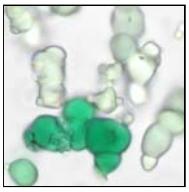

OPTICAL AND PHYSICAL PROPERTIES OF PIGMENT PARTICLES FROM POLARISED LIGHT MICROSCOPY

THE PIGMENTUM PROJECT

© The Pigmentum Project, 2006

OPTICAL AND PHYSICAL PROPERTIES OF PIGMENT PARTICLES FROM POLARISED LIGHT MICROSCOPY

Nicholas Eastaugh, Valentine Walsh, Tracey Chaplin and Ruth Siddall

"Those who have never used a polarized-light microscope will be surprised at the great beauty and vividness of the colours that arise as a result of the interference of the light waves passing through the specimen" (Robinson and Bradbury, 1992).

INTRODUCTION

Polarised light microscopy is perhaps the most widely applied analytical technique currently used for the identification of historical pigments. Despite the advent of newer methods, polarised light microscopy has maintained a place in this field as a routine and effective approach to the determination of the compounds to be found on painted artefacts.

The following document presents a discussion of the various properties used to make such determinations. While not specifically an instruction manual of how to determine each value, it will none-the-less provide an understanding of what needs to be examined and how to document the results.

THE PIGMENTUM PROJECT

CRYSTALLINE SUBSTANCES AND CRYSTAL SYSTEMS

As many compounds encountered as pigments are crystalline, and because this underlies the phenomena observed in optical microscopy, a brief excursion examining the concept of crystallinity is included here. Every crystalline substance has a definite internal structure in which the atoms occur in specific proportions and are arranged in an ordered geometric pattern. This systematic arrangement of atoms is one of the most significant aspects of a compound in the crystalline state. It exists throughout the entire body of the material and, if crystallisation occurs under ideal conditions, this internal arrangement will be expressed in outwardly perfect crystal shapes. Not all crystalline compounds have perfect crystal faces or form because of restrictions in the environments in which they crystallise. However, compounds with poor or imperfect crystal faces do still possess a systematic internal structure, expressed by features such as *cleavage*, the fracturing along lines of particular weakness in the crystal structure.

All crystalline materials belong to one of seven crystallographic 'systems' based on the symmetry of the crystalline forms. On an atomic level the structure of all crystalline forms is periodic, with each repeating unit defining the crystal system. This smallest of crystallographic building blocks is called the *unit cell*. These are three-dimensional blocks, defined partly by the relative lengths of their three axes, a, b and c, and the angles between these axes, α, β and γ. For systems where the axes are of different lengths, c is conventionally the longest axis and a the shortest. Crystal systems are defined also by the rotational and bilateral symmetry displayed. The unit cell dimensions in terms of relative axial lengths, angles between them and the essential symmetries are outlined in the Table below.

TABLE 1 The seven crystal systems (adapted from Putnis, 1992). The essential symmetry is in terms of a rotation axis.

Crystal System	**Relative Unit Cell Dimensions**	**Essential Symmetry**
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	None
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	One 2-fold axis
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Three perpendicular 2-fold axes
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	One four fold axis
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	Four 3-fold axes
*Trigonal	$a = b = c$ $120° > \alpha = \beta = \gamma \neq 90°$	One 3-fold axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	One 6-fold axis

*Crystals in the trigonal system may be described by an hexagonal unit cell, even though they do not have a 6-fold rotation axis. Many texts therefore list trigonal as a subset of the hexagonal system.

THE PIGMENTUM PROJECT

Compounds may change their crystal system in response to variations in temperature, pressure or deformation and also after substitution of trace or major elements into the crystal structure. Examples here are distortions to the structure of lazurite and the other feldspathoids by substituting elements, and fluorapatite, which has a hexagonal structure but becomes monoclinic as hydroxyl groups substitute for the fluorine. Crystals are also never perfect, and are characterised by defects and dislocations (planar defects), the presence of defects actually facilitating crystal growth.

A *solid solution* series represents the variation in chemistry between two pure end-member crystalline phases whereby complete mixing can occur between the end-member compositions. For example, a hypothetical crystal with composition A and another of composition B can form solid solutions A_xB_{1-x}, where $0 \leq x \leq 1$. The end members do not necessarily belong to the same crystal system, this property changing from one to the other at some intermediate point. A system with members in which mixing cannot occur is called a *eutectic*; the result of crystallisation of phases showing this behaviour is always a mixture of pure phases.

Materials that do not posses a crystalline structure are described as being *amorphous*. Amorphous substances that have undergone rapid solidification, which proceeds too fast for crystal nucleation to occur, are glasses; this term is applied irrespective of chemistry.

The processes of crystallisation and the relationship of the resultant morphologies to the conditions under which a substance was formed appears to be a relatively little

studied aspect of historical pigments. For those interested in pursuing this aspect, a thorough review of the mechanisms of crystallisation can be found in Mullin (2001).

PHYSICAL PROPERTIES OF PIGMENTS

Colour

Colour is, naturally, a fundamental property of interest in pigments and most pigment phases appear strongly coloured under the microscope. However, the occurrence of colour is a far from simple concept. Observed colour arises from the transmission of some wavelengths of light and the absorption of others. Transmission of light – and therefore colour – is controlled by the crystal structure and chemical composition of the material. A full discussion of the production of colour on an atomic, molecular or bulk scale is far beyond the scope of this text and the interested reader is therefore referred to standard texts such as Nassau (1983), Putnis (1992) and Burns (1993) for further information.

While the origin of colour in pigments is a field of interest in its own right, the documentation of colours is of more direct importance in the characterisation of these compounds. A number of systems for recording colour are available to the analyst, these falling into two broad groups – colour comparison charts and direct measurement. Discussion of these is beyond the scope of this text and the reader is referred, for example, to the discussion by Johnston-Feller (1986) regarding standard colour notation and the section on micro-spectrophotometry below. However, the formal specification of colour in particles seems to be generally more of a documentation ideal than a common practice. In this text the issue has been dealt with by giving broad colour categories only, or using qualifiers that are reasonably wide in their use and apprehension.

THE PIGMENTUM PROJECT

The analyst should though be aware of the external factors which can affect the appearance of a particle. Specifically, these are the illumination conditions of both the microscope itself and the general laboratory environment. All colour judgements for this book were made with a high-colour temperature microscope light source with a suitable dichroic filter to achieve illumination close to natural daylight and an ambient daylight (or equivalent fluorescent lighting) in the laboratory to minimise metameric effect during observation. Additionally, the impact of different lens qualities cannot be underestimated; as certain authors have noted elsewhere, the appearance of colour in particles under the microscope can shift significantly between lenses with and without substantial chromatic aberration. Optical systems in the microscopes employed for this book all had substantial levels of colour correction such that they provided highly accurate renditions.

Particle size and particle size distribution

Particle size can be described either relatively or absolutely. In simplest terms, particle size may be regarded relatively as very fine, fine, medium, large and coarse. Given the typically small particle size of pigments compared to, say, minerals observed in petrography, it is important that this classification be linked to known size ranges. The standard unit of measurement is the micrometre (1 µm = 10^{-6} metres, formerly known as a micron). Absolute measurement of particle size may be carried out using a stage micrometer, typically marked out in 1, 5 and 10 µm divisions. Feller

and Bayard (1986) have proposed a particle size classification, based partly on the Paint Research Station Classes (1956).

