Colour and Colorimetry
Multidisciplinary Contributions

Vol. X B

Edited by
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The effect of particle size on pigments colour

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1. Introduction

The knowledge of the optical characteristics of pigments used by craftsmen in the olden time represents an important starting point for the study and characterization of paintings.

In ancient time the pigments, depending on their nature, were often used in the form of powder. Depending on their physical structure, the particles can be distinguished into primary particles, conglomerates and aggregates [1]. The pigments most often show up in the form of conglomerates from which, depending on the grinding degree, particles of different form and dimension are obtained.

The optical properties and, in particular, the hiding power, the tinting strength and the colour depend on the dimension and size of pigment grains [2].

The hiding power is the pigment capacity to make opaque the medium in which it is dissolved. The hiding power is proportional to the difference between the refractive index of the pigment and that one of the dispersing medium and it also depends on the size and shape of the particles. It is known that, for a given size, spherical shaped particles have higher hiding power [2].

The ability of a pigment to impart colour to the medium in which it is applied is called tinting strength [2].

The pigment colour can be defined in terms of hue, brightness and saturation [3], parameters that depend on the light interaction with the pigment. In addition to incident light scattering and/or reflection, the selective absorption of different wavelength photons is decisive in colour perception.

Unlike the modern ones, the hand-ground pigments used in the olden time were not constituted by particles having all the same dimensions. In ancient times the painters knew, on the basis of their experience, that excessive grinding of some pigments determined the loss of colour or a saturation change. It was known that each pigment had to be ground with different fineness degrees. They knew, for example, that colour of cobalt blue, malachite and azurite would desaturate if they were ground too finely. This is due to the fact that pigment colour depends on the selective absorption of spectral components and, in the case of grains with too small dimensions, the contribution of diffused white light component is prevalent [4].

Depending on particle size, two types of pigments can be distinguished: "*fine grain*" pigments with dimensions of grains lower than 1 μm, "*medium grain*" if the dimensions fall within the *range* between 1 μm and 10 μm e "*coarse grain*" if they are constituted by particles with a diameter of more than 10 μm. The dimensions of the artistic pigments cover a range from 30 to 40 μm with some larger and smaller particles [4].

The particles dimension determines smoothness, gloss and uniformity of the paint layer. Pigments consisting of "*coarse grain*" particles induce very saturated colour but have poor hiding power unlike those with "*fine grain*", that, instead, have an

increased hiding power. In a film consisting of larger and irregularly shaped pigments particles, in fact, the light easily penetrates through the different paint layers and therefore the contribution of the support to the reflected light is greater.
On the other hand, for some pigments, very thin and homogeneous grains have good hiding power but little tinting strength. This evidence is not generally applicable, in fact, for other pigments, colour saturation is not decreased by the grinding. They maintain both a good hiding power and a good tinting strength even in the case of smaller particles.
The present work is part of a larger research project whose objective is to investigate, by spectrophotometry, a non-invasive and non-destructive technique, the optical characteristics of historical pigments, considering the most used by artists of the past, depending on particle size. On this occasion we present the results obtained on a first group of pigments chosen and selected in order to realize paints with powders belonging to different size classes.

