Effect of Processing Speed on Microstructure and Colour Properties of the Iron Ore-Derived Red Colour Pigment

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Abstract. This study proposes a novel technique to convert local iron ores into industrial grade red colour pigments. The methods employed in this work include high-energy milling, ball milling, rod milling and high-energy blending. It was observed in the TEM results that high-energy milling using ø 3 mm balls running at 550 rpm produced the finest particles with a value of 73.13 nm and a specific surface area of 178.62 m² g⁻¹, while ball milling and high-energy blending methods were similarly effective in producing nanoparticles with size of 78.54 nm and 88.65 nm, respectively. The sample of high-energy milling at 550 rpm displayed noticeable alterations in colour values, but the lightness of high-energy blending samples was low in comparison to other methods. CIE L*a*b* colour values were analysed for all the samples and the results indicated that the value of a* for all the samples was greater than 18.0. This indicated that the samples are suitable for use as raw materials in red colour pigment production. Generally, the processing speeds utilized by the above mentioned methods resulted in significant changes in colour properties and its microstructure.

Keywords: Iron ore, Colour pigment; Ball milling; High energy ball milling; CIE L*a*b* colour values

1. Introduction

Natural iron oxide colour pigments of high quality are confined to a limited amount of iron mines around the world. This is due to the difficulty of ensuring consistency within colour values as well as ensuring pigment performance properties of the harvested iron ores. Malaysian lands are well equipped with an abundance of iron ores [1-3]. However, research and development interests in harvesting, and converting Malaysia iron ores into colour pigments with quality have been frail, hence resulting in a loss of pace in the contention for valuable market shares in the pigment manufacturing industry, which is projected to expand over the next decade [4,8,11]]. As such, local producers of paints and other pigment-related products are dependent on foreign imports for pre-selected colour pigments, thus assuming a role of interim consumers in the supply chain and more susceptibility to global economic fluctuations and price changes. Furthermore, foreign imports with considerable quality come with expensive price tags [5-7]. The formation of new industries, job opportunities, lower costs, and increased profitability are potential advantages if raw materials such as iron ores were to be obtained from local sources.

Recently, the values of iron ores and steel products have been gradually dwindling due to reduction in construction and infrastructure development. This decline dampens the investment and development interests presented by local and international companies aiming to cater to the steel
production industry in Malaysian ore-mining facilities [9,10]. The introduction of natural iron oxide pigments using local iron ores will serve as an alternative product or solution to the Malaysia mining and pigment industries. Moreover, the profit margins for local colour producers can be lucrative due to a high global demand, competitive pricing of colour pigments, and lowered iron ore prices [12].

The following issue can be tackled by presenting successful conversion of Malaysian iron ores into industrial grade colour pigments (particle size of 200 nm to 600 nm) by utilization of various size reduction methods such as high energy milling, high energy blending, ball milling and rod milling with different processing speeds aimed at studying its effects on the microstructures and colour values [13-15].

2. Experimental Procedure

The raw iron ores were obtained from iron mines in Malaysia. Elemental composition and phase stability of the raw iron ores were analysed as well as the type of iron oxide present in the ore samples prior to size reductions attributable to the utilized techniques. Presence of contaminants would significantly affect the quality of pigment and requires a tedious cleaning process. The X-ray diffraction (XRD), or the phase analysis was performed in order to detect the compound in the samples. This analysis was conducted by a CuKα (1.5418 Å) source (45 kV, 40 mA) from PANalytical Empyrean. The scans were executed with 2θ starting from 20° to 80°.

Upon completion of XRD, raw iron ores were hammered, and consecutively crushed into fine powder. The feed powder was then subjected to size reduction techniques with various speeds for different milling machines. High-energy ball milling, also known as planetary ball milling, was carried out in wet conditions, while the other techniques were performed in dry conditions. Subsequently, 5g of the feed powder was placed in a high-energy milling (Retsch, PM100) steel milling jar with distilled water. The charges used were steel balls with diameters of 3 and 11 mm. The machine was operated for 8 hours at 350 rpm and 550 rpm. In addition, a steel ball of diameter 5 mm was used for the conventional ball milling, while for the rod milling, steel rods with diameter of 7 mm and length of 134 mm were selected. Both ball milling and rod milling were operated at 64 rpm for 24 hours. Lastly, a high-energy blender (DM-6) was utilized at 25000 rpm for 5 minutes. The milling was conducted in a closed environment to secure the milling atmosphere.

Particle sizes of the milled powder were measured via a particle size analyser (Malvern Instruments Mastersizer 2000), based on the principle of evaluating the intensity of laser diffraction. The powder was dispersed in water beforehand with the assumption of possessing a spherical particle shape. Specific surface areas of the samples was also evaluated with the use of the same machine. TEM was further employed to confirm the particle size and particle shape. The evaluation of colour values were conducted by using a colourmeter (Konica Minolta CR 10) in order to provide measurements in terms of L*a*b*. The colourmeter was equipped with a gas-filled tungsten lamp as the light source and six silicon photocells as the detector.

