increasing Mica-CaCO$_3$ content for some extent but at 40% loading it was increased upto 0.799.
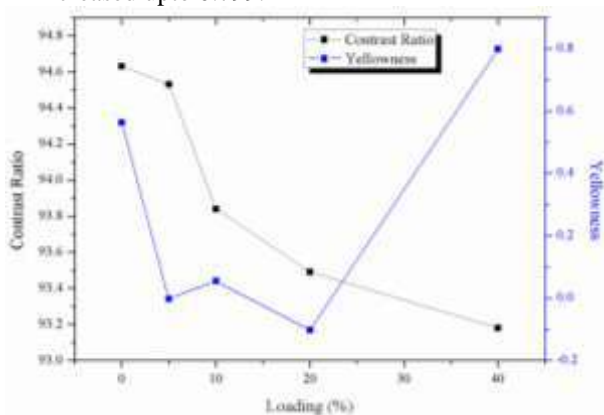

Fig. 2 Influence of replacement of TiO$_2$ by Mica-CaCO$_3$ on whiteness and yellowness of the surface coating

Gloss: The influence of replacement of TiO$_2$ on the gloss of the surface coating is shown in fig. 3. Addition of Mica-CaCO$_3$ is more important on the gloss of the coating compared to other optical properties, since it increases significantly even with small additions of Mica-CaCO$_3$. Replacement of TiO$_2$ by Mica-CaCO$_3$ affects negatively on the gloss of the surface coating.
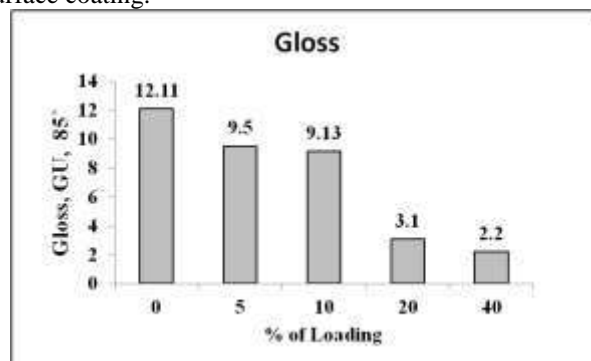

Fig. 3 Influence of replacement of TiO$_2$ by Mica-CaCO$_3$ on Gloss of the surface coating

Mechanical and physical properties of coatings
Hiding Power: The phenomenon of hiding power is based on refractive indices to have good hiding power its refractive index needs to be much higher than that of the binder. The hiding power of prepared paint samples were carried out using P-Fund Cryptometer. Mica-CaCO$_3$ has a particle size and refractive indices about the same as the TiO$_2$ pigment; hence Mica-CaCO$_3$ results in better efficiency of replacement and can save about 20% in prime TiO$_2$ pigment. Fig.4 shows hiding power decreases with increase in % loading of Mica-CaCO$_3$.
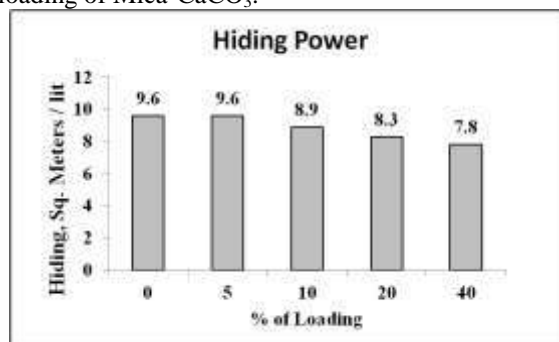

Fig. 4 Influence of replacement of TiO$_2$ by Mica-CaCO$_3$ on Gloss of the surface coating

Wet Scrub test: It is directly related to washability and stain removal, which is duly required for interior latex paints. This test has been carried out with a wet abrasion tester. The paint sample of 50 μm were applied on a paper and dried for 96 hrs. These panels were soaked in water for 10 min, followed by an additional 5 min of soaking in 0.5% soap solution and were used for a scrub resistance test. The test panel was mounted firmly on the plate, the soap-filled brush was placed in a position, and the motor was started. The addition of soap solution drops over the panel is

arranged at a fixed rate of 12 drops per min. [ASTM D-2486–69]. This test continued up to 2000 cycles. The samples loading upto 20% have passed the test.

The mechanical properties of coated samples were shown in Table 2. There is no remarkable effect of properties such as mar resistance, dry film thickness, pencil hardness, adhesion test, Wt/Lit, %NVM and viscosity.

Table 2 Water Based (Acrylic) paint testing

Sr. No.	Test	Mica-CaCO$_3$ loading				
		0	5%	10%	20%	40%
A	Wet film test					
1	Fineness of grinding	7+	7+	7+	7+	7+
2	Wt / litre	1.36	1.37	1.31	1.33	1.34
3	% NVM	41.66	41.66	41.66	41.66	41.66
4	Visocity (Sec)	35	40	35	36	40
B	Dry film test					
1	Pencil Hardness	3B	3B	4B	4B	3B
2	Mar Resistance	1200 Pass (Red)	1200 Pass (Red)	1200 Pass (Red)	1200 Pass (Red)	1200 Pass (Red)
3	DFT	45-50	45-50	40-45	40-45	45-50
4	Cross cut adhesion	3B (5-15%)	3B (5-15%)	3B (5-15%)	3B (5-15%)	2B (15-35%)

IV. Conclusions

In the summery, the preparation of mica-CaCO$_3$ was successfully carried out using co precipitation reaction and utilized in the formulation of durable decorative coatings. The decorative coatings formulated using mica-CaCO$_3$ shows better physical, mechanical and chemical resistance properties as per required standards. The faster reactive events under ambient conditions, stabilized crystal growth, higher yield of mica-CaCO$_3$. Thus, mica-CaCO$_3$ was found as an acceptable substitution for TiO$_2$ since its contribution to superior opacity and hiding power. As a result of the investigation, 20% of TiO$_2$ can be substituted with mica-CaCO$_3$ without any adverse effect on main paint properties of which economical beneficiations has been explained.

Acknowledgements

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