Doctoral School
of the
Hungarian University of Fine Arts

Light microscopic detection and analysis of black and grey pigments of organic and inorganic origin

Anna Vihart

Theses of DLA dissertation

2011

Supervisor: László Kriston, physicist

The light microscopic examination methods of black pigments differ from the general practices of pigment analysis. Very few reports have been published on the analysis of these materials. Black particles do not transmit incident light; consequently, numerous optical properties yielding valuable information in the course of typical pigment analysis cannot be determined by microscopy. Black pigments include several types of materials with different characteristics, and their analyses raise different fundamental questions. The majority of black pigments consist of carbon of plant origin; some minor groups are composed of materials originating from soot, bones and minerals. In order to provide a foundation for studying these materials, it was necessary to elucidate their structure and to develop test methods suitable for differentiating between them.

These 1

Since the most widely used black pigments have been various types of charcoal, a primary question in these studies was to what extent black pigments of plant origin could be differentiated according to the species of origin. To this end, pigment samples were prepared by carbonization and grinding of more than fifty arboraceous species.

Based on the sample collection it can be established that there are particle types that occur abundantly in certain groups of trees and are extremely rare in other species.

There are species-specific features such as scalariform perforation plates, spiral cell wall thickening, or bordered pits with unusually small apertures (~1 μm) on the tracheary wall, which may be observed in transmission microscopy as well as on polished specimens. In case if characteristic fragments of these types appear in the sample, the species of origin can be narrowed down to a specific group of tree species.

Some characteristics are associated with the wall thickness of the supporting tissue of the material. Such are transversely broken pieces of longitudinally elongated plant tissues, which are mainly characteristic of trees with massive tissues. Conversely, the bordered or simple pits of vessel walls are more often observable in wood from trees consisting of fine tissues, simply because thin-walled fibres, vessels etc. will more readily disintegrate to yield small lamellae, whereas hard tissues will produce larger blocks upon disintegration.

Since in the course of the examination of charcoal fragments information can only be obtained by morphological analysis, finely ground charcoal particles most often fail to yield any specific information: the chance for the occurrence of characteristic tissue elements decreases with decreasing particle size. The probability of the occurrence of characteristics suitable for group identification is also very low when only a small amount of black particles is available for analysis.

These 2

It is an important question from a painting technical point of view whether black pigments prepared from certain tree species are better than those obtained from others, and whether there is a characteristic pattern in the utilization of certain tree species.

After the preparation and grinding of charcoals and utilization of their fractions with different particle sizes, it was established that the quality of black pigment obtained from members of the pine family does not come up to that prepared from other tree species. The remarkably stringy, characteristically elongated particles of pine pigment do not form a contiguous coat of paint. Although the properties of charcoal prepared from finely ground pine wood were improved, its quality never came close to that of pigments prepared from deciduous trees. This observation leads to the conclusion that pigment prepared from pine wood must have been utilized mainly for purposes where fine particle size, good hiding power and deep black colour were not required. Its occurrence is improbable among top-quality pigments and on panel paintings of high quality.

Of black pigments of plant origin, the special literature most often recommends vine-shoot charcoal, and not without reason: the pigment prepared from vine-shoots has proved to be one of the best plant charcoals. The reason for this probably is that, unlike the wood of trees many years old, the structure of the one-year-old vine-shoot does not accumulate large amounts of mineral deposits. Since vine-shoots are thin, they are rapidly carbonized; vine charcoal is easily and rapidly ground to a fine particle size due to its loose structure, and the end result is nearly pure carbon.

In addition to vine-shoots, plant pigments of excellent quality can also be prepared from the carbonized wood of various angiosperms; excessive carbonization will also remove the majority of birefringent minerals. Grinding of the harder structures naturally requires more time.

Black pigments prepared from carbonized seeds are also recommended by several books on painting. This material is indeed of good quality, as confirmed by several samples of our black pigment collection. These pigments may have been utilized more widely than known today, although there is no way to determine their abundance from samples taken from paintings. The appearance of black pigments from carbonized seeds differs from charcoals in that the elongated forms characteristic of charcoals are not typical in them. Since, however, the proportions of extensively carbonized and ground charcoal particles may be similar, the two cannot be differentiated on the basis of appearance. In addition, similarly to charcoals, the structure of black pigments of seed origin also exhibits small holes/pits.

These 3

The colour of carbon black pigments under the microscope ranges from light, transparent brown to deep black. The examination of our sample collection revealed that the colour and transparency of the particles depend on the conditions of pigment preparation and the duration of carbonization, and do not contribute to the identification of the species of origin.

These 4

It is a general problem in studies on black pigments that the usual test methods do not provide sufficient information about the material studied. The question we addressed was which methods can be used to differentiate between black pigments of plant and mineral origin.

One test procedure is based on the analysis of light reflected from the surface of the pigment particle.

In reflected light, with the analyzer in parallel position (or even in a stereomicroscope or, in the case of relatively large particles, with the naked eye) it can be observed that the particles absorb and reflect the incident light to different extents. Light reflexion (mirror reflection) of minerals is higher than that of carbons of plant origin. Nevertheless, studies on reflecting surfaces are still a great help in studying carbons of plant origin, because this method yields information on the structure and wall thickness of charcoal.

In reflected light, with the analyzer in parallel position the polished surfaces of the particles, whereas in particle samples (also in reflected light) their broken surfaces can be studied.

Polished surfaces of minerals consisting of large particles give a strong reflection. Formations detectable on their surfaces are e.g. chipping associated with cleavage planes, or uneven, pitted areas, sometimes even resembling charcoal or plant fibres.

The surface and cleavage planes of mineral-derived black pigments with relatively smooth, well-developed crystals are best studied in particle samples. For example, galenite disintegrates along its regular cleavage planes to yield particles with smooth surfaces, which strongly reflect light. The structure of manganite has more of a fibrous character. The surfaces of bone and charcoal particles also reflect light, although, naturally, to a much smaller extent.

Mirror reflection is also related to particle size: pigments consisting of very small particles (e.g. artificial iron oxide, lead sulphide) do not have any contiguous planar surfaces large enough to behave like mirrors, consequently they do not give visible reflection.

These 5

Black pigments of mineral origin are known to include isotropic and anisotropic materials. Since light only penetrates into the surface layer of black particles and cannot pass through them, the birefringence of these materials is quite different from that of coloured, transparent minerals.

In reflected light, with the polarizer and the analyzer crossed, the intensity and in some cases even the colour of the light reflected from anisotropic black mineral particles changes when the objective table is turned around, and their glimmer becomes periodically stronger and weaker. This phenomenon is known as reflection pleochroism or bireflection, i.e. the direction dependence of reflecting power. The best known materials of this type are mineral stibnite, graphite and bismuthinite. The presence of bireflection is proof for the presence of some materials and may exclude others.

Birefringence of the particles may also become visible in transmitted light in the form of a shining band of light along the outlines of the particle; the intensity of the shining band changes as the objective table is turned around. The visibility of the band of light increases as the illumination aperture is opened up. Due to the presence of binders and pigments, the majority of which exhibit birefringence, studies in transmitted light on the birefringence of the particles of samples taken from works of art can only yield reliable results if the sample was non-contaminated.