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A multi-analytical approach for the characterization of contemporary paint materials

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The most beautiful thing we can experience is the mysterious.
It is the source of all true art and science.
Albert Einstein

All art has been contemporary.
Neon installation by artist Maurizio Nannucci

Contents

General introduction

Scope of the thesis

Nowadays, while the physical-chemical analysis of traditional paint materials may be considered a consolidated practice, the characterization of compounds used in Modern and Contemporary Art deserve a major attention because of a lacking of knowledge on the fast ageing processes undergone by the new industrial materials used in artworks.

Talking about conservation issues of Contemporary Art may sound, on the one hand, a contradiction, because recent artworks should not need any restoration yet. On the other hand, contemporary artworks show degradation pathways sometimes even quicker and more severe compared to those occurring in ancient works of art. The main reason of this fragility lies in the physical-chemical properties of the materials they are made of. In Contemporary Art, the materials are not chosen in order to last for centuries; they are often the expression of an artistic will or meaning, so that the artwork appearance is closely linked to the constituting materials, and to the techniques adopted by the artist. In contemporary artworks, traditional paint materials are frequently substituted or mixed with modern products, designed for industrial or domestic use. These new materials and their behaviour over time are often unknown, compared to that of the classic materials used for oil paints, frescoes, marble, bronze or wood sculptures [1].

In recent years, synthetic resins used as paint media have been extensively studied, while oils used in modern oil-based paint media are often considered the same traditional oils used in the past. This is not correct because the botanical origin is often different, these oils undergo industrial treatments, and additives have been admixed in industrial paint formulations. Moreover, in the last years, the study of synthetic organic pigments is gaining importance because they have almost completely replaced traditional pigments from natural sources. Unfortunately, the very large number of synthetic pigments introduced on the market does not facilitate their study; moreover, their ageing pathways have yet to be investigated and described.

This work presents the chemical characterization and ageing studies of several materials currently found in contemporary artworks. Specifically, the study is aimed to the characterization of synthetic organic pigments and oils used in modern oil-based paints and their behaviour under accelerated ageing. To study these materials, a multi-analytical approach was used, the analyses being performed with several techniques: Gas Chromatography/Mass Spectrometry (GC/MS), Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), High-Performance Liquid Chromatography coupled to Electrospray Ionization-Quadrupole-Time-of-Flight Mass Spectrometry (HPLC-ESI-Q-ToF), Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR), micro-Raman, colorimetric measurements. Moreover, several Contemporary Art case studies were investigated and are herein presented.

This thesis aims at contributing to expand the knowledge on the materials found in contemporary artworks and on their ageing behaviour, in order to prevent and slow down the decay processes of the artworks, to allow their preventive conservation, and to plan appropriate restoration strategies.

Brief summary of the major movements in Contemporary Art

It is an hard task to unambiguously define Contemporary Art, and it is not even simple to decide what could be considered art: it includes works produced with several techniques and languages such as video art, painting, photography, sculpture, digital art, drawing, music, happenings, performance, installation. In general, Contemporary Art comprehends art that has been and continues to be created during our lifetimes. There is not a specific starting date of Contemporary Art, but generally it is considered to begin after World War II, with the end of Modern Art.

The political instability before World War II led artists, writers, as well as important art collectors and dealers, to leave Europe and to seek safety in the United States. By the time the War was over, New York had replaced Paris as the new centre of the art world [2]. In the United States a new generation of American artists called Abstract Expressionists began to emerge and dominated the art scene between 1940 and 1950 [3]. This artistic movement combined the lessons learned from Henri Matisse, Pablo Picasso, Surrealism, Joan Miró, Cubism and Fauvism. Sometimes called the “New York School”, it included both colour field painters and action painters. Abstract Expressionism is best known for large-scale paintings that break away from traditional processes, often taking the canvas off of the easel and using unconventional materials such as house paint. The main figures associated with this movement are Jackson Pollock, Barnett Newman, Willem de Kooning, Mark Rothko and Clyfford Still. The Abstract Expressionists were committed to an expressive art of profound emotion and universal themes. They were interested in myth and archetypal symbols, and understood painting as a struggle between self-expression and the chaos of the unconscious.

Between 1950 and 1960 new artistic movements such as Neo-Dada and Pop Art made their way into the art scene. In Neo-Dada, artists such as Jasper Johns and Robert Rauschenberg aimed at shifting the focus of art away from the existential angst of the artist, and towards the audience and the influence of popular culture.

Neo-Dada artists provided a bridge between Abstract Expressionism and Pop Art, by introducing fragments of pop culture inside their artworks and by employing a wide range of mediums, materials and techniques never previously used by artists.

Rauschenberg, for example, introduced many innovations, spanning the mediums of painting, sculpture, drawing, prints and photography. He employed images and references from the mass media [4] and his use of serigraphy, a commercial reproduction equipment, linked him directly to the Pop Art. His paintings evolved from traditional oil paint brushed on canvas to include collage, assemblage, and the direct transfer of images by means of imprinting on the widest array of support materials: from wood panels, silk and nylon to sheet material, Plexiglas, and plaster [5]. The addition of found materials and waste objects was labelled negatively as Neo-dada.

The now famous New York Pop artists Andy Warhol, Roy Lichtenstein, Claes Oldenburg and James Rosenquist emerged in the 1960s in the footsteps of the Neo-Dadaists. The term “Pop Art” is the abbreviation of “Popular Art”. Pop artists celebrated commonplace objects and everyday people, in this way seeking to elevate popular culture to the level of fine art. The Pop Art movement was characterised by an imagery drawn from popular culture, comic books and celebrities photographs, as well as by the use of bright colours [6]. The use of the newly marketed synthetic products by pop artists was fundamental for the development of the movement’ aesthetics [7]. Another artistic movement widely influenced by these new synthetic products was Minimalism, emerged in the early 1960s in New York in opposition to Abstract Expressionism. One of its backgrounds was the Bauhaus movement, particularly Josef Albers. Its leading figures - Donald Judd, Frank Stella, Robert Morris, and Carl Andre - created objects characterized by unitary, geometric forms and industrial materials. The emphasis was on pure shape, without a narrative or reference content [8]. This cool anonymity was often achieved with monochromatic surfaces. A sentence by Donald Judd perfectly explains the philosophy behind this movement: "A*n artwork doesn't need to possess many elements to observe, compare, analyse one by one. What really matters is the thing as a whole, with its characteristics. The most important things are alone and they are more intense, clear and powerful*." [8].

Developed simultaneously in the mid-1960s in the United States, Latin America and Europe, Conceptual Art favoured ideas over the formal or artistic value of the design of an artwork. Sometimes called Post-Modernism, Conceptual Art removed every trace of emotion form the artistic production, in contrast with Abstract Expressionism. It is a movement focused on defining the concept of "art". Conceptual artists denied the materiality of objects, the means of expression and the intrinsic meaning of visual expressions [9]. American artist Sol LeWitt defined Conceptual Art as where the "*idea itself, even if not made visual, is as much a work of art as any finished product*" [10]. Conceptual artists were influenced by the simplicity of Minimalism, but they linked their work to Marcel Duchamp, whose ready-mades had rattled the very definition of the work of art.

Between the 1960s and the 1970s other important movements such as Arte Povera [11] and Performance Art [12] were born.

Neo-Expressionism flourished internationally in the 1980s. Disaffected with the intellectualism of Minimalism and Conceptual Art, many artists returned to painting in an expressionist style, which reasserted the creative power of the individual. Neo-Expressionists revitalized painting with strong colours, as well as motifs drawn from Cubism, Fauvism, German Expressionism, Surrealism, and Pop-Art. Though most closely associated with a group of New York-based artists that included Julian Schnabel, David Salle, and Eric Fischl, the term is also often used—not without controversy—to encompass trends in European painting at the time, including the Italian Transavanguardia (Francesco Clemente, Sandro Chia, Enzo Cucchi, Nicola De Maria e Mimmo Paladino) and the generation of German painters born during World War II (Georg Baselitz, Markus Lüpertz and Anselm Kiefer). The movement was marked by interests in primitivism, graffiti, and the revival of historical styles [13].

From the invention of the Duchamp's ready-mades onward, every common object can be considered an artwork; thus, commercial products entered in the artist' studio. Traditional natural binders and pigments such as proteinaceous media, drying oils, natural resins and inorganic pigments were gradually replaced by a variety of organic synthetic paint materials. The plethora of materials that can be encountered on contemporary artworks includes modified vegetable oils, but also synthetic resins such as acrylic and vinyl polymers, styrene copolymers, alkyds and nitrocellulose, as well as synthetic organic pigments.

Moreover, in Contemporary Art is not infrequent to deal with artworks that show damages and alterations such as holes, lacerations, burned parts, stains and spots already at the very moment of their first exhibition. The damage is usually produced by the artist himself, or it is present on the support. The lived-in look of these materials entails that, most often, the artworks already contain at the moment of their creation the cause of their degradation.

This complexity, compared to the traditional paint materials and techniques used by the Old Masters, accounts for the specific challenges represented by the preservation of Contemporary Art.

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Chapter 1

State of the Art

1.1 Paint binders

The paint binder, an organic material commonly called the vehicle, is the film-forming component of the paint. It should possess very precise physical, chemical and optical properties. During the formation of a film, a substance switch from its liquid state to a solid state trough three main mechanisms: evaporation of the solvent, solidification, or formation of chemical bonds.

The essential physical properties for a good binder are the cohesive properties, to keep the pigment particles together, and the adhesive properties, to interact with the support. A binder should have film-forming properties and the film formed should be thin, flexible, with good mechanical properties. Furthermore, the binder should wet the pigment particles. As for the optical properties, a binder should be transparent, colourless, and with a proper reflection index. Lastly, the required chemical properties for a good binder include lightfastness, weather-fastness and chemical compatibility with the pigments.

This set of properties have limited, in the course of the history, the choice of suitable binding media.

The main classes of paint binders are:

- tempera binders – in an aqueous dispersion – which may be based on proteinaceous materials (i.e. egg, animal glue) or polysaccharidic materials (vegetable gums, water-soluble natural polymers);
- oil binders, based on siccative oils;
- mixed binders;
- modern binders, constituted by synthetic polymers.

Historically, the artists themselves prepared their own paints, by mixing a binding medium, traditionally egg or a drying oil, with the grounded pigments. The artists who operated in the tradition of the Old Masters had a deep knowledge on the materials they employed, and the painting techniques, developed in centuries, were transmitted in the art schools and in ateliers.

In Modern and Contemporary Art, siccative oils are still commonly used, together with synthetic polymers, while, in the tempera technique, egg and other natural substances were often replaced by synthetic polymers in an aqueous emulsion.

In the 20th century, many new synthetic products were introduced on the market and some artists started to experiment with them, often employing industrial paints developed for household or for the automotive industry.

1.2 Synthetic paint binders

1.2.1 Brief history

The 19th century saw the birth of modern science, with a surge of technological progress, bringing a revolution in thinking and in the founding of the scientific method. It is no coincidence that the same period saw the birth of Modern Art. Prior to the mid-1800s, art was used to produce realistic depictions of scenes. Subjects were almost always religious or mythical scenes, historical events or portraits of eminent people. Artworks were usually commissioned, and artists painted what their wealthy customers requested. The first step in a new direction in the art scene was the emergence of Impressionism in the 1860s. The keys to the Impressionists' success were several scientific discoveries and new manufacturing techniques that changed their paint materials. Science was applied to the development of paints. New pigments based on recently discovered elements such as chromium, cadmium, zinc and cobalt provided high saturated, intense colours, while the manufacture of synthetic pigments added completely new colours to the artists' palette [1]. The introduction of ready to use tube colours in the mid-1800s radically changed the way artists approached painting. In 1841, the American portrait painter John Goffe Rand invented the squeezable metal tube. Winsor & Newton, the famous London-based paint manufacturer, was soon using tubes for its oil and watercolour paints. With the introduction of tube colours, the paint was not only ready to use, but was also easy to carry around, enabling *en plein air* (outdoor) painting. This "revolution" most likely contributed to the development of the impressionist movement, to the extent that artist Pierre Auguste Renoir said: "*Without tubes of paint, there would have been no Impressionism*" [1] [2].

The technologic progress, from the invention of the tube colours onwards, became more and more important in the artistic production, providing new materials to the artists.

Industrial synthetic paints were first introduced on the market for the automotive industry. These new materials were subsequently employed also for household and for domestic use. Artists were attracted by these new synthetic products because of their cheap price and quick drying time.

After the introduction on the market of the first synthetic resins, initially for industrial use, paint manufacturers used synthetic resins to develop their particular artists' products [3].

1.2.2 Review of the main classes of synthetic polymers used as paint binders

Polymers have a molecular structure in which the monomer is repeated *n* times; the monomer is the building block from which the polymer originates.

The first semi-synthetic products to be used as paint binders were based on nitrocellulose. The discovery of nitrocellulose by Schoenbein dates back to 1846. Nitrocellulose is highly flammable and was first used as a film base in photography and in motion picture films. Nitrocellulose was also used as a varnish; it was dissolved in an organic solvent together with natural resins and the result was a hard, glossy varnish with a quick drying time. Nitrocellulose varnishes were very popular products in the automotive industry, because they provided new shades of colours for the cars. One of the most famous brands of nitrocellulose was DuCo, of the DuPont Coatings.

Alkyd resins were introduced as binding media in the 1930s as an industrial evolution of the classical oil paint media. They are semi-synthetic, obtained by condensation polymerization of polyols (with at least three hydroxyl groups), polybasic acids and a source of fatty acids (either siccative oils or free fatty acids). Their main advantage is their speed of drying [4]. The polyester is typically hard; with the introduction of monobasic fatty acids the degree of crosslinking can be reduced or modulated. One of the first alkyd paint products for artists was the DuLux series, which DuPont began marketing in 1931. During the 1940s DuPont replaced nitrocellulose with an alkyd resin in the DuCo brand. Alkyd paints dry more quickly than oil paints, but less quickly than nitro paints. The final appearance is very similar to that of an oil paint. Alkyd resins represented a major innovation both for the industrial paints and for household paints markets. The adoption of these oil-based industrial polymers by artists is one of the milestones in the evolution of painting techniques in the 20th century art scene. Artists such as Frank Stella, Jackson Pollock and Picasso experimented with alkyd-based paints [5]. As for the alkyd paints available nowadays, the most important brand is Griffin, by Winsor & Newton, introduced on the market during the 1970s. Moreover, many common paint formulations are “oil colours” where the medium is a mixture of an oil and an alkyd resin.

The first acrylic artist paints were introduced on the market by Leonard Bocour and Samuel Golden in 1947 as acrylic solutions, called Magna. These colours were dissolved in turpentine and dried quickly by evaporation of the solvent. The quick drying time, the high quality of the paint films and the intensity of the colours made these new binders popular among artists, who exploited them to obtain particular aesthetic effects. Morris Louis, Barnett Newman and Roy Lichtenstein all used these acrylic solutions for their artworks. Roy Lichtenstein, in particular, used only Magna colours for all his life, and when in the 1980s the production stopped, the artist bought all the warehouse provisions. A limit of these solvent based acrylic paints was that the paint layer remained partly soluble after drying. This means that the paint layer was partly re-dissolved when in contact with the solvent contained in a new layer applied over it. Henry Levinson in 1954 introduced the first acrylic colours in a water-based emulsion, called Liquitex. Acrylic polymers are not soluble in water, but they can be applied in water emulsions in the form of dispersed drops, that do not maintain water solubility after drying. The impact of the water-based acrylic binders on the art scene was remarkable: the first artists to use them were the Mexican muralists, and soon all the artists belonging to the Pop Art movement like David Hockney and Andy Warhol started to experiment with them. Furthermore, the acrylic colours allowed the painters to obtain an opaque, flat painted surface, without traces of brushstrokes, perfect for those artists who were looking for an impersonal style, like Barnett Newman and Clyfford Still. Their painting technique, called “colour field”, was based on wide and continuous fields of colour. The hardness and flexibility of acrylic paints largely depends on the glass transition temperature (Tg) of the acrylic medium. The polymers employed in these paints require high Tgs, to obtain a non-sticky film, but also Tgs low enough to avoid fragility and consequently disruption of the film formed. The polymer used for the synthesis of the acrylic resins was generally a methylmetacrylate (MMA) - ethylacrylate (EA) co-polymer. At the end of the 1980s, several formulations switched to n-buthylacrylate (nBA) - metylmethacrylate (MMA) co-polymers [3] [6] [7]. The co-polymers characteristics depend on the percentages of acrylates versus methacrylates: acrylates confer flexibility, while methacrylates stiffness and strength.