2. Materials and methods

2.1 The pigments and dyes

The use of pigments and dyes that are selected for the study is documented in the historical sources. Both dyes and pigments colour a substrate. The dye is molecularly dispersed in the substrate which is being coloured. A pigment, in contrast, is a colouring agent with particulate dimensions and is heterogeneously dispersed in the medium being coloured. Hence the distinction between a dye and a pigment is not always a sharp one. Historically, organic compounds have been used as dyes and inorganic compounds used as pigments. The materials used have been prepared by the companies Zecchi and Kremer Pigments GmbH & Co. KG and their formulation was made according to old recipes. The choice of the materials analysed in this work was mainly made by considering the pigments and dyes for which it was possible to select different size classes. They are also chosen because non-toxic and compatible with various solvents and mediums [5].
The materials examined in this work are represented by the red colour: cochineal, dragon's blood, morellone brown, red bole, sinopia, and by the yellow colour: gamboge, natural Sienna earth, French ochre, yellow ochre [6,7-10]. Gamboge, cochineal and dragon's blood are dyes and have organic nature, their use is documented in *Plinio Il Vecchio* (*Naturalis Historia*) and Cennino Cennini [11]. All the other pigments, which are inorganic and have a mineral origin, have been widely used in the paintings of the past.
The pigments were examined in the form of paints made by mixing pigment powder consisting of different sizes grains appropriately classified with the same medium. The compound "pigment + medium" was created with a 1:2 ratio of the components; the mixture for each size fraction was then painted on 10x15 cm^2 canvas prepared with synthetic gypsum.
For all paints, casein, one of the most used historic mediums, was used [12]. It is a phosphoprotein that is obtained from milk in the form of colloidal dispersion. The optical properties of casein are the transparency and the absence of colour so that it does not introduce a contribution like altering the exclusive pigment colouring properties [5].

2.2 Selection of the particle size of the pigments

In this work, two methods were adopted to operate the particle size selection of pigments.

Particle size of gamboge, cochineal, and dragon's blood, which represent pigments available in the form of agglomerated, was selected using a method (method 1), which makes possible, through exclusive mechanical sieving, to have a large grain dimension range. This method consists of two phases. First, they were ground in an agate mortar to break up the particles of different sizes. In the second step the proper selection of the grains took place using sieves with meshes in order to cover a range between 40 and 500 µm in diameter (500, 280, 200, 150, 100, 75, 40 µm).

The application of the first method does not make possible to operate a restricted selection and to obtain classes of grains whose size is less than 40 microns. A second method was therefore used in order to exceed the limits imposed by mechanical and manual sieving and to get "fine and medium grain" pigments more precisely.

The second method (method 2) has been applied for the selection of particle size powders of three yellow (yellow ochre, natural Sienna earth and French ochre) and three red (red bole, morellone and sinopia) pigments. The main steps of this method can be summarized as follows. The powder whose size was less than 40 µm was separated in size, according to Stokes' law, by sedimentation for different times in distilled water. After drying it in the oven at 40 °C, the various size classes of each pigment were collected. The grains dimension was checked by using the Optical Microscopy (OM) and the Scanning Electron Microscopy (SEM) [13].

The pigments analyzed and the various size classes obtained are listed in Table I, along with the colour index and the related chemical formula [2,4,14].

Pigments	Colour Index	Chemical Formula	Particle size (µm)
Yellow ochre	PY-43	Fe $(OH)_3$	<10, 10-20, 20-30, 30-40
French ochre	PY 43	$SiO_2 + AlO_3 + FeO_3$	<10, 10-20, 20-30, 30-40
Gamboge	NY 24	80% resin acids, 13% gum, 7% water	<40, 40-75, 75-100, 100-150, 150-200, 200-280, 280-500
natural Sienna earth	PY-43	$Fe_2O_3{\cdot}nH_2O + MnO_2 + Al_2O_3{\cdot}SiO_2{\cdot}2(H_2O)$	<10, 10-20, 20-30, 30-40
Red bole	PR-102	$Al_2O_3{\cdot}SiO_2 + Fe_2O_3$	<10, 10-20, 20-30, 30-40
Cochineal	NR 4	Coccus Cacti	<40, 40-75, 75-100, 100-150, 150-200, 200-280, 280-500
Morellone brown	PR-102	$Fe_2O_3 + H_2O_3 + MgO + Al_2O_3 + TiO_2 + MgSO_4 + SiO_2 + C$	<10, 10-20, 20-30, 30-40
Sinopia	PR-102	$Fe_2O_3 + H_2O_3 + MgO + Al_2O_3 + TiO_2 + MgSO_4 + SiO_2$	<10, 10-20, 20-30, 30-40
Dragon's blood	NR 31	$C_{18}H_{18}O_4$	<40, 40-75, 75-100, 100-150, 150-200, 200-280, 280-500

Table I. Pigments used: yellow (yellow ochre, French ochre, gamboge, natural Sienna earth) and red (red bole, cochineal, morellone, ochre, dragon's blood) with the corresponding colour index, chemical formula and classes particle size obtained.