TABLE 2: Feller and Bayard's (1986) particle size classification for pigments

Absolute particle size	Relative particle size
> 40 µm	Very coarse
10-40 µm	Coarse
10 – 3 µm	Large
3 - 1 µm	Medium
1.0 - 0.3 µm	Fine
< 0.3 µm	Very fine

To this scale has been added a 'very coarse' size class for particles greater than 40 µm. This classification is particularly applied to mineral-based pigments. The scale is based on a logarithmic increase in particle size, with the smallest optically distinguishable particles being around 0.3 µm, the diffraction limit for visible light. Consequently, the very fine category is unlikely to be used by the majority of analysts. Description of particle size may be more complex when describing particles with a high aspect ratio; in such cases, both length and width of the particle should be quoted. For particles of lower aspect ratio, at least one of the standard 'diameters' should be explicitly recorded – for example the major axis, or Feret's diameter.

THE PIGMENTUM PROJECT

Further qualitative description of particle size distributions may be required when particle size is not uniform. This is particularly relevant to naturally occurring and traditionally prepared pigments, such as the ochres and other earth pigments. Where this occurs the range of particle sizes present should be given. It may be convenient to describe this in terms of a normal distribution curve, implying a mean sample size and deviations away from that mean. Distributions of grain size may therefore be described as being broad or narrow, the former implying a large range of grain sizes, the latter implying a very limited range in grain size, whilst allowing for the rare particle which falls outside the stated range.

If there are two clear particle size ranges (say, one population of fine grained particles and another of large particles) then the sample may be described as having a bimodal particle size distribution. Clearly this can be extended to trimodal and so forth. The term 'seriate' is synonymous with a broad particle size distribution and refers to a sample population with all particle sizes between very fine and coarse.

Particle Shape

Particles in pigments may include mineral fragments, natural and synthetic organic and inorganic crystals, particles of glass or other amorphous substances, mineral fragments supporting organic lakes, fragments of shells, fossils and vegetable remains. These may have been prepared by crushing, grinding and milling larger particles and aggregates, as precipitates, or even simply by sieving naturally occurring substances. Therefore particle shape can be highly variable, but diagnostic of certain substances and certain preparation processes. Description of particle shape borrows largely from the fields of crystallography and petrography, where there is a well defined terminology describing precisely mineral shapes; in these fields, particle

shape is referred to as ‘habit’. Some additional terms relevant to the identification of pigments are also added here.

All materials may form crystalline solids. Crystals, by definition have an ordered, repeating and predictable structure. Despite the thousands of geometrical forms crystals may adopt, they may all be reduced in terms of their symmetry into the seven crystal systems: *cubic*, *tetragonal*, *orthorhombic*, *trigonal*, *hexagonal*, *monoclinic* and *triclinic*. Crystals belonging to these systems may well adopt the shape defined by their system. So, for example, pyrite and halite (common salt) both belong to the cubic system and adopt cubic habits. However, pyrite may also adopt polyhedral forms, such as the 'pyritohedron', which has twelve pentagonal crystal faces. Quartz and calcite on the other hand both belong to the trigonal system, but neither forms triangular prisms. Rather, it is the symmetry of these crystals as observed in three-dimensions that will prove which system they belong to.

When crystals are allowed to grow in unrestricted environments, they will develop crystal faces and, as discussed above, these are a reflection of the symmetry of the underlying crystal system to which the phase belongs. Crystals observed under the microscope showing all crystal faces may be described as being *euhedral*. Those showing no crystal faces are *anhedral*. Intermediate forms showing some, but not all, faces are *subhedral*. Obviously these terms give no idea of the exact shape of the phase present although they are important qualifiers.

Terms that simply describe a geometrical figure may be used to describe euhedral crystals, such as ‘rhombic’, ‘rectangular’, ‘hexagonal’, ‘cubic’, ‘triangular’, ‘polyhedral’ and so forth. Additionally, some further useful and more specific terms are listed below:

THE PIGMENTUM PROJECT

Equant – any shape where length = width = height. A sphere is an extreme example of an equant shape. A cube is also equant and in fact the minerals adopting the cubic crystal system will form equant crystals. Members of other crystal systems can form crystals with a close approximation to equant forms.

Prismatic – forms of crystals having one axis greater than the other two. Terms applied to prismatic forms commonly include the following:

- *Acicular* – needle-shaped.
- *Fibrous* – an extreme case of acicular shape, with particles resembling textile fibres.
- *Bladed* – like a knife-blade; flattened but elongated.
- *Lath-shaped* – similar to bladed, particles appear as elongate rectangles with length much greater than width.

Platy – forming thin plates.

Lamellar – a stack of plates, like pages in a book.

Tabular – forming thicker tablet-like plates.

Columnar – forming crystals with an aspect ratio similar to a column.

Dendritic – forming branching, tree-like shapes. These usually represent phases that have rapidly crystallised.

Pennate – (also 'pinnate'), refers to elongate particles having bilateral symmetry and the shape of a feather or leaf.

Subhedral and anhedral particles may occur naturally or as a result of pigment preparation. If some faces are apparent, then an indication of the crystal's ideal shape can be acquired. In the absence of any crystal shapes, anhedral particles may be described using the following criteria and terminology.

The degree of angularity of a particle's shape can be defined qualitatively, using the following series of terms: angular, subangular, subrounded and rounded, where particles range from sharp-edged to smooth-edged morphologies respectively (Powers, 1953). Highly angular particles, with morphology representing that of broken glass may be called *shards*. Importantly, angular particles defined by cleavage (see below) may appear to be euhedral; they are in fact anhedral. The mineral calcite commonly adopts such forms, with rhombic crystals defined by the three cleavage planes.

The qualifier 'rounded', however should not be confused with 'sphericity'. The concept of sphericity refers to the general aspect ratio of the particle. Particles with high sphericity are equant whereas particles with low sphericity are elongated. A ball, for example, has high sphericity and is rounded, whereas a cigar is also rounded but has low sphericity.

Many particles may show no evidence of crystal shape, nor do they fit with descriptive terms defined above. The terms *irregular*, *crumb-like* or *ragged* may be used to define shapes with the appropriate morphologies. All imply embayed margins on various scales.

THE PIGMENTUM PROJECT

Very fine and fine-grained particles are at the limits of the resolution of the optical microscope. It is therefore impossible to define their exact shape without the aid of an electron microscope. All particles in this range often appear to be small spheres or slightly elongate, rounded, 'capsule'-like shapes. The term *bacterioid* is used here to refer to such habits.

Some particle forms are directly biological in origin. If possible these should be identified and described using appropriate terminology. They will commonly be calcium carbonate-derived shell or fossil fragments, or intact calcium carbonate or siliceous microfossils. The former may typically include crushed shell (which has a lamellar structure), while the latter may include coccoliths (which are at the limit of optical resolution) and diatoms. For further information concerning such forms see Adams *et al*. (1991) and Tucker (1991). Terms for descriptions of these particles are discussed below and in the relevant entries.

Aggregation

Aggregates of several crystals of the same variety may form further diagnostic habits. An aggregate of euhedral crystals may be generally called a *glomerocryst*. However, where individual crystals are poorly defined or a particle appears to be composed of several crystals, then the term polycrystalline may be applied.

Elongate crystals often form glomerocrysts radiating from a single nucleation point. These give rise to *stellate* and *spherulitic* forms. Stellate forms are two-dimensional aggregations with the appearance of stars. Spherulites (or spherules) are three-dimensional and have the overall appearance of pom-poms. Fan- or cone-shaped aggregates of fibrous crystals are said to have *variolitic* texture. The latter are generally composed of fibrous or acicular crystals.