Acrylic-vinyl co-polymers are another type of binders used in the paint industry. The styrene-acrylic polymers are the most widespread.

Another synthetic resin widely used in paint formulations is PVAc (polyvinyl acetate). PVAc resins were first introduced in the 1930s. The first paint formulations contained an organic solvent; non-toxic aqueous formulations followed in 1940s [8]. Water-based vinyl paints were cheap household products readily available in supermarkets. Despite the lack of success in the artists' paint market, PVAc resins have remained the principal type of binder used in interior emulsion house paint until today and they are frequently encountered on modern paintings [3]. In the case of a omo-polymeric PVAc binder, the resulting film is stiff and fragile, thus the majority of the vinyl formulations contain plasticizers to make the film softer. In the first commercial formulations the amount of plasticizers could reach 20% w/w. These substances over the time were prone to migrate outside of the paint film with dramatic consequences, such as embrittlement of the film. Nowadays this problem has been solved with the co-polymerization of vinylacetate with co-monomers such as acrylates or highly branched ester co-monomers (C9 or C10) as in VeoVa series (vinyl esters of versatic acid). The co-polymers obtained are more plastic and transparent compared to PVAc omo-polymers. One of the artists who extensively employed PVAc resins is Yves Klein. He experimented several synthetic resins to fix his blue pigment on the surfaces of his artworks, but only vinyl resins satisfied him. Currently the only relevant brand of PVAc artist paint on the market is Flashe®, by the French manufacturer Lefranc & Bourgeois.

Other synthetic polymers not developed for artistic purposes, but widely employed by contemporary artists are polyurethane, chlorinated gum, epoxy resins, silicone resins.

It is important to add that the majority of synthetic paints contains high amounts of additives, like dispersing agents and surfactants, to keep the emulsion stable, or like fluidizers, to modulate the viscosity. With the exception of some volatile ones, all the additives remain inside the paint film after the drying process. For a list of the most common additives used in paint formulations see Section 1.3.5.

1.3 Modern oil-based paint media

Even with a wide range of synthetic resins to choose from, several professional artists still use oils as paint binders. The reasons for this choice are various, such as to keep using traditional materials, or to obtain specific results on the painted surface that cannot be achieved with synthetic media.

Since remote times, drying oils have been used in the artistic production for their property of binding the pigments to the ground layer. One of the oldest written sources of the use of drying oils in painting techniques is that by Cennino Cennini, who describes in *"Il Libro dell'Arte"* a painting procedure that combines tempera paint and oil [9]. Drying oil paints became popular during the 15th century and almost universal by the 17th century. The oil painting technique, initially used on wood supports by the Flemish painters, from the 16th century onward was also applied on canvas, eventually becoming the only medium used for this type of support until the introduction of acrylic colours.

Vegetable oils consist of mixtures of triglycerides, glycerol tri-esters of fatty acids. The most common fatty acids in drying oils are saturated acids with 12, 14, 16 or 18 carbon atoms (lauric, myristic, palmitic and stearic acids, respectively) and C18 polyunsaturated acids with 1, 2 or 3 conjugated double bonds (oleic, linoleic and linolenic acids, respectively) [10]. Drying oils are characterized by a particularly high content of polyunsaturated fatty acids. In Fig. 1.1 a generic molecule of a triglycerol constituted by C16:0, C18:1 and C18:2 fatty acid moieties is shown.

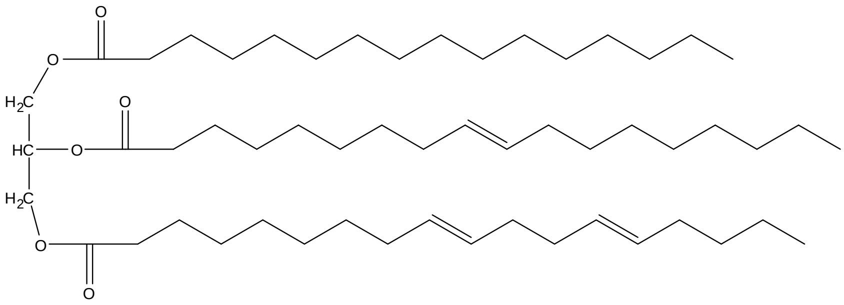

Fig. 1.1 A triglyceride molecule with C16, C18:1 and C18:2 fatty acids moieties.

In addition to the triglycerides (TAGs), siccative oils contain a non-saponifiable fraction (1-3%) constituted mainly of phytosterols (60-90%). Other minor components are free fatty acids.

Having a high content of di- and tri-unsaturated esters, siccative oils are susceptible to polymerization reactions upon exposure to light and oxygen. This polymerization, which is called "drying process", results in the rigidification of the material and in the formation of a stable film. This drying process is explained in detail in Section 1.3.1.

1.3.1 Drying mechanisms and degradation

Drying oils harden to a tough, solid film after a period of exposure to air. The hardening of drying oils has been the subject of several studies [11] [12] [13] [14] [15] [16], but it is still far from being completely understood. The drying, or, more properly, curing of oils is the result of autoxidation reactions, involving the addition of oxygen, and the subsequent crosslinking. This process begins with an activated (triplet) oxygen molecule in the air inserting into carbon-hydrogen (C-H) bonds adjacent to one of the double bonds within the unsaturated fatty acid. The resulting hydroperoxides are susceptible to crosslinking reactions. Bonds form between neighbouring fatty acid chains, resulting in a polymer network with high molecular weight. This polymerization results in stable and elastic films that do not deform readily [15].

Not all vegetable oils are drying oils. The ability to form a film depends on the presence, amount and type of unsaturated fatty acids in the oils. Precisely, when an oil contains at least 66% of unsaturated fatty acids it is considered siccative: the key fatty acids that confer the drying property are linoleic and linolenic acids. Linseed oil, for example, contains more than 50% of linolenic acid and about 20% of linoleic acid, while poppyseed oil is constituted by more than 70% of linoleic acid. Semi-siccative and non-siccative oils, such as cottonseed and castor oils respectively, are not able to form a solid film because they contain low percentages of polyunsaturated fatty acids.

The autoxidation is a free radical chain process consisting of three steps: initiation, propagation and termination [17] [18].

Initiation $RH \xrightarrow{hv} R\bullet + H\bullet$ (scheme 1)

Propagation $R\bullet + O_2 \rightarrow ROO\bullet$ (scheme 2)
$ROO\bullet + RH \rightarrow ROOH + R\bullet$ (scheme 3)

Termination $ROO\bullet + ROO\bullet \rightarrow ROOOOR$ (scheme 4)
$ROO\bullet + R\bullet \rightarrow ROOR + R$ (scheme 5)
$R\bullet + R\bullet \rightarrow RR$ (scheme 6)

In the initiation step, the hydrogen atom in the fatty acids or acylglycerols is removed and lipid alkyl radicals are produced. Heat, metal catalysts, and ultraviolet and visible light can accelerate free radical formation of fatty acids or acylglycerols. The resulting lipid free radical (R•) reacts with oxygen to form peroxy radicals (ROO•) and hydroperoxides (ROOH and ROOR). Termination occurs when radical species react with each other or with neutral species to form a non-radical product.

Together with the formation of the high-molecular weight crosslinked polymer, several low-molecular weight molecules are formed by the oxidative scission of chemical bonds. If the scission occurs on the glyceryl ester side of the radical, the fragment remains in the network; otherwise, if the scission occurs on the side of the hydrocarbon end of the fatty acid, the fragments are compounds with low molecular weight, which remain liquid inside the network [16]. Alkoxy radicals, RO•, evolve by fragmentation of adjacent C-C and C-H bonds to produce mainly aldehydes and ketones, which may evaporate from the oil matrix [19]. The aldehydes may be further oxidized to carboxylic acids. The most abundant dicarboxylic acid formed is azelaic acid, together with sebacic and suberic acids (Fig. 1.2).

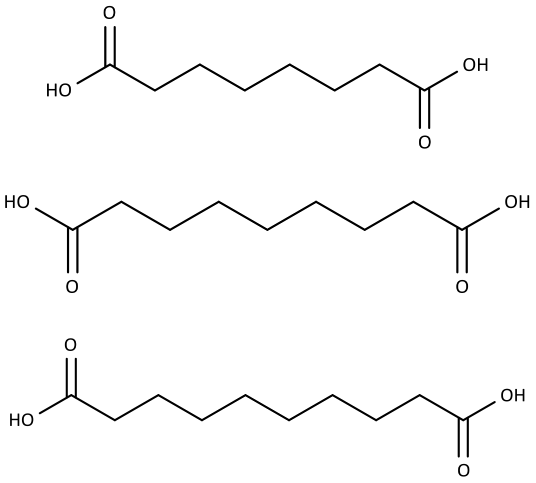

Fig. 1.2 From top to bottom: octanedioic (suberic), nonanedioic (azelaic) and decanedioic (sebacic) acids.

Azelaic acid derives from the oxidative scission of a double bond at C9 in unsaturated fatty acids (oleic, linoleic and linolenic acids).

The radical oxidation reaction is in competition with the di-hydroxylation reaction, which leads to the formation of di-hydroxyacids and hydroxyacids, the most common being the 9,10-dihydroxyoctadecanoic acid.

The photo-oxidative degradation of linseed oil may simply be considered as the continuation of the hardening process. After hardening, the dried oil shows a noteworthy stability, and degradation occurs only at long ageing times, through slow and progressive oxidation of the alkyl chains [16] or hydrolysis of the polymeric structure. The robustness of the oil-based film slowly decreases because it becomes more sensitive to humidity. Initially the film is constituted by a hydrophobic material, but with time its nature is modified: the chemical degradation due to oxidative and hydrolytic processes leads to the breaking of the polymer chains and to the formation of hydrophilic compounds (hydroxylated and carboxylated), which facilitate the penetration of water [20].

The set of the reactions described above leads to an heterogeneous mixture where the porous polymeric fraction, partially oxidized, is characterized by a wide range of molecular weights.

The processes taking place during the drying and the ageing of an oil paint are summarized in Table 1.1 [20] .

Table 1.1 Processes occurring during the drying of an oil paint, readapted from [20].

Process	**Disappearance**	**Formation**
polymerization and oxidation	unsaturated fatty acids	peroxy groups secondary stable alcohols dicarboxylic acids C_3-C_{10} inter-chain ether bonds inter-chain C-C bonds
reversible O_2 addition and isomerisation of allyl radicals	non-conjugated *cis* unsaturations	conjugated *cis-trans* and *trans-trans* systems
hydrolysis of TAGs	ester bonds	acidic groups

A relevant physical consequence of the drying of oils, besides the formation of a rigid material, is the visual effect of yellowing. This effect is particularly important in the art field, because it can lead to aesthetical alterations and a loss of the visual message/meaning of a painting. The yellowing of oil paint layers is a very complex phenomenon and has been the topic of several studies [11] [21] [22] [23] [24]. Liquid siccative oils employed as paint binders are colourless; the yellowing occurs during the hardening of the film. The possible causes of yellowing were summarized by Mallegol et al. [24] and are mainly four: the formation of conjugated compounds resulting from the decomposition of hydroperoxides, the formation of yellow compounds resulting from condensation reactions between fatty acids chains and throughout oil drying, the condensation of atmospheric contaminants containing nitrogen atoms with fatty acids chains, and, lastly, the presence of contaminants and impurities not eliminated during the refining processes of the oil.

Highly unsaturated drying oils like linseed oil tend to yellow the most. Thus, in white paint tubes, linseed oil is very often substituted with other types of oils, such as walnut or safflower oils, which have less tendency to yellow than linseed oil.

1.3.2 Composition of traditional and modern drying oils

The three main types of oils traditionally used by the Old Masters were linseed, poppyseed and walnut oil, which are three siccative oils, extracted from plant seeds and characterized by high levels of polyunsaturated fatty acids.

The fatty acids composition of these traditional oils is summarized in Table 1.2 [25] and it is referred to “fresh” oils, which have not started the drying process yet.

Table 1.2 Characteristic fatty acids of the traditional siccative oils used for painting [25].

Drying oil	**Fatty acid (%w/w)**				
	Palmitic	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**
Linseed	4-10	2-8	10-24	12-19	48-60
Poppy seed	9-11	1-2	11-18	69-77	3-5
Walnut	3-8	0.5-3	9-30	57-76	2-16

The range of oils found in contemporary artists’ oil paints is different to that of the Ancient Art. Although linseed oil is still frequently used, walnut oil is not very widespread today in commercial formulations and poppyseed oil is very rarely employed. Other oils such as sunflower, safflower, soy, castor, coconut, cotton, oiticica, peanut, rapeseed, tall and tung, sometimes mixed together, have partially replaced traditional oils [26].

In the present work we took into consideration six oils used in modern paint formulations, namely linseed, safflower, soybean, sunflower, tung and castor oils.

Linseed oil is considered to have the best drying properties, and it is still the most used oil in artists’ paints, even if it has the tendency to yellow. It is obtained from the dried ripe seeds of the flax plant (*Linum usitatissimum*) and has a distinctive fatty acid profile, containing an unusually large amount of α-linolenic acid . Specifically, the constituent fatty acids in a typical linseed oil are: the triply unsaturated α-linolenic acid (C18:3) about 50%; the monounsaturated oleic acid (C18:1) about 22%; the doubly unsaturated linoleic acid (C18:2) about 16%; the saturated palmitic (C16) and stearic acid (C18) respectively about 7% and 4% [3] [26] [27].

Safflower oil is obtained from the seeds of *Carthamus tinctorius*. There are two types of safflower that produce different kinds of oil: one high in monounsaturated fatty acids (oleic acid) and the other high in polyunsaturated fatty acids (linoleic acid). The former is currently used as edible oil, while the latter is used in paint formulations in the place of linseed oil, particularly with white pigments, as it does not have the yellow shade that linseed oil possesses. This paint material contains about 70% of linoleic acid and about 11% of oleic acid [26] [28].

Soybean oil is extracted from the seeds of the soybean (*Glycine max*). The major unsaturated fatty acids in soybean oil triglycerides are 7–10% α-linolenic acid (C18:3); 51% linoleic acid (C18:2); and 23% oleic acid (C18:1). It also contains the saturated fatty acids stearic acid (4%) and palmitic acid (10%) [26] [29].

Sunflower oil is the oil expressed from sunflower (*Helianthus annuus*) seeds. The British Pharmacopoeia lists the following profile [30]: palmitic acid: 4–9%; stearic acid: 1–7%; oleic acid: 14–40%; linoleic acid 48–74%. The high variability is due to the fact that several types of sunflower oils are produced, like the high oleic or high linoleic varieties.

Tung oil or China wood oil is a drying oil obtained by pressing the seed from the nut of the tung tree (*Vernicia fordii*). As a drying oil, tung oil hardens upon exposure to air. The resulting coating is transparent and plastic-like, a property exploited in most of its applications, which include wood finishing and the composition of oil paints and printing inks. The oil and its use are believed to have originated in ancient China and appear in the writings of Confucius in the 5th century [31]. Tung oil is constituted by about 80-90% of α-eleostearic acid, with small amounts of oleic and linoleic acids [26]. Eleostearic acid - (9Z,11E,13E)-octadeca-9,11,13-trienoic acid - is a conjugated fatty acid and its high degree of unsaturation gives tung oil its properties as a drying oil.

Castor oil is a vegetable oil obtained from the seeds of *Ricinus communis*. It is characterized by approximately 90% of ricinoleic acid [26]. Oleic and linoleic acids are the other significant components. Ricinoleic acid (12-hydroxy-9-cis-octadecenoic acid), a monounsaturated, 18-carbon fatty acid, has a hydroxyl functional group in 12. This functional group causes ricinoleic acid (and castor oil) to be unusually polar.

