Dyes and Pigments **14** (1990) 49–58

Fractal Analysis of Organic Pigment Crystals

Robert R. Mather

Department of Technology, Scottish College of Textiles, Netherdale,
Galashiels, Selkirkshire TD1 3HF, UK

(Received 11 September 1989; accepted 17 October 1989)

ABSTRACT

The surface geometries of two series of organic pigments, β-copper phthalocyanines and calcium 4B toners, have been analysed by a fractal approach, in which surfaces are characterised by a dimensional scale, D. For surfaces of progressively higher irregularity, the value of D rises from 2 (perfectly two-dimensional) towards 3 (perfectly three-dimensional). In view of the anisotropy of both types of pigment crystal, values of D were determined in terms of two crystal dimensions. The values, 2·26 and 2·29, obtained with respect to breadth and length of the β-copper phthalocyanine crystals suggest that their surfaces are by no means smooth. Fractal analysis of the calcium 4B toners suggests that the side faces of their crystals are smoother ($D = 2{\cdot}06$), but information about the main faces is less clear. The nature of the aggregate structures also has a bearing on fractal analysis and examples are discussed for both series of pigments.

INTRODUCTION

Organic pigments are composed of tiny molecular crystals, typically of dimension 0·02–0·5 μm.[1,2] Being insoluble in the media into which they are incorporated, they have to exist in these media in a finely divided state for the achievement of high colour strength. However, the pigment crystals have a large surface energy by virtue of their small size and thus have a high tendency to become aggregated. Aggregation is nearly always undesirable technologically, for by reducing the level of subdivision of the crystals it hinders the attainment of high colour strength.[1,2]

Dyes and Pigments 0143-7208/90/$03·50

The geometry of the aggregates can be strongly influenced by the bulk geometry of the crystals.[3] With blue β-copper phthalocyanine pigments, for example, rod-shaped crystals are often assembled into open aggregate structures, whereas less well-developed brick-shaped crystals are more closely packed together. Nevertheless, larger rod-shaped crystals may also become closely packed, through substantial face-to-face packing.[4]

One objective, therefore, for the pigment manufacturer is the production of pigments of desired crystal geometries. Moreover, the geometries of the crystal surfaces, across which aggregation occurs, are also likely to play an influential role. Pigment crystals with smoother surfaces may adhere to each other less readily than those with rougher surfaces of the same chemical type and so will be less prone to severe aggregation. It would thus be useful to be able to compare surface irregularity in the crystals of a series of pigments, especially if the comparison could be made in simple quantitative terms.

In practice, the surfaces of solid particles are nearly always highly irregular, in that they may consist of pores, steps, fractures and other features. Examples of particles with highly homogeneous surfaces are therefore rare, yet it has traditionally been the practice to treat a surface, whether smooth or irregular, as two-dimensional, with surface heterogeneity being considered as a deviation from ideality.

A more realistic approach is to start with the premise that irregularity is a *normal* feature of surfaces.[5] Two extremes can them ne identified. At one extreme, irregularity in particle surfaces is totally absent, so that the surface is indeed truly two-dimensional. At the other extreme, surface irregularity in solid particles may be so pronounced that the surface is essentially a dense porous maze supported by thin walls of solid.[5] In this case, adsorption of molecules from a gas or a liquid may in effect amount to their penetration into virtually all the solid. The adsorbed molecules form an almost three-dimensional array. In general, therefore, adsorbed molecules can be considered to form an arrangement which is intermediate between two- and three-dimensional.

The fractal approach to surface geometry, developed recently by Avnir & Pfeifer[5-7] from the pioneering concepts of Mandelbrot,[8] imposes just such a dimensional scale, D, on a surface, such that $2 \leq D < 3$. For perfectly smooth surfaces, which can be properly treated as two-dimensional, $D = 2$; for progressively higher surface irregularity, the value of D rises from 2 to 3. The state $D = 3$ would correspond to a completely three-dimensional network.

