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The degree of dispersion of pigments in powder coatings

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Abstract

Assessment of the state of a pigment dispersion in powder coatings is hindered by the lack of a simple and effective method of evaluation, particularly during the production process. A method for evaluating dispersion quality in cured powder coatings or in samples taken immediately after the extrusion process is described in this paper. Quantitative information of pigment dispersion were obtained using plasma etching-SEM-image analysis. In order to correlate the differences in the extrusion equipment and, consequently, the energy input of the dispersion process, two different formulations were studied, each prepared using three different extrusion units. The procedures are described in detail and the results are compared to those obtained using colour difference measurements. Pigment size distribution plots correlate well with measured colour differences and with the energy inputs of the different extrusion units used.

Keywords: Powder coatings; Pigment dispersion; Image analysis; Colour measurements

1. Introduction

The powder coatings (PC) segment of the coatings industry is popular due to its low inherent organic volatile compounds (VOC) emission and high (95% and more) recovery during the application process [1]. The term “pigment dispersion” in the /PC/ industry describes the relative amount of pigment aggregates and agglomerates that are present in solid media. It is known that the dispersion of a pigment in powder coatings is usually incomplete and is influenced by the properties of the pigment itself, the binder and, to a large extent, the extrusion process [2]. Several properties of the coatings formulation influence the dispersing process namely the viscosity of the binder, its ability to wet the pigment surface, the attractive forces operating between the pigment primary particles and the production process [3,4]. There are eight distinct stages in conventional PC manufacturing of which the most important, with respect to the properties of the final PC, are, premixing, extrusion and grinding [5]. Sufficient premixing of the ingredients is especially important for materials that are used in small quantities. Pigment clusters are separated to primary particles during the extrusion process, which lasts, typically, for 20–30 s. Differences in the extrusion equipment and, therefore, extrusion shear force,

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also influence the final state of the pigment dispersion. It is believed that grinding in the final stage of the production process does not affect the pigment dispersion process. The presence of large pigment clusters in the coating affects its appearance by reducing gloss and increasing haze values; the presence of large clusters also affects the viscosity of the final PC system. Consequently, inadequate levelling during the curing process is observed. Recently [2], different approaches have been used to improve dispersion which include the use of pigment predispersions in coating formulations, different additives to improve wetting of the pigment surface and modifications in equipment design.

The assessment of the state of the pigment dispersion is hindered by the lack of simple and effective methods of analysis particularly, during production. While in classical coatings, the presence of large pigment clusters can be observed easily in situ using a grindometer, the degree of a pigment dispersion in a PC can only be evaluated at the end of the extrusion process or at the end of manufacture of the PC. The main indirect method for evaluating the state of the pigment dispersion in PC involves measurement of the differences in PC hiding power and shade using colorimetry.

There are few quantitative methods for the determination of the state of pigment dispersion in a dry coating film; one of these involves direct visual observation using microscopy. Although there are other methods, such as flocculation-gradient techniques or colour strength and hiding power determination, during optimisation of the production parameters and during development of the powder coating formulation, microscopy gives a direct view of the pigment particle size and size distribution.

One of few, suitable direct methods that can be used for the quantitative determination of the state of pigment dispersion in PC is that of scanning electron microscopy (SEM) [6–8]. Such measurements have been applied to dry paint film to evaluate the degree of flocculation [2,9]. The approach can be modified and used on PC although such SEM methods based on PC samples involved only qualitative examination. In order to assess the particles within the solid coating film, oxygen plasma etching is required.

This paper describes a quantitative method for the evaluation of the degree of the pigment dispersion in PC by the use of oxygen plasma etching, scanning electron microscopy and image analysis. The main advantage of this method is that it permits quantification of the pigment dispersion in cured samples. Two different PC formulations were studied each being prepared in three ways, differing in the type of the extruder used and, consequently, in energy input. Firstly, selective oxygen plasma etching was used and details of removal of the binder matrix are given. Scanning electron microscopy of etched surfaces was then used and micrographs were analysed using public domain software. The distribution of the particle sizes inside PC layer was given in graphical form and the results compared. A comparison with colorimetric measurements is also made in order to illustrate the usefulness of the developed technique.

