Chapter 3
Analytical Approaches to the Analysis of Paintings: An Overview of Methods and Materials

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Abstract The analysis of paintings is based on a combination of non-invasive and sampling approaches – which provide different types of information about different areas of paintings. In this chapter the principal methods for analysis applied to the study of paintings are presented to provide information about the evidence that each can yield. This is followed by a review of the materials found in different layers of paintings, from the support to paint layers and coatings. While intended as an introduction, the chapter highlights the large variety of techniques employed, and the significant complexity of paintings which is an analytical challenge and requires very careful interpretation. Within the context of authentication, the interpretation of analysis requires understanding of the limitations and accuracy of analytical methods, and reference to historical trends and to the chronological use of materials for painting is necessary.

Keywords Analytical methods · Technical analysis · Chemistry · Dating · Chronology

3.1 Introduction

Scientists are often asked to evaluate unattributed works of art. Identifying the author of an artwork may be a crucial step in establishing its value from a cultural, historical, and economic perspective but it is our view that making decisions of attribution is not the responsibility of the scientist or conservator. Instead, scientists and conservators can provide key information that may refute the attribution of a

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work to a specific historical period, or identify paint materials or additions that may be consistent with a particular period or workshop practice.

Forgeries are endemic in the art world: old Masters and modern Masters paintings are commonly faked and forged. Therefore, great caution is necessary when providing assessments of attribution with a significant burden of proof resting on scientific and historical analysis. Sound knowledge of the history of a particular painting and its provenance, of the artistic technique of the painter, and on the identification of the constituent materials are often essential in the interpretation of the significance of results from the chemical analysis of works of art. Within this context, the accuracy and the limitations of scientific analysis are particularly important; while some techniques are ideal for the identification of bulk composition, others may provide evidence of trace materials or identify specific binders or pigments. In this book we have aimed to provide a balanced description of advantages and limitations of analytical methods and the extent to which each method provides qualitative and quantitative information.

Paintings are complex objects, and contain different materials (that may include wood, canvas, pigments, binders, varnishes, added materials from conservation, as well as degradation that may originate from the environment). Each component of a painting can be analysed or assessed using scientific methods and offer clues regarding the origin and physical history of paintings. A thorough visual examination by an art historian, curator, and conservator, all of whom may be familiar with the production of the supposed author, is a first step in assessing authorship of works of art. Scientific analysis and documentation rely on the choice and application of a large array of documentation techniques that range from consolidated methods including X-radiography and Infrared Reflectography and UV Fluorescence imaging (see Chaps. 4, 8, and 11), as well as hyperspectral imaging and complementary data analysis (see Chaps. 4 and 5). Imaging is often followed using analytical methods that rely on spot-analyses or sampling to identify artistic techniques and materials. Analysis may provide information that can be used to date a painting or to corroborate the compatibility of materials with a specific period. Synergistic interpretation of data between art historians, conservators, connoisseurs, and heritage scientists allows careful assessment of paintings, and can lead to the detection of forgeries.

Conservation and art history evidence will clarify the following issues:

- Documentary information and conservation history reveal the condition of a painting in terms of the presence of restoration and original material, damage and legibility. Past treatments of paintings may have introduced significant changes to the size and shape of a painting. For example, it is common that large canvases and panel paintings may be cut into smaller multiple paintings for sale, with well-known examples including Manet's 'Execution of Maximilian' (Execution of Maximilian n.d.). Past conservation treatments and in particular both lining of canvases where a new support is adhered to a canvas painting, or cradling where wooden panel paintings were thinned and a rigid structure (a cradle) was attached to the back may permanently change the appearance of a painting and destroy evidence of the original materials. It is also worth noting that damage to paintings can be masked by restoration or reintegration – and it is critical for art historians and conservators to be able to assess the condition of a painting and distinguish original materials from past restorations. The use of UV Fluorescence imaging (see Chap. 8) is particularly important for highlighting varnishes and past retouching, and may be complemented by X-radiography, IRR and, more recently with data from elemental mapping with XRF. When a painting is significantly compromised due to damage, being able to assess restoration is particularly important since in this case the authenticity of the work may no longer be a prime concern. It is noted that decisions regarding acceptable damage and the extent to which reintegration can mask or restore a damaged painting are in the hands of curators and conservators of collections, and that in many cases paintings which have suffered damage may indeed be restored without compromising the legibility of the artist (e.g. the successful restoration of Raffaello's Madonna of the Goldfinch (Madonna of the Goldfinch n.d.)). Compensation for loss is commonplace in painting restoration but needs to be considered carefully and thoroughly documented. There are ethical guidelines for the use of easily identifiable restoration paint that can be removed with solvents for retouching (Schenck 1994). With the aim of making reintegration more easily identifiable to the public and to experts, conservators and indeed entire conservation schools have developed varying methods for retouching (see the documents produced by the Retouching of Cultural Heritage workgroup at (Rechgroup.pt. n.d.)).