For a surface to be correctly described in terms of a fractal dimension D, it must generally exhibit self-similarity.[5,8] This means that the same type of geometrical features are identifiable either at different magnifications or when probes of different sizes are used to examine the surface. For adsorption studies, the probes are molecules of adsorbate. Thus, by following the adsorption on a given solid of molecules of different sizes, the fractal dimension D can be evaluated from the relation:[5]

$$n \propto r^{-D}$$

where n is the number of adsorbate molecules of radius r required to give a monolayer coverage over the adsorbent surface.

An alternative, and usually more practical, method is to use the same adsorbate on a family of related solid adsorbents. In this approach, their specific surface areas are analysed as a function of their particle sizes, d. The adsorbate very often used is nitrogen: specific surface areas, S_{BET}, may be determined by application of the Brunauer–Emmett–Teller (BET) equation[9] to nitrogen adsorption isotherms.[10] If the adsorbent surfaces are fractal, then $S_{BET} \propto d^{D-3}$. A plot of $\log S_{BET}$ against $\log d$ should, therefore, be linear: D is obtained from the slope of the straight line.

The fractal approach thus provides a means of analysing the surface geometry of particles, such as the crystals constituting organic pigments. However, crystals of organic pigments are in practice anisotropic and fractal analysis of such crystals has yet to be fully exploited. The anisotropy of these crystals implies that different crystal faces may have different geometries and so should be described by different values of D. In this paper, fractal analysis is applied to series of well-defined β-copper phthalocyanine crystals (major blue colourants) and calcium 4B toner pigment crystals (major red colourants).

β-COPPER PHTHALOCYANINE PIGMENTS

McKay & Mather[4] published data showing the effect of treating a 'semi-finished' copper phthalocyanine pigment, possessing both α- and β-character, with a variety of organic liquids at 60°C for 24 h. In every case, crystals of copper phthalocyanine with a β-lattice structure were produced, which were appreciably larger than those of the starting material. From transmission electron micrographs, the mean length, L, and the mean breadth, B, of the crystals of each pigment could be determined. On the basis that the crystals were of square cross-section perpendicular to the major axis,[4] crystal volumes, LB^2, and axial ratios, L/B, were determined. The latter is a measure of crystal shape. The size and shape of the pigmentary crystals were found to be highly dependent on the liquid in which they had been grown.

The geometric specific surface area, S, was also derived from crystal dimensions and compared with the BET specific surface area, S_{BET}, determined by nitrogen adsorption. The ratio, S_{BET}/S, indicates the extent of face-to-face packing of pigment crystals. Where S_{BET}/S is about unity, the crystal surfaces are all accessible to nitrogen and form open aggregate structures, essentially free of face-to-face contact. Where S_{BET}/S is considerably less than unity, a more closely-packed aggregate structure with substantial face-to-face packing of crystals is indicated.

McKay & Mather[4] showed that, with two exceptions, the crystals had to be about eight or more times larger than those in the original $\alpha\beta$-pigment before face-to-face packing between crystals was effectively eliminated. Indeed, in some pigments, the crystals were still small enough to exhibit an appreciable degree of close packing. The very low values of S_{BET}/S, 0·54 and 0·56, found for the two exceptional pigments demonstrated strongly coherent face-to-face crystal contact, which signalled the start of a secondary growth process.

Further information on these pigment crystals can be gained from fractal analysis of their surface geometry. Avnir *et al*,[7] have already demonstrated the utility of this approach to a series of iron oxide pigments. Following Avnir *et al.*, a mean crystal dimension, *d*, for the copper phthalocyanine crystals may be taken as $(LB^2)^{1/3}$, the cube root of the mean crystal volume. Figure 1, taken from the data of Mather & McKay, shows a plot of log S_{BET} against log *d*. If the points labelled ● are ignored, corresponding to the two exceptional pigments where there is secondary growth, the correlation between S_{BET} and *d* is highly significant. The fractal dimension *D*, calculated from the slope of the line of best fit, is 2·45 ± 0·10.