2. Materials

Different types of PC were examined based on formulations that are used in standard production process. The formulations include a mixture of inorganic pigments and organic pigments of different textures and dispersibilities. The binder in all samples was a mixture of carboxy–polyester polymer and on hydroxyalkylamide. It was proven that the nature of the binder had no significant influence on pigment dispersion evaluation. A formulation of the yellow PC is shown in Table 1 and a formulation for the orange–yellow PC is given in Table 2. Average particle sizes of applied pigments are also given. Most data for primary particle sizes were obtained from manufacturers. Particle sizes for products, where no information was available, were estimated from SEM micrograph of pigment powders.

3. Experimental

3.1. Preparation of the powder coating samples

Two formulations of PC samples namely yellow (Y) and orange–yellow (OY) were prepared

Table 1
Formulation of yellow PC

Amount (mass%)	Component	Information	Average particle size
70.3	Binder	–	–
10.1	Filler $BaSO_4$		2.10 μm
16.0	C.I. Pigment White 6	TiO_2-rutile	0.24 μm
0.02	C.I. Pigment Red 101	Red iron oxide	0.17 μm
3.1	C.I. Pigment Yellow 194	Monoazo (benzimidazolone)	0.31 μm
0.02	C.I. Pigment Yellow 110	Tetrachloro-isoindolinone	0.30 μm
0.4	C.I. Pigment Yellow 42	Yellow iron oxide	0.40 μm

Table 2
Formulation of orange–yellow PC

Amount (mass%)	Component	Information	Average particle size
70.1	Binder	–	–
14.9	Filler $CaCO_3$	Min. 97% $CaCO_3$	0.1–1.0 μm
7.5	C.I. Pigment White 6	TiO_2-rutile	0.24 μm
7.5	C.I. Pigment Yellow 83	Dis-azo yellow	0.33 μm
0.01	*Irgazin Red 2031* (Ciba-Specialty Chemicals)	Diketo-pyrrolo pyrrole	($\leqslant$0.4 μm)[a]

[a] Average particle size was estimated from SEM micrographs of the pigment powders.

according to three different extrusion technologies. Details are given in Table 3. The samples are denoted by indices 1, 2 and 3, identifying the production technology route.

3.2. Oxygen plasma etching and scanning electron microscopy evaluations

Selective plasma etching was used to remove the surface polymer matrix from the samples. The procedure is based on the selective interaction of reactive gaseous particles with paint films. As we wanted to etch the polymer matrix while leaving the particles unchanged, etching was performed in a pure oxygen plasma. Plasma parameters were measured using a double Langmuir probe and catalytic probe. At the neutral gas temperature of about 50 °C, the electron temperature was about 60,000 °C, the density of positive ions about 1×10^{16} m^{-3} and the density of neutral oxygen atoms 2×10^{21} m^{-3}. Electron and neutral gas temperatures were derived from their average random velocity. In order to prevent sample overheating, plasma was applied in time intervals of 20 s. The removal of the polymer matrix was completed in the topmost layers within 2–4 min, as was found out from SEM micrographs, taken at different time intervals. The etching process is highly selective

Table 3
Production description of PC samples

	Technology 1	Technology 2	Technology 3
Extrusion equipment	Twin-screw extruder ZSK 50	Single-screw extruder PCS 70	Single-screw extruder PCS 30
L/D[a]	20	8	7
Extrusion chamber diameter (D)	2×50 mm	70 mm	30 mm
Capacity	570 kgh^{-1}	380 kg h^{-1}	9 kg h^{-1}
Extrusion chamber length (L)	1000 mm	560 mm	210 mm
Process speed	0.57 kg mm^{-1} h^{-1}	1.02 kg mm^{-1} h^{-1}	0.04 kg mm^{-1} h^{-1}
Input power	43.2 kW	14.4 kW	2.4 kW

[a] Ratio of the extrusion chamber length to the extrusion chamber diameter.

and leaves all the pigment and filler particles left intact. Selectivity is achieved due to difference in coherent energy between amorphous polymer and crystalline pigments. Each PC formulation was exposed to a different etching time in order to determine the best effect, where pigment particles were completely exposed from the polymer matrix. It was realised that longer exposure times could remove the polymer matrix to an extent that the pigment particles would become clogged together and unsuitable for further examination in SEM.