The fatty acid composition of the oils described above is summarized in Table 1.3 and it is referred to “fresh” oils, which have not started the drying process yet.

Table 1.3 Fatty acids composition of the oils used in modern oil-based paint media [26].

Oil	**Fatty acid (w/w%)**					
	Palmitic	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Other**
Castor	1	1	7	3		ricinoleic 87
Coconut	48	15	29	9		
Cotton	23	3	25	45	1	
Linseed	6	4	19	24	47	
Oiticica	6	10	14	21		licanic 48
Peanut			54	26		
Rapeseed	1	1	15	15	8	erucic 60
Safflower	7	3	18	69	4	
Soybean	11	4	23	54	8	
Sunflower	7	5	23	65		
Tall oil			46	41	3	rosin 8
Tung	2	2	5	3		α-eleostearic 87

1.3.3 Interaction with pigments and metal soaps formation

Pigments containing metal salts with different degrees of oxidation (i.e. Co, Mn, Pb) facilitate the curing of the oils. Other pigments, for example cinnabar (HgS), have a long-term negative effect, because they accelerate the oxidative degradation of the oils.

The reactivity between the oil binders and the pigments has been extensively studied, particularly in relation with the formation of metal soaps. It is known that metal salts, present as driers or pigments in painted artworks, can react with the triglycerides constituting the binder, leading to the formation of metal carboxylates (soaps) [32] [33] [34]. These saponification reactions have important consequences on both the visible appearance and the state of conservation of the paintings. As the saponification progresses, paintings appear darker due to gradual loss of the pigment hiding power [35] and carboxylates can appear in the form of extrusions on the paint layer. Boon et al. [36] [37] proposed a mechanism to explain the metal soap formation, which consist in a transition from a cross linked plant oil to a metal coordinated paint system.

The oils ageing study in the present work has been performed on mock-ups containing titanium white (TiO_2). Titanium white is a very popular white pigment in contemporary artworks that does not form metal soaps. After its discovery in 1821, and its mass production started in 1916, titanium white was one of the most popular pigments in the 20th century and it is still the most employed white pigment nowadays, especially after the interdiction of the use of lead pigments in household and artist paints. Titanium dioxide pigment is not exempt from having an influence on the binders, in fact it performs a multiple role in the durability of paint films. On the one hand, it acts as an oxidation catalyst in the photolysis of the binder, but on the other hand it provides protection by its ability to scatter and absorb UV light [38] [39].

1.3.4 Extraction methods and refining processes

Prior to extraction, the plant seeds are subjected to several treatments, such as cleaning, drying, size reduction, hull removal, heating/drying, flaking, and extruding. Oil can be extracted from these prepared seeds by either mechanical extraction or solvent extraction methods [40]. There are mainly three methods to extract the oils from the plant seeds:

1. raw or cold pressing method, where the seeds are mechanically pressed while the maximum temperature does not exceed 120 °C;
2. expelled pressing method, where oils are mechanically pressed from the botanical material at high pressure to obtain maximum yield and the temperature often rises above 120 °C;
3. solvent extraction, where a solvent, usually hexane, is employed and then removed by distillation from the oil. Palm, soybean, grapeseed and sunflower oils are typically solvent extracted.

The first method is mainly used when the oil is intended for edible purposes, while the other methods are employed in all the other industrial fields, including the production of paints.

After extraction, vegetable oils often undergo various treatments to improve some of their characteristics to be used as paint binders [41]. The refining processes used in antiquity were limited to few basic treatments, such as heating to obtain a pre-polymerized product, or adding driers, to speed the drying process [42].

The most common chemical treatments, still carried out nowadays, are heating in the presence of oxygen, and heating in the absence of oxygen, which leads to the formation of the “stand oil”, defined as an oil heated at high temperatures (300 °C) and in anaerobic conditions. Heating pre-treatments induce pre-polymerization and in some cases trans-esterification reactions. In the case of castor oil the reactivity of the 12-hydroxy group towards condensation is exploited to pre-polymerise the material. Stand oils or pre-polymerised oils dry more slowly but the film formed is more long-lasting, resistant, and less prone to yellowing.

As for the addition of the driers, the most common procedure in antiquity was the use of lead oxide, sometimes simply by heating the oil inside lead containers.

The modern procedures, instead, very often entail some refining steps: some oils undergo a refinement process in order to remove impurities, improve the color or texture, or stabilize the shelf life of the oil. Alkali refining is a very common treatment, in which the oil reacts with a weak base solution to saponify the free fatty acids into a soap. The oil is then centrifuged and washed with water until the pure oil remains.

1.3.5 Additives

Besides the oil and the pigment, commercial paint formulations very often contain a wide variety of miscellaneous additives [43]. Some examples include additives to modify surface tension, improve flow properties, or the finished appearance, increase wet edge, improve pigment stability, impart antifreeze properties, control foaming, control skinning, etc. Other additives include catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), biocides to fight bacterial growth, low cost oleochemicals including free fatty acids. Pigments are bought by paint manufacturers in the form of concentrated liquid emulsions that can be mechanically mixed with the binder containing up to 20% of surfactants and fluidizers. Thus, modern oil formulations cannot be compared to those used in antiquity, because the long term effects of these additives are unknown and ageing studies on modern paint materials are lacking. Other additives to be considered are those added by the artists themselves, for example resins, turpentine or extra oils. The same additives listed above are often found in synthetic paints, where the medium is a synthetic resin.

1.3.6 Commercial formulations

Very often companies do not publicize confidential information about the “ingredients” in their paint products. The main reason is to protect their “secret formulas” from the competitors, but this approach leads to a general lack of knowledge on the chemistry of modern paints.

The generic term “oil” is often employed to describe the type of binder on museums’ labels, but many paint manufacturers use mixtures of oils. Linseed oil is often mixed with other siccative or semi-siccative oils. For instance, blending with tung oil increases drying rate, while blending with a bodied oil or with an alkyd resin increases viscosity [44].

The declarations of the composition of oil-based paints by the main paint manufacturers for the European and International markets are reported in Table 1.4. As we can see, some manufacturers (Da Vinci, Grumbacher, Lefranc&Bourgeois) do not even declare which type of oil they use for their formulations, neither the type of treatments the oil has undergone. Some manufacturers specify the employed oil only for the more expensive brand of colours, but are secretive about the oils employed in the cheaper formulations. In other cases, they give an idea of the treatments underwent by the oils; for example Gamblin, RGH and Spectrum declare that their oil has been alkali refined. Other manufacturers label the oil as cold-pressed, pure, virgin, pharmaceutical grade, etc. to highlight the purity of their products, even if these are very generic terms and do not clarify the treatments performed to obtain such characteristics.

Table 1.4 Declarations of the oils used in paint formulations by the main paint manufacturers.

Paint manufacturer	**Country**	**Brand**	**Declaration**
BLOCKX	France	→ Huile extra-fine	poppyseed oil (linseed oil for iron oxides, earth pigments and blacks)
Da Vinci	USA	→ Oil Colors	/
Daler Rowney	UK	→ Artists' oil colour → Georgian oil colour → Graduate oil colour → Simply oil colour	linseed oil + beeswax / / /
Ferrario	Italy	→ Ferrario 1919 → Van Dyck → Idroil → Oil Master	/ / / /
Gamblin	USA	→ Artist grade oil color	alkali-refined linseed oil
Grumbacher	USA	→ Oil/Academy → Oil/Pre-tested → Max (water-miscible oil)	/ / /
Holbein	Japan	→ Artists oil colors → Ecolse oil	cold pressed linseed oil safflower oil
Kremer	Germany	→ Kremer oil colors	linseed oil (walnut oil for whites)
Lefranc & Bourgeois	France	→ Huile Extra-fine Lefranc → Huile Fine → Huile Louvre	/ / /
Lukas	Germany	→ 1882 Oil Colors → Studio Oil Colors → Berlin Water-mixable Oil Colors → Terzia Oil Color	cold pressed “pharmaceutical grade” linseed oil + sunflower oil + beeswax linseed oil + sunflower oil + beeswax linseed oil + sunflower oil + beeswax linseed oil + sunflower oil +

			beeswax
M. Graham	USA	→ Oil color	walnut oil
Maimeri	Italy	→ Maimeri puro → Rinascimento → Artisti → Classico → Mediterraneo → Maimeri olio → Olio HD	oil (?) without additives cold pressed walnut oil / does not contains waxes / / /
Michael Harding	UK	→ Oil colours	cold pressed linseed oil (poppyseed or walnut oil for whites)
Old Holland	Holland	→ Classic oil colours	cold pressed extra-virgin linseed oil
RGH	USA	→ Oil colors	alkali refined linseed oil without extenders
Schmincke	Germany	→ Mussini Oil Colours → Norma Professional → Akademie	linseed oil + dammar resin (added in colloidal solution) linseed oil linseed oil (sunflower oil for whites)
Sennelier	France	→ Huile Extra-fine → Huile Etude	safflower oil /
Spectrum	UK	→ Studio oil colours	refined linseed oil
Talens	Holland	→ Rembrandt → Van Gogh → Amsterdam → ArtCreation Expression	linseed oil and safflower oil linseed oil and safflower oil linseed oil and safflower oil linseed oil and safflower oil
Winsor&Newton	UK	→ Artists' Oil Colour → Winton Oil Colour → Artisan Water-mixable Oil Colour	linseed oil (safflower oil for whites) / linseed oil and safflower oil

The exact composition of the commercial paint formulations is frequently a trade secret. Furthermore, the formulations are constantly changing. The lack of information on the chemical composition of these products is thus challenging for conservation scientists. Therefore it is of paramount importance to study the oils used in modern paint media, to better understand their chemical composition and ageing pathways. It is of great interest to understand the mechanisms of the chemical evolution that occurs in these drying and semi-drying oils during long-term aging with light exposure.

1.4 Synthetic organic pigments

The majority of the paintings, even the contemporary ones, have a structure composed by layers, one of which is always a paint layer. The paint layer has typically a thickness of about

10 µm [45] and is generally composed by fine particles (pigments), dispersed in a transparent medium (binder) in the form of thin layers. These layers may be covered by a varnish. Thus, the pigment is the component that determines the colour to a greater extent, since the medium and the varnish are almost non-coloured.

The colour of each pigment depends on the property of the pigment itself to absorb the radiation at a specific wavelength; the colour is originated by the combination of the reflected radiation.

A distinction is usually made between a pigment, which is insoluble in its vehicle (resulting in a suspension), and a dye, which either is itself a liquid or is soluble in its vehicle (resulting in a solution). Dyes dissolve during application, losing their crystal or particulate structure in the process. The difference between pigments and dyes is therefore due to physical characteristics rather than chemical composition. In some cases, a pigment can be manufactured from a dye by precipitating a soluble dye with a metallic salt (“mordant”). The resulting pigment is called a lake pigment. Confusingly, the same compound can be referred to as a dye when discussed as an individual molecule, and as a pigment after it has been precipitated. Strictly speaking, all paints are made with pigments (organic or inorganic), not with dyes.

Pigments are classified as either organic or inorganic. Organic pigments are based on carbon chains and carbon rings. However, they may also contain metallic (inorganic) elements that help stabilize the properties of the organic component. Inorganic pigments, chemical compounds not based on carbon, are usually metallic salts precipitated from solutions.

Synthetic organic pigments are true pigments and not dyes, being insoluble in the medium in which they are dispersed. The molecular structures of synthetic organic pigments contain carbocyclic ring skeletons. Most of these ring systems are aromatic and their mobile electrons cloud is the chromophore of the pigment. They may also include metal ions or auxochromic functional groups [46]. The chromophore groups are unsaturated functional groups (-N=O, -N=N-, C=O, C=C, etc.). Auxochromic functional groups are not able to confer colour by themselves, but they increase the efficacy of the chromophores, bringing non-bonding electron pairs ($-NR_2$, -NHR, $-NH_2$, -OH, $-OCH_3$). The term “synthetic organic pigment” specifically refers to those pigments that are synthesised in a laboratory and must be distinguished from natural organic pigments obtained from plants or animal sources [46].

To the present, about 160 synthetic pigments have been mentioned in artists' colour catalogues and archives such as those from The Royal Talens, Schmincke, Winsor & Newton, Lefranc & Bourgeois, Ferrario and Liquitex, but the number of pigments that can be found in modern and contemporary works of art exceeds this number, due to the application of paints that were never intended specifically for artists' use, such as household or industrial paints. Moreover, several synthetic pigments were produced for only a few years and then withdrawn from the market due to poor lightfastness or toxicity. Synthetic pigments are classified in the Colour Index, a reference record for all the commercial dyes and pigments, created in 1924 by the Society of Dyers and Colourists. The pigments are recorded by a generic name and a number [47]. Today, the total number of synthetic organic pigments listed for different applications in the Colour Index International exceeds 500; when dyes are also considered, the number of synthetic organic colorants listed is a few thousands [48].

1.4.1 History

Traditionally, the pigments were obtained by using coloured earths or by grinding stones, but also by chemically manipulating the minerals to obtain specific products. Examples, in this respect, are, respectively, yellow and red ochres, lapislazuli, and Egyptian blue, obtained in 3000 b.C. by heating silica, malachite, natron, calcium carbonate and sodium carbonate.

Before the advent of synthetic organic pigments in the 19th century, synthetic inorganic pigments were first synthesized during the 18th century. These inorganic products began to appear on the market, gradually replacing some expensive traditional inorganic pigments. The first artificial inorganic pigment was Prussian Blue (1704), used in place of the more expensive ultramarine. The discovery of new elements played an important role in the synthesis of new inorganic pigments, one of the most important elements discovered being cadmium [49]. This discovery led to the production of cadmium yellow, started in 1840. Other important synthetic inorganic pigments are zinc white (1792), cobalt blue (1802), cerulean blue (1805), emerald green (1814).

The development of synthetic pigments goes along with that of synthetic paint binders. At the beginnings of 20th century the number of colours available was still limited, while nowadays the paint industry has a wide variety of pigments to choose from. The rapid development of synthetic chemistry during the 19th century, partly driven by the textile dying industry, led to the development of synthetic organic pigments.

In 1856, William Perkin, an eighteen-year-old student at the Royal College of Chemistry (London), was trying to produce a synthetic alternative to quinine from coal tar in his improvised laboratory at Greenford, Middlesex. By using potassium dichromate as an oxidizing agent, he produced a compound that, when dissolved, gave a purple solution. He had carried out an oxidation of aniline. At first he called the compound Tyrian purple, then changed the name to Mauveine, which later became Mauve. Mauve rapidly became the most fashionable colour for Victorian ladies and Perkin became the rich manufacturer of the dye [50]. At the time, all dyes used for colouring clothes were natural substances, many of which were expensive and labour-intensive to extract. Furthermore, many lacked stability, or fastness. The purple colour, which had been a mark of aristocracy and prestige since ancient times, was especially expensive and difficult to produce — the dye used, known as Tyrian purple, was made from the glandular mucus of certain murices. Its extraction was variable and complicated. Perkin instead obtained the dyestuff from coal tar, an abundant by-product of the process for making coal gas and coke. Perkin had synthesised the first organic dyestuff.

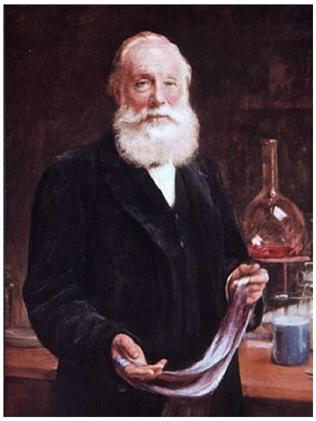
Fig. 1.3 Sir William Henry Perkin.

The colorant industry at that time was mostly based in Britain and France, but, as the 1860s progressed, there was a gradual shift of industrial development to Germany and Switzerland, in the formative days of the strong German empire [49]. At the time of mauveine's discovery, aniline was expensive. Soon thereafter, a new synthesis method reported in 1854 by Antoine Béchamp [51] was applied. The first azo dye was Aniline Yellow, produced in 1861 by C. Mene [52]. 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 these pigments were not tested sufficiently for fastness properties before their introduction on the market.