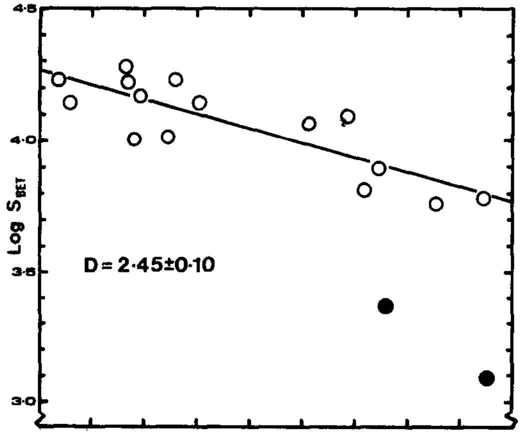
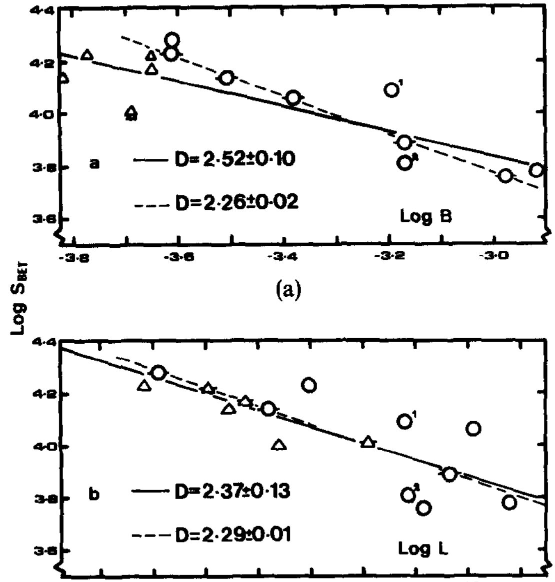


Fig. 1. BET specific surface area, S_{BET}, as a function of mean crystal dimension, *d*, for a series of β-copper phthalocyanine pigments. The two filled symbols, ●, correspond to pigments where there is secondary crystal growth.



(a)

(b)

Fig. 2. BET specific surface area, S_{BET}, as a function of (a) mean crystal breadth B, and (b) mean crystal length L, for a series of β-copper phthalocyanine pigments. Continuous lines represent the best linear fits to all points. Broken lines represent the best linear fits to the points labelled –○– and –△–. 1 Signifies crystals grown in 2-nitrotoluene and 2 signifies crystals grown in acetylacetone.

The dimension d, however, accommodates both mean crystal length L and mean crystal breadth B, yet for anisotropic crystals the value of L is always several times that of B. It is appropriate, therefore, to monitor S_{BET} in terms of B and L separately, and Figs 2(a) and 2(b) show the respective log–log plots (denoted by the continuous lines). The calculated fractal dimensions are $D = 2\cdot52 \pm 0\cdot10$ in terms of breadth B, and $D = 2\cdot37 \pm 0\cdot13$ in terms of length L. These two values are not significantly different in a statistical sense.

However, six of the points labelled △, correspond to pigments with the smallest crystals, for which $S_{\text{BET}}/S < 1$. The crystals of these pigments had grown insufficiently for complete elimination of face-to-face packing. Hence, their aggregate structures are different from the much more open structures of the pigments represented by the points labelled ○. For these latter pigments, $S_{\text{BET}}/S \simeq 1$, and the derived fractal dimensions are now $D = 2\cdot28 \pm 0\cdot10$ in terms of breadth B, and $D = 2\cdot28 \pm 0\cdot22$ in terms of length L. These values appear identical, but their standard errors are considerable. Nevertheless, they do suggest that the surfaces of the pigment crystals are by no means smooth.

