Journal of Chromatography, 517 (1990) 395–403
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 1969

Sedimentation field-flow fractionation for pigment quality assessment

L. KOCH*, T. KOCH[a] and H. M. WIDMER
Central Analytical Department, CIBA-GEIGY Ltd., CH-4002 Basle (Switzerland)

ABSTRACT

Sedimentation field-flow fractionation is presented as an alternative method for pigment particle size characterization for the purpose of industrial quality control. The technique is demonstrated for three pigments of variously broad particle size distributions having average particle diameters ranging from *ca.* 0.1 to 0.6 μm. The analysis times compared favourably with those of disc centrifugation, and the reproducibility of the shape and mean particle size distributions were sufficient to obtain a reliable quality standard "fingerprint" with which samples of unknown quality could be compared.

INTRODUCTION

Pigments are always virtually insoluble materials that exist in the form of very small crystals that are incorporated into a colourless binding agent in the solid state. Whereas the properties of dyestuffs (soluble colorants) are determined by their molecular structure and by their interaction with the substrate, the properties of pigments are determined to a large extent by their physical characteristics. Through controlled changes in these physical characteristics, especially the particle size distribution, the properties of pigments can be optimized for certain applications or shifted in a desired direction. In certain instances, these physical properties can have such a significant impact on the final properties of the pigment that a certain pigment must be preferentially selected for use in an application where the chemically identical pigment in another physical form led to problems in processing or other unsatisfactory application results in the coloured medium.

As pigments are not soluble compounds but rather dispersed, microscopically small crystals, the particle size influences all application properties, albeit to various extents. Hue and strength, important properties of both pigments and dyestuffs, are primarily a function of the absorption wavelength region and the molar absorption coefficient. With pigments, however, the particle size also plays a significant role. After

[a] Present address: Heinz Schlegel Ltd., CH-4313 Möhlin, Switzerland.

0021-9673/90/$03.50

synthesis, the pigment aggregate must be reduced in size through milling. Down to a certain level, the smaller are the pigment particles, the stronger is the colour of the pigment. In addition, the particulate structure of the pigment gives rise to light scattering which is responsible for the extremely important application property of hiding power, *i.e.*, the ability to obliterate from view a background substrate. In many instances, unattractive substrates are covered through painting or lacquering, which also acts to provide protection against corrosion or degradation. The more strongly the non-absorbed light is scattered, the better is the covering power of the pigment. There is a need for pigments possessing either high or low hiding power, depending on their intended use. For example, pigment systems with high hiding power are required for heavy-duty industrial paints for machinery, whereas a transparent packaging film necessitates a low hiding power. The hiding power can be influenced through the choice of the pigment, the particle size distribution and additives.

Unfortunately, physical or physico-chemical measurements on dry pigment powder usually provide no real relevant conclusions on the final application properties of the pigment system. Untreated pigment powder is always in an aggregated state, and these aggregates and agglomerates must undergo a multi-step process of dispersion, through which they are wetted, reduced in size, dispersed and stabilized, in order to attain and maintain a sufficiently fine distribution. Almost all important properties of pigments or pigmented systems are, in fact dependent on how successful this dispersing process is. The optimum dispersed state of a pigment distribution is obtained when all primary particles, *i.e.*, either pigment aggregates or crystals as colloidal stabilized single particles, are homogeneously distributed. A series of different methods are suitable for the determination of the dispersibility as a function of various parameters, and most of these methods accomplish this through evaluation of the particle size distribution. These methods commonly include electron microscopy, various light-scattering techniques rheological measurements, Joyce–Loebl photosedimentometry, sedigraphic methods and Coulter Counter measurements. Our aim is to develop and utilize field-flow fractionation (FFF) methods and related techniques, *i.e.*, split-flow lateral transport thin (SPLITT)[1] separation cells, to help solve industrial particle sizing problems in situations where more conventional techniques have not yielded satisfactory results. When the pigment is most effectively analysed in a specific medium, or when the particle size distribution is characterized by multi-modality or shows non-Gaussian behaviour, FFF is likely to be the analytical method of choice. In this paper we propose and, using several examples from practice, demonstrate the use of sedimentation field-flow fractionation for the determination of particle size distributions for the purpose of pigment quality assessment in industry.

