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Evaluation by nitrogen adsorption of crystal aggregation in organic pigments

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Dedicated to Arnold Peters on his retirement as editor of *Dyes and Pigments*

Abstract

Organic pigments consist of tiny molecular crystals with a propensity to cluster into aggregates. Such aggregation is commercially undesirable. The properties of the crystal aggregates can be investigated by the use of nitrogen adsorption isotherms. The review describes how a measure of the extent of crystal aggregation can be provided from the combined application of nitrogen isotherms and transmission electron microscopy. The application of full nitrogen isotherms to the study of crystal aggregation is also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Organic pigments are composed of tiny molecular crystals, of cross-section typically from 0.02–0.5 μm [1]. Such crystals have a great tendency to cluster into aggregates. Crystal aggregation is commercially very undesirable, because it reduces the effective level of subdivision of the crystals in dispersion and hinders the attainment of high colour strength. In commercial samples of organic pigments, additives such as abietyl resin and dyestuffs may also be present, and these too will influence crystal aggregate properties.

The effective dispersion performance of organic pigments is crucial for their successful application. The dispersion properties are in turn strongly influenced by crystal aggregation, which is also likely to be affected by any additives present. Technical insight into the problem of aggregation is consequently highly important.

The most direct approach to the study of organic pigment crystals and their aggregates is by microscopy, and indeed transmission electron micrographs have revealed that organic pigments possess crystals of widely differing size and shape and highly different aggregate structures [1]. However, attempts to draw further conclusions on aggregate structure can often be misleading. Prior to examination under the electron microscope, the pigment sample is normally dispersed in a suitable liquid and then dried on a grid. Thus, the aggregate

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structure, as observed under the electron microscope, could well be affected by the method of preparation of the pigment sample. Moreover, many types of organic pigment will be damaged by the electron beam in the microscope: there may be rounding of the edges and corners of the crystals or even degradation.

An effective alternative approach to investigating crystal aggregate behaviour is the use of gas adsorption isotherms, especially nitrogen adsorption isotherms at 77 K. This approach has been especially valuable in providing insights into the strength of crystal aggregation in a given pigment. It has also helped to provide a quantitative measure of the degree of crystal aggregation, although the determination of this measure does additionally require the application of electron microscopy and, for some pigments, X-ray diffraction as well. From a practical point of view, the gas adsorption method is attractive in that the technique is very well established. Moreover, no modification to the pigment sample is required, except evacuation to very low pressures before the start of the isotherm experiment. The principles underlying the determination of gas adsorption isotherms are very fully described elsewhere [2,3].

2. Degree of crystal aggregation

One important parameter which can be calculated from nitrogen adsorption isotherms is the specific surface area, S_{BET}, of a pigment sample, using the Brunauer–Emmett–Teller (BET) equation [4]. Values of S_{BET} can be usefully compared with values of S, the geometric specific surface area, whose determination from transmission electron micrographs and X-ray diffraction patterns of organic pigment crystals has been discussed elsewhere [5,6]. With very few exceptions, the ratio, $S_{\mathrm{BET}}/S \leqslant 1$. It has been suggested that those values of S_{BET}/S which are slightly greater than unity may be accounted for by the fractal roughness of the pigment crystal surfaces [7].

Where S_{BET}/S closely approaches unity, it is concluded that the surfaces of all the pigment crystals are readily accessible to nitrogen molecules during the course of a nitrogen adsorption isotherm. The pigment crystals, therefore, form quite open aggregate structures, which are virtually free of face-to-face contact between the crystals. Where, by contrast, S_{BET}/S is considerably below unity, the surfaces of the crystals are much less accessible to nitrogen molecules and there is now considerable face-to-face contact between adjacent crystals. A much more closely packed aggregate structure, therefore, exists. The value of S_{BET}/S thus acts as an indicator of the extent of face-to-face contacts between crystals. The lower the value of S_{BET}/S, the more closely packed is the aggregate structure. Thus, a measure of the extent of aggregation is provided.

Values of S_{BET}/S for a wide range of β-copper phthalocyanine pigments [5] and calcium 4B toner pigments [6] have been reported. Much larger variations in S_{BET}/S have been found amongst the β-copper phthalocyanine samples than amongst the calcium 4B toner samples. McKay investigated a total of 31 toner pigments, consisting of samples prepared on production and laboratory scales [6], and concluded that in the main there was no extensive crystal aggregation of a strongly coherent type.