Closer scrutiny of Figs 2(a) and 2(b) reveals that several points in each graph (those identified by –○– and –△–) can be selected which provide a particularly close linear fit (denoted by the broken lines). There are five such points in Fig. 2(a) and six in Fig. 2(b). Moreover, two pigments provide points on both broken lines. The derived fractal dimensions are now $D = 2{\cdot}26 \pm 0{\cdot}02$ in terms of breadth B, and $D = 2{\cdot}29 \pm 0{\cdot}01$ in terms of length L. These values are very close indeed to one another and are also close to the values derived previously. Moreover, the standard errors are now considerably smaller, being similar to those reported elsewhere for many other types of particulate solid.[6,7]

In Fig. 2(a), all the points labelled △ lie below the broken line. These points correspond to pigments for which $S_{\mathrm{BET}}/S < 1$. If these points are then considered in Fig. 2(b), only if $S_{\mathrm{BET}}/S < c.\ 0{\cdot}8$ do they lie below the broken line. Points corresponding to pigments for which $0{\cdot}8 < S_{\mathrm{BET}}/S < 1{\cdot}0$ now also lie on this line. On this basis, then, it appears that the breadth B of the crystals has more influence than their length L on the complete transition to an open aggregate structure.

This assertion is tested in Figs 3(a) and 3(b), which show plots of S_{BET}/S against B and L, respectively. A clear pattern is revealed in Fig. 3(a), where S_{BET}/S is plotted against B, but not in Fig. 3(b), where S_{BET}/S is plotted

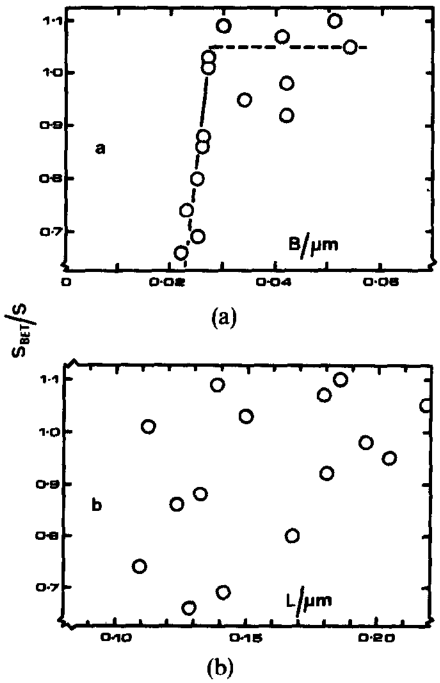


Fig. 3. Plots of the ratio, S_{BET}/S, against (a) mean crystal breadth B, and (b) mean crystal length L, for a series of β-copper phthalocyanine pigments.

against L. Thus, although growth of β-copper phthalocyanine crystals is preferred in the direction of their length L, the lesser growth at right-angles to L apparently has a key influence on opening up the aggregate structure. The crystal breadth at which this process appears just to be complete is *c.* 0·027 μm, and indeed no point in Fig. 2(a) lies on the broken line below this value (equivalent to −3·61 on the logarithmic scale). It is noteworthy that this value is only *c.* 1·4 times the breadth of the crystals of the $\alpha\beta$-starting material.

There are, however, a few points labelled ○ which are situated well away from the broken lines. Although it is too early yet to provide a detailed explanation, it seems evident that they mostly reflect accelerated or diminished growth of the crystals in particular directions. The departures from the broken line are more frequent in Fig. 2(b), where length L is considered. This is perhaps not surprising in view of the generally more rapid growth along this axis, where the effect of liquids in inhibiting or promoting growth would be more readily detectable.

One pigment, whose crystals were grown in 2-nitrotoluene, appears unusual in giving rise to points above the broken lines in both figures. Its crystals are thus both longer and broader than would be expected for its value of S_{BET}. By contrast, another pigment, with crystals grown from acetylacetone, gives rise to points below the broken lines. The value of S_{BET}/S for this pigment is 0·92, which suggests that secondary growth of the crystals has just begun.

CALCIUM 4B TONER PIGMENTS

McKay[11] has published extensive data on the crystals of 31 calcium 4B toner pigments, prepared both on the laboratory and production scales. The pigments all contained plate-like crystals, which (with the exception of four pigments) were coated with a resin, incorporated to control crystal size during preparation and to promote dispersibility in application media.