Sedimentation field-flow fractionation (SdFFF) has emerged as a versatile technique for the characterization of both simple and complex particle populations[2–5]. A particulate sample is entrained in a stream of liquid within the flat, circular channel of a specially designed, flow-through centrifuge rotor. The spinning of the centrifuge produces a field, oriented perpendicular to the direction of longitudinal channel flow, which causes sample particles denser than the mobile carrier to sediment radially outward towards the outer channel wall. Larger, or denser, particles interact more strongly with this applied field than the smaller, or less dense, particles in the sample mixture. Opposing this accumulation at the outer wall is the diffusion of the particles towards the centre of the flow channel. The combination of these two phenomena

culminates in the formation of thin steady-state concentration layers, or particle "clouds", which lie parallel to the accumulation wall, and which exhibit a characteristic degree of compression known as the steady-state layer thickness. The extent to which this layer protrudes into the parabolic flow streamlines on initiation of flow down the channel determines the average downstream particle velocity and thus the resulting elution sequence. The elution times can therefore be related by exact theory to particle size, mass and density[6].

However, although this separation principle has been used successfully to analyse a variety of submicron-sized particles relatively very few of the numerous FFF publications have dealt with its use in industrial applications. Our aim is to make use of FFF or related methods where other, more conventional techniques do not yield satisfactory results, *e.g.*, for multi-modal particle size distributions or in cases where a particular dispersing agent is required to ensure retention of certain particle properties.

Although Joyce–Loebl photosedimentometry (disc centrifugation), Coulter Counter and light-scattering methods are frequently used for pigment characterization, they all exibit certain intrinsic limitations which restrict their applicability. By requiring the use of density modifiers in the spin fluids, disc centrifugation cannot provide an analysis of the particles in their "as marketed" state. In contrast, by allowing an almost unrestricted choice of carrier, field-flow fractionation techniques are able to maintain the most meaningful environment for the pigment in terms of application properties. In addition, the use of the optimum carrier type greatly reduces the possibility of inducing additional aggregation and flocculation of the sample. The Coulter Counter has the disadvantage of not providing a particle size continuum. This limits the use of the instrument for quality assurance purposes, for which an accurate "fingerprint" of the sample, *i.e.*, a continuous particle size distribution curve, would be desirable for comparison with a standard "fingerprint" already on file. Light scattering is not an elution technique, *i.e.*, it does not separate as it analyses, and hence it cannot provide samples for further analysis by microscopy. This latter possibility can be extremely useful when, for example, it is necessary to determine whether anomalies in the particle size distribution are due purely to multi-modalities in size or if the particle shape is a contributory factor.

EXPERIMENTAL

Instrumentation

All measurements were performed on a DuPont SF[3] Model 1000 sedimentation field-flow fractionator (DuPont Instrument Systems) with a Hewlett Packard 9000/217 data-processing system. The initial temperature of the SdFFF system was 23°C (room temperature) in all instances. A temperature probe inserted in the centrifuge served to monitor the temperature of the air around the channel throughout the runs.

The various mobile phases were prepared with either Tween 20 (Fluka) or Teepol (Fluka) and doubly distilled water to the specifications given in Table I; 0.01% sodium azide (Merck) was added to retard bacterial growth. Samples were prepared by dilution in the mobile phase to *ca.* 1% by weight. Immediately before injection into the SdFFF channel, all samples were sonicated for precisely 1 min using a Branson Model

250 Sonifier, on high power, fitted with a micro-tip for use directly within the sample tubes.

For the evaluation of the fractogram in terms of actual particle diameters it is essential to know the density of both the sample and the carrier very accurately. Mobile phase densities were determined on a Paar Model DMA-60/602 densitometer, and found to be 1.00 g/ml in all instances. The densities of solid samples were precisely measured in the Physics Department at CIBA-GEIGY. Pigment A, an organic DPP (diketopyrrolopyrrole) colorant, was thereby found to possess a density of 1.55 g/ml. Pigments B and C, both azo colorants, each possessed a density of 1.3 g/ml. When analysing pigments, it is particularly important that the solid density be determined on the same crystal modification as that to be analysed by FFF. As the purpose of this study was to demonstrate "fingerprinting" of the particle size distribution of a particular pigment type by SdFFF, exact values for the particle and carrier densities are not required. They were necessary later, however, to evaluate the instrument performance when retention times were in question.