The Béchamp reduction for aniline enabled the evolution of a massive dye industry in Germany. Thus, Germany took the lead in the manufacture of synthetic organic pigments. A small group of German businessmen and chemists founded the Hoechst dyeworks (Meister, Lucius & Co.) at the village of Hochst, near Frankfurt, in 1863 [53]. In the same year, Friedrich Bayer & Co. was established in Barmen and within a few years had moved to nearby Elberfeld [54]. Since 1861, the Clemm brothers had been involved in the manufacture of magenta at Mannheim, and this became the nucleus of the *Badische Anilin & Soda Fabrik* (BASF), founded in 1865.

In the same years the approach to chemistry shifted from trial-and-error experimentation to solid chemical theory. This approach occurred partly thanks to the work of August Kekulé in 1865, who proposed the six-member carbon ring structure for benzene [49]. This discovery allowed chemists to have a better knowledge on the structure of organic molecules.

In 1868 the industrial production of the synthetic madder, alizarin, began and caused the total demise of the natural madder industry throughout Europe. Alizarin was synthesized by the German chemists Adolf Bayer, Carl Gräbe and Carl Lieberman, and still sold today as alizarin crimson (PR83 in the Colour Index). This compound is the same contained in the coloured dye that had been extracted from the roots of the madder plant (*Rubia tinctorum*) for centuries. It has high tinting strength and high transparency. It is a popular pigment with artists despite its relatively poor permanence rating.

In 1884 insoluble salts of azo dyes were discovered. They were true pigments, so they did not need to be adsorbed onto an insoluble carrier material.

In 1897 the industrial production of synthetic indigo, synthesized by Adolf Bayer, began. The triumph of the indigo synthesis foreshadowed the end of natural dyestuffs as a major economic force. By 1914 over 90% of all indigo used came from synthetic manufacturing routes. The demise of natural indigo and madder marked the end of an era for natural colorants. It was no longer economically viable to grow plants, collect lichens or crush rocks to obtain colorants [49].

During the first decade of the 20th century, the Hoechst company brought out the first modern organic pigment: “Arylide Yellow”, also known as Azo or Hansa Yellow. Red azo pigments were similarly developed and from the 1920s onwards these new pigments began to appear in artists' materials.

In 1936 the first phthalocyanine pigment, Monstral Blue, was introduced by ICI. Phthalocyanines quickly came to dominate the blue and green pigment markets in all applications.

The first quinacridones, a very important group of pigments, were introduced in the 1950's. They have excellent fastness and resistance properties and have been used in high-quality artists' materials.

In 1974 diketopyrrolopyrrole (DPP) pigments were synthesized [49] .

Today synthetic organic dyes and pigments dominate the colorant market and have almost completely replaced traditional natural organic materials. The dye market is nowadays centred in the Far East where the textile industry migrated from the United States and Europe to take advantage of higher economic growth rates and lower labour costs.

1.4.2 Pigments' physical-chemical properties

Pigments are generally described with their specific chemical and physical properties, the most important being the colour appearance, the refractive index, the particle size, the crystal structure, the lightfastness and the tinctorial strength. While the properties of soluble dyes are determined almost exclusively by their chemical constitution, the characteristics of pigments are largely controlled by their crystalline constitution, i.e., by their physical characteristics [55].

<u>Colour appearance</u>. The principal characteristic of a pigment is, obviously, its colour. Colour is essential because in many cases is the most important feature which define an artwork. Colour is not an objective property, because it changes depending on the light source (the illuminant), on the observer, and partly on the object dimensions and on the background. Colour has physical causes: it derives from the spectrum of light interacting in the eye with the spectral sensitivities of the light receptors. The human eye is only sensitive to the electromagnetic radiations between 380 and 780 nm, called the visible light. An object possesses the colour resulting from the combination of the wavelengths reflected. If an object does not absorb any of the wavelengths of the incident (visible) light, and it is opaque, all the wavelengths will be reflected (scattered), and it will appear white. An object absorbing all the wavelengths, will appear black. An object absorbing selective wavelengths, will achieve the sensation to the eye of a colour resulting from the wavelength reflected.

The colour of pigments and dyes arises from the absorption of light in the visible region and is generally the result of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. These compounds generally contains conjugated double bonds responsible of these transitions. Like typical organic molecules, dyes and pigments also absorb in the higher energy UV region of sunlight, usually producing higher energy π → π* transitions [56].

Colorimetry is the science that measures and systematically defines colour. Colours are defined by associating to each colour a series of numbers. Colorimetric measurements require the convolution of the illuminant's spectrum, of the reflectance spectrum of the object under study and of the standard response of the human eye (the observer). The convolution of these three parameters leads to the Tristimulus values X, Y and Z. From X, Y and Z it is possible to obtain the chromaticity coordinates (x, y and z), usually represented in a chromaticity diagram. The chromaticity diagram is supplanted for subtractive colour space[i] (pigments and dyes) by the CIELAB space. CIELAB is a reference colour space specified by the French *Commission Internationale de l'Eclairage* and it describes all the colours visible to the human eye. The three coordinates L*, a* and b* of CIELAB represent the lightness of the colour (L* = 0 yields black and L*= 100 indicates diffuse white), its position between red and green (a*, negative values indicate green while positive values indicate red) and its position between yellow and blue (b*, negative values indicate blue and positive values indicate yellow). Through the CIELAB values it is possible to express the colour difference ΔE*:

$$\Delta E^{*} = \sqrt{(\Delta L^{*})^2 + (\Delta a^{*})^2 + (\Delta b^{*})^2} \qquad \text{(equation 1)}$$

The human eye appreciates colour differences ΔE* > 1. Colour could be altered in time mainly by light and deposition of pollutants on the object surface.

Colour appearance is defined by three visual attributes that describe our colour perception under normal conditions of lighting and display. These are hue (the spectrum name of a colour, such as red, orange, yellow, green, blue and violet), lightness (the value of the colour in comparison to pure white) and chroma (or saturation, the richness or intensity of the colour in comparison to a colourless grey of the same lightness) [57]. The hue of a pigment is primarily defined by the molecular structure of its chromophores. For example, the hue of a red azo pigment lake carrying sulfonic acid functions is determined to a

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[i] An important distinction must be made between additive and subtractive syntheses: the additive synthesis concerns light, while the subtractive synthesis concern matter. The sum of the three primary colours (red, green and blue) in the additive synthesis gives white, while the sum of the three colours (magenta, yellow, cyan) in the subtractive synthesis gives black. The additive synthesis explains the colour appearance of pigments, whereas the subtractive synthesis is the reference synthesis when pigments or dyes are mixed together. For example, the mix of a yellow pigment with a magenta pigment will give a red colour.

considerable extent by the metal counter ion. The shift of hue from yellowish to bluish red increases in the Na → Ba → Sr → Ca → Mn series [55].

Refractive index & particle size. The refractive index (RI) of a pigment (optical medium) is a dimensionless number that describes how light, or any other radiation, propagates through that medium.

The interactions between light and a non-transparent matter (for example a paint layer) can be summarized as follow:

a) specular reflection, in which light from a single incoming direction is reflected into a single outgoing direction;
b) scattering, in which the incident light is reflected in multiple directions, for example by irregularities in the propagation medium;
c) selective absorbance.

In the case of pigments in a paint layer, the interactions involved are usually light scattering and selective absorbance, because the surface of a painting is most often non-specular, but rough and irregular. The scattering is directly related to the pigment's particle size. In general, the smaller the particle size, the greater the scattering. The scattering is also related to the ratio between the RI of the pigment and the RI of the binder: the higher this ratio, the more opaque the paint film.

Generally, inorganic pigments have a higher RI than organic pigments. Consequently, most inorganic pigments are opaque, whereas organic pigments are semi-transparent.

To conclude, the more a pigment is finely grinded, the higher its RI compared to the medium, the greater the film ability to cover the ground layer.

The values of the RI ratio between some classes of pigments and a watercolour vehicle (gum Arabic) are reported in Table 1.5 [57].

Table 1.5 Values of refraction index for some classes of pigments, readapted from [57].

RI	pigment/vehicle RI ratio	Pigments classes
1.47	1	gum Arabic (watercolour binder)
1.4	0.95	phthalocyanine, arylide yellows
1.5	1.02	indanthrone blue
1.6	1.09	naphthol reds
1.7	1.16	perylene red, benzimidazolone yellows
2	1.36	quinacridones
2.5	1.70	titanium white

Whereas the RI of a compound cannot be altered, the pigment manufacturer can influence the particle size of pigments; consequently particle size selection has become one of the principal developments in pigment technology in recent years.

Particle size of pigment particles in paint is a critical parameter that affects surface finish. Typical ranges are:

- carbon black: 0.01 to 0.08 µm;
- organic pigments: 0.01 to 1.00 µm;
- inorganic pigments: 0.10 to 5.00 µm (e.g. TiO_2: 0.22 to 0.24 µm).

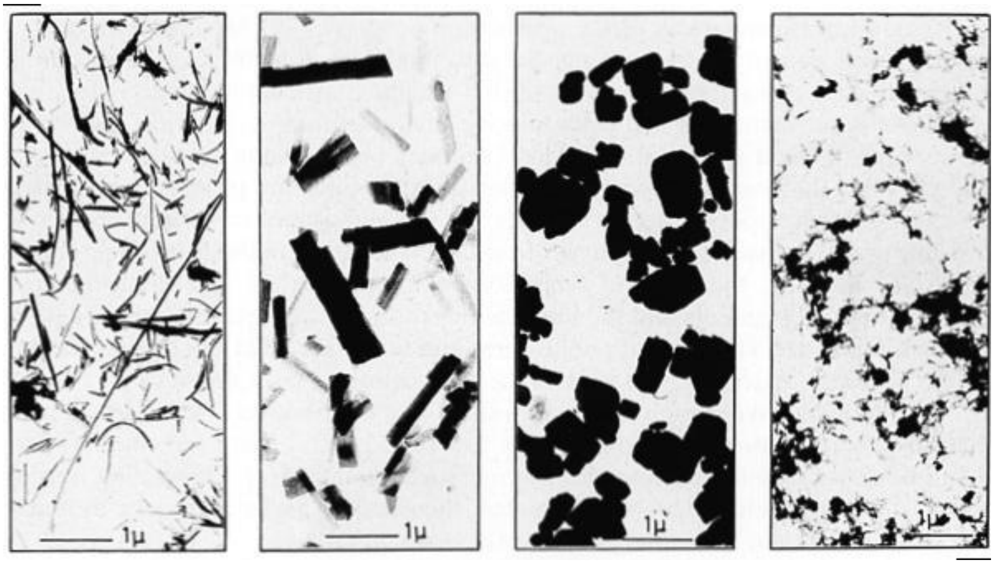


Fig. 1.4 Examples of crystal forms of organic pigment particles [55].

Inorganic pigments have a much larger average particle size than organic pigments. The optimum particle size needed to achieve maximum light scattering – resulting in opacity – is between 0.4 and 0.8 µm. More precisely, pigments should be described by a particle size distribution. For surface energy reasons, with the decreasing of the particle size, the tendency to agglomerate and form crystallites increases. Pigment particles may assume a variety of shapes, such as cubes, platelets, needles, or bars, as well as a number of irregular shapes [55]. Fig. 1.4 shows some examples.

<u>Lightfastness</u>. Lightfastness is the ability of a pigment to maintain its original colour appearance under exposure to light. There are several methods to measure the lightfastness of a material. One of the most used methods is the Blue Wool Scale [58], traditionally developed for the textile industry. The Blue Wool Scale consists of eight blue-

coloured woollen samples that differ in their fastness to light and are ranked from #1 to #8, #1 indicating extreme sensitivity to light, while #8 high resistance to light. These woollen standards are commercially available and can be exposed to light together with the sample under test. The lightfastness is measured by assessing which one of the eight strips on the blue wool standard card has faded to the same extent as the sample under test.

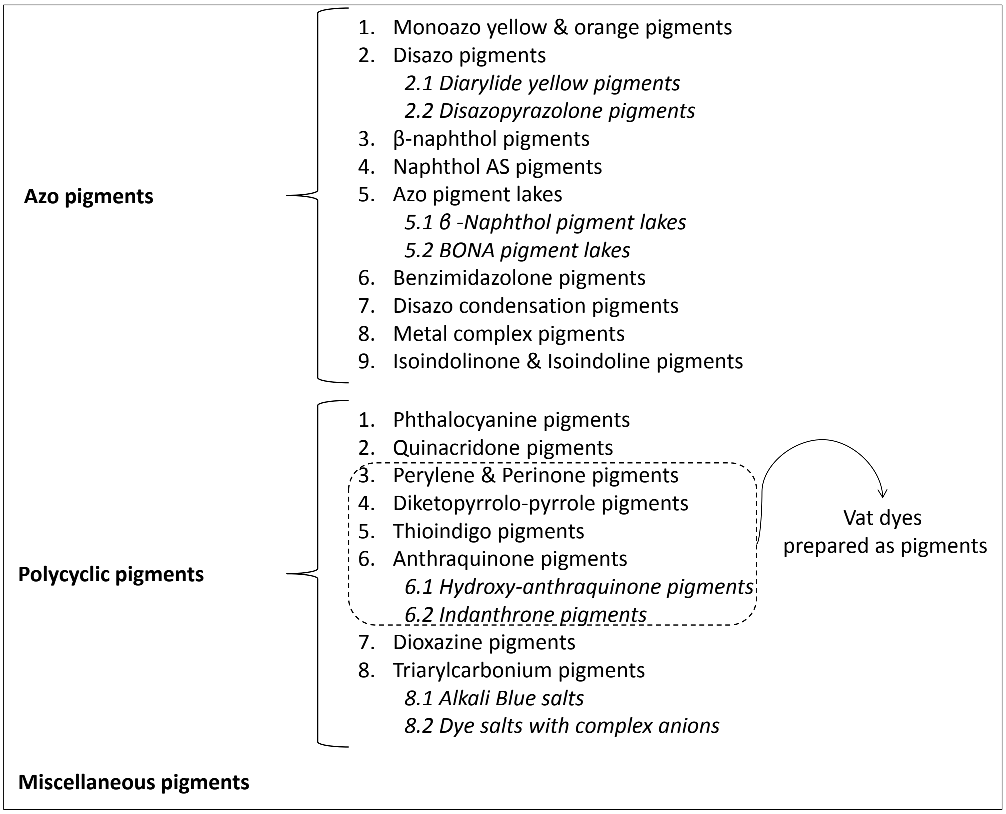
A relatively new method for evaluating the lightfastness is the use of a Xenon lamp equipped with specific filters, which reproduces the radiation of natural sunlight and can be used for accelerated ageing of the materials [59]. In a chamber called “weather-ometer”, where temperature and relative humidity are strictly controlled, the samples are exposed to the Xenon lamp at a specific distance. Lightfastness is evaluated by comparing the exposed samples to unexposed ones and the colour difference is expressed in CIELAB values.

The American Society for Testing and Materials (ASTM) has rated the lightfastness of several synthetic organic pigments, but the ratings are always referred to a pigment with a specific binder, for example with oil, or watercolour, or with an acrylic resin. The ratings have a 5 level scale: categories I and II include pigments with excellent and good lightfastness, respectively, while categories III, IV and V include pigments that should not be used in paints formulations, because they have fair, poor and very poor lightfastness, respectively.

Tinctorial strength. The tinctorial strength of a pigment is its colorant power in relation to its mass. In general, synthetic organic pigments have a higher tinting strength than inorganic ones.

1.4.3 Review of the classes of synthetic pigments

The most comprehensive text for synthetic organic pigments classification, synthesis, attributes and applications is *Industrial Organic Pigments*, by Willy Herbst and Klaus Hunger [55], where the pigments are classified according to their chemical structure. In the present work we adopted their classification, reported in Fig. 1.5.