Fibrous or acicular crystals arranged in layers may develop what is known as *botryoidal* habit, referring to the surface on a macro-scale resembling a bunch of grapes. The mineral malachite frequently displays this form; however, the defining structure is generally lost when the mineral is crushed to make a pigment. Bundles of parallel fibres may be called *sheaves*.

Other aggregates of anhedral crystals may be very irregular and have the appearance of bread-crumbs, the term *crumb-like* is simply used here. *Framboidal* aggregates are clusters of rounded, equant particles with the general appearance of (literally) raspberries.

Very fine aggregates of crystals such as those developed by so-called chalcedonic silica and calcite may be referred to as being *cryptocrystalline*. Calcite is a special case. Cryptocrystalline masses of this phase are described as *micrite*, whereas calcite that forms crystals visible down the microscope is called *sparite*. These terms should not be applied to other phases.

THE PIGMENTUM PROJECT

For some pigments, precipitates of one phase may be found adhering to a second phase and this relationship should be described as observed.

Particle Surface

Using a binocular microscope a good impression of the surface texture of a particle can be obtained. This feature is highly influenced by the relief of the mineral, itself a function of refractive index (see below for definitions of both terms). Particle surfaces may straightforwardly be defined as being rough or smooth. Other descriptive qualifiers such as powdery, pitted, undulating, fractured and striated may also be applied to rough surfaces. Glass and some minerals show characteristic conchoidal fractures, which may be visible on crystal surfaces as scoop-shaped fracture surfaces with concentric pressure ridges (their appearance resembles a shell, hence the name). A surface showing several well developed crystal faces may be described as being faceted (this phase will already have been described as euhedral). Particles with very high relief may appear domed (or convex).

Inclusions and other inter-particle relationships

Few naturally occurring and synthetic crystals are completely pure. They can contain inclusions which may be gas- and/or liquid-filled cavities (called fluid inclusions), or solid inclusions of another phase. Inclusions of both sorts may strongly influence the colour of a crystal both negatively and positively. The colour of some minerals is directly related to the presence of inclusions (for example the purple and yellow colours of the Blue John variety of fluorite, which is thought to be influenced by sub-microscopic inclusions of hydrocarbons; see: Dunham, 1937). However abundant inclusions of separate phases may also diminish the colour and attempts to remove the bulk of these will be part of the pigment processing.

Fluid inclusions may contain both gas and liquid phases. In this case the gas will appear as a bubble in the liquid, which will start to move around as the light from the microscope heats the crystal. Fluid inclusions may be randomly orientated cavities and/or may have a crystallographically defined alignment.

Solid inclusions may well show a colour or relief contrast with the host particle and this should be noted. Where abundant solid inclusions occur, the particle may be described as being *poikilitic*. The host particle may be called the *oikocryst* and the included particles *chadocrysts*. Worm-like inclusions of one phase in another may be called vermiculate texture.

Other intergrowth textures, not strictly inclusions, may also occur. A *pseudomorph* is a crystal that grows replacing another crystal of different composition, but replicating its habit and, occasionally, some internal features such as cleavage. *Intergrowths* are where two crystal phases of different composition have grown simultaneously and interpenetrated each other as they do so. Complex, interfingering intergrowths between two phases may be called a *symplectite*. These are common in some minerals. Intergrowths between distinct phases all have specific, distinguishing names. For example, perthites are emulsions of one feldspar variety in another of slightly different chemistry. These relationships are rarely important in identifying pigment phases, particularly because they occur on scales greater than the ground pigment, and the interested reader is therefore referred to relevant mineralogical texts such as Hibbard (1995), MacKenzie and Guildford (1980), MacKenzie *et al.* (1984), Yardley *et al.* (1990) and Shelley (1992) for description and mode of formation of these textures.

THE PIGMENTUM PROJECT

Variations in chemistry within a single crystal (zoning) and the 'intergrowth' of two or more crystals of the same chemistry (twinning) are features generally only observable in cross-polarised light. These features are discussed in further detail below.

Fracture and Cleavage

The way that crystals break may be a diagnostic feature. Many crystals possess a cleavage; that is, they will break along straight, parallel and equally spaced, crystallographically defined planes that represent weakness inherent in the crystal structure. Crystals may have one, two, three, four or even six sets of cleavage, or none. Because cleavage is crystallographically controlled, in crystals that display two or more cleavages the angle at which the cleavages intersect may be used to distinguish two otherwise similar crystals.

Crystals with strong, well-defined cleavage can be said to possess *perfect cleavage*, while a weak cleavage may be described as a *parting*. Some crystals (notably quartz) do not possess planes of weakness within their structure and therefore do not possess a cleavage.

Fracture refers to breaks within a crystal unrelated to cleavage. Fractures may be even, that is broadly planar, or uneven, that is leaving behind a rough surface. Conchoidal fracture is typical of glasses and some minerals including quartz.

Conchoidal fracture forms curved, shell-like fracture surfaces, often with concentric pressure lines. Conchoidal cracks within a crystal are visible as curved lines.

As discussed above, the cleavage or fracture possessed by crystals can strongly influence their habit on crushing.

Diaphaneity

The degree of light transmittance through a substance, its diaphaneity, can be described in terms of transparency, translucency and opacity. Transparent phases do not impede the passage of light. Translucent phases transmit some, but not all, light and opaque phases do not transmit any light. The latter will appear black in dispersions.

Reflected light

Although much examination of optical properties is carried out using transmitted light ('dia-illumination'), dark-field epi-illumination is an effective method of determining the colour (as well as the texture) of phases that are opaque, or particles of such a pale colour that characterisation of the hue is difficult by transmitted light. It is common therefore to document the appearance of samples under these conditions. For this book, reflected light illumination was achieved using a polariser inserted in the epi-illumination path and a corresponding analyser. Using this approach it was possible to additionally observe the phenomenon of bireflectance (see below).

Red transmission

THE PIGMENTUM PROJECT

The degree to which certain, primarily blue and green, pigments transmit at the red end of the visible spectrum has been used as a means of distinguishing them. Most commonly this is via the application of the so-called Chelsea filter, a device inserted into the light train. However, the more general study of pigment transmission spectra across the visible spectrum is a field of recurring interest.

The Chelsea filter was originally developed by gemmologists to distinguish emeralds from other green stones. Emeralds have the unusual property of absorbing part of the yellow-green wavelengths of light and transmitting red light. Thus an emerald observed through the green glass of the Chelsea filter appears deep red, the filter absorbing the remaining green wavelengths (Liddicoat, 1993). However, other minerals have similar effects. For example, lazurite transmits a strong red light, despite the fact it is blue. Azurite, in contrast, appears blue-grey when observed using a Chelsea filter. Though generally designed for use on items of jewellery, a Chelsea filter may be used for microscope analysis, simply inserted above the transmitted light source of a microscope (below the stage and polariser). Chelsea filters are available from suppliers to jewellers and gemmologists.

A more sophisticated approach (outside the scope of this text) is micro-spectrophotometry, whereby the transmission spectrum of particles under the microscope can be measured directly. This technique is potentially effective for such otherwise difficult applications as the differentiation of indigo and Prussian blue (Leona and Winter, 2001), detection of cobalt absorption bands in pigments such as cobalt blue and smalt (Bacci and Picollo, 1996), characterisation of red lake pigments (Kirby, 1977) and study of phthalocyanines (Talsky and Ristic-Solajic, 1987).