The injection volumes were 50 μl, and injection was carried out automatically with two Rheodyne pneumatically activated injection valves that had been fixed inside the system to minimize the prechannel dead volume. These valves were connected to a Gilson Model 221 sample changer which controlled the injection procedure, and a Gilson Model 401 diluter, which served to pump the sample very accurately onto the channel for the relaxation process. The eluate was detected at 254 nm with a Spectroflow Model 783 programmable absorbance detector (Applied Biosystems).

As most of the sample preparation was not performed within our laboratory, *e.g.*, the dispersion step was done in the plant, the concentrations varied slightly from sample to sample. However, the detector response is dependent on both particle concentration and size (as a consequence of their light scattering), which necessitates a correction of the response if a true concentration distribution is to be obtained from the fractogram[7]. Through moment analysis one may calculate the area under the retained peak, which reflects the total amount of retained particles, and the centre of the peak, reflecting the average diameter of retained particles. Future implementation of this in our data collection system will permit accurate computer comparison of fractograms.

Fractions for subsequent electron microscopy were collected with a Gilson Model 203 fraction collector.

Operating conditions

Time-delayed, field-decay programming was used in all instances. The proper functioning of the SdFFF equipment was routinely checked by injection of a mixture of Seragen Diagnostics standard polystyrene latex sphere particles of known density and diameter [0.460 $\pm$ 0.0048 μm, 0.318 μm (standard deviation unknown) and 0.204 $\pm$ 0.0020 μm]. The resulting fractograms were evaluated in terms of consistency in position of the void peak and the particle peak and shape of the particle peak.

All runs for a given pigment type were performed under identical FFF operating conditions. These conditions are given in Table I.

The fractogram obtained from all three pigment systems were repeatable and showed no undue noise or apparent distortion other than that which could be attributed to the properties of the particle populations themselves. The raw data

TABLE I

FFF OPERATING CONDITIONS

Pigment code	*Initial rpm*	*Relaxation time (min)*	*Time constant (= delay time) (min)*	*Carrier*	*Flow-rate (ml/min)*
A	600	10	8	0.01% Tween 20	3.0
B	2000	10	3	0.01% Teepol	2.0
C	3000	10	5	0.01% Teepol	2.0

(fractograms) were examined to identify and evaluate the void peak, which contains all particles and macromolecules small enough to be unaffected by the centrifugal field as they pass through the channel and the particle peak.

RESULTS AND DISCUSSION

The average particle diameters of the three pigments ranged from *ca.* 0.1 to 0.6 μm. The shape of the particle size distributions, as previously determined by either Coulter Counter or disc centrifugation measurements, also varied. The samples were crystalline and, while primary particles of pigment A were small, stable aggregates, B and C consisted of single crystals. Thus, any measurement of pigment A was actually a measurement of aggregate size. This made the decision to sonicate these samples before running them in the FFF particularly difficult, as it was not our intention to disrupt the particles from their natural states. In fact, SdFFF experiments on pigment A showed significant reductions in the mean particle size with increasing sonication time, leading us to believe that, with extended sonication time, aggregates had been reduced to an artificially high degree of fineness.

Electron micrographs of the three original samples (after 1 min of sonication) are shown in Fig. 1. Micrographs of samples B and C showed that they contained particles from the submicron range up to more than 100 μm in diameter, and thus spanned the ranges of both normal and steric FFF. For these cases, a more meaningful particle size determination would include either an off-line preseparation step (filtration), or an on-line preseparation realized by performing two subsequent runs at different conditions. The latter strategy permits the analyis of the submicron particles separately from the particles larger than 1 μm. This can be very useful for complex mixtures, and ensures that a steric foldback[8], which distorts the fractograms and limits their information content, is avoided.