Scanning electron micrographs were obtained using a Joel 5500 LV at a 20 kV accelerating voltage. Prior to the SEM analyses the samples were covered with a thin layer of gold using a Bal-tic SCD 005 sputter coater.

3.3. Image analysis

The degree of pigment dispersion in PC was evaluated by distribution of pigment particle sizes inside coatings. The particles are seen on etched micrographs where they were quantified according to their area. The area distribution was converted to their size distribution.

The SEM micrographs of etched samples were quantified using *Image-J* public domain software [10]. This program identifies the pigment particles, calculates their area and generates an area distribution graph. The procedure has the following steps:

1. contrast black/white conversion of the SEM micrographs;
2. detection of particles with *Image-J* software;
3. program parameter modification;
4. scale calibration;
5. graphical presentation of the particle area distribution;
6. transformation of the *Image-J* results into size distribution data.

As the *Image-J* program demands contrast black/white micrographs the necessary conversion of gray-scale SEM micrographs to such a form was made. Any capable computer program such as PaintBrush® or PaintshopPro® can be used. Such contrast micrographs enable the *Image-J* program to distinguish between the pigment particles and the background. Parameters that have to be optimised are the threshold, the minimum particle area and the number of intervals to which the area distribution data are divided. In order to quantify the area, scale calibration is made using known distances on the SEM micrograph.

Transformation of the particle area to particle dimensions and the graphical representation of these results was achieved using computer programs developed in *Matlab 5.3* software. These programs are available on request. Some graphical presentations of data were made using a Microcal Origin (Microcal Software, USA) software package.

3.4. Colour difference measurements

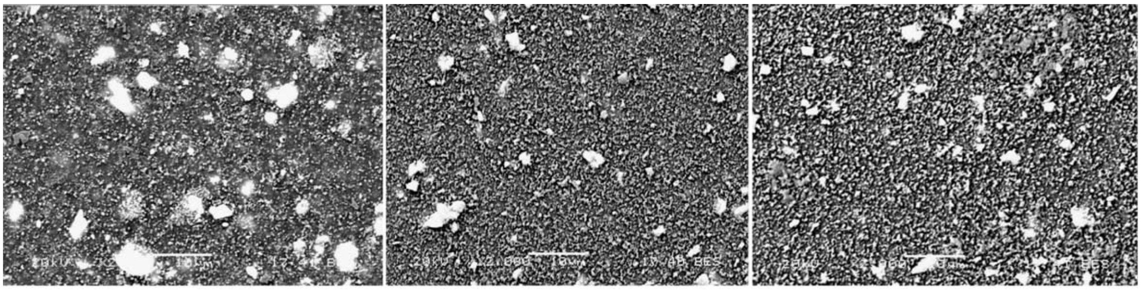
The colour difference between each sample and selected RAL standard [11] was calculated using CIE 1976 $L^*a^*b^*$ space using illuminant D_{65} and 10^0 standard observer. The diffuse reflectance of coatings was measured using a CS-5 CHROMA-SENSOR System (Datacolor). Large area sample measurement aperture and specular included scanning mode were applied.

4. Results and discussion

In order to study the influence of the procedures, namely plasma etching, SEM and image analysis of the pigment particle size, particle size analysis of pigments and filler was undertaken prior to the dispersing process and comparisons were made with the results that were obtained after plasma etching of the cured PC film. It was shown that during etching, no changes in the particle size distribution of pigments occurred.