2.3 Spectrophotometric analysis

The reflectance in the visible spectroscopy is a technique of optical investigation based on the measurement of the Spectral Reflectance Factor (SRF) of the sample analyzed in function of the wavelength (range 400-700 nm) of the incident radiation. The SRF is expressed as the percentage ratio between the intensity of the reflected radiation and the incident radiation, as a function of wavelength. In order to investigate the relationship between the optical properties of the pigments analyzed and the grain size, the present study was carried out with the aim of highlighting any changes in the paint layer of the SRF factor obtained with the different size classes selected from each pigment. The analysis was conducted using a Konica Minolta spectrophotometer, model CM-2006d with measurement geometry d/8°, selecting an area of 6 mm in diameter (SAV mask, Small Average Value). The results are related to 10° standard observer and the D65 light was selected. The values were obtained by repeated measurements (5 different acquisitions) and the elaboration concerned SPEX/100 data (SPecular component EXcluded and UV component included). The acquisition step was performed with the SpectraMagic ® software [15] while Origin ® software (OriginPro 8) was used for data processing. The PH3DRA laboratories routine protocol [16,17] was used for spectrophotometric measurements by selecting homogeneous and covering paint layer areas. The scale adjustment was carried out by using a reflectance standard with spectral properties close to that the perfect reflecting diffuser [18], "white standard", and a box (CM-A32), simulating a totally absorbent body, as "black standard".

3. Results and discussion

Spectrophotometric analysis was conducted to assess the possible change of the optical characteristics when the particle size of the pigments used in paintings vary. The graphs are presented in the form of reflectance spectra with *SRF%* as a function of wavelength (λ) and in terms of the derivative of SRF% (*dSRF*) as a function of the wavelength (λ). The behaviour of *dSRF* allows us to detect the characteristic points of the colour pigment and it is useful to highlight any changes in the optical behaviour considering the shift of these points [19]. The spectrophotometric analysis carried out on the two red pigments, cochineal and dragon's blood, and the yellow pigment gamboge, for which a wide range of particle sizes (from 40 μm to 500 μm) was available, showed that, with the decreasing of grain size, SRF% values increase. The graphs of the reflectance derivative factor do not show changes in the position of the maximum points for any particle size class investigated. This testifies that the colour of the pigment is not substantially modified when the size of the grains vary. This result was obtained for all the analysed pigments. The SRF% behaviour and the values of the related *dSRF* of the dragon's blood red pigment (figure 1) and the gamboge yellow pigment (figure 2) were below reported as an example.