By adhering to a fixed set of experimental conditions for each of the three pigments A, B and C, the fractograms become directly comparable for a rapid evaluation of similarities or differences in the particle size distributions. Our approach was thus to obtain a reproducible fractogram in which sample components were well retained, and for which the total run time had been reasonably well optimized, and to use this as a standard fractogram with which others could be compared. These standard fractograms are shown as solid lines in Fig. 2a, b and c. The traces denoted by dashed lines in Fig. 2a represent additional samples of pigment A which were drawn from the same production line at periodic intervals. Even small differences in mean particle diameter could be seen by comparing fractograms. Concentration differences,

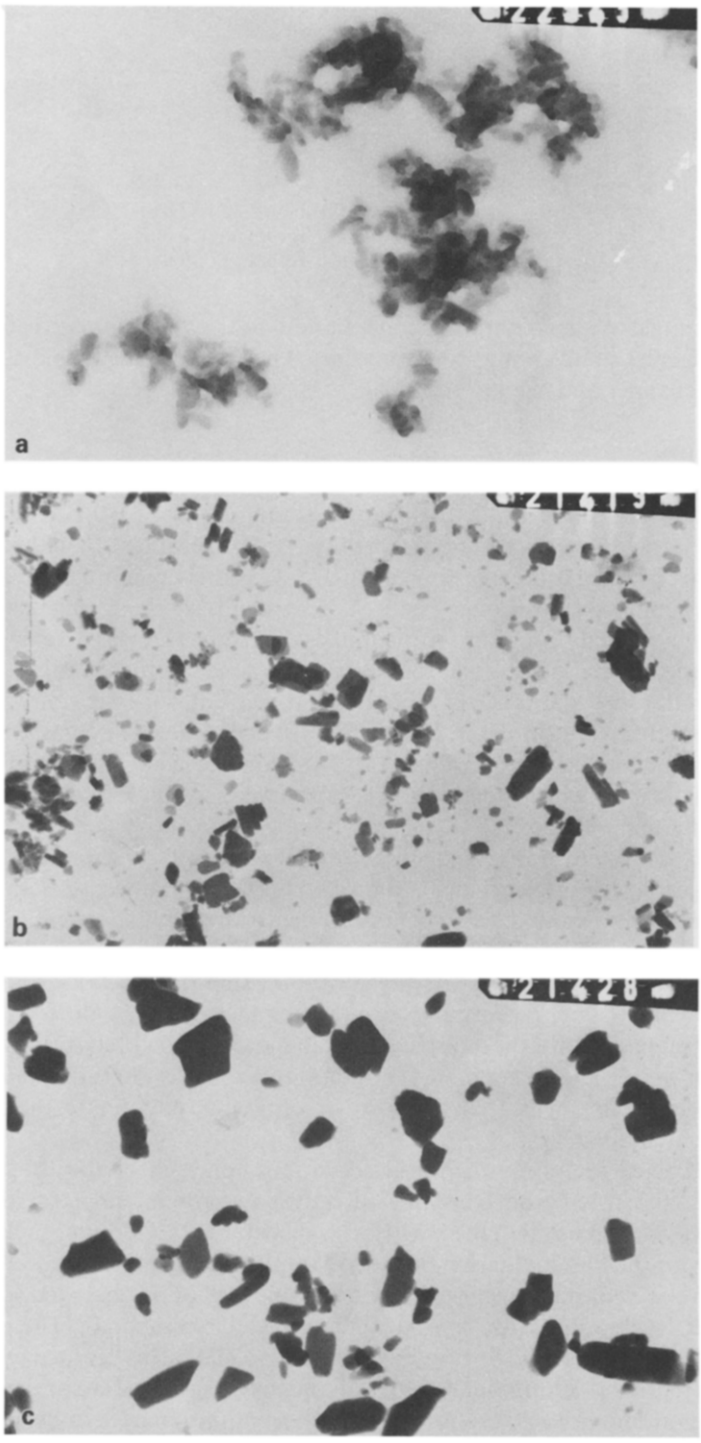

Fig. 1. Electron micrographs of the original pigment samples: (a) A; (b) B; (c) C. The magnification of A is twice that of B and C.