Fluorescence

Fluorescence is becoming an increasingly standard adjunct to paint microscopy due to its use in selective staining techniques as applied to media in cross-sections. However, it is a potentially useful tool in some cases for extending the examination of pigment dispersions.

Fluorescence is the phenomenon whereby a material absorbs light at one wavelength and then promptly re-emits it at another, longer, wavelength that is shifted towards the red end of the spectrum or beyond. Underlying this is absorption of energy from the light so that when it strikes the material, interacting with it, it is subject to a loss of energy. Since energy and wavelength are directly related, the wavelength (colour) of the light returned is therefore longer (redder). Fluorescence originates from the absorption of light photons by components within particular molecules, the absorption being associated with changes of energy levels of electrons in the molecular structure. Since such electron transitions are fairly precise, so the minimum energy (wavelength) of light required for fluorescence is also well defined. The shift in wavelength to the longer, redder, less energetic end of the electromagnetic spectrum is then related to gradual loss of energy of the electrons, generally through loss of heat, before the electrons fall back to lower molecular levels with the re-emission of another photon. This also affects the form of the range of emitted wavelengths, with the most photons being emitted at the higher end of the range. Fluorescence takes place rapidly, typically within around 10^{-9} to 10^{-8} seconds. The process of fluorescence can in fact take place at all wavelengths, not just in the visible light region, so that, depending on the substance, fluorescence can occur over a wide range of illumination (excitation) conditions.

THE PIGMENTUM PROJECT

In fluorescence microscopy it is important to define two values, the excitation (Ex) and emission (Em) wavelengths, with the excitation wavelength being that used to excite fluorescence, the emission wavelength being that which is given out by the material. Usually these values are effectively fixed by the microscope system, with standardised Ex/Em filter blocks targeted at specific fluorophores such as FITC and Rhodamine B.

A number of pigments have known fluorescence. Examples include zinc white, which has a strong yellowish fluorescence, cadmium sulfides, which fluoresce in the yellow to red part of the spectrum, certain lake pigments and some coals. For further information the papers by de la Rie (1982) and standard works on fluorescence microscopy such as Rost (1995) should be consulted.

OBSERVATIONS IN PLANE-POLARISED LIGHT

Polarised light

The technique of polarised light microscopy relies on the fact that light travels in waves. A ray of light from a light source travels out in every direction form that source. For microscopes not fitted with polarisers, this is the light observed and it is simply called transmitted light. However, on passing through a polariser, the light is forced to vibrate in a single plane; it is polarised and this is called plane-polarised light (PPL). The appearance of plane-polarised and transmitted light appear identical when observed by the human eye. When a second polariser (the analyser) is inserted, orientated at right angles to the first polariser, then the field of view is in cross-

polarised light (XPL) and will be dark as the light is vibrating in the wrong plane and cannot pass through it. When a transparent or translucent crystalline material is placed between the polariser and the analyser, as light enters the crystal, two things will happen. First, the velocity of the light will be retarded (refracted) and second, the light beam will be split into two rays (of differing velocities), each vibrating perpendicular to the other. Therefore light can now be passed through the analyser and the crystal is said to be birefringent and interference colours will be observed.

The theory of polarised light microscopy is standard and further explained in texts including Patzelt (1974), Gribble and Hall (1992) and Robinson and Bradbury (1992).

Pleochroism

The phenomenon of pleochroism is observed as a crystal changes colour or colour intensity as the stage is rotated. For uniaxial phases, crystals may be pleochroic (or strictly speaking 'dichroic') in two colours. For biaxial phases, three colours may be observed (although all three will not be observed in the same particle). Each extreme in the two colours observed in a crystal will be observed twice in a 360° rotation. The phenomenon arises as a result of a difference in absorption of light in different crystallographic orientations. The more that light is absorbed, the darker the colour observed.

The intensity and colour changes observed should be noted. Pleochroism is a feature of all non-cubic phases. However, it may be very subtle or take place at wavelengths outside the visible region and therefore may not be apparent.

THE PIGMENTUM PROJECT

Refractive Index and Relief

As light passes from a vacuum into any substance, its velocity is reduced; it is refracted. The factor by which the light is slowed by the substance through which it is transmitted compared to its speed in a vacuum is known as the refractive index (RI) and may be expressed mathematically as:

$$\text{RI} = \frac{\text{Velocity of light in a vacuum}}{\text{Velocity of light in the substance}}$$

RI is a unit-less quantity. Substances that have the same refractive index in all directions are called *isotropic*. These include non-crystalline solids (such as glasses), liquids and gases as well as crystalline forms belonging to the cubic crystal system.

In *anisotropic* substances the refractive index varies with the orientation of light propagation through the crystal lattice. These crystals are classified as being either *uniaxial* or *biaxial*.

For a uniaxial crystal (belonging to the hexagonal, trigonal or tetragonal crystal systems) a beam of light entering it is split into two rays. One ray, the *ordinary* ray (with a refractive index n_ω) continues in a straight line through the crystal, whereas the second ray, the *extraordinary* ray (with a refractive index n_ε) is displaced. It is because of this that the phenomenon of double refraction occurs, which is particularly visible in the mineral calcite. For many uniaxial crystals, the RI of the extraordinary

ray is greater than that of the ordinary ray and such materials are described as being optically positive (+). Less commonly, this is reversed and the ordinary ray has the greater RI. Such crystals are described as being optically negative (-). This is, in some cases, a useful diagnostic feature.

For a biaxial crystal (belonging to the orthorhombic, monoclinic or triclinic crystal systems) a beam of light entering it can experience three distinct RIs, these having values normally designated n_α, n_β and n_γ. In a similar manner to the uniaxial crystals, biaxial crystals may also be stated to be optically positive or negative. However, the designations refer in this case to the more complex relationship of whether $|n_\alpha - n_\beta|$ is greater or less than $|n_\beta - n_\gamma|$; such determinations are normally difficult, requiring a high level of expertise to carry out, especially on very small particles like those encountered in pigment analysis.

The difference in refractive indices of the rays, δ_n (or more usually just δ; calculated as $|n_\varepsilon - n_\omega|$, or $|n_\gamma - n_\alpha|$) is known as birefringence. Birefringence is responsible for the interference colours observed under crossed polars (see below); it is always zero for cubic crystals and amorphous substances.

Refractive index (RI) is an important and potentially diagnostic phenomenon. For each pigment in this book, numerical values for RI are given where known. A single refractive index is available for amorphous substances, two refractive indices are given for uniaxial minerals (for the ordinary ray and extraordinary ray n_ω and n_ε) and three refractive indices are given for biaxial minerals (for the minimum, intermediate and maximum, n_α, n_β and n_γ). Quantitative refractive index is difficult to determine for particles and involves immersing materials in a series of oils of different but known refractive index. However, a relative refractive index value compared to that of the medium in a dispersion (or adjacent particles in a cross-section) can be determined by observing the relief and using the Becke line test.

THE PIGMENTUM PROJECT

Relief is a three-dimensional optical effect that occurs as a direct function of the relative refractive indices of adjacent substances. The degree of relief observed increases the greater the difference between the two RIs. For example, if a pigment particle has a RI very similar to that of its mounting medium, it will have particle boundaries barely distinguishable from the medium. Alternatively a particle with a RI either substantially lower or higher than the medium will appear to stand out from the medium, with clear, well-defined particle boundaries.