- Provenance, or the history of ownership and documented sale history of a work is often essential in attributing a work. Insecure provenance or falsified provenance may compromise the authentication of paintings, while ownership and documented evidence of purchase can instead provide key and important art historical information regarding perception, taste and value. Excellent examples of the way documentary evidence can contribute to the study of provenance can be found in the Raphael Research Resource from the National Gallery London (https://www.nationalgallery.org.uk/paintings/research/provenance) (Cooper and Plazzotta 2004). While masterpieces in collections may have uninterrupted and documented provenance, this may not be the case for newly discovered paintings and this constitutes a significant dilemma: without provenance, authenticity is compromised.
- Another key aspect of studying a painting is the careful examination of the way a work is executed, or technical study. This may be as important as the identification of compatible materials in excluding or confirming authorship. For example, a close study of brushstrokes, drawings, signatures and other paint details are elements of the style of a painter (see Chap. 5). An intimate knowledge and visual memory of style and familiarity with the evolution of a painter's style is at the heart of close examination of paintings, and the work of the connosieur (Van De Wetering 2008). Advances in image-based automatic artist attribution is under development to improve visual examination by learning to recognize visual features from data rather than from prior knowledge (Noord et al. 2015).

Technical analysis entails the use of a large set of techniques to analyse the materials constituting a painting. Since it is fundamental to ensure that the paintings are not subjected to significant damage during sampling, analytical campaigns start with the application of non-invasive methods (Hyperspectral/multispectral imaging, point analysis and mapping by XRF, XRD, FTIR, FORS, Raman, X-ray radiography). Following non-invasive approaches, sampling is often required to obtain information about stratigraphy and specific components of paint layers and binding media. The principal methods applied during analysis are summarised in Table 3.1, and can be classified as:

- Non-destructive techniques (MO, SEM-EDX; microRaman, ATR, SIMS, XRD, XRF, Synchrotron based spectroscopies) applied on cross-sections or powdered samples;
- Sampling and microdestructive methods (analytical pyrolysis, GC-MS, HPLC-MS, ICP-MS, Raman SERS).

3.2 Materials

While different analytical methods provide data which can be used to identify materials, the interpretation of results requires significant knowledge of the composition of paintings and conservation materials. In order to provide context, a summary of the current understanding of the use of materials and their historical usage is given in the following sections.

3.2.1 Supports

The term “support”, which is an integral part of the painting itself, refers to any material onto which paint is applied: it may be a flexible material like cotton or linen canvas (stretched over a wooden frame, the stretcher) and paper, or a rigid one as a wall, wooden panels, metal, glass or plastic. The types of materials used for supports are very much influenced by their availability in the historical periods: wooden panels and linen canvas were extensively used for tempera painting in medieval age; plywood and hardboard became prominent from the twentieth century onward; modern supports often consist of composite materials and include paper, illustration board, wood, tarpaulin, plywood and hardboard (Nevin and Sawicki 2019). Dendrochronology, X-radiography and Tomographic studies may be particularly important both for the dating and the identification of the type of wood employed as well as its condition, and are essential when considering complex constructions as commonly found in polychrome wood.