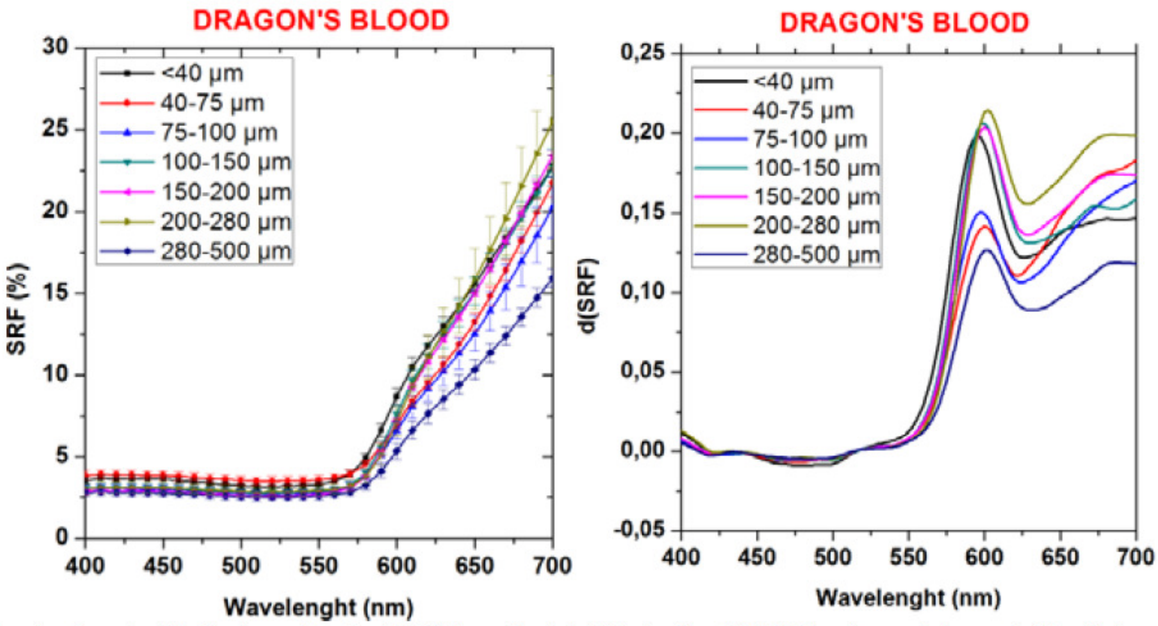

Fig. 1 – *Spectral Reflectance Factor* (*SRF%*) and related derivative (*dSRF%*) values of dragon's blood pigment.

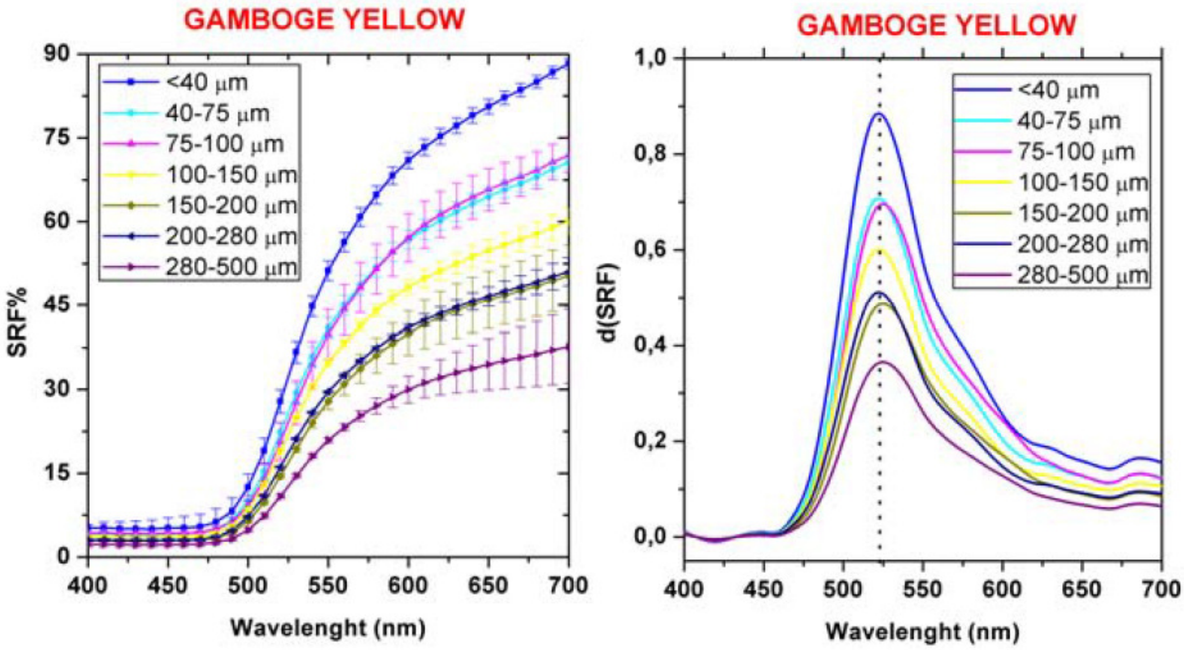

Fig. 2 – *Spectral Reflectance Factor* (SRF%) and related graphic derivative (*dSRF%*) values of gamboge pigment.