Azo pigments

1. Monoazo yellow & orange pigments
2. Disazo pigments
    2.1 Diarylide yellow pigments
    2.2 Disazopyrazolone pigments
3. β-naphthol pigments
4. Naphthol AS pigments
5. Azo pigment lakes
    5.1 β -Naphthol pigment lakes
    5.2 BONA pigment lakes
6. Benzimidazolone pigments
7. Disazo condensation pigments
8. Metal complex pigments
9. Isoindolinone & Isoindoline pigments

Polycyclic pigments

1. Phthalocyanine pigments
2. Quinacridone pigments
3. Perylene & Perinone pigments
4. Diketopyrrolo-pyrrole pigments
5. Thioindigo pigments
6. Anthraquinone pigments
    6.1 Hydroxy-anthraquinone pigments
    6.2 Indanthrone pigments
7. Dioxazine pigments
8. Triarylcarbonium pigments
    8.1 Alkali Blue salts
    8.2 Dye salts with complex anions

Vat dyes
prepared as pigments

Miscellaneous pigments

Fig. 1.5 Classification of synthetic organic pigments according to their chemical structure.

Synthetic pigments can be divided in two large groups, the azo group and the polycyclic group. These two large groups are divided into many classes according to the chemical structure. All the pigments that do not belong to one of these two groups are classified as miscellaneous. Table 1.6 summarizes the structures, characteristics, date of introduction, major uses and important members of each class of synthetic pigments. The characteristics of the main classes are discussed in detail in the following paragraphs.

Table 1.6 Synthetic organic pigments and their characteristics, readapted from [46].

Pigment class	Structure	Characteristics	Dates of use	Major uses	Important members
Monoazo	acetacetarylamide coupling component	good lightfastness, poor solvent fastness	1910	artists’ paints	PY1, PY3, PY73, PY74, PY75, PY98
Disazo	two azo groups and the diaminodiphenyl skeleton	not as lightfast as monoazo, more solvent fast	patented 1911, not widely used until 1930s	printing inks	PO16, PY12, PY14, PY55, PY126, PY127
β-naphthol	2-hydroxynaphthalene coupling component	may be neutral or salts, not good fastness properties	PR1 in 1985, most others introduced in early 1900s	printing inks, artists’ materials	PR3, PR4
Naphthol AS	derivatives of 2-hydroxy-3-naphthoic acid	good lightfastness	first synthesized in 1911	automotive, architectural and artists’paints	PR2, PR7, PR9, PR112, PR146, PR170, PR253, PR256
Azo pigment lakes		poor lightfastness, good solvent fastness	first discovered 1899	artists’ paints, printing inks, plastics	PR48, PR49, PR52, PR53, PR57, PR63
Benzimidazolones	5-aminocarbonyl benzimidazolone grouping	good lightfastness and solvent fastness	first paptented 1960s	automotive, artists' paints, printing inks	PO36, PO60, PO62, PR175, PY154, PY175
Disazo condensation	aromatic diamino carbonamide likage	excellent lightfastness and solvent fastness	first patented 1950s	automotive, artists' paints, plastics	PBr23, PO31, PR214, PR242, PY128, PY166
Metal complex	metallized azo pigments	excellent lightfastness	developed 1945	automotive, artists' paints	PG10
Isoindolinone & Isoindoline	containing the isoindoline ring	excellent lightfastness and solvent fastness	introduced mid 1960s	automotive and industrial paints	PO61, PO66, PO69, PY109, PY110, PY130
Phthalocyanine	metal porphirins	excellent lightfastness and solvent fastness	blues introduced in 1935, greens 1938 and 1959	automotive, artists' paints, plastics, textiles	PB15, PB16, PG7, PG36
Quinacridone	based on linear trans quinacridone	excellent lightfastness and solvent fastness	introduced in 1955	automotive, artists' paints, plastics, textiles	PO48, PO49, PR206, PR207, PR209, PV19
Perylene & Perinone	diimides of perylene tetracarboxylic acid (Perylenes), naphthalene-1,4,5,8-tetracarboxylic acid (Perinones)	excellent lightfastness and solvent fastness	introduced 1950	automotive, industrial and artists' paints, plastics	PO43, PR149, PR178, PR179, PR194, PR224
Diketopyrrolo-pyrrole	based on 1,4-diketopyrrolo(3,4c)-pyrrole ring system	excellent lightfastness and solvent fastness	introduced 1980s	automotive and artists' paints, plastics	PR254
Thioindigo	structurally related to indigo	excellent lightfastness and solvent fastness	first discovered 1907	automotive and other paints, plastics, textiles	PR88
Hydroxy-Anthraquinone	anthraquinone skeleton	poor lightfastness and solvent fastness	chemical structure first described in 1963	artists’ paints	PR83
Indanthrone	anthraquinone skeleton	excellent lightfastness and solvent fastness	introduced in early 1950s	automotive and artists' paints, plastics, inks	PB60
Dioxazine	dioxazine type structure	excellent lightfastness, moderate solvent fastness	first synthesized 1928; patented as pigment 1952	automotive, artists' paints, plastics, inks	PV23
Triarylcarbonium	triarylcarbonium cations with complex ions	moderate lightfastness	patented 1913	printing inks	PR81, PV3, PV27

1.4.3.1 Azo pigments

Pigments belonging to the azo group contain the azo function (-N=N-). Azo pigments are by far the largest fraction of organic pigments on the market today thanks to their relativevely cheap synthesis process. The synthesis of azo pigments is based on a the diazotization of an aromatic amine, yielding a diazonium compound, which subsequently reacts with a coupling component. These pigments can be grouped according to the coupling component.

A brief description of the various classes of azo pigments follows.

Monoazo yellow & orange pigments. Yellow monoazo pigments were discovered by Meister Lucius & Brüning in Germany (later Hoechst AG) in 1909 and entered the market in 1910 under the trade name of "Hansa Yellows" [55].

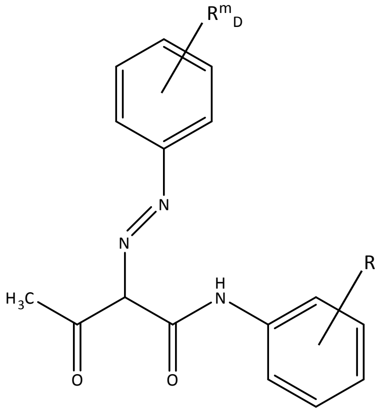


Fig. 1.6 General structure of the monoazo pigments. R_D: substituents of the diazo component; R_K: substituents of the coupling component; m, n: between 1 and 3. R_D and R_K = CH_3, OCH_3, OC_2H_5, Cl, Br, NO_2, CF_3.

They have good lightfastness and weather resistance but are susceptible to discoloration when heated. They were commonly used as inexpensive substitutes for cadmium yellows in paints and plastics. Winsor & Newton currently uses PY3, PY65 and PY74 in its high grade artists' oil colours. The general structure of the monoazo pigments is reported in Fig. 1.6.

Disazo pigments. The disazo pigments have the general structure shown in Fig. 1.7, based on the diaminodiphenyl skeleton. They were developed in 1940s and their colour range is limited, including mostly yellow and red hues. They are used mainly in the printing ink industry. Disazo colours have generally low solubility in organic solvents and fair to good lightfastness. The disazo class can be divided in two groups, depending on the coupling component: the diarylide yellows and the disazopyrazolone pigments. Diarylide yellows have a high tinctorial strength and a small particle size, compared to monoazo pigments. Although the diarylides are often more saturated and have higher tinting strength than the monoazo pigments, the doubling of the molecule also significantly reduces the lightfastness. The most important diarylide pigments are PO16, PY12, PY14, PY55, PY126 and PY127, while the most important disazopyrazolones are PO13, PO34, PR37, PR38 and PR41.

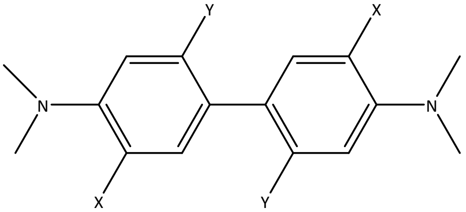


Fig. 1.7 Disazo pigments general structure. X = Cl, OCH_3 or CH_3 and Y = H, Cl or the diaminophenylene moiety.

β-naphthol pigments. Para Red (PR1), obtained in 1885 by coupling β-naphthol with diazotized 4-nitroaniline, is considered the oldest of all known synthetic organic pigments and was one of the first compounds successfully used in textile dyeing and printing [55]. Other pigments of this class include Toluidine Red (PR3), launched in 1905, chlorinated Para Red (PR4), which appeared in 1906, and Dinitroaniline Orange (PO5), introduced in 1907.

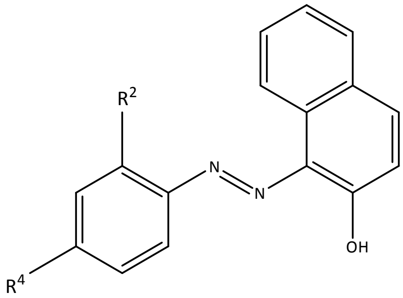


Fig. 1.8 General structure of the β-naphthol pigments.
R_2, R_4: H, Cl, NO_2, CH_3, OCH_3, OC_2H_5.

Most of these are still used nowadays in several applications. The coupling component of this class is the β-naphthol (2-hydroxynaphthalene) and the general structure is reported in Fig. 1.8. The commercially available pigments belonging to this class are PO2, PO5, PR1, PR3, PR4 and PR6.

Naphthol AS pigments. Naphthol AS is the most important group of azo pigments in the paint industry; these pigments were first synthesized in 1911. In the USA they are known as Naphthol Reds and their diffusion started in the 1940s only. Naphtol AS is a trade name of Hoechst AG, Germany. Naphthol AS pigments are derivatives of 2-hydroxy-3-naphthoic acid, where AS stands for Amid einer Saure. The general structure of this class is reported in

Fig. 1.9. Several Naphthol AS pigments, including PR112, PR146, PR170 and PR188, were extensively used in artists' paints [60].

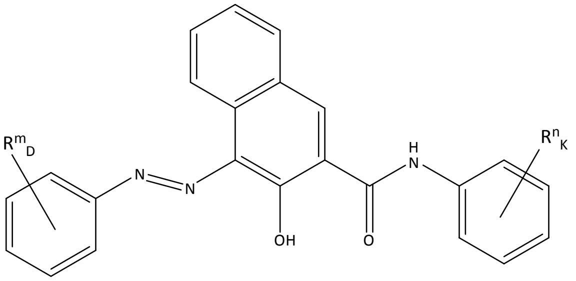


Fig. 1.9 General structure of the Naphthol AS pigments. $R_D = R_K$, $COOCH_3$, $CONHC_6H_5$, $SO_2N(C_2H_5)_2$. $R_K = CH_3$, OCH_3, OC_2H_5, Cl, NO_2, $NHCOCH_3$. m and n are numbers between 0 and 3.

Azo pigment lakes. Historically, "lakes" referred to the first type of synthetic organic pigments made from water soluble dyes by formation of insoluble Al^{3+} complexes with alum. Today these compounds are used as pigments after being precipitated by conversion into insoluble alkali earth or manganese salts [55]. We will focus on β-naphthol pigment lakes and BONA pigment lakes.

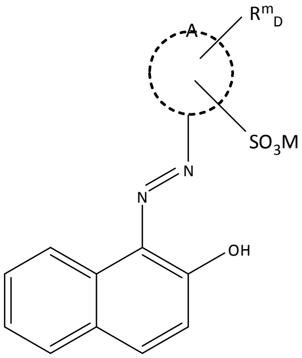


Fig. 1.10 General structure of the β-naphthol pigment lakes. A is typically a benzene or a naphthalene ring, R_D = Cl, CH_3, C_2H_5, COOM, m between 0 to 2, M is a metal ion, such as manganese, aluminium, or sodium.

β-naphthol pigment lakes originated with the discovery of Lithol red (PR49) by Julius at BASF in 1899 [61]. Lithol red is one of the earliest colorants specifically developed as a pigment rather than a dyestuff. The most important β-naphthol pigment lakes are PR49 (with its various metal salts), PR51, PR53, PO46. PR49 and PO46 are currently used as inexpensive industrial paints, especially in the USA. PR53:1 is found in inexpensive colour pencils and watercolours. The general structure of the β-naphthol pigment lakes is shown in Fig. 1.10. As a result of their salt character, β-naphthol pigment lakes are faster to solvents and more resistant to migration than β-naphthol pigments, but also less lightfast [55].

BONA pigment lakes derive their name from Beta-OxyNaphthoic Acid (BONA) which is used as a coupling component in their synthesis. The general structure of this sub-class is reported in Fig. 1.11. The most important BONA lakes are PR48, PR52, PR57, PR63. They have poor to good lightfastness depending on the substituents.

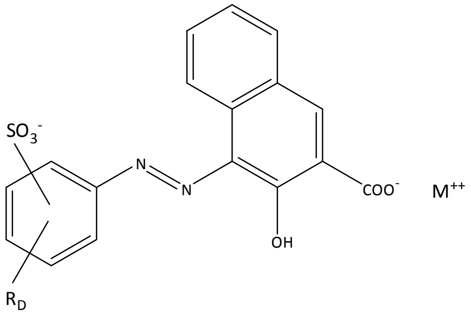


Fig. 1.11 General structure of the BONA pigment lakes. R_D = H, Cl, CH_3. M is a divalent metal ion such as calcium, barium, strontium or manganese.

Benzimidazolone pigments.

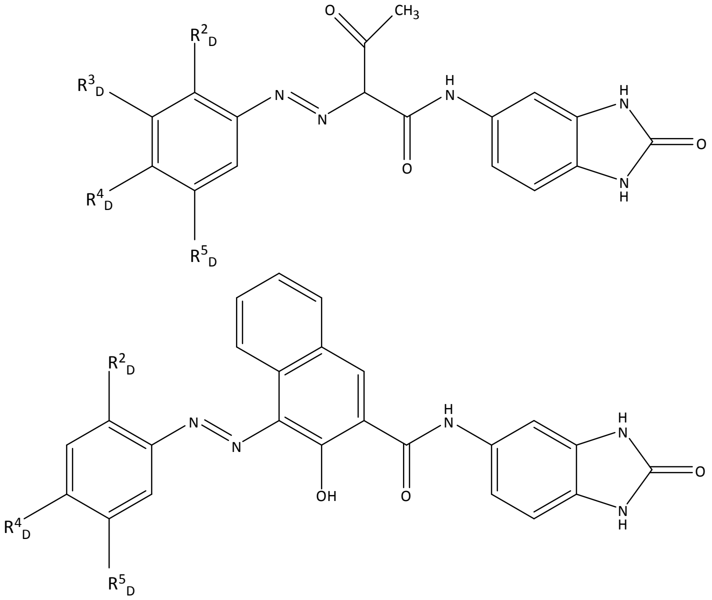


Fig. 1.12 General structure of the yellow and orange benzimidazolone pigments (top) and of red and brown series (bottom). R_D = Cl, Br, F, CF_3, CH_3, NO_2, OCH_3, OC_2H_5,COOH, COOAlkyl, $CONH_2$, $CONHC_6H_5$, $SO_2NHAlkyl$, $SO_2NHC_6H_5$.

The general structure of this class is shown in Fig. 1.12. Developed and patented by Hoechst in 1960, the benzimidazolones are monoazo pigments with the 5-aminocarbonyl benzimidazolone group. They provide a series of yellow, brown, red, and violet pigments that are very lightfast. They are relatively expensive, but are also among the most durable pigments used in artists' paints. Winsor & Newton, for example, employs a benzimidazolone pigment, PO62, for its "Winsor yellow" and "Winsor orange" oil colours. Another example is PR176, found in Royal Talens "Carmine" oil colour [60], and PBr25, found in several brown colours of the Winsor & Newton series.

Disazo condensation pigments. In the early 1950s, Ciba researchers succeeded in synthesizing red disazo compounds of relatively high molecular weight.

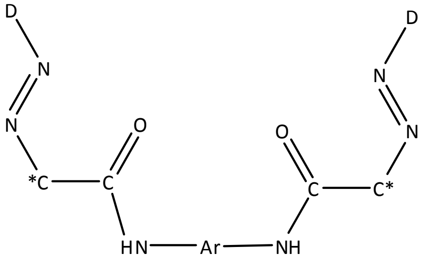


Fig. 1.13 General structure of the disazo condensation pigments. D = diazo component; C* = coupling component; Ar = bifunctional aromatic group.