Canvases are widespread and often have a distinct texture that in most cases can be easily recognized in the painting: coarse canvas imparts a softness to the surface,

Table 3.1 Overview of the main analytical methods used for the analysis of the paint surface or on powder samples or on cross sections

Instrument	Information provided	Notes
Optical microscopy (OM)	Visual information in visible and ultraviolet light on the stratigraphy of cross sections	
Scanning electron microscopy with energy dispersive X-ray detection (SEM-EDX)	Cross section morphology and elemental identification in the paint layers	
Micro-Fourier transform infrared spectroscopy (μFTIR)	Molecular information on inorganic and organic composition in the painting and in cross sections	Inorganic signals are more intense. Being the paint layers very thin, the analysis of cross sections often refers to two layers
Micro-Raman spectroscopy (μRaman)	Molecular information on inorganic and organic composition. Particularly useful to identify inorganic and organic pigments	Important in the study of cross sections, but also used on paint fragments: spatial resolution is generally compatible with the paint layer thickness
X-ray fluorescence (XRF)	Elemental information on inorganic composition of the painting surface and of paint layers in the cross section	XRF of paint surface contains information from all the layers up to the preparation (Moens et al. 2000)
X-ray diffraction (XRD)	Identification of inorganic pigments	Particularly useful for differentiating pigments with the same chemical structure but with different crystalline phases
Fibre optics reflectance spectroscopy (FORS)	Identification of inorganic and organic pigments	The presence of sooth/particles, degraded varnishes can affect position and shape of reflectance bands
Direct mass spectrometry (DTMS, MALDI, ESI-MS, LDMS)	Ionization techniques enable the detection of organic compounds	Mostly used for varnish and organic pigments identification
Secondary ion mass spectrometry (SIMS)	Identification of organic and inorganic compounds also in cross sections	It shows a major sensitivity for glycerolipid compounds
Analytical pyrolysis (Py-GC-MS and EGA-MS)	Information on thermal behavior of organic compounds and detection of specific makers and profiles of synthetic and natural materials	To volatilize all compounds, it is necessary to use derivatization agents for acidic and alcoholic moieties. All the polymers are detected
Gas chromatography-mass spectrometry (GC-MS)	Information on specific profiles of proteins, glycerolipids, waxes, natural resins and pitches, gums	Wet treatments of samples to break chemical bonds in macromolecules
Liquid chromatography-mass spectrometry (LC-MS)	Information on specific profiles of proteins, lipid, waxes, resins and organic dyes	Wet treatment of samples to solubilize compounds of interest

whereas a painting on a wooden or metal panel looks hard and smooth. Interestingly, by X-radiography it is possible to understand the type of weave of the cloth, the orientation, thickness, and density of the threads (Hendriks and Van Tilborgh 2001). Thread counting, determination of the orientation of warp and weft, the width of canvas strips, and weave matches link certain canvases together, informing on their production and sometimes determine unexpected relationships between paintings. These features help to understand which canvases an artist used in a specific historical period and in a specific geographical location: this can help to confirm an attribution of a painting to a specific artist, or to date it in a specific period (Pozzi et al. 2021). Instead of manual thread counting, a software was designed to compute a trustworthy average thread count in a repeatable, readily documented procedure (Johnson et al. 2009; Johnson and Sethares 2017). This software can be applied to the X-rays digital images and can be freely downloaded from the GitHub repository [https://github.com/sethares/CountingVermeer]. Canvases by Vermeer and Van Gogh have been extensively analysed by this method (Van Tilborgh et al. 2012).

Generally, the support is sized by a diluted glue, most typically made from animal skins, to prevent absorption of the binder into the support. In the case of canvas, a ground covers the sized support to further protect it from the adverse effects of organic paint materials. The ground is a mixture made of materials compatible with the support and the paint to be used over it, acting as a reflective surface beneath the paint film. For centuries, a mixture composed of gypsum or chalk (calcium carbonate) and animal glue was used as a ground for both wooden panels and canvas. The most common ground preparation used today is gypsum dispersed in a binder of acrylic polymer, which replaces the animal skin glue used in "traditional gesso".

