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Optimisation and analysis of bead milling process for preparation of highly viscous, binder-free dispersions of carbon black pigment

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A R T I C L E I N F O

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A B S T R A C T

Lab scale milling equipment is often employed to prepare dispersion formulations that possess considerably different characteristics from each other. The viscosity of a pre-mixed dispersion is one of the main parameters to consider when selecting a particular milling equipment for grinding of pigment. Generally, high viscosity dispersions are not easy to grind using a lab-scale re-circulating bead mill. There are numerous factors that can potentially result in changes in the starting point formulations. It is therefore crucial to assess any variations in the pigment loading occurring during milling for extended time periods. In this study, rheological characterisation, thermogravimetric analyses and surface resistivity measurements have been carried out on multiple dispersion formulations and it is shown that pigment loading after milling can be different from that in the starting point formulation.

1. Introduction

The property requirements for various coating systems are often significantly different from one another [1]. Thus, the technological aspects of the corresponding production processes are also different. A typical coating production process involving bead milling is depicted in Fig. 1. However, there are huge varieties of manufacturing equipment that are designed to meet specific requirements of a specific coating manufacturing process. The selection of equipment and the sequence of the steps that are involved in preparation of a coating system are primarily dependent on the type of coating and the quantities being manufactured [2]. In addition, the important factors pertaining to the formulation include the viscosity of the premix, the vehicle, the solids content in the formulation, the pigment hardness, temperature limitations, aeration tendencies and so on [3]. The main target to be achieved in a coating manufacturing process is proper blending of all of the formulation components, in general, and an optimal dispersion of the pigment, in particular. Detailed accounts of the mechanisms involved in dispersing a pigment are reported in literature [4–6].

Depending upon the design of milling equipment, single or multiple passes through a mill may be required to achieve the required reduction in particle size, a narrow particle size distribution and to improve stability [8–10]. It is important to note that the main manufacturing cost in coating preparation is associated with the cost of pigment milling which has two components. One is the cost that is associated with the duration of the milling which in turn dictates the total energy that is consumed during the process [11]. The other component of cost is associated to the wear and tear on the milling equipment. The wear of the conventional ceramic or metallic grinding media needs to be considered as this can lead to contamination of the dispersion [12–15]. The optimum milling process parameters, i.e., the milling time and the milling speed, to prepare pigment dispersion depends on a number of factors including the pigment hardness, the pigment aggregate size, the solubility of pigment in the dispersion medium, the effectiveness of the dispersant(s) and the design of the milling equipment [16–19]. Mathematical models have also been developed to identify, predict and optimise the most significant pigment grinding parameters [20,21].

As new applications of coatings are envisaged, increasing numbers of pigments are employed as functional materials [22,23]. As a result, a coating system manufacturer has to frequently deal with formulations that possess significantly different characteristics from each other. In many cases, the cost of pigment is a major consideration due to which the coating manufacturer is faced with the challenge of maximising the desired functionality while using an optimally low amount of the pigment. The optimum amounts of all of the other formulation ingredients also have a direct influence on the properties of the end product. In addition, it is crucial to assess the capabilities and limitations of the available milling system for each unique type of formulation. This is commonly done by preparing a series of dispersions using lab scale milling equipment followed by characterisation of the same using a

Abbreviations: DOWP, Amount of dispersant (gm) on the weight of pigment; OAN, Oil absorption number

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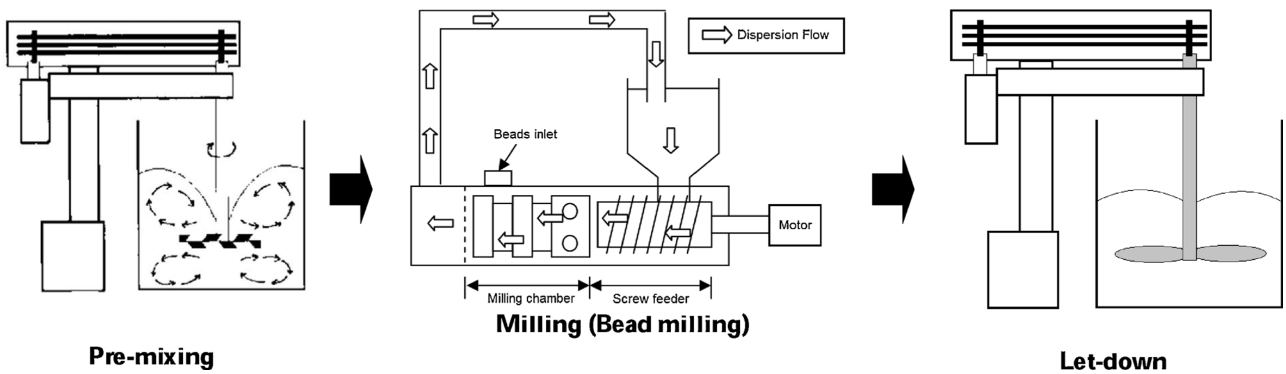

Fig. 1. Typical steps involved in manufacturing of a pigmented coating system [7].