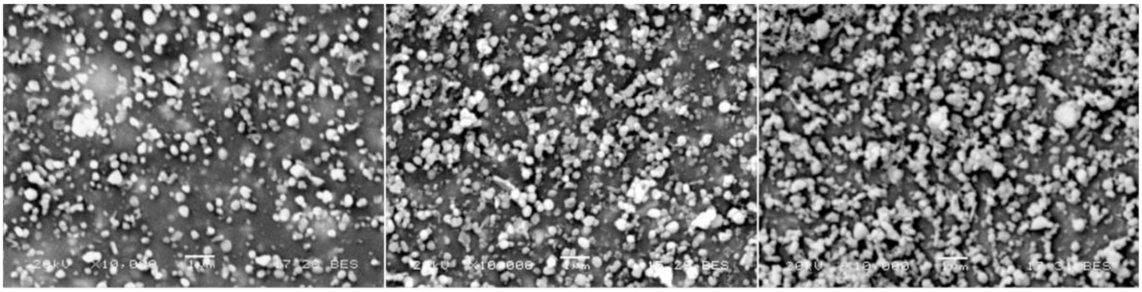
4.1. Yellow PC

The formulation includes barium sulphate filler (average particle size 2.1 μm) and a mixture of inorganic and organic pigments (average size distribution between 0.17 and 0.40 μm). SEM micrographs were obtained at different magnifications of 2000 times and 10,000 times (Figs. 1 and 2).



Y1 Y2 Y3

Fig. 1. SEM micrographs at 2000× magnification of the Y1, Y2 and Y3 plasma etched samples.



Y1 Y2 Y3

Fig. 2. SEM micrographs at 10,000× magnification of the Y1, Y2 and Y3 plasma etched samples.

The particles showing a diameter of more than 2 μm are the barium sulphate. These can be clearly distinguished from the particles of other pigments. The presence of the agglomerates and aggregates in samples Y2 and Y3 is caused by the incomplete pigment dispersion process as seen in these micrographs.

The micrographs shown in Fig. 1 were then processed using *PaintShopPro®* software to improve contrast and to convert each micrograph into a negative contrast black/white micrograph. An example of such a transformation is presented in Fig. 3 for the Y1 system, at 10,000× magnification, before and after conversion. The other micrographs were converted in a similar manner. The third part of Fig. 3 shows the results of particle detection using the *Image-J* program.

The results of the image analysis of these three micrographs are presented in the Fig. 4, where the size distribution of pigment particles is shown. Large particles, of diameter greater than 2 μm, were excluded from the calculation because of their small population in the micrographs.

The quality of the dispersion process can be evaluated from the distribution graph given in Fig. 4. The smallest particles in Y1, Y2 and Y3 samples have a diameter of 0.22 μm. They are present in all three samples, as primary particles and, most likely, are primary particles of the C.I. Pigment White 6. This is because the C.I. Pigment White 6 is present at the highest pigment loading with a diameter that is equal to the product specifications. The higher relative amount of the primary particles (between 0.22 and 0.40 μm) and lower relative amount of the larger pigment clusters in the Y1 sample indicate superior dispersion relative to that of Y2 and Y3. The pigment particles in Y1 are better dispersed than are those in Y2 and the pigment particles in Y3 are the least well dispersed. The distribution graphs are in good agreement with the energy input of the extrusion process since Y1 was produced with the highest energy input, Y2 with less and Y3 with the smallest energy input (see Table 3). The colour differences according to CIELAB definitions are shown in Fig. 5.

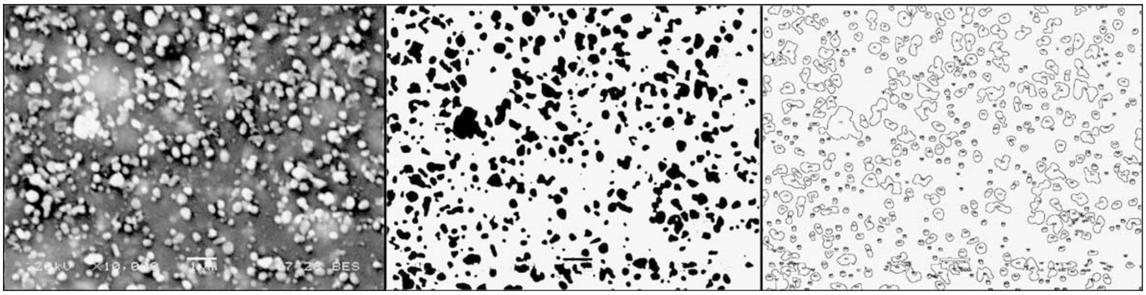


Fig. 3. SEM micrograph at 10,000× magnification of the Y1 sample before and after the image modification and outlined particles detected with *Image-J* program.