Relief is easy to qualify and the observed ability of the particle to 'stand-out' from the medium can simply be stated as being low (particle boundaries almost indistinguishable from the medium), moderate and high (very distinct, thick, black lines defining particle boundaries).

Some phases, notably the carbonate minerals and their biogenic analogues, have variable relief. This is because the refractive index varies widely depending on the orientation of the crystal to the light source. For example in calcite, RI varies from 1.658 to 1.486. This is observed as the particle edges fading and then reappearing as the microscope stage is rotated.

The relative refractive index of two adjacent substances may be determined by observation of the *Becke line*. The Becke line is a bright fringe formed by refraction and/or diffraction at the boundary between two substances of differing refractive index. Clearly this is of use if the refractive index of, say, the embedding medium of a microscope sample is known since one can then establish whether the unknown material has a higher or lower RI. When the focus of the microscope is adjusted the Becke line will move either into or out of the substance being examined, the direction being dependent upon whether the separation is increasing or decreasing, and the relative refractive index of the substances. As the distance between the sample and the objective lenses is increased, so the Becke line will move into that substance of *higher* refractive index. Consequently, it is simple to determine whether the particle has a RI greater than (>) or less than (<) that of the medium. For fine-grained particles the Becke line may be difficult to observe, however for particles with refractive index greater than that of the medium, a bright spot appears in the particle centre as the stage is racked down.

As a consequence of this technique, it is important to know the RI of the medium being used, information that will be readily available from manufacturers. Meltmount™ is currently available in seven refractive indices, though that most commonly used for mounting pigments has a RI of 1.662. Canada Balsam, and materials of similar refractive index (RI ~ 1.54) are routinely used by mineralogists and petrologists. Therefore a mineral exhibiting moderate relief in Canada Balsam may have low relief in Meltmount™. Analysts should be aware of this when changing from one medium to another or, more particularly, when reading estimates of relief from texts intended primarily for petrologists (for example Gribble and Hall, 1992). The RI of glass typically used in the manufacture of microscope slides is ~ 1.52, a value which may vary slightly with composition.

THE PIGMENTUM PROJECT

TABLE 3: Relationship of RI to relief for a medium with RI = 1.662

RI	Description of Relief
1.40 - 1.50	High
1.50 - 1.60	Moderate
1.60 - 1.70	Low
1.70 - 1.80	Moderate
1.80 - 2.0	High
>2.0	Very high

Dispersion

Refractive index also varies with wavelength of light, this being the phenomenon that underlies the splitting of light by a prism. Known as *dispersion*, blue light generally has a higher refractive index than red light. Dispersion also varies between substances, from a virtually negligible difference to marked levels. It should be noted that for some phases, where dispersion is high, interference figures might be difficult to obtain (Gribble and Hall, 1992; McCrone *et al.*, 1979). Dispersion may also strongly affect interference colours of minerals with low birefringence, leading to anomalous colours (see below). Dispersion has not been systematically measured for

the samples used in this book; where available, data from the literature has been incorporated.

OBSERVATIONS IN CROSS-POLARISED LIGHT

Isotropism

Cubic and non-crystalline (amorphous) substances are isotropic – that is, the material behaves identically in all directions – and therefore has only one refractive index. Because the axial difference in refractive index is zero, isotropic phases do not transmit light through crossed polars and thus appear black. It is not usually possible to differentiate whether phases are cubic or amorphous using polarised light microscopy alone.

Anisotropism: Birefringence and interference colours

Light is transmitted through crossed polars when non-cubic crystalline structures with different refractive indices are placed between them. Such phases are anisotropic and birefringent. As discussed above, uniaxial minerals have two refractive indices, and biaxial minerals have three. Birefringence (δ) is a quantitative value, measured as the difference between the refractive indices of a crystal. As polarised light is transmitted through a crystal and then observed through another polariser, an array of colours is observed. These *interference colours* (also known as 'polarization colours') are a function of the birefringence and the thickness of the sample through which the light is passing. A crystal exhibiting this property can be said to be *birefringent*. The colours that appear are graded according to Newton's Scale which is divided into orders of colours. *First order colours* are dark grey, through white, dull yellow and red. *Second order colours* are brighter and range through violet, green blue, yellow and red. The jewel-like *third order colours* are bright blues, greens, yellows and pinks. *Fourth order* and above are increasingly subtle shades of pinks and greens. Above fourth order, the orders become difficult to distinguish by the eye. Because the colours observed depend upon sample thickness as well as birefringence, the thicker the sample, the higher the order of colours observed. For further discussion of this phenomenon, see Robinson and Bradbury (1992).

THE PIGMENTUM PROJECT

Mineralogical texts, such as Deer *et al*. (1992), MacKenzie and Guildford (1980) and Hibbard (1995) illustrate photomicrographs of minerals showing their 'standard' interference colours, which for petrographers are based on a mineral section 30 µm thick. As pigment particles are of variable particle size range (from less than 0.3 µm to substantially greater than 10 µm) then the order of interference colours observed may differ from the mineralogically expected norm, and in fact, will usually be lower. An estimation of interference colours based on particle size may be gleaned from the Michel-Lévy Chart (see insert), where birefringence is shown as a series of rays plotted against particle thickness. Where the ray for the particular birefringence intersects the desired thickness, the position in Newton's Scale is given. In this way it can be shown that all crystals can show orders of colours up to the maximum.

As a consequence of the refractive index variation of minerals with crystallographic orientation, the birefringence will also vary depending upon the section observed. Therefore orientations where the difference between refractive indices is small (generally the basal sections of crystals) will show lower interference colours than sections where the variation in refractive indices is large (that is, prismatic sections).

If, as in the case of many pigment-related phases, the crystal has a strong body colour, this will effectively 'mask' the interference colours. However as a rule of thumb, the brighter the crystal appears under crossed polars, then the higher the order of colours. In these cases it is possible to qualitatively describe the interference as low, moderate, high and very high, these categories broadly corresponding to first order, second order, third order and fourth to fifth order colours respectively.

Anomalous colours may form in many phases with strong body colours and, technically, low birefringence. True anomalous colours are blue, indigo, purple and brown, which do not equate to colours appearing on Newton's Scale; they are thus abnormal colours. Chlorite and copper acetate compound F (a form of 'verdigris') are good examples of crystals exhibiting this phenomenon. Anomalous interference colours arise as a function of dispersion. Modification of interference colours in phases with strong body colours and high birefringence may also be termed as being anomalous, and this is the case for phases such as minium and cobalt phosphate.

For the entries in this book, only the standard value of birefringence, δ, is given. From this value, using the Michel-Lévy chart, the interference colours may be calculated using the variable of particle size.

Internal reflection

Some minerals which have very high relief and a RI much higher than that of the medium (greater than 2) often exhibit internal reflections, where light is trapped inside the particles and causes them to appear to glow. The same phenomenon is responsible for the 'fire' in diamonds. The reflections will be the same colour as the mineral. For extreme cases, the whole microscope slide will appear to glow in the respective colour. This phenomenon is usually more obvious under crossed polars and may be mistaken for birefringence, especially in fine-grained samples.

THE PIGMENTUM PROJECT

Extinction

In cross-polarised light, as the microscope stage is rotated through 360°, the observed crystal will be aligned such that it will not transmit light (that is, it will go black) at four positions, 90° apart, throughout the rotation. Uniaxial crystals possess 'straight' or 'parallel' extinction; they are extinct when a long axis of the crystal is parallel to the north-south or east-west cross-hairs at the 90°, 180°, 270° and 360° positions. Orthorhombic biaxial minerals also possess straight extinction (*ortho* meaning straight in Greek); however other biaxial minerals possess inclined or oblique extinction – that is, they become extinct at an angle to the cross-hairs. The angle through which the crystal must be rotated from the extinction position to the nearest cross-hair is known as the extinction angle and this may be diagnostic of the chemical composition of some mineral phases. This feature is readily applied to the feldspar, amphibole and mica groups of minerals.

