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

N.P. Badgujar, Y.E. Bhoge and T.D. Deshpande
Institute of Chemical Technology, North Maharashtra University Jalgaon, India
B.A. Bhanvase
Department of Chemical Engineering, Laxminarayan Institute of Technology, Nagpur, India
P.R. Gogate
Department of Chemical Engineering, Institute of Chemical Technology, Mumbai, India
S.H. Sonawane
Department of Chemical Engineering, National Institute of Technology, Warangal, India, and
R.D. Kulkarni
Institute of Chemical Technology, North Maharashtra University Jalgaon, India

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

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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 ($C_{32}H_{16}C_lN_8$, 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).

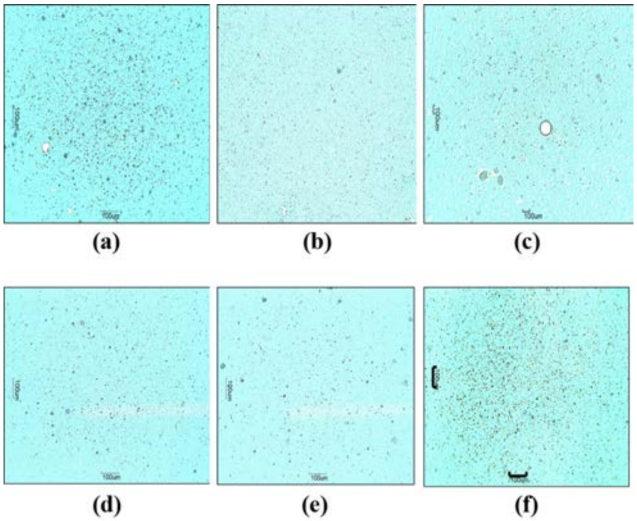
Characterisation

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

Figure 1 Microscopic images at 40 × magnification of the ultrasound-assisted dispersed blue pigment in the water-based system using



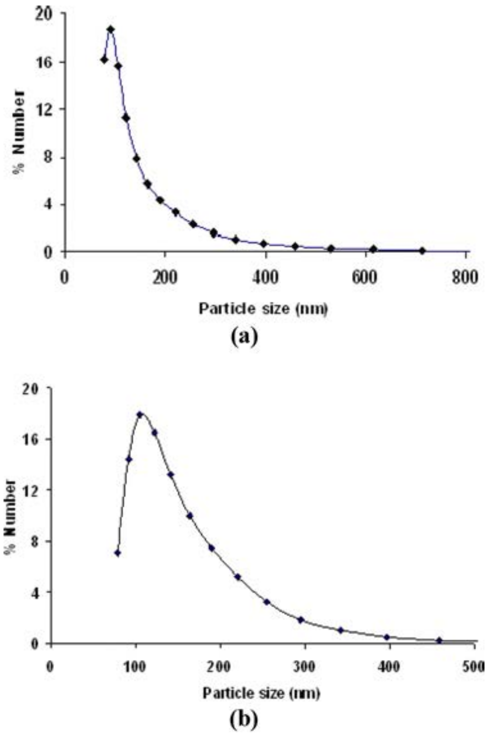
Notes: (a) 10-mm probe; (b) 20-mm probe ; (c) the high-speed dispersion mill along with SDS surfactant and in organic solvent-based system using; (d) 10-mm probe; (e) 20-mm probe; (f) the high-speed dispersion mill along with Tween 80 surfactant

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 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 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.

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



(a)

