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Investigation of the heterogeneity of organic pigment particle surfaces using a film flotation method

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Abstract

The film flotation method, described by Fuerstenau DW, Williams MC. Particle Characterization 1987; 4: 7, is extended to a variety of organic pigments, to provide information about the surface heterogeneity of their constituent particles, and some preliminary results are reported. Differences in surface heterogeneity amongst four copper phthalocyanine pigments are discussed, and the data for these pigments are compared with those for a metal-free phthalocyanine pigment and two azo pigments. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Film flotation; Organic pigment; Surface heterogeneity; Cumulative distribution; Frequency distribution

1. Introduction

It is well established that organic pigments consist of tiny molecular crystals (typically of dimension 0.02–0.5 μm) in various states of assembly [1,2]. As with many other types of powdered solid, the crystals comprising an organic pigment are highly heterogeneous. Not only do they exhibit appreciable variation in size and shape, but their surface characteristics may also extensively differ. This surface heterogeneity may, for example, arise from variation in porosity and surface topography, and also from the differing structures of the individual crystal faces.

The surface properties of a pigment exert an important influence on its dispersion quality in commercial application media, for example in the production of printing inks and paints. It is clearly beneficial to both pigment manufacturer and user to be able to assess the distribution of surface properties in a given pigment. Well-established techniques, such as gas adsorption and immersion calorimetry [3–5], have proved valuable in characterizing the surface and aggregation properties of pigment crystals, but these techniques provide an overall picture. For many types of organic pigment, such as copper phthalocyanines [4], calcium 4B toners [6] and bisarylamide yellows [7], an impression of variation in pigment crystal size and shape has been gained from transmission electron microscopy and X-ray powder diffraction, but no information on variation in surface character is gained from these techniques. By means of the film floatation method, however, information about surface heterogeneity can be provided.

The film flotation method has been exploited by Fuerstenau et al. [8–10] on particles of a variety of

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different substances, including coal, quartz, sulfur and silver iodide. Their method is based on the earlier work of Hornsby and Leja [11] and of Yara and Kaoma [12]. The method has been fully described elsewhere [8,9], so only a brief description is given here. In the method, the surface tension of a liquid is determined at which the liquid will just wet solid particles. In a film floatation experiment, the particles are sprinkled gently onto the surface of the wetting liquid (commonly an aqueous alcohol solution), and the proportion of particles which sink into the liquid is determined. Fuerstenau et al. [9–10] have shown that this proportion is determined almost completely by the surface character of the pigment particles. With liquids of high surface tensions, the particles will all remain on the surface of the liquid. With liquids of low surface tensions, the particles will all sink. At intermediate values of the liquid surface tension, however, only some particles will sink whereas others will float. By using aqueous alcohol solutions as the test liquids, a wide range of surface tensions can be covered, and any desired surface tension within this range can be prepared, using the correct ratio of alcohol to water.

The fraction by weight of particles which float can be plotted against surface tension. A cumulative distribution of the wetting surface tension for the sample is thus determined. From this distribution curve may be determined the critical wetting surface tension, γ_c, at which 50% of the pigment is wetted, the minimum wetting surface tension, γ_c^{min}, and the maximum wetting surface tension, γ_c^{max}.The greater the heterogeneity of the surface character of the particles, the greater is the difference between γ_c^{max} and γ_c^{min}. It is generally useful too to determine a frequency distribution from the cumulative distribution. The frequency distribution gives an expression for the surface heterogeneity of the pigment sample.

In this paper, the film flotation method is extended to the characterization of organic pigments, and some preliminary results are reported.

2. Materials and method

A wide range of commercially available organic pigments was used, and these are indicated in Table 1.