These products were known as disazo condensation pigments. Such compounds may be structurally visualized as disazo pigments, formally composed of two monoazo units, which are attached to each other by an aromatic diamino carbonamide bridge [55]. Available hues range from yellow, orange, red and brown. PY128, for example, is found in Winsor & Newton artists' oil colours. In Fig. 1.13 the general structure of these pigments is shown.

Metal complex pigments. First developed around 1920, many metal complex pigments did not appear on the market until the late 1940's. Copper, nickel, and cobalt complexes are the most industrially interesting products within this class. PY150, a nickel complex pigment, is used in Winsor & Newton artists' oil colours.

Isoindolinone & Isoindoline pigments. This high-quality products class was introduced in the mid-1960s and is characterized by the isoindoline ring. The hues range from yellow (PY109, PY110, PY139, PY173, PY185), to orange (PO61, PO66, PO69) and red (PR260). PY139, for example, is employed for the Winsor & Newton "Indian yellow" high grade artists' oil colour. The structure of isoindolinone and isoindoline pigments is shown in Fig. 1.14.

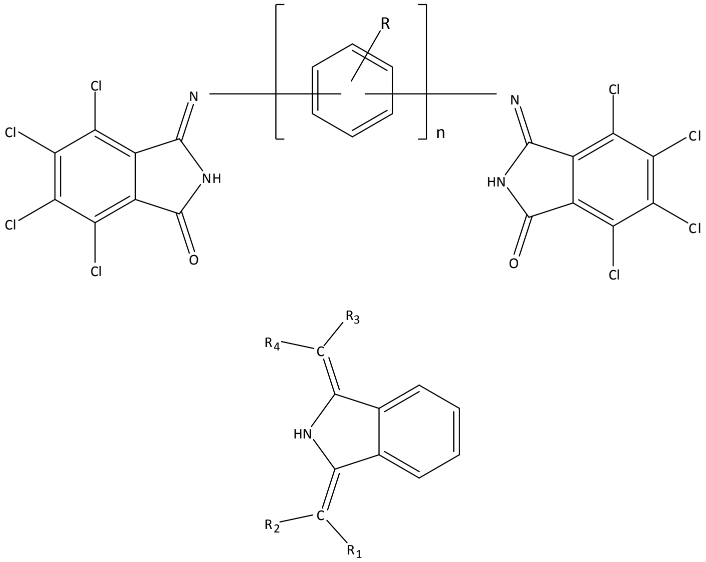


Fig. 1.14 General structure of the isoindolinone pigments (top) and isoindoline pigments (bottom). For isoindolinones, R = H, CH_3, OCH_3, CL and n =1. For isoindolines, R_1 through R_4 = CN, CONHAlkyl, CONHAryl, heterocyclic ring system.

1.4.3.2 Polycyclic pigments

The second big group of synthetic pigments, besides the azo group, is that of polycyclic pigments. Polycyclic pigments are characterized by condensed aromatic or heterocyclic ring systems. Except for the phthalocyanine pigments, they are more expensive than azo pigments.

Phthalocyanine pigments. Phthalocyanines are among the most important modern synthetic organic pigments used in artists' paint formulations and were adopted by many famous 20th century artists, including R. Lichtenstein, P. Delvaux, W. Kandinsky, Y. Klein, S. Francis, E. Kelly and B. Newman [62]. The general structure of phthalocyanine pigments is reported in Fig. 1.15 and it is similar to the chemical structure of porphyrin, the basis of haemoglobin and chlorophyll. Phthalo blues were first introduced in 1935, while phthalo greens in 1938 (chlorinated) and 1959 (chlorinated and brominated) [46]. Phthalo blue is the most important blue pigment synthesised since cobalt blue (1804) or ultramarine blue (1828); phthalo green is the most important green pigment since emerald green (1814) or viridian (1838). The hues range comprehends all the blue and green shades.

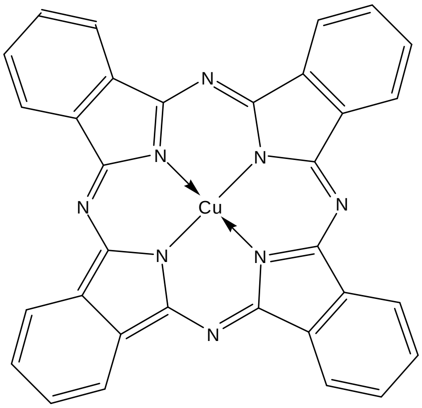


Fig. 1.15 General structure of the phthalocyanine class.

Quinacridone pigments. The first quinacridones were marketed in the mid-1950s as auto body paints and artists' materials and were promptly adopted by New York abstract expressionist painters. Quinacridones have excellent fastness and resistance properties and have been exploited since their appearance on the market in high-quality artists' materials [55].

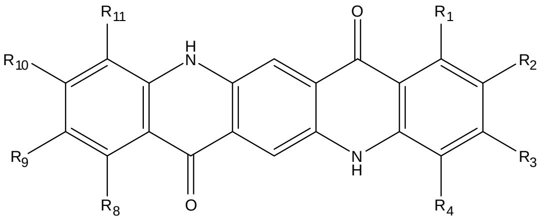


Fig. 1.16 General structure of the quinacridone pigments. R1 through R11 = H, Cl, CH_3.

The available hues range from yellow/orange (PO48, PO49) to red (PR122, PR202, PR206, PR207, PR209), and purple (PV19, PV42). PV19 is one of the most important and popular pigments of this class, sharing the violet pigment market only with dioxazine violet PV23. Another important quinacridone pigment is PR122. The general structure of quinacridone pigments is shown in Fig. 1.16.

Perylene & Perinone pigments. The group of perylene pigments is derived from perylene-3,4,9,10-tetracarboxylic acid. These compounds have been used as vat dyes since 1913 and were first introduced commercially as pigments in 1950. The general structure of these pigments is shown in Fig. 1.17. PR149 is currently used in “Winsor red deep” oil colour by Winsor & Newton.

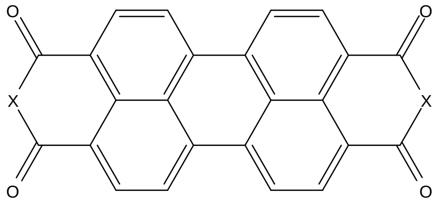


Fig. 1.17 General structure of perylene pigments. X = O or N-R, where R is H, CH_3 or a substituted phenyl moiety.

Diketo pyrrolo-pyrrole (DDP) pigments. DDP pigments are the most recent class of synthetic pigments introduced on the market. In the early eighties, Ciba-Geigy discovered a new type of heterocyclic pigments, based on a symmetric chromophore, the 1,4-diketopyrrolo(3,4c)pyrrole system, shown in Fig. 1.18 [55]. DDPs are based on this chromophore. They are widely used in the paint industry, for example PO73, or PR254 and PR255, which are now used in Winsor &Newton oil colours to replace PR188 (Naphthol AS pigment), used in previous formulations.

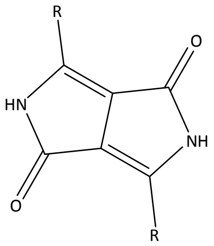


Fig. 1.18 The 1,4-diketopyrrolo(3,4c)pyrrole system, on which the DPP pigments are based. R = alkyl, aryl, Cl, Br, CF_3.

Thioindigo pigments. Thioindigo pigments were first synthesised in 1907 and are structurally related to indigo, the natural dyestuff derived from *Indigofera tinctoria*.

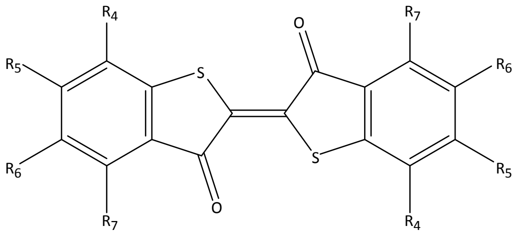


Fig. 1.19 General structure of the thioindigo pigments. R = H, Cl, CH_3.

The replacement of the NH groups of indigo by sulphur atoms leads to thioindigo. This class covers the violet, brown, orange and red shades. PR88 is the most important pigment of this class and is mainly found in watercolour paint materials, such as in “Thioindigo violet” watercolours by Da Vinci. Fig. 1.19 shows the structure of thioindigo pigments.

Anthraquinone pigments. This class groups those pigments sharing the 9,10-anthraquinone skeleton. One of the most popular pigments is PR83, alizarin crimson, an hydroxyanthraquinone pigment. PR83 (Fig. 1.20) is the synthetic counterpart of the natural madder lake, extracted from the root of *Rubia tinctorium*. Even if characterized by poor lightfastness, it is still employed even in high grade paints, such as in Winsor & Newton “Alizarin crimson” artists’ oil colours or in Royal Talens “Alizarin crimson” and “Madder lake D” Van Gogh oil colours.

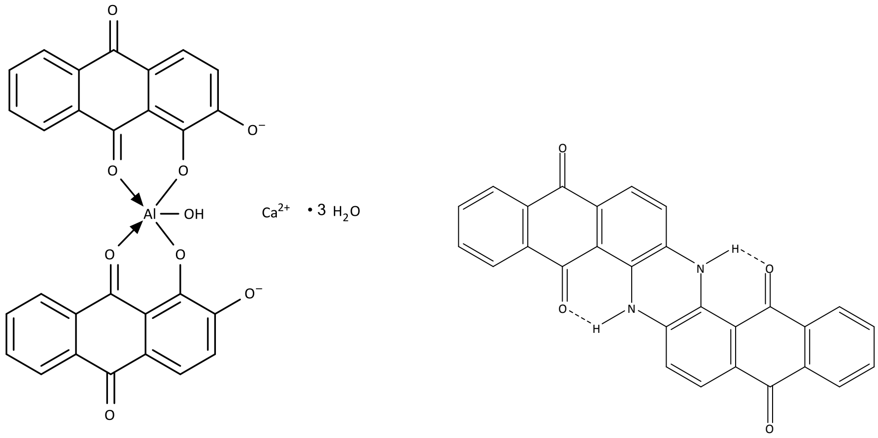


Fig. 1.20 Structure of PR83, an hydroxyanythraquinone pigment (left) and of PB60, an indanthrone pigment (right).

Another sub-class of the anthraquinone family is the indathrone group. In 1901, R. Bohn synthesized indanthrone and flavanthrone. Both compounds are thus among the oldest synthetic vat dyes [55]. Indanthrone blue PB60 (Fig. 1.20) is currently the only significant pigment of this class still used in the paint industry. It is produced from the 2-aminoanthraquinone and can be used with almost all binding media.

Dioxazine pigments. The dioxazine pigments were first synthesized in 1928, but patented as pigments only in 1952. The dioxazine molecule is derived from triphenodioxazine, a linear system of five anellated rings. PV23, Carbazole Violet, is the commercially most important pigment of this class and it is used in almost all media, from coatings and paints to plastics and printing inks. The structure of dioxazine pigments is shown in Fig. 1.21.

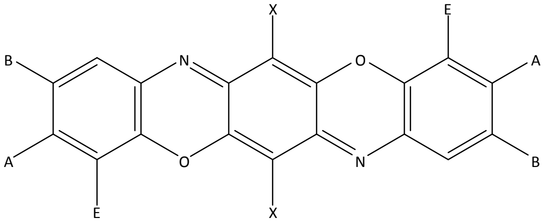


Fig. 1.21 General structure of the dioxazine pigments. A = ethoxy groups; B = acetylamino or benzoylamino moiety; X = chlorine or $NHCOCH_3$.

Triarylcarbonium pigments. These pigments were patented in 1913 and first used as dyes for textiles.

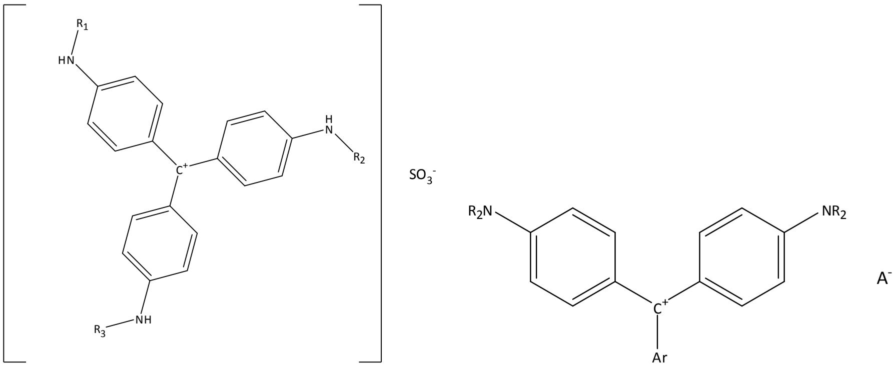


Fig. 1.22 General structures of the triarylcarbonium alkali blue salts (left) and of the triarylcarbonium dye salts with complex anions (right). For the alkali blue salts, R_1 and R_2 = $C_6H_4CH_3$, C_6H_5 and R_3 = H. For the dye salts, R = CH_3, C_2H_5. A = heteropolyacid, such as PMA (phosphomolybdic acid), PTA (phosphotungstic acid), PTMA (phosphotungstomolybdic acid), SMA (silicomolybdic acid) CF (copper ferrocyanide).

Triarylcarbonium pigments are obtained by precipitating basic dyes as lakes and are divided into two groups: inner salts of triphenylmethane sulfonic acids, and complex salts with heteropolyacids containing phosphorus, tungsten, molybdenum, silicon, or iron. The first group is characterized by poor lightfastness and limited solvent resistance. The second group includes the complex salts of basic pigments that are common in the dyes industry. The general structure of both groups in shown in Fig. 1.22. The available colours are blue, green, red and violet.

1.4.4 Photo-chemical degradation of synthetic pigments

The photo-chemistry of dyes and pigments can be understood with the use of the Jablonski diagram (Fig. 1.23).

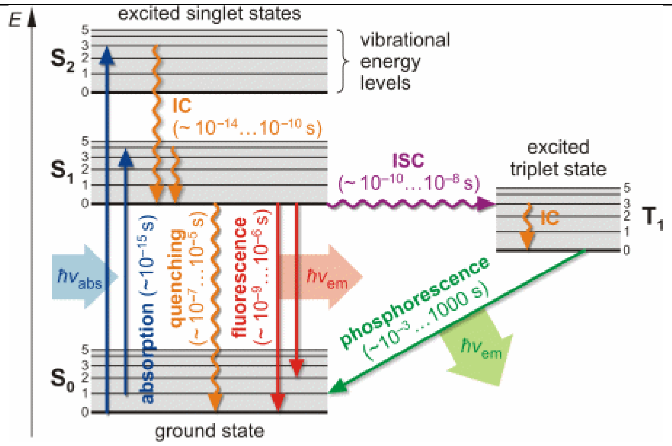


Fig. 1.23 Jablonski energy diagram illustrating the transitions between electronic states of a molecule. Waved lines mark non-radiative transitions. IC means internal energy conversion, ISC intersystem crossing. (Figure taken form [63]).

Absorption of light raises the molecule from the ground state S_0 to excited electronic states. Once there, the molecule tends to return rapidly to the ground state as excited states tend to be extremely short-lived. The absorbed energy can be lost in the following ways:

- non-emitting transitions due to intersystem crossing (ISC) or internal energy conversion (IC);
- emission of radiation, i.e. fluorescence or phosphorescence;
- photochemical reactions.

Photochemical reactions are at the basis of photo-induced degradation. In general, most conventional photo-chemical reactions originate from triplet states, which have lifetimes in the range 100 ns to 10 s, but also the lowest singlet state may be sufficiently more long-lived to induce degradation reactions [56].