McKay[11] determined both the thickness, t, of the crystals and their cross-sectional area, A, at right-angles to the direction of t. By assuming that the resin coats the crystal surfaces uniformly, he also calculated a thickness x, for the coating. Thus, the thickness of the coated crystals becomes $(t + 2x)$ and the mean dimension across the crystals is $(A^{1/2} + 2x)$. As with β-copper phthalocyanine pigments, the geometric specific surface area, S_c, of each toner pigment was also determined and compared with the BET surface area, S_{BET}. For the majority of the toner pigments, S_{BET} is a substantial fraction of S_c: the crystals form open aggregate structures, in which compact face-to-face packing is minor. Values of S_{BET}/S_c are commonly 0·8 or more.

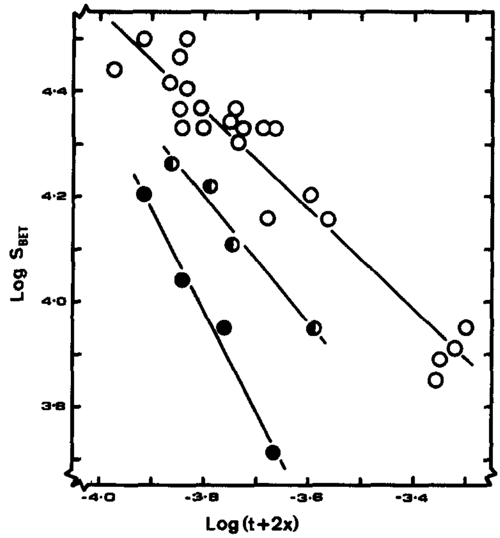


Fig. 4. BET specific surface area, $S_{\rm BET}$, as a function of mean crystal thickness, t, for a series of calcium 4B toner pigments.
○, $D = 2\cdot05 \pm 0\cdot06$, pigments for which $S_{\rm BET}/S \geq 0\cdot80$.
◐, $D = 1\cdot82 \pm 0\cdot15$, pigments for which $S_{\rm BET}/S = 0\cdot76$.
●, $D = 1\cdot09 \pm 0\cdot15$, pigments for which $S_{\rm BET}/S < 0\cdot76$.

A fractal analysis can also be conducted on the data for these pigments. Figure 4, for example, shows a plot of log $S_{\rm BET}$ against $\log(t + 2x)$, and there is clearly a correlation between the two parameters. If the points in Fig. 4 labelled ◐ and ● are ignored, corresponding to pigments for which $S_{\rm BET}/S_{\rm c} < 0\cdot8$, the fractal dimension calculated from the straight line of best fit is $D = 2\cdot05 \pm 0\cdot06$.

The correlation between $S_{\rm BET}$ and $(A^{1/2} + 2x)$, whilst statistically significant, is nevertheless much less clear. The calculated fractal dimension is $D = 2\cdot05 \pm 0\cdot34$. The large standard error could indicate substantial variation in the character of the main faces of the crystals.

The points in Fig. 4 corresponding to the more aggregated pigments are also of interest. They fall into two categories, the points in each being fitted well by a linear plot. It is noteworthy that the four points labelled ◐ on the upper line correspond to pigments for which $S_{\rm BET}/S_{\rm c} = 0\cdot76$ ($\pm 0\cdot01$), whilst for the four on the lower line labelled ●, the values of $S_{\rm BET}/S_{\rm c}$ lie below this range. The fractal dimensions are $D = 1\cdot82 \pm 0\cdot15$ for the upper line and $D = 1\cdot09 \pm 0\cdot15$ for the lower line.

It is noteworthy that the values of D for the two sets of aggregated pigments are both below 2, although the value of $1\cdot82 \pm 0\cdot15$ referring to only four samples is not significantly different from 2. By contrast, the result $D = 1\cdot09$ is intriguing, for being so close to unity it would at first sight

TABLE 1
Variation of S_{BET}/S_c with Pigment Crystal Volume in the Most Aggregated Calcium 4B Toner Pigments

Pigment	*Crystal volume* ($\mu m \times 10^4$)	S_{BET}/S_c
1	1·386	0·63
3	1·644	0·74
17	1·951	0·68
11	2·319	0·54

suggest that adsorption of nitrogen molecules is one-dimensional and, therefore, largely confined to crystal edges. However, the result could also be explained if the crystal aggregates become more compact as crystal size increases.[5] Table 1 compares S_{BET}/S_c against crystal volume, calculated from McKay's results.[11] Although the Table offers some indication that the bigger crystals are assembled into more compact aggregate structures, the explanation for such a low value of D still appears complex.