Many crystals show complete extinction; that is, as the extinction position is reached particles become completely dark. Variation in crystal growth mechanisms or subsequent deformation of the crystal may produce incomplete extinction phenomena. The terminology for description of these observations is given below.

Undulose extinction occurs in particles that have undergone deformation. In this case, the entire crystal does not go black all at once, but 'undulates' across the crystal in patches.

Sweeping extinction is typical in aggregates of fibrous minerals and occurs because each crystal is orientated at a subtly different angle to its neighbours. In this way the extinction sweeps across the crystals. A special case occurs in spherulitic or stellate glomerocrysts, where crystals are orientated through the full 360° range. This means that even when the stage is rotated, there are always crystals orientated parallel to the extinction position. The resulting phenomenon is a cross-shaped extinction pattern that does not rotate, known as a fixed cross, standing extinction cross or 'Maltese' cross.

Mottled extinction is shown by carbonate minerals, micas and some clays. This is because sub-microscopic deformation of the crystal results in a very fine undulose extinction, which means that the crystal is never completely black when in the extinction position, but has a fine mottled appearance.

Cryptocrystalline materials are too fine to record accurate extinction positions. As the stage is rotated, the birefringent particles are clearly observed to 'flicker'. This phenomenon is described here as *twinkling extinction*.

Zoning and Twinning

Zones in crystals develop as the crystal grows. These usually form concentrically to the particle margins and represent changes in composition. Some phases may develop zoning in sectors, like slices of a cake. When zoning is optically apparent, subtle changes of the colour of the crystals either in plane-polarised or cross-polarised light (or both) may be visible.

THE PIGMENTUM PROJECT

Twinning is another function of the mechanisms of crystal growth. Simple twinning is where a crystal and either its mirror image or a rotated crystal appear joined together. Multiple, lamellar, or polysynthetic twins are all terms applied to repeats of this phenomena. Each twin in a pair will have different optical properties. Cross-hatched twins are two sets of twins at different angles to each other.

Elongation

As discussed in the section concerning refractive index, non-cubic crystal structures have orientations at which the transmission of light is fastest or slowest, these directions corresponding to the principal crystallographic orientations of lowest and highest refractive index. In elongated crystals the major axis may correspond to either of these axes, leading to the designation of so-called 'length-fast' and 'length-slow' particles. (Length slow is also sometimes referred to as 'positive' elongation, length fast as 'negative' elongation.) This phenomenon can be diagnostic for some phases where other optical information is insufficient for differentiation. Determination of this property is usually achieved using the sensitive tint (or 'Red-1') retardation plate, an optical device that introduces an additional wavelength shift into the light train which thereby raises or lowers the birefringence in the aligned crystal axes.

Determination of elongation may be made for suitable particles with straight (or weakly inclined) extinction. It is important that the crystal be brightly illuminated

when in the 45° position as this corresponds to the orientation of the accessory plate insertion slot in optical microscopes. Insertion of the accessory plate will lead to a rise or fall in the order of interference colours visible. A rise in colours will be observed if the slow direction of the plate corresponds with the slow direction of the particle or, correspondingly, when the fast direction of the plate corresponds to the fast direction of the particle; such phases are said to be length slow. Conversely, a fall in the order of the interference colours denotes that the particle is length fast. (The stage may also be rotated through 90° so that the colour change can be checked.) For phases with very high birefringence it may prove impossible to determine which direction is fast or slow, as the orders of colours are very similar; in such cases if smaller particles of the substance are present then these can be used for the determination.

OBSERVATIONS IN CONOSCOPIC LIGHT

Using conoscopic light (on insertion of the *Bertrand lens* or removal of the eyepiece) an interference figure may be observed on basal sections of crystals (these may be determined as those having the lowest birefringence or, where appropriate, no pleochroism). Determination of interference figures is impossible for phases with birefringence so low that they are to all intents and purposes isotropic.

Uniaxial minerals (hexagonal, trigonal and tetragonal crystal systems) have, as the name suggests, a single optic axis and in conoscopic light a cross-shaped interference figure, or *isogyre*, is produced; the optic axis lies at the centre of the cross. For biaxial crystals (those belonging to the orthorhombic, monoclinic and triclinic systems) there are two optic axes that intersect at their mid points. Here the interference figure is of two separate curved isogyres. The optic axis corresponds to the hinge point of the isogyres. The smaller angle between the two axes is called the axial angle, or *2V*. 2V can vary from almost zero to 90°. 2V may also be a diagnostic feature for some phases and may be estimated from the degree of curvature of the isogyres observed in conoscopic light. As 2V increases, the isogyres move further apart and become less curved. For 2V approximating zero, the isogyre has an almost right angle bend, whereas for 2V close to 90°, the isogyre is straight and revolves like a propeller in the field of view. Determination of optic sign and 2V ('2V' is zero for uniaxial phases) may be made using the conoscopic or Bertrand Lens and a sensitive tint plate.

In practice, for particles of less than 50 µm in diameter it is almost impossible to observe interference figures. Some microscopes may be fitted with mask devices to aid with the conoscopic analysis of small particles.

MICROSCOPY OF ORGANIC PARTICLES

A small but significant group of pigments utilise organic materials as colouring agents, substrates or extenders. In addition, the humic earths and hydrocarbon-based pigments are derived from organic material and, although these are predominantly amorphous, they may also contain recognisable components with organic structures.

Description of properties observed using polarised light microscopy including relief, colour, birefringence, particle size and so forth broadly follows that outlined above

ARCHIVE DOCUMENTUM PROJECT

for inorganic phases. Particle morphology, however, is likely to be biological in origin and therefore requires a separate terminology.

Fossils, Shells and Eggshell

Microfossils and fragments of macrofossils as well as unfossilised shells are not infrequent components of limestones of all varieties. Crushed shell has also been used as a pigment. Description of the morphologies of fossilised flora and fauna generally requires specialist language and reasonable coverage of this broad topic is beyond the scope of this book. However, simple descriptions of visual appearance and broad identification of organisms is straightforward enough. Entries are included in this book for avian eggshell, oyster shell and diatomites, and appropriate terminology is given therein. Additionally, the calcareous microfossils, coccoliths and associated microflora are described under the entry for chalk, a rock in which they are particularly abundant. Basic descriptive terminology for these components is given where appropriate. Further information general to the recognition of shells, fossilised or otherwise are to be found in Adams *et al*. (1991) and in McCrone *et al*. (1973-80).

Bone

Bone in various stages of calcination may be encountered as pigments (bone blacks and bone ash white). Crushed particles of uncalcined bone have a composition of calcium hydroxylapatite and the optical properties of this phase are close to those for apatites of geological occurrence (see: Deer *et al*., 1992; McCrone *et al*., 1973-80). The biological structure of bone is often observable. Particles appear fibrous and have sweeping extinction. Some grains show the typical bone structure of flat plates (*lamellae*) and channels (*canaliculi*). Bone ash typically has irregularly shaped particles and very low birefringence. The authors and McCrone *et al*. (1973-80) have also observed pitted, bubble-rich particles associated with this phase. Fully coked bone and ivory is opaque and black.