The film flotation experiments were conducted at room temperature in mixtures of methanol and deionised water. The surface tensions of these mixtures were measured using a du Nuoy ring tensiometer. 50 cm^3 beakers were filled to at least three-quarters of their volumes with liquids of different surface tensions, ranging from 30 mN m^{-1} to 64 mN m^{-1} in intervals of 2 mN m^{-1}. A known mass of the pigment under investigation was carefully passed through a #60 sieve onto the surface of each liquid. The sieve was held as closely as possible over the beaker. After the pigment

Table 1
Wetting parameters of some pigment samples, determined from film flotation with aqueous methanol solutions

Sample	Pigment colour index reference	Chemical type	γ_c[a] mN m^{-1}	γ_c^{max}[b] mN m^{-1}	γ_c^{min}[c] mN m^{-1}	γ_c^{m}[d] mN m^{-1}
A	Blue 15:3	β-CuPc	49.9	58	32	50.2
B	Blue 15:1	CuPcCl	51.6	57	34	52.0
C	Green 7	$CuPcCl_{15-16}$	53.3	59	41	56.6
D	Green 36	$CuPcCl_{10}Br_6$	54.0	60	40	55.0
E	Blue 16	H_2Pc	47.4	52	42	47.6
F	Yellow 3	Monoazo	48.4	52	<34	48.6
G	Yellow 13	Bisazo	43.9	50	36	44.0

[a] γ_c = critical wetting surface tension at which 50% of the pigment is wetted.

[b] γ_c^{max} = maximum wetting surface tension.

[c] γ_c^{min} = minimum wetting surface tension.

[d] γ_c^{m} = surface tension corresponding to the maximum of the frequency distribution.

particles had been left in contact with the liquid for at least 5 min, those particles still remaining on the surface of the liquid were skimmed off. Those particles which had sunk were filtered, dried and weighed, and hence the fraction of pigment particles which had sunk could be determined. Subtraction of this value from unity gives the proportion of pigment particles which had not sunk into the liquid and represents the lyophobic fraction of the pigment sample at a particular surface tension [9]. A plot of the lyophobic fraction against surface tension gives a cumulative distribution. Differentiation of the cumulative distribution gives a frequency distribution. Fig. 1 gives an example of a cumulative distribution and the frequency distribution derived from it.

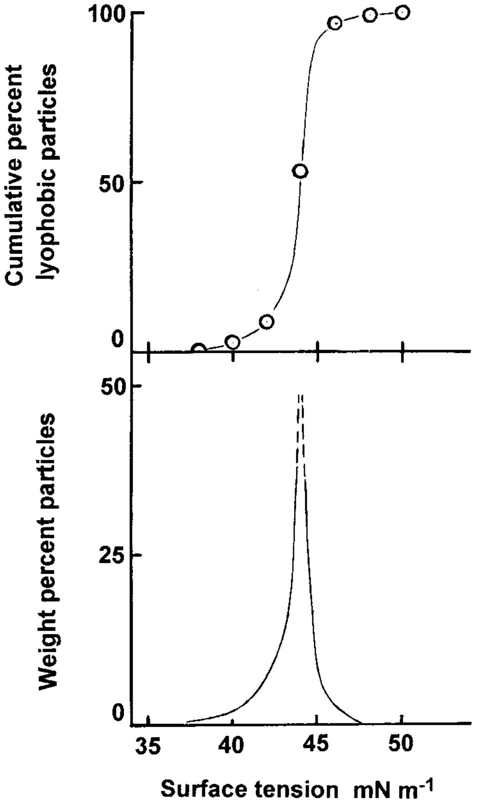

Fig. 1. The cumulative percentage (top) and frequency distribution (bottom) of lyophobic particles of Sample G as a function of wetting surface tension.

3. Results

Table 1 lists values for γ_c, $\gamma_c^{\min}$ and $\gamma_c^{\max}$. The higher the value of γ_c, the more easily wetted is the pigment expected to be. Thus, it is interesting to note that, amongst the four pigmentary copper phthalocyanine samples, Sample A possesses the lowest value of γ_c, the value for Sample B is intermediate, and the values for Samples C and D are highest. It appears then from Table 1 that the greater the degree of substitution by halogen atoms, the less hydrophobic is the sample. The values of γ_c for Sample E, a metal-free phthalocyanine pigment, and for the two yellow azo pigments, Samples F and G, are all lower than those for the copper phthalocyanine pigments.