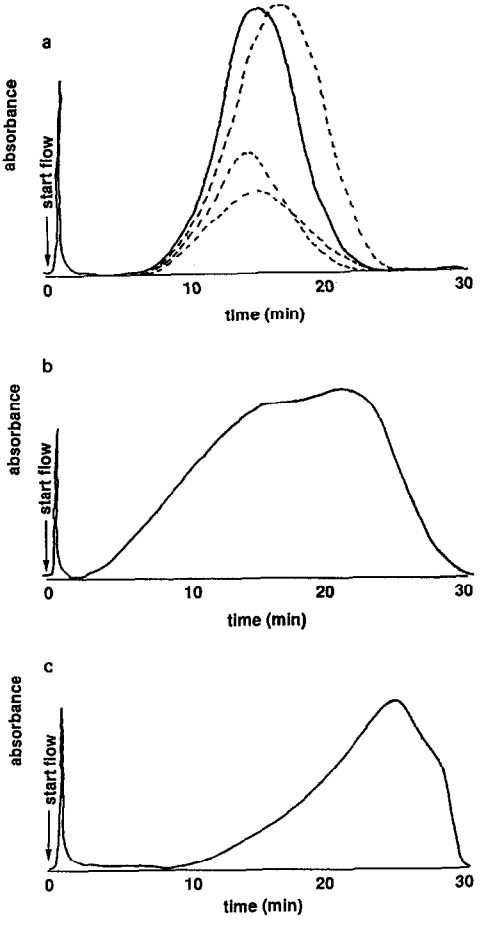

Fig. 2. Standard fractograms of (a) pigment A (solid line), (b) pigment B and (c) pigment C. The dashed lines in (a) correspond to fractograms of samples subsequently drawn from production.

visible as differences in peak amplitude, can be traced to the sample preparation step (dilution). The standard analysis procedure for these pigments within our company is disc centrifugation, and the total SdFFF run times, of the order of 30 min, were comparable to the times required for a disc centrifugation analysis.

As for any analytical technique, method development in FFF can be very time consuming. This learning process is considerably accelerated when the approximate particle diameter and densities, and a suitable dispersing agent, are known in advance. Fortunately, this information is generally readily available or obtainable for pigment particles. However, even when this basic knowledge exists, the varying complexity of samples can lead to great differences in the time needed for method development, as was the case for the three pigments examined in this study. Pigment A, which exhibited monomodal Gaussian distributions in the SdFFF, and indicated no significant interaction with the accumulation wall, required only an extremely short method development (two or three preliminary runs) and could have actually been analysed

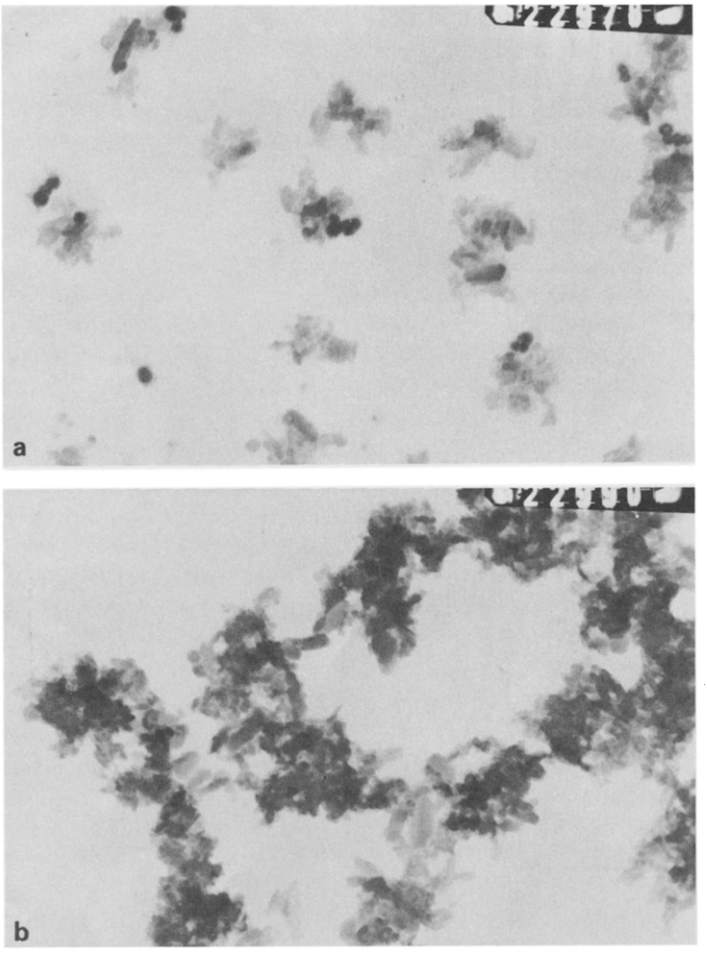

Fig. 3. Electron micrographs of fractions collected during a SdFFF run of pigment A, (a) at $t = 20$ min and (b) at $t = 30$ min.