THE PIGMENTUM PROJECT

Starch

Starch is major component of turmeric rhizomes and starch from various other sources has been used as substrates for lakes. Although produced in leaves, fruits and barks, starch is only available in amounts suitable for commercial uses in tubers, roots and rhizomes of plants and in the seeds of legumes and cereals. This is so-called 'reserve starch'. Starches from different sources are differentiable using optical microscopy and are described in terms of their shape (globular, lenticular, ellipsoidal, ovoid, truncated or polygonal), degree of aggregation, size and *hilum*, or organic centre of the particles. The *hilum* is conspicuous in some starches, but difficult to observe (certainly in plane-polarised light) in others. *Hila* may be spots, small rings, elongated, or even dark clefts in various starches. *Hila* may also be situated centrally in the grain or off-centre. Under crossed polars, starch grains exhibit a distinctive extinction cross or ‘Maltese Cross’, the centre of which is the location of the *hilum*. (It should be noted, however, that legume starches that have large, cleft-shaped *hila* have an extinction ‘cross’ with a central bar.) The appearance of extinction crosses may again be diagnostic and varies with the degree of crystallisation of the starch grains. Starch grains also frequently show concentric rings around the *hilum*. Again, these may be unobservable, faint or conspicuous. Rings are more obvious in oblique illumination. Observation of many starch grains with a sensitive tint or gypsum plate reveals a ‘beautiful play of colours’ (Winton, 1906) that may also aid in identification. The morphology of starches has additionally been described by Singh

et al. (2003) and the optical properties applied in the determination of a variety of starches have been detailed by Winton (1906).

Gums and resins

Gums and resins, such as gamboge, are predominantly amorphous and therefore isotropic. Some examples may be characterised by the presence of air bubbles, thus having a spongy appearance.

Plant tissue

Plant tissue may be present in various states in organic derived pigments. Cell structure is often well preserved, and frequently even survives charring (Winter, 1983). Woody plant material (lignin) is also frequently well preserved in low-grade coals and lignites and a common component of impure humic earths.

Cellular material from plants, roots and rhizomes is immediately recognisable under the microscope and has a polygonal network structure. The simplest form of plant tissue, with cellulose walls is called *parenchyma*. The term *sclerenchyma* describes a variety of cellular plant tissues with noticeably thickened walls and composed of lignin. *Sclerenchyma* can contain rounded or polygonal cells, known as *stone cells*. These may occur singly or as dense groups; the latter case forms components such as peach and cherry stones. Sclerenchyma may also contain bundles of fibrous elements called *bast fibres*. The outer layers of plant stems, roots and rhizomes are formed of *cork cells*. These also have polygonal morphologies in surface view, but are elongate and arranged radially. These are particularly diagnostic of cork char blacks, especially apparent when observed using a scanning electron microscope. It should be noted that vegetable chars, whilst preserving tissue structure, are characterised by having substantially thinned cell walls, these structures being easily destroyed during grinding (Winter, 1983).

THE PIGMENTUM PROJECT

Crystallites of phases primarily including amorphous silica ('plant opal'), calcium oxalate (which can also occur in finely acicular habits known as *raphides*) and microconcretions of calcium carbonate may also be encountered. The microscopic identification of vegetable material has been described in some detail by Winton (1906). Further useful illustration of the appearance of plant tissue is encountered in McCrone *et al*. (1973-80).

Pollen and spores are common constituents of dust and are remarkably resistant to degradation. Although not directly used as pigments, pollen may appear as unintended impurities. Again, as a first general reference, McCrone *et al*. (1973-80) have an excellent section illustrating these particles.

Coals

As fossilised peat beds, coals may be regarded as rocks rather than organic deposits. The various components of coals are called macerals and these may be considered analogous to minerals. Identification is complex and based on the classification of the organic matter preserved. Coal macerals are divided into three main groups – *vitrinites*, *liptinites* ('*exinites*') and *inertinites* – based on their origin, reflectivity and UV fluorescence. Coal macerals are opaque and isotropic in polarised light. The *vitrinites* are derived from woody plant material and include the macerals telocollinite and textinite, both identifiable by their cellular appearance, as well as desmocollinite

and eugelinite which are amorphous, precipitated humic gels. Vitrinites have poor or no UV fluorescence and are moderately reflective. The liptinites are derived from fatty and waxy parts of plants; spores and pollen are preserved as sporinite, leaf cuticle wax as cutinite, resins, gums and bark oils as resinite. Liptinites are highly distinctive in that they have very low reflectance but strong green or yellow UV fluorescence. Finally the inertinites (most commonly the maceral fusinite) are natural charcoals, having been oxidised or aromatized during the coalification process. Inertinites are of strikingly high reflectance and exhibit no fluorescence under UV light.

UV fluorescence of coal macerals has been described by Rost (1995). General texts on coal microscopy are uncommon. However, Seyler (1929) provides a thorough and well-illustrated introduction, but understandably does not employ modern terminology.

VARIANTS AND COMPOSITE PIGMENTS

Two practical aspects of the examination of samples should be stressed. These are, first, the differentiation of variants – pigments of the same composition, but arising (for example) from different manufacturing processes or sources – and, second, composite pigments, where a number of different compounds are intermixed as a result of their origin or use. The analyst should consequently be aware of the range of normal variation within a pigment, other compounds found commonly or uncommonly in association with it and the implications such observable differences may have on the interpretation.

THE PIGMENTUM PROJECT

Sample homogeneity should normally be noted in a specimen and should be expressed in terms of percentage estimates of each phase present. Inhomogeneity may, of course, result from intentional mixing of pigment phases or from the presence of naturally occurring impurities or contaminants. All phases present should be described.

FURTHER READING

The aim of this book is to provide a first and encyclopaedic description of the optical properties of pigment-related materials. Pigment analysis is mainly concerned with the examination of naturally occurring minerals, synthetic crystalline compounds and amorphous substances, including the substrates of lake pigments. As such, pigment analysis borrows largely from the terminology devised for petrography with a few notable, but nevertheless, important differences. Consequently there are additional works already widely available that deal with the optical properties of materials encountered in other disciplines, but which overlap with those of our own. As further reading the authors therefore recommend the works below.

Examination of particles using the polarising microscope has been standard practice in many disciplines for over 100 years though the technique has perhaps found most routine employment in the fields of crystallography and petrography (that is, the description of rocks and their constituent minerals). Listings and descriptions of the optical properties of minerals are readily accessible in standard texts including Gribble and Hall (1992), Deer *et al*. (1992), and Hibbard (1995). Colour atlases of

photomicrographs of rocks, minerals and fossils are also useful *aide memoires* (see: MacKenzie and Guilford, 1980; MacKenzie *et al*., 1984; Adams *et al*., 1991; Yardley *et al*., 1990). For heavy minerals in dispersions ('grain mounts') see Mange and Maurer (1991). For the discussion and identification of strongly coloured minerals used as gems, decorative stones and their synthetic (or even fake!) analogues, including a great many varieties used as pigments, see Liddicoat (1993) and O'Donoghue and Joyner (2003). The technique also has applications in engineering, biology and material sciences. McCrone *et al*. (1979, 1973-80) give a detailed overview of the scope of applications. More recently, polarised light microscopy has been applied to other fields as a diagnostic tool including the analyses of archaeological ceramics (see: Whitbread, 1989; Freestone 1995) and, of course, pigments. The *Artists' Pigments* series of volumes edited by Feller (1986), Roy (1993), FitzHugh (1997) and Berrie (forthcoming) deals with a selection of the more prevalent pigment phases, including discussions of physical, chemical and optical properties.