The photo-degradation of synthetic dyes and pigments is originated from two types of mechanisms: photo-reductive and photo-oxidative pathways. In general, photo-reduction is associated with absorption of the UV radiation due to excitation to more reactive high-energy states, and the rate is not generally influenced by the presence of oxygen. The photo-oxidative route becomes progressively more important when the dye is subjected to lower-energy visible excitation in the presence of oxygen. In some cases oxygen can retard dye fading by re-oxidizing reduced molecules; in most cases, it can accelerate degradation via radical-initiated oxidation.

Oakes [56] outlined the general mechanisms of degradation of textile dyes, which, to a greater extent, are valid also for dyes and pigments used by paint manufacturers.

The photo-oxidation pathway may take place via singlet oxygen or by superoxide. In the photo-oxidation via singlet oxygen, if the dye is excited to a triple state (^{3}HD), it may undergo triplet-triplet annihilation with oxygen (which has a triple ground state) to produce singlet oxygen, which may initiate dye degradation.

$^3HD^* + {}^3O_2 \rightarrow HD + {}^1O_2$ (scheme 7)

$^1O_2 + HD \rightarrow$ decomposition (scheme 8)

In the photo-oxidation by superoxide, oxygen may participate to the photo-oxidation of dyes via electron-transfer reactions with electronically excited states (HD*) to generate superoxide. Subsequent reaction of superoxide with dye may lead to fading of the dye.

$HD^* + O_2 \rightarrow HD^{+\bullet} + O_2^{-\bullet}$ (scheme 9)

$O_2^{-\bullet} + HD \rightarrow$ decomposition (scheme 10)

Photo-reductive processes generally involve radicals, but high-energy light (UV or near-UV) is required to facilitate their formation via bond cleavage. The reaction pathways are illustrated in Schemes 11-13.

$HD^* + RH \rightarrow H_2D^\bullet + R^\bullet$ (scheme 11)

$H_2D^\bullet \rightarrow$ decomposition (scheme 12)

$R^\bullet + O_2 \rightarrow RO_2^\bullet$ (scheme 13)

Both $R^\bullet$ and peroxy radicals $RO_2^\bullet$ can cause dye degradation (Scheme 14). The radical $H_2D^\bullet$ may also react with RH to generate H_3D and $R^\bullet$.

$R^\bullet/RO_2^\bullet + HD \rightarrow$ decomposition (scheme 14)

Schemes 7-14 collectively represent the so-called type 1 photo-redox pathway, since the primary reaction products are radicals.

If the process shown in Scheme 15 occurs, the dye is not consumed but helps to initiate and propagate free-radical processes.

$H_2D^\bullet + O_2 \rightarrow HD + HO_2^\bullet$ (scheme 15)

However, although in such cases the dye may not be consumed directly, the high built-up of peroxides in the substrate can lead to indirect and irreversible oxidative bleaching of the dye, for example via scheme 16.

$O_2^{-\bullet} + HO_2 + H^+ \rightarrow H_2O_2 + O_2$ (scheme 16)

Metal species are involved in catalytic degradation by peroxide. They can generate hydroxyl radicals via Fenton chemistry (scheme 17), which can degrade dyes via electron or hydrogen atom abstraction or by addition to unsaturated groups or aromatic rings.

$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^{\bullet} + OH^{-}$ (scheme 17)

Radicals can also be generated by bond dissociation upon irradiation by light in the UV region (scheme 18), where $R_1^{\bullet}$ and $R_2^{\bullet}$ represent radicals generated from the dye itself. Subsequent photo-oxidative degradation proceeds according to schemes 13 and 14 as an overall photo-reductive degradation reaction.

$HD^{*\bullet} \rightarrow R_1^{\bullet} + R_2^{\bullet}$ (scheme 18)

The key factors influencing photo-stability of dyes are:

- the wavelength distribution of incident radiation;
- the degree of dye aggregation;
- the presence of moisture;
- the presence of metal ions, either inextricably bound in dyes or bound in impurities;
- the chemical and physical structure of the substrate;
- the particular dye structure [56].

The violet end of the visible spectrum has a detrimental effect for all the pigments. For red and yellow pigments, particularly, damage decreases as the wavelength increases [64].

The presence of moisture tends to enhance many photo-fading reactions, because it facilitates the diffusion of reactants, e.g. oxygen. Also the presence of metals strongly influences the photo-degradation of pigments: not only metal complexes can act as sensitizers for singlet oxygen, but they can also act as efficient quenchers for singlet oxygen or superoxide. On the other hand, dye aggregation on a metal centre has the effect of protecting the dye, with respect to oxidation, by rendering it less accessible.

The ease of photo-degradation of azo dyes tends to follow the order: blues > reds > yellows. This is in line with the order of decreasing conjugation, and hence chemical reactivity. The general susceptibility of dyes to oxidation follows the order: polyenes, poly- and aryl-methines > azos > phthalocyanines > anthraquinones, with the first two members of the series being readily oxidized by singlet oxygen or hydrogen peroxide [56].

1.5 Investigation techniques

This section gives a summary of the analytical techniques used for the characterization of synthetic organic pigments, oils used in paint formulations and synthetic polymers used as binding media. It focuses on how each technique works and which kind of information could be obtained. It is divided into three sections, namely non-invasive, non-destructive and micro-destructive techniques. The micro-destructive techniques section is further divided into the review of the literature about the analysis of lipids, synthetic organic pigments and synthetic polymers.

The identification of the materials in a work of art is of paramount importance, because it may improve the knowledge on the work of art itself, on the historical context, on the artist and on the painting technique. Moreover, it may allow to solve authenticity, attribution and conservation problems. The analysis of 20th century artists' oils paint and of synthetic pigments is fundamental mainly because these materials are not been extensively investigated yet. Moreover, a comprehensive ageing study is lacking, even if contemporary artworks often show very quick degradation rates.

The analysis of synthetic organic pigments presents some peculiar issues, particularly in complex matrices such as paint samples. The main reasons are: the wide range of compounds (hundreds of such pigments, compared to a handful of traditional ones), their small particle size, usually less than 1 µm, and the low concentration of the pigment(s) in paint formulations, sometimes less than 1% or lower, due to their high tinting strength. Moreover, organic pigments, both natural and synthetic, are subjected to photo-induced degradation, which may further reduce their concentration in the paint sample, as discussed above (see Section 1.4.4). Thus, their detection is more challenging, compared to that of inorganic pigments.

1.5.1 Non-invasive techniques

Non-invasive techniques do not require a sample collection from the object under study and therefore are completely safe to use, when dealing with high valuable objects such as works of art. Several of the most widely employed non-invasive techniques include photographic techniques (grazing light, trans-illumination, black/white IR, false-colours IR, UV fluorescence), IR reflectography, radiography, thermography, and tomography.

In the present work a recently developed non-invasive technique, Fibre Optics Reflectance Spectroscopy (FORS), was employed for one of the case studies presented in Chapter 4.

1.5.1.1 Fibre Optics Reflectance Spectroscopy (FORS)

One of the most promising non-invasive techniques used in the field of Cultural Heritage is Fibre Optics Reflectance Spectroscopy (FORS) [65] [66] [67] [68] [69], based on the use of optical fibres, which convey light upon the painting and then collect the light backscattered from the surface of the painting. Optical fibres allow the investigation of a wide range of the electromagnetic spectrum, from about 250 nm up to about 11,000 nm, and thus they cover the UV, Vis, near- and mid-IR ranges. FORS is a portable technique that allows *in situ* measurements. It is mainly employed for colour monitoring and for the identification of pigments by matching the spectra acquired on the paint surface with those in a suitable pigment database. The identification and subsequent discrimination among different pigments depend on the electronic structure of the pigment. Indeed, a variety of electronic (Crystal-Field, Charge-Transfer, Valence-Conduction band transitions) and vibrational processes (Overtones and Combinations transitions), falling within the Vis and near-IR regions, may produce typical intrinsic spectral features that appear in the absorption or reflectance spectra [70]. The IFAC institute of the National Research Council of Italy has recently published an on-line database of reflectance spectra of modern paint materials in the 200-2500 nm range [71], which can be used for the identification of traditional and modern pigments, even if it is not exhaustive. It must be noted, however, that FORS is a "bulk" analysis, being the obtained spectrum due to the sum of all materials on the investigated surface, and it is thus of difficult interpretation when mixtures (e.g. two or more pigments), or other materials with significant absorption in the investigated range, are present.

1.5.2 Non-destructive techniques

Invasive techniques require the collection of a sample from the object under study. Non-destructive techniques do not entail the destruction of the sample during the analysis, thus the sample can be analysed with the same technique or with different techniques afterwards. The non-destructive techniques most frequently employed in the field of Cultural Heritage analysis are Scanning Electron Microscopy (SEM-EDX), X-Ray Fluorescence spectroscopy (XRF), Fourier Transform Infrared Spectroscopy (FTIR) and micro-Raman spectroscopy. SEM-EDX and XRF achieve elemental analysis, while FTIR and Raman spectroscopies collect information on functional groups and are often used for a fingerprint approach by mean of comparison with databases.

SEM-EDX is mainly used for the analysis of paint samples, metallic objects, glasses, fibres, papyri [72] [73] [74] [75]. Moreover, it can be used to detect extraneous materials on the analysed surface, such as salts, atmospheric particulate, biological materials, which can lead to the degradation of a work of art.

XRF is extensively employed in the analysis of paintings, ceramics, manuscripts and archaeological findings for the identification of inorganic pigments [76] [77] [78] [79]. On the one hand, XRF is not useful in the case of synthetic pigments because they are organic compounds. Even in the case of the phthalocyanines, which contains copper, cobalt and chlorine ions, XRF cannot allow their ultimate identification, because these metals are present in very low amounts. On the other hand, XRF may be employed in the analysis of oil paint samples for the detection of inorganic compounds such as inorganic pigments, extenders, fillers, driers.

In the present work both FTIR and micro-Raman spectroscopies were employed; these techniques are described in detail below.

1.5.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

One of the most extensively used techniques in field of Cultural Heritage is Fourier Transform Infrared Spectroscopy[ii] (FTIR) [80] [81] [82] [83].

FTIR allows the identification of the functional groups characteristic of inorganic and organic compounds. The mid-IR (2.5-25 µm) radiation is typically used in this spectroscopy, and the IR absorbance is directly related to the transitions between vibrational energetic levels of the molecules. FTIR is employed in the identification of several organic and inorganic materials, including binding media, varnishes, grounds and pigments. The qualitative identification of the substances in a sample is generally based on the comparison between the spectra of the analysed sample and those of reference materials. It must be noted, however, that in the case of mixtures of many molecular species, being the spectra related to functional groups, materials belonging to the same class cannot always be clearly distinguished. Notably, linseed oil and poppyseed oil are not easily distinguished by FTIR as they contain triglycerides bearing the same functional groups. In pigments analysis, FTIR is mainly used for inorganic pigments. FTIR gives excellent spectra

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[ii] FTIR employs a Michelson interferometer, which scans all the frequencies of the incident radiation. In this way an interferogram in the time domain is obtained. The application of the Fourier transform to the acquired data transforms the interferogram into a spectrum in the frequency domain.

also for organic pigments and could readily differentiate them in their dry, powder form [3]. Unfortunately, other components in a paint film, such as the binding medium and the fillers, frequently mask the pigment’s diagnostic peaks, and consequently the technique often fails to detect the pigment in historical paint films.

A very useful set-up for the study of paint samples is the FTIR-ATR (Attenuated Total Reflectance), which enables samples to be examined directly in the solid or liquid state without further preparation. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered [84]. The FTIR-ATR set-up was used in this work to analyse synthetic organic pigments (see Chapter 3, Section 3.4.1.4).

1.5.2.2 Micro-Raman

Raman spectroscopy is a non-destructive spectroscopic technique widely used for the analysis of paint materials. Raman is based on the scattering phenomenon. The monochromatic radiation of a laser is sent on the sample under study and the scattered light is measured by a detector. The Raman effect, that is the inelastic diffusion of the light, is due to the modulation of the incident radiation by the normal vibrational modes of the molecules. By combining a microscope with the Raman spectrophotometer, a micro-Raman is obtained. In this case, the laser radiation is focused on a small spot (0.8-2 µm) of the surface under study. An increasing number of applications of Raman spectroscopy to art work characterization have been presented in recent years, and some publications contain databases of Raman spectra [48] [85] [86] [87] [88] [89]. In particular, the Raman technique has proven highly effective in detecting a wide range of synthetic organic pigments in paints, but can be employed also for the analysis of binding media [90]. In some cases, fluorescence phenomena due to binding media or varnishes may prevent the identification.

Some authors have proposed Fourier-Transform-Raman (FT-Raman) [91] [86] and Surface-Enhanced Raman Spectroscopy (SERS) [92] [93] for the analysis of pigments. The main advantage of FT-Raman over Raman microscopy with visible excitation is that, by employing infrared excitation, the problem of the fluorescence of materials under analysis can frequently be overcome. SERS, on the other hand, allows an enhanced Raman signal to be obtained, along with a substantial quenching of fluorescence, through the use of noble metal colloidal substrates.

In this work synthetic organic pigments were analysed with micro-Raman (see Chapter 3, Section 3.4.1.5).

1.5.3 Micro-destructive techniques

The non-invasive/non-destructive approach is often not sufficient to gain the information needed. In the field of Cultural Heritage there is the need of very sensible and selective techniques, because the samples are usually very small and constituted by complex mixtures of materials. Thus, in selected cases micro-destructive techniques, which require the collection of a sample from the object under study, are applied. Although the term destructive indicates that the sample is destroyed or corrupted during the analysis and thus cannot be employed for further investigations, the amount of sample needed is usually very small, normally less than 10^{-3} g.

Several micro-destructive techniques are currently applied to the analysis of Cultural Heritage, one big group being the “thermal” techniques, such as Thermogravimetry (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) [94] [95] [96] [97] [98].

Chromatographic techniques coupled with Mass Spectrometry (MS) are probably the most important array of micro-destructive techniques extensively employed for the characterization of organic materials in works of art and archaeological materials. In the present work they were used for the analysis of polymers, synthetic pigments and oils. In the following paragraphs they are described in detail.

1.5.3.1 Mass spectrometry and its coupling with chromatographic techniques

Mass Spectrometry (MS) is one of the most powerful analytical methodologies for identifying, structurally characterizing, and quantifying several classes of materials, ranging from low to very high molecular weight components. Mass spectrometry is the analytical technique that best meets the requirements of the analysis of artworks when molecular information is necessary, because it requires very small samples and it is able to provide valuable information about the nature of the materials analysed.

MS is based on the production of gas phase ions and on their separation according to their mass-to-charge (*m/z*) ratios [99]. The sample is introduced into the spectrometer and its molecules are ionized. After the ionization, the molecules are accelerated into the analyser of the MS, which operates in high vacuum conditions. The analyser uses dispersion methods to separate the ions on the basis of their *m/z* ratios. Finally the detector reveals the ions. A schematic diagram of a mass spectrometer is reported in Fig. 1.24.