3.2.2 Pigments

Both pigments and binders have been used since prehistory for paintings. Over the centuries, craftsmen and artists experimented with traditional and novel materials to impart colour to their paintings, improving the aesthetic appearance and durability of their works-of-art. In some lucky cases, we can estimate the first use of pigments, especially when dealing with synthetic ones. Nonetheless, scientific studies have led to new discoveries regarding the long-term use of historic pigments (e.g. Egyptian blue detected in Raffaello's works of art (Anselmi et al. 2020), or natural carmine found in 19th C. Lefranc-Bourgeois archive materials (Degano et al. 2017; Gabrieli et al. 2016)). Thus, our ability to connect dating and provenance to the occurrence of specific pigments is dependent not only on geographic and historical research, but also on the study of specific artists and their workshops. Information on the most common pigments used in paintings are reported in Table 3.2.

Pigments can be classified by colour or origin, or broad chemical composition as inorganic and organic pigments. The latter can typically be obtained by complexation or adsorption on an inorganic, uncoloured salt, of an organic dye, extracted from natural sources, and are thus generally known as pigment lakes (see Chap. 9).

Table 3.2 Examples of the most commonly-used pigments found in paintings, adapted from (Colombini and Degano 2018)

	Name of the pigment	Formula/chemical class	Details	Notes
White	Lead white	$2PbCO_3 \cdot Pb(OH)_2$	Inorganic, artificial	Most used white until the nineteenth century
	Lime white (San Giovanni white)	$CaCO_3$	Inorganic	Mostly in wall paintings
	Titanium dioxide	TiO_2	Inorganic, synthetic	Synthetic (1920)
	Gypsum	$CaSO_4 \cdot 2H_2O$	Inorganic	Mostly used for ground layers
Blue	Azurite	$2CuCO_3 \cdot Cu(OH)_2$	Inorganic	
	Ultramarine blue (lazurite)	Lazurite is a tectosilicate mineral with sulfate, sulfur and chloride with formula $(Na,Ca)_8[(S,Cl,SO_4,OH)_2 \vert (Al_6Si_6O_{24})]$	Inorganic, natural (but a synthetic lazurite exists, first synthesized in 1828 (Plesters 1966))	Very precious
	Smalt (cobalt glass)	Obtained by including cobalt oxides in a glass melt and grinding the final product	Inorganic, artificial	Mostly used in the seventeenth–eighteenth centuries
	Indigo	Indigoid dye precipitated on an inert substrate (clay, gypsum), is composed mainly by indigotin, with possible secondary components (indirubin, isatin)	Organic, natural (but synthetic indigotin is available since 1882)	Extracted from several plants
	Maya blue	Indigo adsorbed on/ included in palygorskite clay	Lake pigment, artificial	Used in Mesoamerica
Green	Malachite	$CuCO_3 \cdot Cu(OH)_2$	Inorganic	
	Verdigris (copper acetate)	$Cu(CH_3COO)_2 \cdot 2Cu(OH)_2$	Inorganic, artificial	Synthesized by Greek and Roman painters
	Phthalo green	Copper phthalocyanine	Organic, synthetic pigment	Very stable, synthetic (1936)

(continued)

Table 3.2 (continued)

	Name of the pigment	Formula/chemical class	Details	Notes
Yellow	Lead chromate	$PbCrO_4$	Inorganic, synthetic	Commercially available since 1818
	Azo yellow pigments	Series of monoazo, diazo, BONA, etc.	Synthetic organic pigments (first, PY1, syntehsised in 1897 in Germany)	Commercially available since the end of nineteenth century
Yellow-red	Yellow and red ochre	Fe_2O_3 (from yellow to red depending on the hydration)	Inorganic, natural, artificial	
Red, violet and purple	Red lead (minium)	Pb_3O_4	Inorganic	
	Vermilion	HgS	Inorganic	From cinnabar mineral
	Madder lake	Anthraquinones precipitated as a complex with alum	Lake pigment, artificial	Since ancient times, from roots
	Carmine	Anthraquinones (carminic acid mainly) precipitated as a salt	Lake pigment, artificial	Very precious, seventeenth century
	Azo red pigments	Series of monoazo, diazo, etc.	Synthetic organic pigments (first, PR1, synthesized in 1880 in England)	Commercially available since the end of nineteenth century
	Eosin	Organic pigment (xanthene class)	Lake pigment, synthetic	Synthetic, very fugitive
	Crystal violet	Organic pigment, triarylmethine class	Much used in inks, until now	Synthetic, quite fugitive
Black	Ivory black	Amorphous carbon obtained from ivory and animal bones, also containing calcium phosphate and carbonate	Artificial	
	Carbon black/vine black	Amorphous carbon obtained from organic material	Artificial	