REFERENCES

ADAMS ET AL. (1991) Adams, A.E.; MacKenzie, W.S.; Guilford, C. *Atlas of sedimentary rocks under the microscope* Longman Scientific & Technical (1991)

BACCI & PICOLLO (1996) Bacci, M.; Picollo, M. "Non-destructive spectroscopic detection of cobalt (II) in paintings and glass" *Studies in Conservation* **41** (1996) 136-144

BERRIE (FORTH.) Berrie, B. (ed.) *Artists' Pigments. A Handbook of their History and Characteristics* **4** National Gallery of Art, Washington (Forthcoming)

BURNS (1993) Burns, R.G. *Mineralogical applications of crystal field theory* 2nd ed. *Cambridge Topics in Mineral Physics and Chemistry* **5** Cambridge University Press (1993)

DEER ET AL (1992) Deer, W.A.; Howie, R.A.; Zussman, J. *An introduction to the rock forming minerals* 2nd ed., Longman Scientific & Technical, Essex (1992)

DE LA RIE (1982) de la Rie, E. Rene "Fluorescence of paint and varnish layers (Parts 1-3)" *Studies in Conservation* **27** 1-3 (1982)

DUNHAM (1937) Dunham, K.C. "The paragenesis and color of fluorite in the English Pennines" *American Mineralogist* **22** (1937) 468-478

EASTAUGH (2002) Eastaugh, N. "The realities of digital image acquisition, integration and access in a large database project" *Digital Imaging for the Paintings' Conservator. Preprints for a conference held in the Starr Auditorium at Tate Modern on Friday 6th December 2002* UKIC, London (2002) 46-52

FELLER (1986) Feller, R.L. (ed.) *Artists' Pigments. A Handbook of their History and Characteristics* **1** National Gallery of Art, Washington & CUP (1986)

FELLER & BAYARD (1986) Feller, R.L.; Bayard, M. "Terminology and procedures used in the systematic examination of pigment particles with the polarizing microscope" *Artist Pigments; a handbook of their history and characteristics* **1** Feller, R.L. (ed.) National Gallery of Art, Washington and Cambridge University Press (1986) 285-298

FITZHUGH (1997) FitzHugh, E.W. (ed.) *Artists' Pigments. A Handbook of their History and Characteristics* **3** National Gallery of Art, Washington and Oxford University Press, Oxford (1997)

FREESTONE (1995) Freestone, I.C. "Ceramic Petrography" *American Journal of Archaeology* **99** (1995) 111-115

GRIBBLE & HALL (1992) Gribble, C.D.; Hall, A.J. *Optical Mineralogy: Principles and Practice* UCL Press, London (1992)

HIBBARD (1995) Hibbard, M.J. *Petrography to Petrogenesis* Prentice Hall (1995)

JOHNSTON-FELLER (1986) Johnston-Feller, R. "Standard Specification of Pigment Composition and Color" *Artists' Pigments. A Handbook of their History and Characteristics* **1** Feller, Robert L. (ed.) National Gallery of Art, Washington and Cambridge University Press (1986) 299-300

KIRBY (1977) Kirby, J. "Two panels by the Master of St Giles. Materials, paint structure and techniques" *National Gallery Technical Bulletin* **1** (1977) 49-56

LEONA & WINTER (2001) Leona, M.; Winter, J. "Fiber optics reflectance spectroscopy: a unique tool for the investigation of Japanese paintings" *Studies in Conservation* **46** #3 (2001) 153-162

LIDDICOAT (1993) Liddicoat, R.T. *Handbook of Gem Identification. Chapter IX; Colour filters and fluorescence* 12th ed., Gemmological Institute of America, Santa Monica, California (1993) 81-84

MACKENZIE & GUILDFORD (1980) MacKenzie, W.S.; Guilford, C. *Atlas of Rock Forming Minerals in Thin Section* Longman (1980)

THE PIGMENTUM PROJECT

MACKENZIE ET AL. (1984) MacKenzie, W.S.; Donaldson, C.H.; Guilford, C. *Atlas of Igneous Rocks and their Textures* Longman (1984)

MANGE & MAURER (1991) Mange, M.A. & Maurer, H.F.W. *Heavy minerals in colour* Harper Collins (1991)

MCCRONE ET AL. (1973-1980) McCrone, W., et al *The Particle Atlas: An Encyclopedia of Techniques for Small Particle Identification* 2nd ed.Ann Arbor Science, Ann Arbor (1973-1980)

MULLIN (2001) Mullin, J.W. *Crystallization* 4th ed., Butterworth-Heinemann, Oxford (2001)

NASSAU (1983) Nassau, K. *The Physics and Chemistry of Color: The Fifteen Causes of Color* John Wiley & Sons (1983)

O'DONOGHUE & JOYNER (2003) O'Donoghue, M.; Joyner, L. *Identification of Gemstones* Butterworth Heinemann (2003)

PAINT RESEARCH STATION CLASSES (1956) *Pigment Particles* **6** Paint Research Station, Teddington (1956)

PATZELT (1974) Patzelt, W.J. *Polarized-light microscopy: principles, instruments, applications* Ernst Leitz Wetzlar GMBH (1974)

POWERS (1953) Powers, M.C. "A new roundness scale for sedimentary particles" *Journal of Sedimentary Petrology* **23** (1953) 117-119

PUTNIS (1992) Putnis, A. *Introduction to the mineral sciences* Cambridge University Press (1992)

ROBINSON & BRADBURY (1992) Robinson, P.C.; Bradbury, S. *Qualitative Polarized-Light Microscopy. Royal Microscopical Society Microscopy Handbooks* **9** Oxford Science Publications (1992)

ROST (1995) Rost, F.W.D. *Fluorescence Microscopy* Cambridge University Press, Cambridge (1995)

ROY (1993) Roy, A. (ed.) *Artists' Pigments. A handbook of their history and characteristics* **2** National Gallery of Art, Washington & Oxford University Press (1993)

SEYLER (1929) Seyler, C.A. *The microscopical examination of coal* Fuel Research: Physical and Chemical Survey of the National Coal Resources, No. 16. HMSO, London (1929)

SHELLEY (1992) Shelley, D. *Igneous and Metamorphic Rocks under the Microscope* Chapman and Hall (1992)

TALSKY & RISTIC-SOLAJIC (1987) Talsky, G.; Ristic-Solajic, M. "High resolution/higher order derivative spectrophotometry for identification and estimation of synthetic organic pigments in artists' paints" *Anal. Chim. Acta* **196** (1987) 123

TUCKER (1991) Tucker, M.E. *Sedimentary petrology* 2nd ed., Blackwell Scientific Publications (1991)

WHITBREAD (1989) Whitbread, I.K. "A proposal for the systematic description of thin sections towards the study of ancient ceramic technology" *Archaeometry* **31** (1989) 127-138

WINTER (1983) Winter, J. "The characterization of pigments based on carbon" *Studies in Conservation* **28** (1983) 49-66

WINTON (1906) Winton, A.L. *The Microscopy of Vegetable Foods* John Wiley & Sons, New York (1906)

YARDLEY ET AL. (1990) Yardley, B.W.D.; MacKenzie, W.S.; Guilford, C. *Atlas of Metamorphic Rocks and their Textures* Longman Scientific and Technical (1990)

THE PIGMENTUM PROJECT