A correlation can be made in Samples A–D between the values of γ_c and the extent of halogenation in the copper phthalocyanine molecule, although such a correlation can only be tentative at this stage. Sample A, an unchlorinated copper phthalocyanine pigment containing largely β-phase crystals, possesses the lowest values of γ_c. The value of γ_c for Sample B, however, which contains one chlorine atom per molecule of copper phthalocyanine, is intermediate, whereas those for Samples C and D, whose molecules contain 15–16 halogen atoms, are the highest. Thus, a greater degree of halogenation of the copper phthalocyanine molecule apparently renders the pigment more lyophilic. An analogous observation has been made in the examination of copper phthalocyanine pigment surface properties using nitrogen adsorption isotherms [3]. It may be significant too that the value of γ_c for Sample D, whose molecules contain some bromine atoms, is perceptibly higher than that for Sample C, which contains no bromine atoms.

From the values of $\gamma_c^{\max}$ and $\gamma_c^{\min}$ listed in Table 1, it can be seen that the difference between the two values varies widely amongst the pigments. There are clearly extensive differences in surface heterogeneity. A fuller picture of these differences emerges when the frequency distributions are plotted, and some examples are illustrated in Figs. 1 and 2. For the copper phthalocyanine samples, A–D, the frequency distributions tail towards lower values of surface tension; the distributions

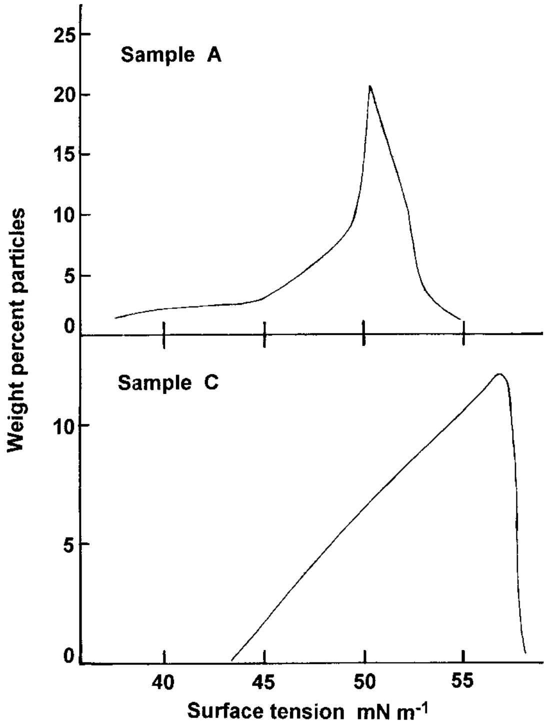

Fig.2. The frequency distributions of lyophobic particles of Sample A and Sample C as a function of wetting surface tension.

are clearly not Gaussian. An extreme example of this behaviour is given by Sample C (illustrated in Fig. 2). Thus, the value of the surface tension, γ_c^m, which corresponds to the maximum in each frequency distribution, will exceed the value of γ_c. This difference in values is borne out in Table 1.

The frequency distributions for the remaining pigment samples, E–G, are very much closer to Gaussian (though for Sample F there is some evidence of very slight tailing to lower values of surface tension). Fig. 1 illustrates the distribution of Sample G as an example. Table 1 confirms that the values of γ_c and γ_c^m appear very nearly identical.

4. Conclusion

It is proposed that the film flotation method devised by Fuerstenau et al. [8,9], can be usefully extended to organic pigments. It should be noted, however, that organic pigments differ from the materials investigated by Fuerstenau et al., in that organic pigments consist of much smaller primary particles. The consequent propensity for crystal aggregation [3] may lead to entrapment of air within a pigment sample. In addition, care has to be taken that the liquid does not age the pigment sample, though appreciable aging is unlikely under the experimental conditions adopted.

Nevertheless, the preliminary results reported in this paper do suggest that the film flotation method may provide a simple approach to studying the surface heterogeneity of organic pigment samples. The pattern of the frequency distributions for samples, E–G, is clearly different from those for samples, A–D, and may reflect differences in the methods by which the pigmentary particles in the samples studied were formed. In addition, there is a good correlation between the values of γ_c for the copper phthalocyanine samples and their degree of halogenation.

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