Amongst the synthetic organic pigments, some molecules are already insoluble in the paint binder, or can be precipitated as a salt, being strongly acid or alkaline.

Traditionally, pigments were obtained from coloured earth pigments (iron oxide containing clays) or by grinding precious stones. In few cases, specific products were obtained by chemically modifying natural substances, e.g. Egyptian blue, obtained in 3000 b.C. by heating silica, malachite, natron, calcium carbonate and sodium carbonate; lead white, consisting of basic lead carbonate ($2Pb(CO_3)_2 Pb(OH)_2$) was made by stacking lead strips in porous jars with vinegar and burying the jars in animal manure, whose mild temperature promoted the reaction. Thanks to the modern understanding of chemical properties and processes, many synthetic inorganic pigments were produced during the eighteenth century: Prussian Blue (1704) replaced the more expensive ultramarine (Barnett et al. 2006). Cobalt containing pigments shortly followed: Cobalt blue, developed in 1802 by Thenard; Cobalt green developed by Rinmann, a Swedish chemist in 1780; Cobalt violet (either cobalt phosphate or cobalt arsenate) appeared in 1859 and Cobalt yellow (cobalt aluminium nitrite) discovered by Fischer in Breslau in 1830. Zinc was also very important: in 1834 Winsor & Newton of London, working with Michael Faraday, invented Chinese white (zinc oxide). Finally, Cadmium metal was discovered by Stromeyer in 1817, and Cadmium yellows were in use in Europe since 1829.

Lake pigments have been used since antiquity for colouring vases, for mural paintings, and later on wood panels and for easel paintings. Few water insoluble pigments were precipitated on inert supports as gypsum or clay, e.g. Maya blue (Grazia et al. 2020), or Tyrian purple used in Ancient Greek and Etruscan mural paintings (Sotiropoulou et al. 2021). Water soluble dyes were instead mostly precipitated as metal complexes on colourless salts, in particular with alum. Madder, kermes, lac and cochineal lakes are the most famous red ones, followed by brazilwood lake; few yellow lakes are known, such as weld lake. In the last decades of the nineteenth century, the deeper understanding of inorganic and organic chemistry influenced the availability of reactants, thus impacting on the preparation of a wider variety of new colours for paint materials. By modulating the extraction process and using different salts as precipitating agents, it became possible to obtain different modified madder and cochineal based products (e.g. carmine), with different colours.

The development of synthetic organic pigments (SOPs) was driven by the textile dying industry. In 1856, William Perkin synthetized the first organic dye, mauve. The success of the dye encouraged the production of other aniline/coal tar-based pigments used in paintings. At the beginning of twentieth century the number of colours available was still limited, while nowadays the paint industry has a wide variety of pigments to choose from. Due to their high performances, cheapness, and wide range of brilliant hues, SOPs were exploited for many industrial applications including printing inks, food and drink additives, plastics, and textiles. The first azo dye was Aniline Yellow, produced in 1861 by C. Mene. It was manufactured by reacting aniline with nitric acid and commercialized in 1864 as the first commercial azo dye. Several azo dyes were precipitated as lakes as new pigments for artists, but unfortunately many of the new products were not tested sufficiently for fastness properties before their introduction on the market. For instance, Eosin (Acid Red 87, C.I. 45,380), belonging to the family of xanthenes and commercialized as "Geranium lake", was one of the most attractive and interesting early synthetic colorants which unfortunately is highly fugitive. Vincent Van Gogh used this pigment lake in several paintings during the Arles period (1888–1890), which now show clear discoloration: the fading of the red lakes in still lives *Irises* and *Roses* has resulted in pink paints that now look white and in purple paints that now look blue (Centeno et al. 2017).