This experimental evidence is also confirmed by data obtained in paint layers with smaller particle size of red (red bole, morellone and sinopia) and yellow (French ochre, yellow ochre and natural Sienna earth) pigments selected by method 2 (Table I). We show, for example, the *SRF%* and *dSRF* behaviour for the red bole (figure 3) and for the yellow natural Sienna earth (figure 4).

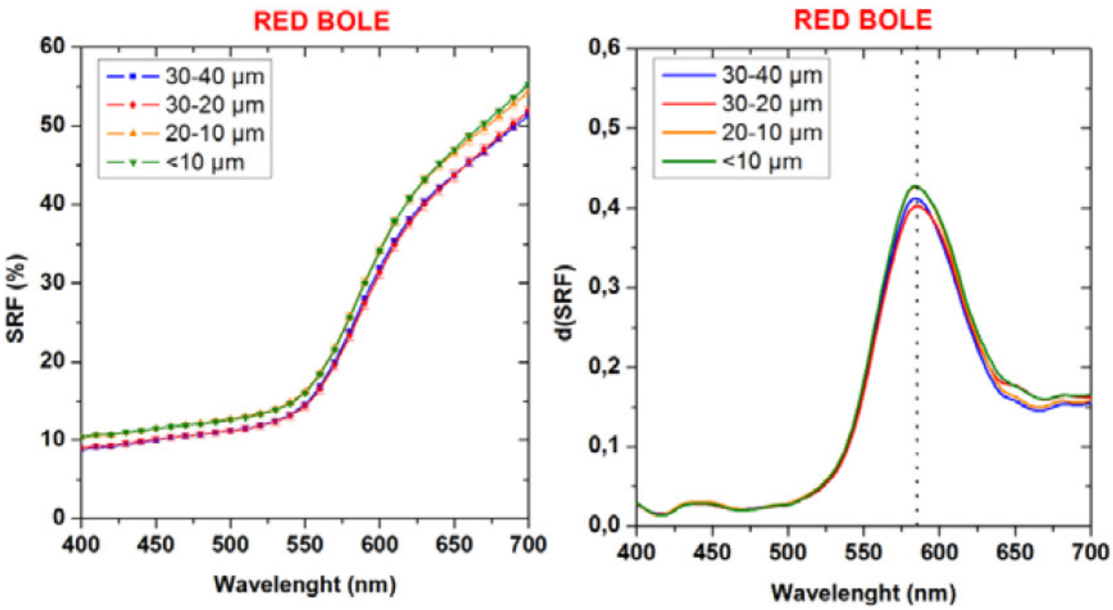

Fig. 3 – Spectral Reflectance Factor (SRF%) and related derivative (*dSRF*) obtained for the red bole pigment.