after the first run. In contrast, samples B and C, with very broad, complex distributions, required several days of method development before a satisfactory, reproducible fractogram could be obtained. It should be noted that the system parameters for the last two pigments were not necessarily optimized, but rather a stable, reproducible fractogram was produced which could serve for comparison with latter fractograms. Whether the phenomenon leading to the non-Gaussian particle size distributions is adsorption, steric foldback or multi-modality in particle sizes remains unknown and is not of significant importance to this study. In fact, the shapes of the particle size distributions were in good agreement with those obtained by light scattering and disc centrifugation. There was, however, some discrepancy in the mean particle diameter.

In all instances the particles were considerably under-retained in SFFF. This may be a consequence of an incorrect value for the channel void volume. The effect

became more pronounced with increasing diameter, culminating in a size discrepancy of up to 30% for particles eluting at the peak maximum. In order to gain an insight into this discrepancy, we collected fractions of the continuously eluting sample for further analysis by electron microscopy. Fig. 3a shows a fraction collected from sample A at $t = 20$ min and Fig. 3b a fraction collected at $t = 30$ min. While the microscopy clearly served to verify the separation, the mean diameters of the particle population were difficult to assess with microscopy because of the non-spherical nature of the particles. However, careful evaluation of the microscopy data supported the disc centrifugation particle size data. The cause of the observed under-retention is still being investigated.

The results obtained show that SdFFF, when used as part of a "fingerprinting" strategy, is suitable for the quality assessment of pigments within the particle diameter range studied. Further developments are necessary to ensure that the excellent reproducibility of the distributions is coupled with reliable particle size data. Careful study is required to locate the cause of the discrepancies between actual and experimental particle size, likewise exhibited in runs with polystyrene standards.

Because the analysis times were comparable to those for disc centrifugation analyses, and because field-flow fractionation systems lend themselves to fully automated operation with an autoinjector (difficult to implement in a disc centrifugation system), SdFFF shows great promise for unattended, constant use for quality control purposes in the production plant itself. The realization of this goal would be facilitated by the development of simple, inexpensive FFF analysers which monitor the industrial pigment milling process through periodic, automated analyses and actually serve to determine the end-point of the milling process. This would provide a considerable advantage over the present method of allowing the milling process to proceed for an extended time to ensure that the particles have definitely reached the desired size. In addition, the high densities of pigment particles could ideally be exploited with the development of a simple SdFFF system which utilizes only gravitational force as the applied field. With such a simple system it would be feasible to couple an analyser to each mill in production.

REFERENCES

1 J. C. Giddings, *Sep. Sci. Technol.*, 23 (1987) 119.
2 S. M. Mozersky, K. D. Caldwell, S. B. Jones, B. E. Maleeff and R. A. Barford, *Anal. Biochem.*, 172 (1988) 113.
3 L. E. Schallinger, E. C. Arner and J. J. Kirkland, *Biochim. Biophys. Acta*, 966 (1988) 231.
4 H. K. Jones, B. N. Barman and J. C. Giddings, *J. Chromatogr.*, 455 (1988) 1.
5 L. E. Oppenheimer and G. A. Smith, *Langmuir*, 4 (1988) 144.
6 J. C. Giddings, G. Karaiskakis, K. D. Caldwell and M. N. Myers, *J. Colloid Interface Sci.*, 92 (1983) 66.
7 F. S. Yang, K. D. Caldwell and J. C. Giddings, *J. Colloid Interface Sci.*, 92 (1983) 81.
8 S. Lee and J. C. Giddings, *Anal. Chem.*, 60 (1988) 2328.