Carbon based and organic pigments have been also used in the production of inks. The adoption of fluid inks has been attributed to China around 2700 b.C. (Edwards 2018). The first inks produced were made of carbon black suspended in water and gum Arabic solutions; sooth of different origin was later widely employed. In mediaeval times, iron gall ink replaced carbon black ink as the favored medium of writing, which was produced by reacting aqueous solution of iron(II) sulfate and extract of gallnuts with the addition of gum Arabic. Red inks were produced with brazilwood lakes, whose fugitive nature made it a better candidate for writing and manuscript illuminating than for painting purposes. Following upon Perkin's synthesis of mauveine in 1856, several developments in ink manufacture occurred, thanks to the availability of a new range of organic dye-based colored inks.

3.2.3 *Traditional Paint Binders*

Traditional binding materials are natural substances produced by plants or animals. Naturally occurring materials may contain proteins, lipids, carbohydrates, and waxes as reported in Table 3.3.

From a chemical point of view, these natural materials can be described as follows:

(a) **Proteins**. They are macromolecules made up of one or more unbranched chains of amino acids joined together by peptide bonds between the carboxyl and

Table 3.3 Classification of traditional natural binders

Class of organic compound	Natural material	Uses in painting
Proteins	Animal glue Egg white Egg yolk (proteins + lipids + sugars) Milk/Casein (+ lipids and sugars) Vegetable proteins (e.g. garlic)	Water-soluble binders for *tempera, tempera grassa* and *gilding* techniques
Carbohydrates	Honey, starch contain simple sugars Plant gums: Arabic gum, tragacanth, karaya, ghatti, guar, locust bean, fruit tree gum	Water-soluble polysaccharide binders mainly for *watercolor* and *gouache* techniques, ink components
Glycerolipids	Vegetable drying oils: linseed, walnut, poppy seed, Tung oil Animal fat	Not water-soluble binders for *oil* techniques
Waxes	Beeswax	*Encausto* and *ceroplastic* technique

amino groups of adjacent amino acid residues. Several (yet in limited number) amino acids are commonly found in animal and vegetable proteins: glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), methionine (Met), proline (Pro), hydroxyproline, (Hyp), threonine (Thr), asparagine (Asn), glutamine (Gln), tyrosine (Tyr), cysteine (Cys), lysine (Lys), arginine (Arg), aspartic acid (Asp), phenylalanine (Phe), tryptophan (Trp), serine (Ser), glutamic acid (Glu), and hystidine (His).

(b) **Carbohydrates**. Plant gums are naturally occurring polysaccharide exudates from several species of plants or extracted from the endosperm of some seeds. The polymers consist of aldopentoses, aldohexoses and uronic acids joined together by glycosidic bonds. Natural gums present variable distributions in mean molecular mass of polymeric molecules, whereas the composition of the constituent sugar percentages remains reasonably constant and depends on the specie of the plant.

(c) **Glycerolipids**. Oils and fats are mixtures of triglycerides, namely esters of glycerol with fatty acids, containing smaller amounts of other compounds, as sterols and vitamins. Unsaturated and especially polyunsaturated fatty acids in the triacylglycerol molecule are commonly subject to oxidation via radical reactions with the inclusion of oxygen in the acyl chain, carbon-carbon bond formation, and the production of lower molecular weight species. This phenomenon causes polymerization and cross-linking processes during the curing of drying oils. It leads to the formation of a polymeric network, generating a solid paint film.

(d) **Waxes**. Beeswax, obtained from the hives of bees, is the most commonly used natural wax for manufacturing works of art, and used since prehistory. The qualitative average composition of beeswax is quite constant and is made up of hydrocarbons (14%), monoesters (35%), diesters (14%), triesters (3%), hydroxymonoesters (4%), hydroxypolyesters (8%), monoacid esters (1%), acid polyesters (2%), free acids (12%) and free alcohols (1%). The aliphatic chains of beeswax compounds are mainly saturated and consequently extremely resistant to ageing.