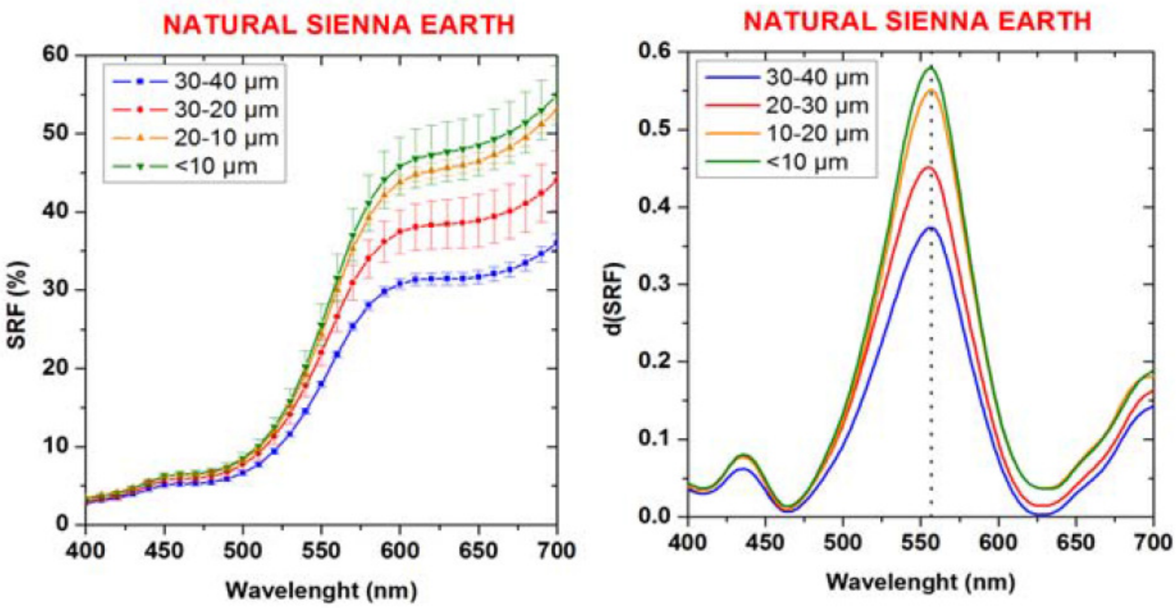

Fig. 3 – Spectral Reflectance Factor (*SRF%*) and related derivative (*dSRF*) obtained for the natural Sienna earth.

As shown by results in the reflectance curve, the SRF% higher values characterize paint layers made from powders of finer particle size (d <10 µm). These data decrease with the increasing of grain size. The lower values are related to greater particle size (range 30-40 µm). The trend reported in figure 2 and figure 3 was found for all analyzed pigments. The *dSRF* behaviour also confirmed that, varying the size, the maximum value corresponding to the dominant wavelengths does not shift.

4. Conclusion

The optical behaviour of yellow (yellow ochre, ochre french, gamboge, natural Sienna earth) and red (red bole, cochineal, morellone, dragon's blood and sinopia) dyes and pigments, differently selected in size, was investigated by spectrophotometric analysis. The grain size selection methods were two. The first one was based solely on manual and mechanical sieving, after grinding some

materials available in the agglomerates form in an agate mortar. It ensured the selection of grains with dimensions between 40 μm and 500 μm. The second method has been applied to obtain smaller particle sizes and has been achieved by sedimentation procedure based on Stokes' law. The spectrophotometry is a selection methodology for painting characterisation because it is non-invasive and non-destructive. In this study, this technique allowed us to assess the relationship between the particle size and the optical behaviour of different dyes and pigments in terms of *Spectral Reflectance Factor*. Measurements concerned paints made with casein and pigment powders of different particle size classes. For both materials, which were separated in larger grain size (method 1) and in finest powder (method 2), the experimental results showed an increase of *SRF%* with decreasing particle size. From the values of the derivative of spectral reflectance factor (*dSRF*) it is also possible to underline that the position of the values of the dominant wavelengths, characterizing the hue of pigments, does not shift.
Since the results cannot be considered generally valid, it is appropriate to confirm by a greater number of dyes and pigments for a wide spectrum of particle sizes preferably obtained with the same method and whose dimensions are lower than those studied in this occasion. The perspectives of this work in fact concern the development of a protocol for size selection in wide ranges optimizing the procedure based on Stokes' law and, if need be, through the test of other methods.
It is similarly important that the measurements are carried out on a larger number of samples and, above all, by choosing dyes and pigments of hues which until now have not been investigated such as blue, green and brown. The extension of the study to black and white pigments, which are pure and in binary mixtures, represents an additional prospect of the research.

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