# The influence of synthesis on the size and morphology of $\alpha$–$Fe_2O_3$ particles

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Iron oxides are very important materials in several fields of industry and science. They are used as catalysts, pigments, gas sensors, abrasives, polishing agents or magnetic recording media. Iron oxides are the basis for magnetic prospecting of archeological areas as well as for the production of iron or ferrites.

It is well known that iron oxides are the oldest-known colorants, chemically stable, non-toxic, non-bleeding and highly durable with excellent suspension properties. $\alpha$–$Fe_2O_3$ (hematite) is the most frequent red inorganic pigment with a very high heat resistance as a superior pigmentary property. In the present comparative study two types of $\alpha$–$Fe_2O_3$ samples have been prepared by non-equivalent ways. "Dry" way of $\alpha$–$Fe_2O_3$ synthesis was based on the thermal decomposition of $FeSO_4 \cdot 7H_2O$ in the air. The synthesis includes several stages: the partial dehydration of ferrous sulfate heptahydrate to monohydrate at 200 ℃, the milling and sorting of particles, calcination at temperatures 600–800 ℃, dissolution of possible sulfato-intermediates in the water, filtration and drying of the final pigment. The size of $\alpha$–$Fe_2O_3$ particles can be varied depending on the calcination temperature and the used sort of the initial particles. When using "wet" way, iron oxide pigment was produced by reacting a ferrous salt, a reducable aromatic nitrocompound (nitro- or azoderivates) and a basic compound, chosen from hydroxides of ammonium and alkali metals, operating at 25-200 ℃, in an aqueous medium. The size (and colour) of pigment particles can be varied by increasing the reaction temperature and the molar ratio between ferrous salt and aromatic nitrogen compound.

The way of synthesis can influence not only an internal structure of $\alpha$–$Fe_2O_3$ but also they can modify the morphology of particles and their size distribution. Just the influence of the method of synthesis on external pigment characteristics and consequently on the pigment colour quality was studied and discussed in the present work.

Samples were characterized by dynamic light scattering method — DLS (particle size distribution), non-contact atomic force microscopy — AFM (the morphology of particles) and the elastic scattering visible spectroscopy (the colour quality of pigments).

Concerning the general description of particles morphology using AFM measurements, all observed particles showed the symmetrical shape like "flat hexagonal scales" (figure 1) — lateral dimensions were about 10–30 times greater than the vertical dimension, independently on the type of pigment. However particles of $\alpha$–$Fe_2O_3$ prepared by dry way showed about 3 times greater the vertical dimension than the crystallites prepared by the wet way, at comparable lateral dimensions.

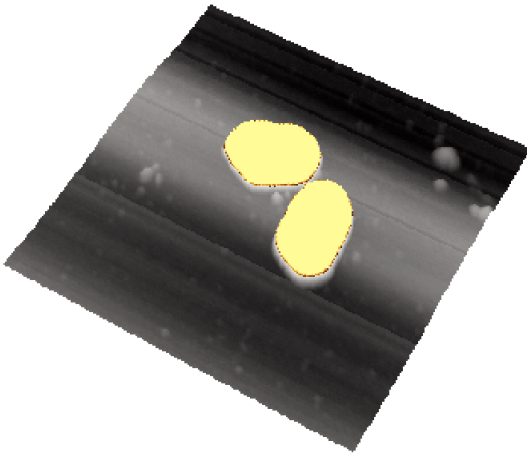

Figure 1: AFM image of $\alpha$–$Fe_2O_3$ particles prepared by wet way, section in $xy$ plane (scan size: 680 × 680 nm)

Particle size distributions were measured using DLS method, experimental data were approximated by log-normal fit from which three basic characteristics — a mean diameter, a half width of distribution curve and an asymmetry parameter — were calculated (see table 1). Results summarized in table 1 indicate that the asymmetry parameters are significantly higher for samples prepared by wet way (average value 0.550 vs. 0.496). Values of mean diameters are dependent not only on the method of pigment synthesis (dry vs. wet) but also on the specific conditions during preparation (reaction temperature). Nevertheless it is evident that samples prepared by wet way show higher values of mean diameters though the half width distribution values are almost the same.

**Table 1. Results of DLS analysis**

| Sample | Mean diameter [nm] | Half width [nm] | Asymmetry parameter |
|---|---|---|---|
| I/A | 278 | 122 | 0.507 |
| I/B | 247 | 122 | 0.480 |
| I/C | 250 | 111 | 0.486 |
| I/D | 309 | 143 | 0.482 |
| I/E | 251 | 102 | 0.526 |
| II/A | 300 | 120 | 0.541 |
| II/B | 377 | 140 | 0.539 |
| II/C | 261 | 86 | 0.538 |
| II/D | 319 | 105 | 0.573 |
| II/E | 318 | 125 | 0.570 |

Samples I were prepared by dry way, samples II by wet way

To assess the colour quality of pigments the elastic scattering visible spectra were measured in the wavelength range of 400–750 nm. The results of these measurements for both sets of pigments are presented in the standard form of two-dimensional colour co-ordinates (figure 2). Two mutually perpendicular directions can be highlighted. The first direction marks changes in the colour quality produced by different values of mean diameters, the second direction corresponds to the shift due to the different asymmetry parameters.

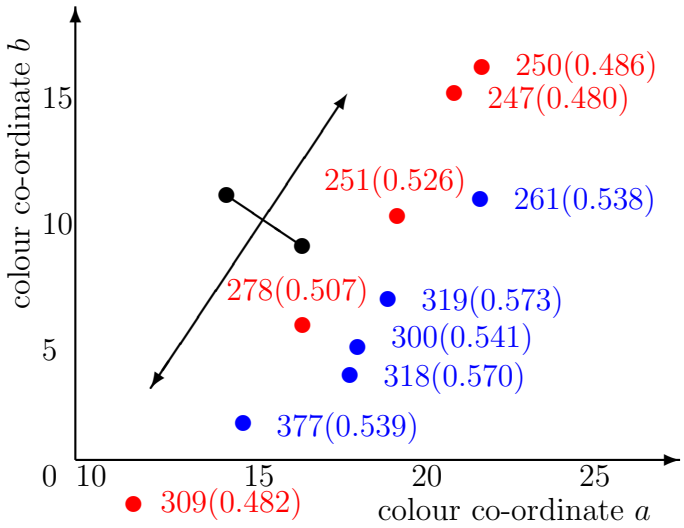


Figure 2: The colour co-ordinates of $\alpha$–$Fe_2O_3$ samples and directions of influence of mean diameter (arrow) and asymmetry parameter (line with disks)