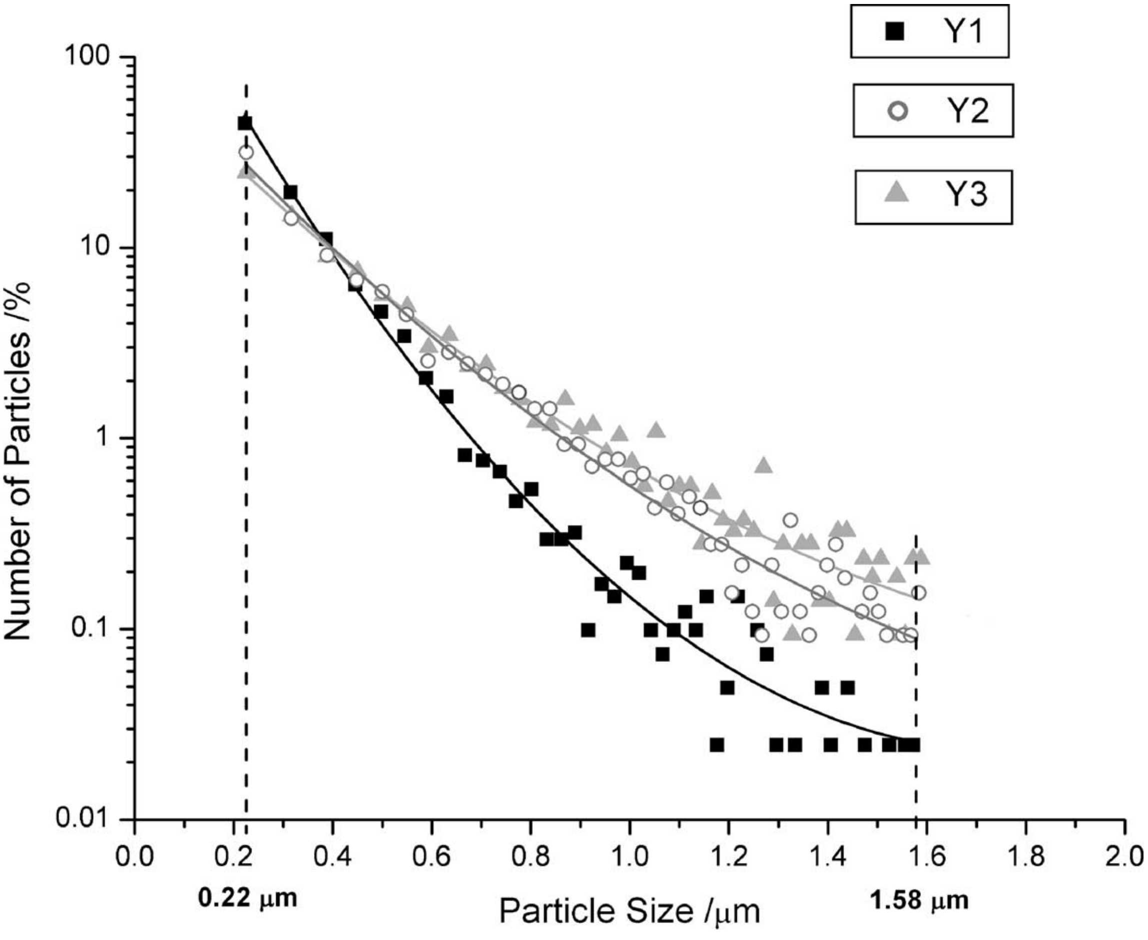


Fig. 4. Particle diameter distribution in Y1, Y2 and Y3 samples.

The total colour difference, ΔE^* increased from Y1 to Y3, relative to the standard (RAL 1018). Both Y2 and Y3 samples had negative Δa^* values resulting in a greener hue compared to that of Y1. Since the pigment formulation contains inorganic white, red and yellow pigments and an organic yellow pigment, it is evident, from these data, that the inorganic pigments were better dispersed than

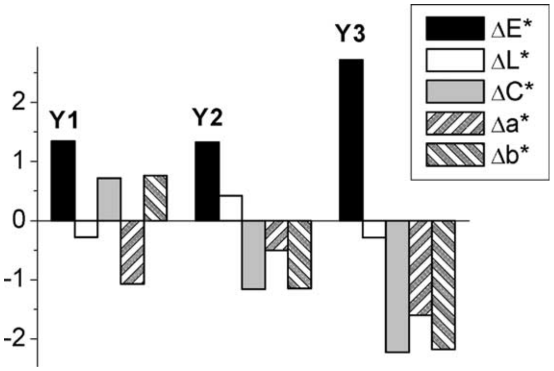


Fig. 5. CIELAB colour differences for Y1, Y2 and Y3 samples, relative to the RAL 1018 standard.