In the case of β-copper phthalocyanine, however, the extent of crystal aggregation is strongly influenced by the mean size and shape of the pigment crystals. The degree of crystal aggregation is pronounced where the mean length-to-breadth ratio of the crystals < 2. On the other hand, larger, rod-shaped crystals are assembled into more open structures, and dispersion performance in application media is improved [8]. It appears too that the rod-shaped crystals of a stabilised α-copper phthalocyanine also form open structures [9].

A β-copper phthalocyanine pigment comprised of rod-shaped crystals is produced by heating an αβ-copper phthalocyanine in an organic liquid. The αβ-form is itself produced by grinding non-pigmentary ‘crude’ β-form material. The crystals of αβ-copper phthalocyanine are generally aggregated in a very compact manner [9], and their dispersion performance is poor. However, when such mixtures are heated in a suitable organic liquid, the larger, rod-shaped β-copper phthalocyanine crystals produced form open aggregate structures [5].

These pigments have good dispersion performance in lithographic media, despite the enlargement of the pigment crystals as a result of the treatment with the organic liquid. Continued treatment, however, tends to induce a secondary mechanism of crystal growth, caused by side-to-side fusion of the rod-shaped crystals [5]. This secondary process is deleterious to colouristic performance.

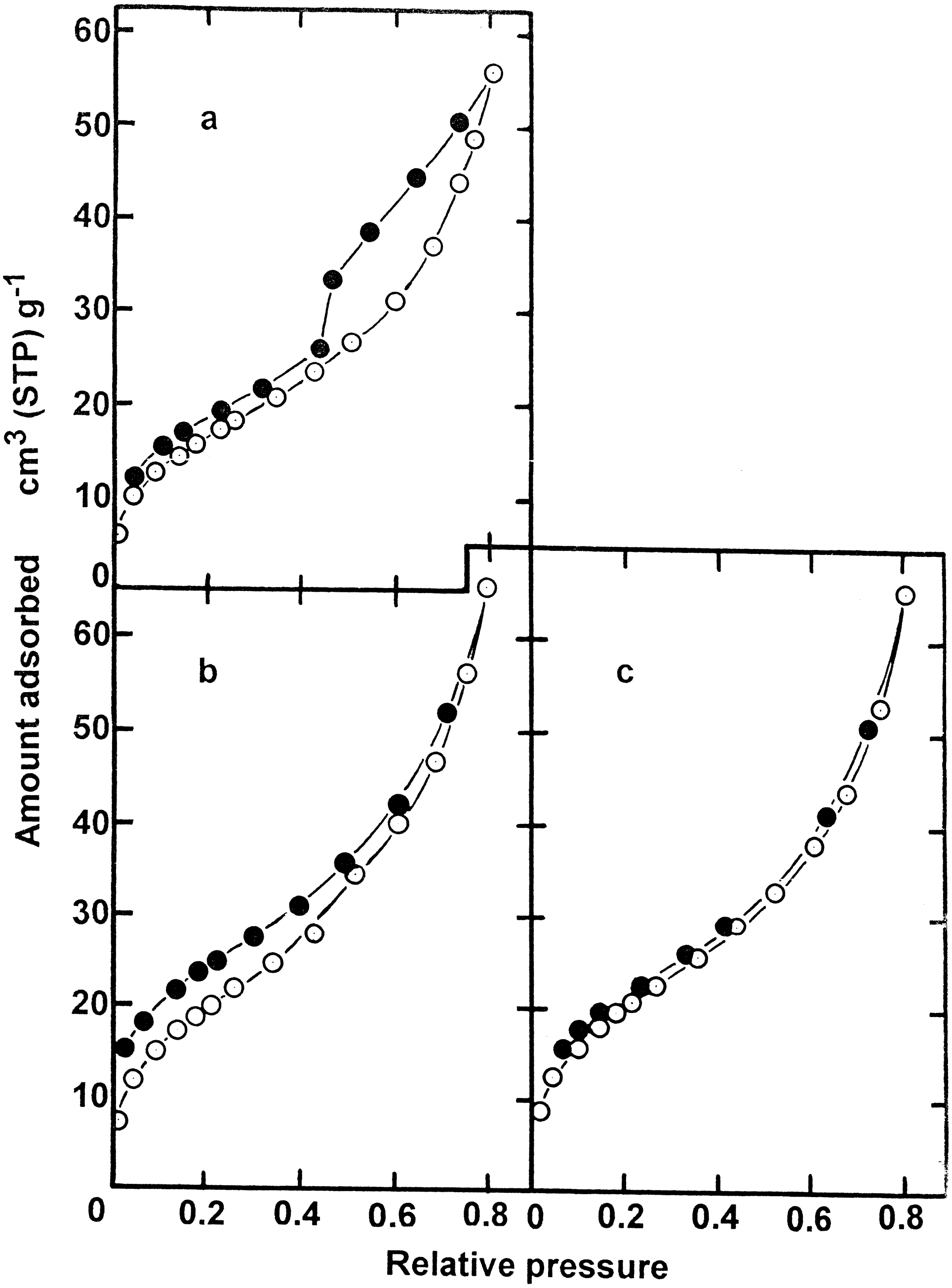

Fig. 1. Nitrogen adsorption isotherms on samples of an αβ-copper phthalocyanine pigment treated with ethyl acetate to (a) 50% β-form, (b) 82% β-form, (c) 100% β-form. ○, Adsorption; ●, desorption.

3. Information from nitrogen adsorption isotherms

Although the adoption of S_{BET}/S as a measure of the extent of aggregation is clearly valuable, further information about aggregate structure is gained from determination of the full isotherm. Fig. 1 shows some nitrogen adsorption isotherms, plotted in the normal manner as adsorption of nitrogen at 77 K versus relative pressure. (Relative pressure is the pressure of nitrogen at equilibrium, divided by the saturation pressure at the same temperature.) The isotherms correspond to the treatment of an αβ-copper phthalocyanine (54%α, 46%β) with ethyl acetate at 40 and 50°C over various lengths of time [10]. The changes in the nature of the isotherms as the conversion towards β-copper phthalocyanine proceeds are illustrated in Fig. 1. It can be seen that when conversion is complete (Fig. 1c), the adsorption and desorption branches are virtually coincident. However, before complete conversion to the β-form, adsorption hysteresis is exhibited in the isotherms (Fig. 1a and b): the desorption branch of the isotherm lies above the adsorption branch.