3.2.4 Modern Paint Binders

The chemical and compositional features of modern oil paints are different from those of classical oil paint used in antiquity. The main ingredients of the first commercial paint tubes, introduced at the beginning of the twentieth century, were traditional drying oils, as linseed or walnut oil, often used in mixtures with less expensive oils as castor, safflower or fish oil, added with new classes of additives such as surfactants, metal soaps and dispersing agents (La Nasa et al. 2015, 2021b). Pastel crayons were also widely used for sketching compositions with precise details, and were ideal for different kinds of supports. The early commercial formulations of pastel crayons still remain undisclosed (La Nasa et al. 2021a).

In the twentieth century a wide range of new synthetic materials were also introduced. Modern art materials include a large number of formulations of synthetic polymers characterized by short drying times, excellent optical properties, flexibility and good resistance to light, humidity and heat. Synthetic polymers are extensively used not only as binders by the artists, but also as materials for conservation (i.e. as consolidants, adhesives or protective coatings). This means that almost any type of polymer structure can be found in historical and modern artworks, either added in some conservation treatment or as constituent materials. Anyway, the most representative classes of synthetic resins used by artists are acrylic, vinyl and alkyd ones, being the most used the acrylic resin. Table 3.4 reports some characteristics of the most used polymer paint binders.

Table 3.4 Characteristics of commonly used synthetic paint binders

Polymer	Production year	Chemical composition	Additives and plasticizers	Notes
Vinyl polymers	~1920	Poly(vinyl acetate): Polymerization of vinyl; poly(vinyl alcohol): acetate monomer hydrolysis of PVAc	Phthalate esters	Water-based paint binder
	~1960		VeoVa (vinyl versatates esters in vinyl acetate polymers)	VeoVa improves hydrolytic stability, adhesion, water and UV resistance
Alkyd resin	1927	Oil-modified polyesters synthesized from glycerol, phthalic anhydride and a drying oil	Unsaturated fatty acids, acrylic, styrene and silicone compounds, driers, dispersing agents	Semi-synthetic polymer
	1960	Glycerol was substituted by pentaerythritol		
Acrylic resins	~1940	*Homopolymers:* ethyl acrylate EA, butylmetacrilate, nBMA		Solvent soluble
	1956	*Copolymers* of MMA, EA, EMA, 2-EHA, nBA	Phthalates, surfactants	Aqueous emulsion, being p(EA/MMA) one of the most used
Polystyrene	~1940	Polymerization of the styrene monomer		Solvent soluble

3.2.5 Varnishes

Varnishes are mixtures of natural or synthetic resins that dry when spread thinly on a surface. Several recipes, reported in numerous historic sources, describe a variety of materials and techniques used to obtain natural varnishes. Basically, they can be classified into spirit varnishes and oil ones. Curing of spirit varnishes consists in the evaporation of the solvent and solidification of the resin; curing of oil varnishes is based on the polymerization capability of the (poly)unsaturated compounds present in both the oil and resin.

Natural varnishes were used by artists for easel painting, and by restorers to protect the paint layer from the environment (i.e. oxygen, moisture). Synthetic varnishes have been used for the same purposes, but also as binding media in modern and contemporary paintings.

Varnishes possess specific optical and physical properties, which confer them transparency and ability to form stable films on the surface of the paintings, without compromising the aesthetics of the work-of-art, and even improving its gloss and general color equilibrium. Plant terpenoid resins are the most used as varnish. They are a complex mixture of mono-, sesqui-, di- and triterpenes, which have, respectively, 10, 15, 20 and 30 carbon atoms per molecule.

In East Asia and Japan, natural polymers called lacquers were used both as varnishes and painting media since ancient times; lacquers consist of the sap extracted from trees and their composition is based on a specific mixtures of catechol derivatives (Heginbotham et al. 2011; Tamburini et al. 2020).