the yellow pigment. The high positive Δ*b** value of sample Y1 indicates that the yellow inorganic pigment was better dispersed than in Y2 and Y3 samples, where the Δ*b** values were negative. These differences in the dispersion process are also shown in the differences in the Δ*C** and Δ*E** values, indicating that Y1 was better dispersed than Y2 and that Y2 was better dispersed than Y3.

That finding is in good agreement with size distribution graphs for the yellow samples (Fig. 4). The presence of greater amount of aggregates and agglomerates is therefore detectable through size distribution graphs and total colour difference values.

4.2. Orange–yellow PC

Samples of orange–yellow PC were prepared in a similar manner to that used for the red PC samples and for the yellow PC samples. SEM micrographs after etching are presented in Fig. 6.

Micrographs (at 6000× magnification) were chosen because these gave a large enough population of particles and because of the good resolution which was better than that obtained with the 2000× magnification. The micrographs were then modified to contrast black/white micrographs and processed with the *Image-J* program. The resulting particle diameter distribution for the three samples is presented as Fig. 7.

Pigment particles in sample OY1 were better dispersed than the pigment particles in the other two samples. Almost 50% of all particles had an average diameter of approximately 0.14 μm, which is the average diameter of primary particles of most of the pigments in the formulation. Only a small number of particles had a diameter of up to 1.5 μm, it is being the diameter of the calcium carbonate filler. It can be concluded from Fig. 7 that OY3 had the least dispersed pigments and filler. The distribution starts at 0.23 μm and is shifted to higher values relative to the OY1 and OY2 samples, clearly indicating the presence of agglomerates and aggregates of pigments. Again, the distribution graphs of samples OY1, OY1 and OY3 respectively, are in good agreement with the energy input of the extrusion process.

The difference in the state of the pigment dispersion was proven also by measurements of the colour differences between the OY1, OY2 and OY3 samples relative to the standard (RAL 1028). The data are represented in Fig. 8. The total colour difference Δ*E** increases from OY1 over OY2 to OY3. The negative Δ*C**, Δ*a** and Δ*b** values indicate the green-blue hue, originating from incomplete dispersion of the yellow and white pigments. Again,

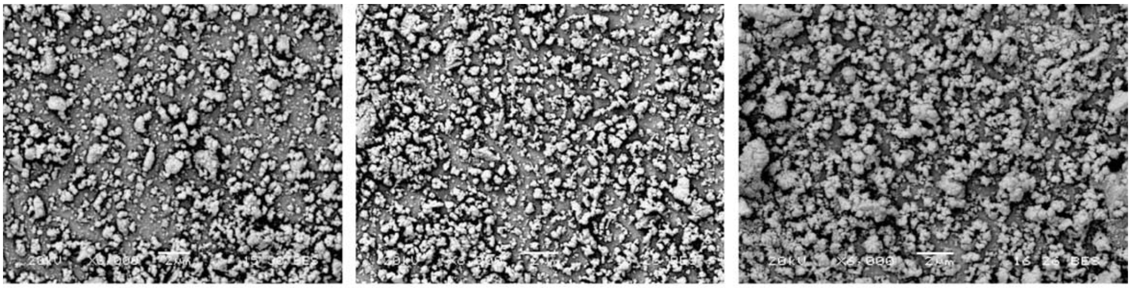

OY1 OY2 OY3

Fig. 6. SEM micrographs at 6000× magnification of plasma etched OY1, OY2 and OY3 powder coating samples, respectively.