3. Results and Discussions

The studies were carried out in accordance to three variables which included the following: average particle size (nm), specific surface area (m²g⁻¹) and colour values. According to Figure 1, the the Ø 3mm ball had undergone a massive reduction from an initial value of 234.77 nm at 350 rpm to a final value of 73.13 nm at 550 rpm. In contrast, the Ø 11mm ball was observed to have reduced from 298.21 nm at 350 rpm to a final value of 231.30 nm at 550 rpm. What can be concluded is that the Ø 3mm ball was more effective in comparison to the Ø 11mm ball in high-energy milling of the iron oxide particles, especially with an increase in milling speed. A further conclusion is that incremental milling speeds allowed for small sized charge media to be used for optimal and effective size reduction processes. While the ball milling at 64 rpm produced a sample with an average particle size of 78.54 nm, the DM-6 high-energy blender produced samples at an average of 88.65 nm. It can, therefore, be concluded that the calibration of suitable milling speed is a crucial factor affecting the particle size of iron oxide pigments.
Regarding the specific surface areas, an increase in speed of high milling energy in both the Ø 3mm and Ø 11mm balls was observed to result in an increase in specific surface areas. Such a trend may also be applied to the high energy blending with 25000 rpm, which produced samples with a specific surface area of 103.05 m²g⁻¹. Regarding the ball and rod milling, the obtained specific surface area values were low due to the adjustment of the milling speed to 64 rpm. As shown in Figure 2 below, it may also be deduced that the changes in specific surface area was contributed to by speed variations in the size reduction methods.
It can be observed on Figure 4, in which Ø 11mm ball were utilized at 550 rpm, that the resulted particles were larger and formed larger agglomerates. This could be due to the low specific surface areas produced by high energy milling as an adsorptive gas layer could not form over each individual particle. In contrast, the particles in Figure 3 were smaller, exhibited less agglomeration, and produced more uniform-size particles. The milling speed in Figure 4 revealed that the particles were crushed in more effective manner. However, some of the particles were found as needle shaped.

![Image](image1.png)

Figure 3: TEM image of high-energy milling (Ø 3 mm ball, 550 rpm, 8 h)

![Image](image2.png)

Figure 4: TEM image of high-energy milling (Ø 11 mm ball, 550 rpm, 8 h)

Each size reduction method requires a unique milling speed in order to produce the desired particle size and shape. This could be observed as the high energy blending which produced rectangular particles, attributed to high random-manner collisions and particle-breakages in the blender. In contrast, the ball and rod milling process produced more circular and uniform particle shapes. This is attributable to slow milling speeds, which allowed the consistent milling pattern of these particle size distributions and shapes.

The lightness was highly noticeable at high-energy milling with 550 rpm, while the rod and ball millings were low in lightness as a result of the low speed. Furthermore, the high speed DM-6 blended samples exhibited lightness as well. This could be attributed to the differences in milling mediums between dry, versus wet, and the particle shapes differing between oval versus circular. A plausible explanation would be that the oval and circular iron oxide particles are more effective at
light reflection and display of colour values. Figure 5 below displays an overview of the lightness recorded graph of the particles.

![Figure 5: L* values with respect to size reduction methods](image1)

As for the redness or a* values of the particles, it was observed that the samples with high specific surface area tend to possess lower redness value. The high energy milling of the Ø 3mm ball with 350 rpm has the highest value of a* at 21.9 followed by Ø 11mm at 550 rpm which has a value of 20.6. The remaining values range from 18.7 to 19.9. Despite the higher specific surface area of DM-6, the sample had the lowest a* value at 18.7. This is likely attributable to the rectangular shape of the particles, which was unique to this sample and was possibly affected the redness display. The b* values of the high-speed conventional milling and DM-6 were similar, suggesting that both methods may produce samples with similar a* values. Selection of either methods depends on the particle shapes and sizes. Figure 6 and 7 below display the overview of both a* and b* values of the iron oxide samples.

![Figure 6: a* values with respect to size reduction methods](image2)
4. Conclusion
The obtained results of this study indicated that the value of processing speed in the various milling techniques is vital in the alteration of the particles sizes, as observed in the Ø 3mm and Ø 11mm balls at 550 rpm, which had noticeable average size reductions. Furthermore, it was concluded that reduction in particle sizes results in higher value of specific surface area. It was concluded that high-energy milling using ø 3 mm balls running at 550 rpm and high-energy blending at 25000 rpm could successfully produce particles with sizes less than 100 nm. Moreover, results indicated that the red colour properties (a* values) were best produced by the high-energy milling.

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