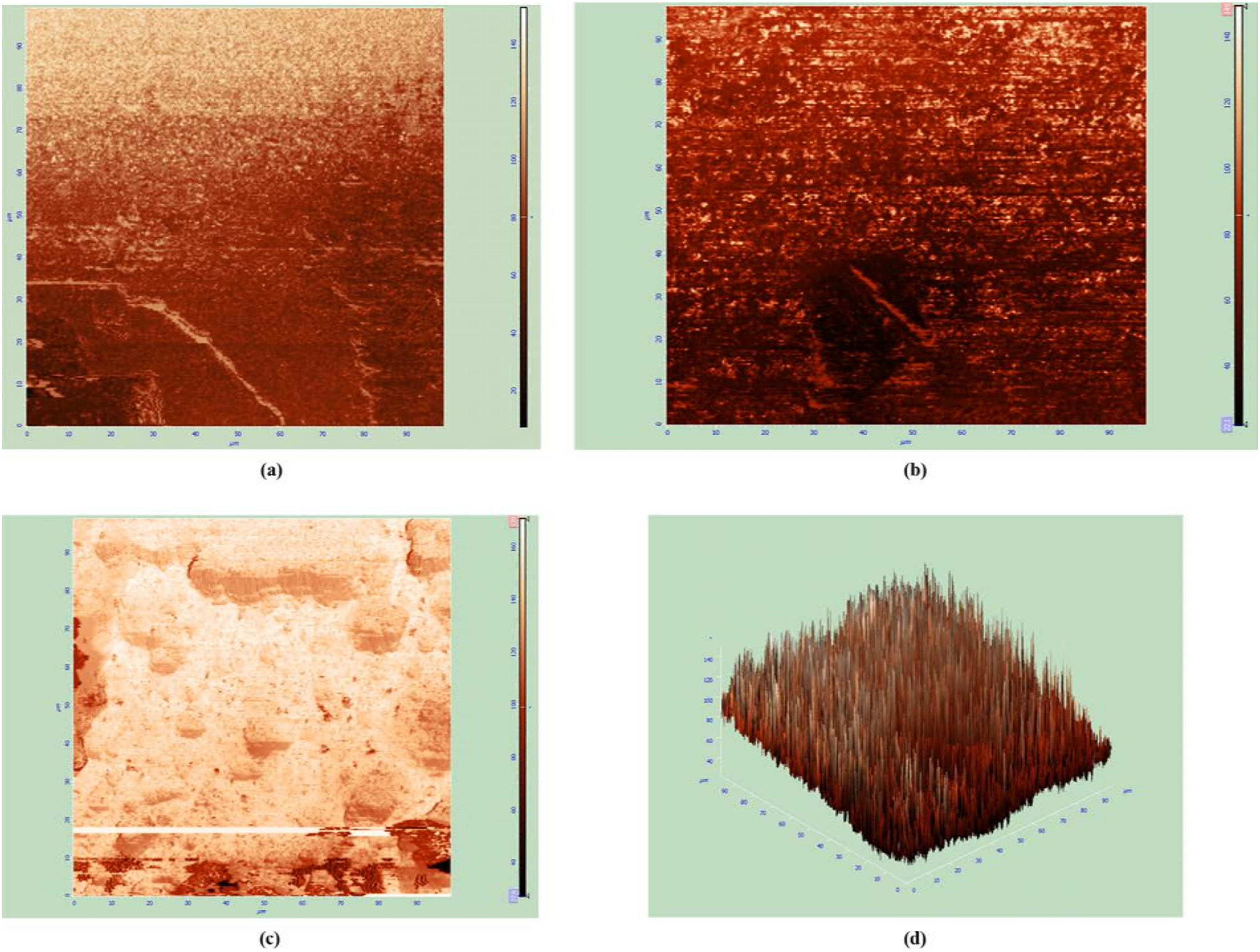
(b)

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

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.

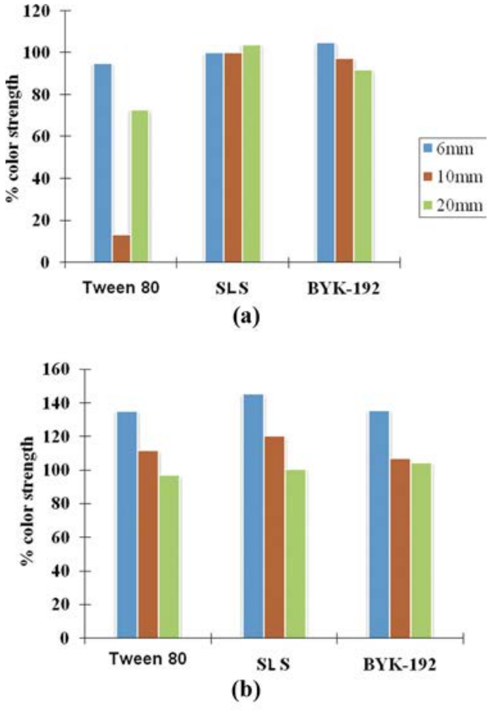
Prediction of deagglomeration using probability analysis

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

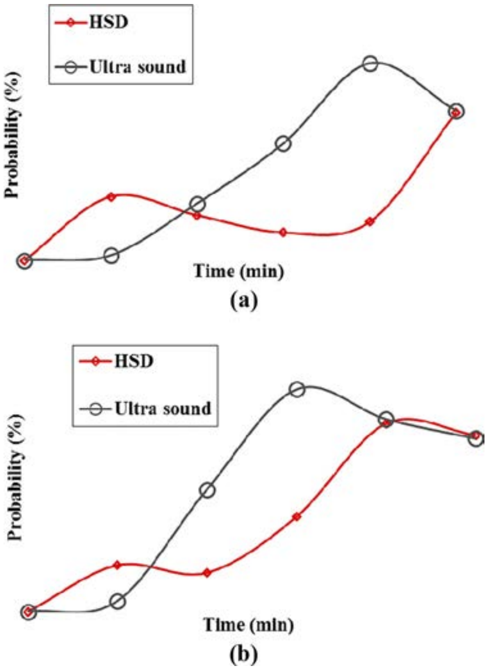
	Probe (6 mm)			Probe (10 mm)			Probe (20 mm)		
Colour	**Tween 80**	**SDS**	**BYK-192**	**Tween 80**	**SDS**	**BYK-192**	**Tween 80**	**SDS**	**BYK-192**
Viscosity values (cps) water-based									
Blue	9.6	7.06	1.302	4.09	0.74	9.11	69.94	63.43	2.79
Viscosity values (cps) organic solvent-based									
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

	Probe (6 mm)			Probe (10 mm)			Probe (20 mm)		
Colour	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).

Corresponding author

S.H. Sonawane can be contacted at: shirishsonawane09@gmail.com