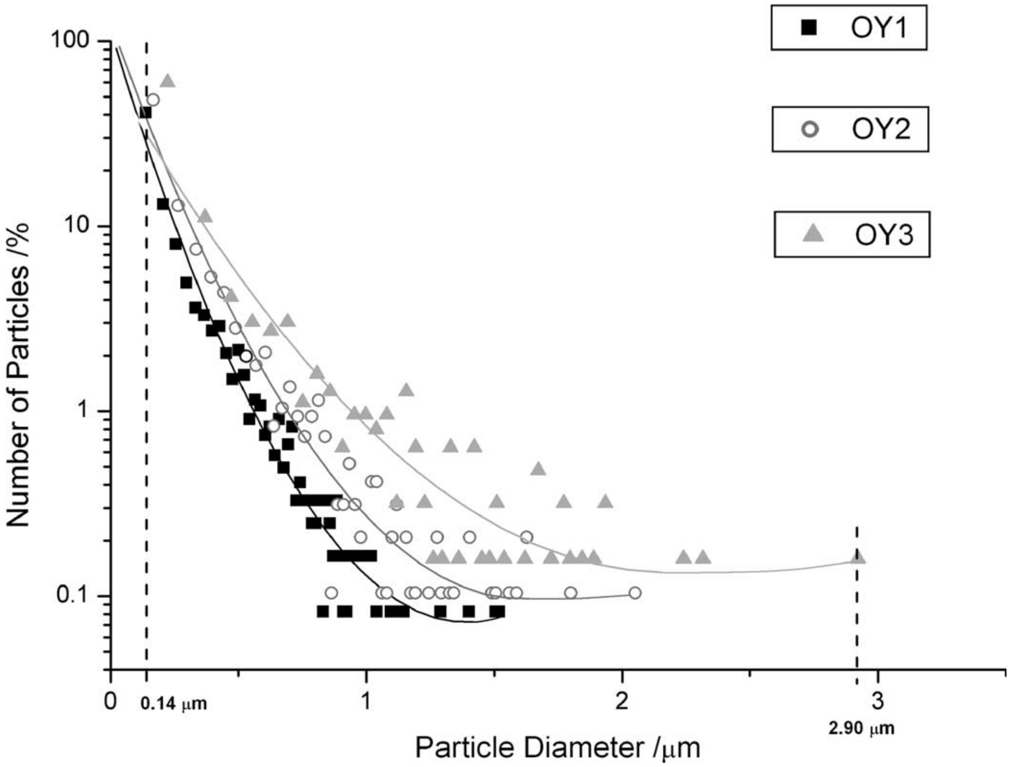


Fig. 7. Particle size distribution in the orange–yellow PC samples.

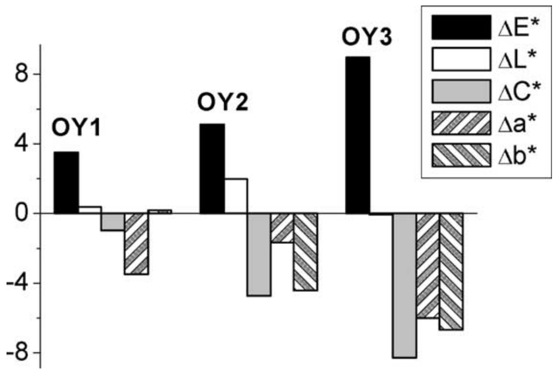


Fig. 8. Colour differences of OY1, OY2 and OY3 samples, relative to RAL 1028 standard.

differences in colour measurement are in good agreement with the image analysis results. According to these results, OY1 had a better dispersed pigment than OY2 which, in turn, was better dispersed than OY3.

5. Conclusions

This paper has given relevant results associated with the evaluation of the state of the pigment dispersion in powder coatings. It was developed to quantify the degree of pigment dispersion in powder coatings as dictated by the process used. As such, this approach offers potential in equipment comparison and production process optimisation. The main advantage of this procedure is the quantification of the degree of the pigment dispersion in cured samples. The approach can also be applied to samples that have been taken immediately after completing the extrusion process, but before final grinding is applied. No significant difference was observed between these samples and samples taken after grinding and curing.

The difference in the extrusion process arising from the different energy input and the different applied extrusion equipment is also manifested through colour difference values. However, the results of colour measurement give only information that the process is incomplete or wrong. The *Plasma etching-SEM-Image analysis* method that has been described gives quantified information concerning the particle size distribution and, consequently, the degree of the pigment dispersion in the system. Such results are in close relation to the total colour difference values.

The particle size distribution graphs for the samples used in this study are in good correlation with the energy input in the process (see Table 3).

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