Amongst the natural and synthetic varnishes, the most common are reviewed in Table 3.5.

The detection of a specific varnish may provide the analyst with information on the painting technique, on the possible restoration occurred, on the presence of re-paintings (especially whenever synthetic varnishes are applied) (Decq et al. 2019). Detecting synthetic or semi-synthetic varnishes may also yield information about the dating of the production of the painting or of a previous restoration (Bonaduce et al. 2013; La Nasa et al. 2017).

3.3 Conclusions

By providing a simplified overview of commonly applied techniques and many of the materials found in paintings it is clear that the identification of specific material in paintings is a complex analytical challenge, and requires experience and careful interpretation as well as caution. Commonly publications include as much data as necessary to support interpretation of results and should highlight accuracy and error as well as the potential analytical limitations, especially when the authorship

Table 3.5 Characteristics of the most used varnishes

Class	Common name	Main content	Provenance	Notes
Diterpenoid resin	Colophony/ turpentine	Abietadienic acids, pimaradienic acids	*Pinaceae* resins	
	Sandarac	Pimaradienic acids (sandaracopimaric acid), communic acid, totarol, agathic acid		Sandarac type I and II are available
Triterpenoid resin	Mastic resin	Euphanes (masticadienonic and isomasticadienonic acids), oleananes (oleanonic and moronic acids), dammaranes	*Pistacia* tree resin	Plant resin from Chios island in the Aegean Sea; already used in ancient Egypt
	Dammar resin	Dammaranes (hydroxydammarenone, dammaradienol), ursanes (ursonic acid, ursonaldehyde)	*Hopea* genus tree	Plant resin, introduced into Europe in the nineteenth century
	Copal resin	Lupane (mainly), ursane and oleanane triterpenoids	*Bursera* spp., *Protium copal*, some *Pinus* spp. (e.g., *P. pseudostrobus*) and a few *Fabaceae* spp	
Sesquiterpenoid resin	Shellac	Mono- and polyesters of hydroxy-aliphatic and sesquiterpene acids, peaking at jalaric and laccijalaric acids, aleuritic and butolic acids	The glandular secretion of an Indian scaled insect (*Laccifer lacca* Kerr)	Animal resin, began to be used in Europe towards the end of the sixteenth century
East Asian Laquers	Japanese lacquer (*urushi*)	Catechol derivatives, peaking at 3-pentadecylcatechol	From the sap of *Rhus vernicifera* (*Anacardiaceae*), native to China, Japan and Corea	Plant resin, used as both varnishes and painting medium (see above) since ancient times
	Laccol	Catechol derivatives, peaking 3-heptadecylcatechol	From the sap of *Rhus succedanea* (*Anacardiaceae*), native to North Vietnam and Taiwan	
	Burmese lacquer (*thitsi*)	Catechol derivatives, including 3-pentadecylcatechol, 3-heptadecylcatechol, alkylphenylphenols and alkylphenyl-1,2-dihydroxybenzenes	From the sap of *Melanorrhoea usitate* (*Anacardiaceae*), native to Thailand and Burma	

Vinyl polymers	Polystyrene, PVC, polyethylene, polypropylene, polyacrylonitrile			Used in plastic objects, as water-based paint binder, adhesive and varnish
Acrylic resin	Perspex, PMMA, Paraloid			Synthetic polymers, available since c.a. 1930, used as varnishes, adhesives
Low-molecular-weight resins	Laropal K80	Urea-aldehyde polymer	Aldehyde resin synthesized from urea, isobutyraldehyde, and formaldehyde	Synthetic resins used as varnishes since c.a. 1930
	MS2A	Reduced ketone polymer	Condensation products of methylcyclohexanones and/or cyclohexanones	
	Regalrez	Hydrocarbon-based resin	Hydrocarbon resin synthesized from vinyltoluene and α-methylstyrene and subsequent hydrogenation of the unsaturated polymer	

or authenticity of works is under scrutiny. Indeed, the interpretation of results from analysis is often based on deduction and comparisons with results from the analysis of similar works, for which there may or may not be reliable studies.

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