Table 1
Specifications of carbon black pigments (as provided by the suppliers).

Pigment (Supplier Code)	Supplier	BET Surface area (m^2/g)	OAN (cm^3/ 100 g)	Volatile content (%)
Vulcan XC605	Cabot	59	148	< 0.1
Ensaco 250G	Timcal	62	191	0.2

Table 2
Dispersants used and their characteristics (as provided by the suppliers).

Dispersant	Supplier	Water solubility	Active Matter (wt%)
Solsperse 44000	Lubrizol	Soluble	50
BYK-190	BYK Chemie	Completely miscible	40
Tego Dispers 760W	Evonik Tego	> 500 g/L	35

number of techniques such as electrophoresis, rheological assessments, particle size analysis, sedimentation tests and adsorption isotherm [24–28]. Another technique called electroacoustics allows zeta potential measurement in concentrated suspensions [29–31]. In order to speed up the formulation optimisation and characterisation processes, in-situ and online analytical techniques have been reported recently [32–34].

It is clear from a review of the available literature that a significant number of studies report on the analysis of dispersion preparation process and characterisation of dispersions. However, there is a clear need to devise a method to estimate any potential changes in the starting point formulation that can occur during the dispersion preparation process, particularly during milling. This is considered to be important and thus the focus of this work because not all pigment milling equipment designs provide air-tight environment and as a result the vehicle (dispersion medium) can evaporate during milling for extended time periods. If the viscosity of a premixed dispersion is high then the loss of vehicle can accelerate due to increased temperatures. In addition, pigment loss can possibly occur in the form of accumulations in various sections of the milling equipment, particularly during the first several minutes of milling if the dispersion flow characteristics are not ideal (shear thinning). The aforementioned potential problems are more likely to occur in lab-scale milling equipment which is often used to grind pre-mixed dispersions possessing significantly different rheological characteristics. This can lead to changes in the starting point formulations and subsequently unexpected product performance. In this work, a simple method is proposed to estimate the optimum milling duration and at the same time record any changes in the starting point formulation in terms of pigment loading.

Table 3
Pigment-dispersant combinations prepared in the present study.

	DISPERSANT		
PIGMENT	Solsperse 44000 (Dispersant1)	BYK-190 (Dispersant2)	Tego 760W (Dispersant3)
Vulcan XC605 (Carbon1)	Carbon1-Dispersant1	Carbon1-Dispersant2	Carbon1-Disperssant3
Ensaco 250G (Carbon2)	Carbon2-Dispersant1	Carbon2-Dispersant2	Carbon2-Dispersant3

Table 4
TGA parameters for dispersion analysis.

TGA parameter	Description
Heating method	Ramp – Isothermal for 10 min at end temperature
Heating rate (°C/min)	10
Start temperature (°C)	25
End temperature (°C)	800–825
Test atmosphere	Nitrogen purge

2. Materials and methods

2.1. Pigments

Carbon blacks of the same particle morphology may vary considerably in their ease of dispersion. Such differences in dispersibility can be attributed to the amount of chemisorbed complexes. On the basis of a consideration of this property, carbon black pigments that contained low volatile matter content were selected for this study. Some of the more important characteristics, as provided by the suppliers of these pigments, are provided in Table 1. In order to put more strain on the milling process, binder-free, waterborne dispersions of these pigments were prepared.

2.2. Dispersants

For the dispersion and stabilisation of non-polar pigments such as carbon black, high molecular weight dispersing additives are generally recommended. In this situation, steric hindrance becomes the primary mechanism by means of which pigment particles are stabilised in the

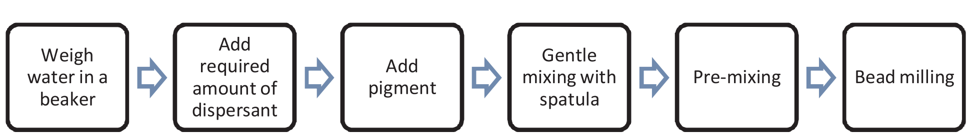

Fig. 2. Sequence of addition of formulation ingredients and the steps involved in milling of dispersions.