Adsorption hysteresis is normally associated with capillary condensation of the nitrogen in mesopores, i.e. pores of dimension between 2 and 50 nm [2,3]. Thus, non-porous solids give reversible (or almost reversible) isotherms, as exemplified by the isotherm in Fig. 1c. Where hysteresis is exhibited, it occurs with most solids only at relative pressures above ca. 0.4 and is not observed below 0.4 [11]. However, with organic pigments, hysteresis almost always extends down to very low pressures, as shown by the isotherms in Fig. 1a and b. Everett et al. [12] proposed that low pressure hysteresis arises from distortion of the solid as adsorption proceeds. In the case of organic pigments, this distortion is considered to arise from changes occurring in the structure of the pigment crystal aggregates. The aggregates are, therefore, not rigid but contain pores whose dimensions alter during adsorption.

At low relative pressures, the internal surfaces of the aggregates cannot be reached by nitrogen molecules. As the relative pressure is raised, however, adsorbed nitrogen molecules begin to penetrate between the crystals and open up some more surfaces. On subsequent desorption, some of the nitrogen molecules become trapped and are difficult to remove. Hence the desorption branch of the isotherm lies above the adsorption branch even at low relative pressures.

It can be observed too that the hysteresis loops in Fig. 1a and b possess different shapes. The loop in Fig. 1a broadens considerably at higher relative pressures. Moreover, the broadening commences at a relative pressure of ca. 0.4, where for many other types of solid, hysteresis is normally only just starting. The broadening may, therefore, be ascribed to capillary condensation of nitrogen within some mesopores whose dimensions are not significantly altered during adsorption. The pigment contains aggregates in which the crystals are tightly held together [10].

The hysteresis loop in Fig. 1b becomes broader at *lower* relative pressures, and its shape presents a contrast to that of the loop in Fig. 1a. Fig. 1b demonstrates that, whilst the pigment crystals are still aggregated to some extent, their aggregates possess much looser structures [10]. Thus, comparison of the three isotherms in Fig. 1 reveals how the crystal phase conversion to the β-form of copper phthalocyanine is accompanied by the extensive diminution or even removal of crystal aggregation.

4. Conclusion

Nitrogen adsorption provides an effective approach to evaluating the aggregation of organic pigment crystals and the technique continues to be a valuable tool. In recent research, for example, it has been applied to a study of the changes which different heat treatments can impart to a variety of toners and bisarylamide yellow pigments [13]. The technique has also been extended to the crystal aggregation of commercial samples of disperse dyes [14].

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