For correlation between S_{BET} and $(A^{1/2} + 2x)$, the two categories of aggregated pigment behave differently from one another. For those pigments for which $S_{BET}/S_c = 0{\cdot}76$, the fractal dimension is $D = 2{\cdot}20 \pm 0{\cdot}09$. However, no value of D can be readily calculated for the four most aggregated pigments.

CONCLUSION

Two examples have been given of the application of fractal analysis to series of organic pigments. In the family of β-copper phthalocyanines, there are authentic indications of surface irregularity in the crystals of each pigment and of structural self-similarity between many of the samples. In most cases, it appears that the degree of surface irregularity in the different crystal faces is almost identical ($D = 2{\cdot}26$–$2{\cdot}29$). In the family of calcium 4B toners, self-similarity is indicated in the side faces of the pigment crystals, and the fractal dimension, $D = 2{\cdot}06$, suggests that these faces are quite smooth. Self-similarity in the main faces is much harder to detect: there may be genuine variation in the roughness of these crystal faces from one sample to another. There may also be greater error in the values of the areas, A, determined by McKay,[11] which arise from the complex geometries of the main faces of the crystals he sampled.

Whilst emphasis has been placed on individual pigment crystals, the nature of the crystal aggregate structure has also been shown to influence the fractal analysis. Crystals aggregated into closely packed structures, which would be undesirable in technological terms ($S_{BET}/S < 1$), do not show self-similarity with those forming the more desirable open aggregate structures ($S_{BET}/S \doteqdot 1$). However, such closely packed crystals may show self-similarity amongst themselves; an example has been given by the crystals of those calcium 4B toner pigments for which $S_{BET}/S_c = 0{\cdot}76$. Since in practice organic pigment crystals are so prone to aggregation, it would be highly desirable to be able to apply fractal analysis to aggregate structures as well as to individual crystals. However, to achieve this aim, the mean number of crystals in an aggregated unit must first be determined. It is hoped that the determination of this number and its application to the fractal analysis of crystal aggregates will be the subject of a future paper.

ACKNOWLEDGEMENTS

Professor D. Avnir, The Hebrew University of Jerusalem, Israel, and Dr R. B. McKay, Ciba–Geigy Pigments, Paisley, Scotland, UK, are thanked for their helpful comments and suggestions during the preparation of this paper.

REFERENCES

1. McKay, R. B. & Smith, F. M. In *Dispersion of Powders in Liquids*, ed. G. D. Parfitt, 3rd edn Applied Science, London, 1981, p. 471.
2. McKay, R. B., *Rev. Prog. Coloration*, **10** (1979) 25.
3. Fryer, J. R., McKay, R. B., Mather, R. R. & Sing, K. S. W., *J. Chem. Tech. Biotech.*, **31** (1981) 371.
4. McKay, R. B. & Mather, R. R., *Colloids and Surfaces*, **27** (1987) 115.
5. Pfeifer, P. & Avnir, D., *J. Chem. Phys.*, **79** (1983) 3558; Avnir, D., *The Fractal Approach to Heterogeneous Chemistry*, John Wiley and Sons, New York, 1989.
6. Avnir, D., Farin, D. & Pfeifer, P., *Nature (London)*, **308** (1984) 261.
7. Avnir, D., Farin, D. & Pfeifer, P., *J. Colloid Interface Sci.*, **103** (1985) 112.
8. Mandelbrot, B. B., *The Fractal Geometry of Nature*, Freeman, San Francisco, 1982.
9. Brunauer, S., Emmett, P. H. & Teller, E., *J. Amer. Chem. Soc.*, **60** (1938) 309.
10. Gregg, S. J. & Sing, K. S. W., *Adsorption, Surface Area and Porosity*, 2nd edn Academic Press, London, 1982.
11. McKay, R. B., *FATIPEC Congr. XVIII*, **2/B** (1986) 405.