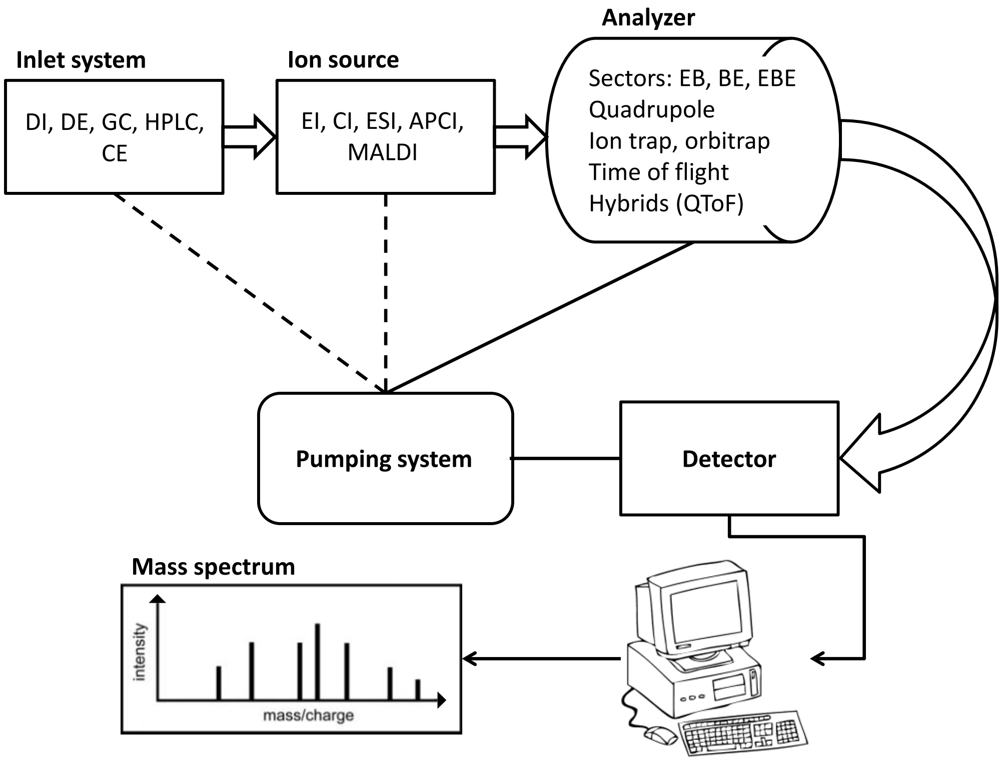

Fig. 1.24 Mass spectrometric approach, readapted from [99]. DI, direct inlet; DE, direct exposure; GC, gas chromatography; HPLC, high performance liquid chromatography; CE, capillary electrophoresis; EI, electron ionization; CI, chemical ionization; ESI, electrospray ionization; DESI, desorption electrospray ionization; APCI, atmospheric pressure chemical ionization; MALDI, matrix-assisted laser desorption ionization; B, magnetic analyser; E, electrostatic analyser.

With regard to the mass analyser of the spectrometer, the most common are the ones based on a magnetic field or on electrostatic field, quadrupole, ion traps and Time of Flight (ToF) types.

In magnetic sectors the ions of a certain *m*/*z* value will have a unique path radius which can be determined if both magnetic field magnitude *B*, and voltage difference *V* for region of acceleration are held constant.

The electrostatic sector analyser, instead, consists of two curved plates of equal and opposite potential. As the ion travels through the electric field, it is deflected and the force on the ion due to the electric field is equal to the centripetal force on the ion. Here the ions of the same kinetic energy are focused, and ions of different kinetic energies are dispersed.

The quadrupole analyser consists of four cylindrical rods, set parallel to each other. Each opposing rod pair is connected together electrically, and a radio frequency (RF) voltage is applied between one pair of rods while a direct current (DC) voltage is applied to the other two rods. Ions travel down the quadrupole between the rods. Only ions of a certain *m/z* ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods. This permits the selection of an ion with a particular *m/z* and the acquisition of SIM (Selected Ion Monitoring) chromatograms.

In the ion trap analyser ions are focused using an electrostatic lensing system into the ion trap. An electrostatic ion gate pulses open (-V) and closed (+V) to inject ions into the ion trap. The pulsing of the ion gate differentiates ion traps from "beam" instruments such as quadrupoles, where ions continually enter the mass analyser. After entry, the electric field in the cavity causes the ions of certain *m/z* values to orbit. As the radio frequency voltage increases, heavier mass ion orbits become more stabilized and the light mass ions become less stabilized, causing them to collide with the walls, and eliminating the possibility of traveling to, and being detected, by the detector. The time during which ions are allowed into the trap, termed the "ionization period", is set to maximize signal. The ion trap is typically filled with helium to a pressure of about 1 mtorr. Collisions with helium dampens the kinetic energy of the ions and serve to quickly contract trajectories toward the centre of the ion trap, enabling trapping of injected ions. Trapped ions are further focused toward the centre of the trap through the use of an oscillating potential applied to the ring electrode.

ToF analysers separate ions by time. The separation is based on the kinetic energy and velocity of the ions. The ion beam formed in the source is accelerated towards the flight tube by the application of an electric field. Since the kinetic energy E_k is related to the mass and the potential energy E_p to the applied field and the charge, the time for each ion to reach the detector in high vacuum conditions (10^{-7} torr) will depend on the square root of its m/z.

MS detectors can be coupled with several separation techniques, as seen in Fig. 1.24. These separation techniques and their coupling with MS allows the study of complex mixtures, that are generally encountered in the field of Cultural Heritage.

In the chromatographic techniques, a mixture of analytes is dissolved in a fluid called the mobile phase, which carries it through a structure (a column) holding the stationary phase. The various constituents of the mixture elute and separate, reaching the detector at different, highly reproducible times. The separation is based on the differential partitioning of the single analytes between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation. The separation can be improved by changing the temperature of the stationary phase, the pressure of the mobile phase or its composition. The time between the injection (time zero) and when elution occurs is referred to as the retention time (RT).

In Gas Chromatography (GC) the typical ionization methods are electron ionization (EI) and chemical ionization (CI), EI being the most common for Cultural Heritage analysis. In EI the molecules are bombed with a high energy (70 eV) electronic beam. The result is the ionization of the molecules, but also the production of fragments caused by the breaking of chemical bonds. CI is another type of ionization where the analytes are subjected to an excess of a ionised reagent gas and the ions are produced by a proton transfer mechanism. The first type of ionisation is called ‘hard’, because it causes an extensive fragmentation and the molecular ion may be undetectable, while the latter is called ‘soft’.

Spray ionization techniques such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) are the typical ionization devices for the High-performance Liquid Chromatography (HPLC) with MS. ESI is produced by forcing a liquid to pass through a capillary, which generates a spray; simultaneously an electric field applied to the capillary causes the ionization of the molecules. ESI mass spectra are characterized by base peaks due to the pseudomolecular ions, i.e. protonated/deprotonated molecules and adducts, such as $[M+H]^+$, $[M+Na]^+$, $[M+HCOO]^-$, $[M-H]^-$. APCI is also carried out at atmospheric pressure. The APCI interface nebulises the LC column effluent in a similar way as ESI, but the ionisation is promoted by a cloud of electrons emitted from the tip of a corona electrode pin. The eluent molecules, which are in vast excess compared to the analyte, are ionised and act as a reagent gas. Analyte molecules are ionised and are subsequently sampled into the nozzle-skimmer region of the mass spectrometer in a similar fashion as described for ESI. APCI is mainly used for nonpolar and relatively nonpolar compounds with a molecular weight of less than 1500 Da, generally giving mono-charged ions.

Matrix-assisted laser desorption ionization (MALDI) is a two-step desorption ionization, produced by a laser beam and assisted by a matrix. It is usually employed for the analysis of high molecular weight organic molecules. ToF is the mass spectrometer most widely used with MALDI ionization, mainly due to its wide *m/z* operating range and high resolution.

Prior to analysis, the sample is added with a suitable matrix. First, desorption is triggered by a UV laser beam. Matrix material heavily absorbs UV laser light, leading to the ablation of the upper layer (~1 µm) of the material. Secondly, the analyte molecules are ionized (more accurately, protonated or deprotonated).

MS can be also used by directly inserting the sample in the ion source with a direct inlet set up. Direct Temperature-resolved Mass Spectrometry (DTMS) is essentially a desorption-pyrolysis mass spectrometry. This technique requires very small amounts of untreated sample (a few nanograms), and can be performed rapidly. The sample, suspended in a suitable solvent, is applied onto a rhenium or a platinum/rhodium (Pt/Rh 9:1) filament of the direct insertion probe. The probe is inserted in the ion source and inductively heated at a rate of 0.5-1 A min^{-1} to a maximum temperature of 800 °C. The desorbed products are ionised and directly analysed by MS or MS/MS. This technique is useful and rapid for obtaining a fingerprint of solid samples.

1.5.3.2 Analysis of lipids

Lipid characterization, together with the study of lipid degradation processes, is an important research area in conservation science. The analysis of lipids in Cultural Heritage is routinely carried out by gas chromatography/mass spectrometry (GC/MS) [10] [25] [100] [101] [102] [103] [104] [105] [106] [107], after suitable sample treatments. GC based methods are highly efficient and deliver additional structure information in combination with mass spectrometry. Lipids are generally identified in paint samples by evaluating characteristic ratio values of fatty acids (FA) amounts and comparing them with naturally or artificially aged reference paint layers. Thus, for the GC analysis of lipids, hydrolysis of the triglycerides and derivatization for enhancing volatility of free fatty acids are mandatory. In particular, acidic hydrolysis [108] [109] or alkaline saponification [102] [103] [104] have been proposed in the literature. Fatty acids and dicarboxylic acids are transformed into the corresponding 2-propyl esters [108], methyl esters [110], ethylcloroformate derivatives [109], *N*-tert-butyldimethylsilyl-*N*-methyltrifluoroacetamide derivatives [102] [104] or *N*,*O*-bis(trimethylsilyl)trifluoroacetamide derivatives [111]. Colombini and coworkers developed a combined GC/MS analytical procedure for the characterization of glycerolipid, waxy, resinous, and proteinaceous materials in a unique paint micro-sample [106] [105]. This procedure is based on a multistep chemical pre-treatment (solvent extractions and microwave-assisted chemolysis) that is able to separate the various organic components of the sample into different fractions, which are suitably treated and derivatized before analysis. In the present work, the GC/MS analytical procedure was derived from this previously published combined procedure, slightly modified and adapted for the analysis of the lipid-resinous fraction only.

Another technique employed for the analysis of lipids is Py-GC/MS with *in situ* derivatisation. Pyrolysis entails the thermochemical decomposition of organic materials at elevated temperatures in the absence of oxygen. The pyrolytic reactions usually take place at temperatures higher than 250-300 °C, commonly between 500 °C and 800 °C. The interpretation of the pyrograms is carried out by comparison with libraries of reference materials analysed in the same conditions. The most common approach is to use thermally assisted reactions, where the sample is pyrolysed in the presence of a suitable derivatising reagent, which transforms polar functionalities into less polar moieties, thus increasing the volatility of the analytes. Thermally assisted hydrolysis and methylation (THM) and thermally assisted silylation are the most commonly used reactions [112]. Tetramethylammonium hydroxide (TMAH) is one of the most commonly used reagents for online methylation of acidic and alcoholic moieties. Other reagents commonly used are trimethylsulfonium hydroxide, tetramethylammonium acetate, or silylating agents such as *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and hexamethyldisilazane (HMDS) [112] [113].

Lipids are routinely analysed for applications in food analysis with HPLC/MS to obtain their triacylglycerols (TAGs) profile [114] [115] [116] [117] [118] [119]. Mass spectrometry detects TAGs and also identifies positional isomers. The ion sources most frequently employed for this purpose are ESI, MALDI and APCI. ESI tandem mass spectrometry and multi-stage mass spectrometry (MS^n) have also proved very informative for the analysis of TAGs. The analysis is usually carried out in a non-aqueous reversed phase HPLC with solvents like methanol/*iso*-propanol/hexane [120], dichloromethane/acetonitrile [121], dichloromethane/acetonitrile/propionitrile [122], pure propionitrile [123], acetone or chloroform with acetonitrile [124], or methanol/*iso*-propanol [114] [125]. The sample pre-treatments are usually quicker than those required for GC/MS analysis: the analyte is generally dissolved in the mobile phase prior to injection.

Capillary electrophoresis (CE) is another extensively used technique for the analysis of the fatty acids content of lipids [126] [127]. CE has been recently employed for the determination and characterisation of long-chain fatty acids and for the analysis of the dicarboxylic acids formed as degradation products during the drying process [128].

Other techniques employed in lipid analysis are MALDI-MS [129] [130] and DTMS [19] [118]. In the present work the HPLC-ESI-Q-ToF was employed for the analysis of oils (both raw and aged as paint films) used in modern oil-based paint media.

1.5.3.3 Analysis of synthetic organic pigments

Synthetic pigments are not generally analysed with GC/MS, being the analytes difficult to vaporize at temperatures suitable for GC. Moreover, HPLC techniques, widely used for the characterisation of traditional organic dyes obtained from plants or animal sources, food colorants, cosmetic dyes and soluble dyes in general, are not widely employed for the analysis of synthetic pigments, because they are often insoluble in the majority of the solvents.

Laser desorption/ionisation mass spectrometry (LDI-MS) is one of the most suitable mass spectrometric techniques for the analysis of synthetic pigments [131] [132] [133].

Other MS-based techniques extensively used for synthetic pigments analysis are DTMS [131] [134] [135] and MALDI-MS [136] [137] [138].

Some authors have proposed pyrolysis coupled with GC/MS (Py-GC/MS) for the analysis of synthetic organic pigments [3] [139] [60]. Synthetic pigments are usually analysed without any derivatising reagent. It must be noted, however, that while extensive Raman libraries already exist, no equivalent library obtained with chromatographic techniques is available, mainly because authors have analysed only few classes of synthetic pigments. Thus, in this study, 76 synthetic organic pigments were analysed with Py-GC/MS to obtain a comprehensive library of characteristic pyrolysis products, to be used as a reference.

1.5.3.4 Analysis of synthetic polymers

GC/MS may be used for the analysis of most modern paint media, but not for all synthetic polymers, due to their high molecular weight. For the analysis of synthetic polymers many authors use Py-GC/MS [7] [140] [141] [142] [143] [144]. The pyrolysis step solves the volatility problem, because the polymers are broken down into volatile fragments, which can be injected and separated by GC. Synthetic polymers may be analysed both with or without the presence of reagents. Other MS-based techniques employed for the analysis of synthetic resins are DTMS [3] [131] [136] and LDI-MS [131] [136].

1.5.4 Accelerated ageing

Accelerated ageing tests are destructive measurements carried out to assess the chemical and/or physical stability of a material, to estimate its long-term stability and to elucidate the chemical reactions involved in the degradation process [59]. The final goal of an accelerated ageing experiment is usually to acquire suitable knowledge to prevent the degradation of a certain material. The material under test can be exposed to rapid (but controlled) changes in temperature, humidity, pressure, strain, etc. Polymers, for example, are often kept at elevated temperatures or exposed to light, in order to accelerate their chemical breakdown.

Colorants and dyes are often subjected to photochemical ageing tests, to assess their lightfastness, i.e. to determine if the dye will fade and the extent of the fading process. The preservation of chromatic properties by a colorant over a long period of years is essential in a work of art. Thus, lightfastness is a fundamental aspect for paint manufacturers, who usually have to declare the resistance to light of the pigments employed in their formulations. The American Society for Testing and Materials (ASTM) has listed four standard test methods for lightfastness of colorants used in artists' materials [145]. The first and second methods are the exposure in southern Florida and in Arizona - respectively - to natural daylight, filtered through window glass. The third and fourth methods consist in exposing the sample under study in a non-humidity controlled and in a humidity controlled – respectively - Xenon-arc device simulating daylight, filtered through window glass. The instrument used in the last method is called weather-ometer. These test methods are used to approximate the colour change (ΔE^* of the CIELAB colour space, see Section 1.4.2) that can be expected over time in colorants used in artists' materials exposed indoors to daylight through window glass, as in museums. ASTM has listed several pigments with suitable lightfastness that can be safely used in paint formulations [146] [147] [148] [149]. The lightfastness of the pigments is always referred to a specific binder, so that the same pigment may have a certain lightfastness rating in an oil binder and a different lightfast rating in a watercolour binder.

1.6 Conclusions

My literature review highlighted a lack of knowledge on the characterization of modern oil media and synthetic pigments as well as their behaviour under accelerated ageing.

This thesis aims at describing the behaviour of:

- selected oils used in modern paints: linseed, sunflower, safflower, soybean, castor and tung oils. The survey took in consideration the fresh oils, but also natural and artificial ageing experiments were performed;
- the synthetic organic pigments commonly employed in paint formulations. Also for this class of compounds an artificial ageing test was carried out.

Lipid materials were aged naturally - for 14 months in indoor conditions – but also subjected to an artificial ageing in a Solar Box, equipped with a Xenon lamp simulating outdoor solar exposure. Two analytical techniques were employed for their characterization: GC/MS and HPLC-ESI-Q-ToF. Moreover, a study of their contact angle was performed.

Synthetic organic pigments were characterized with Py-GC/MS, in order to build a library of characteristic pyrolysis products. They were also subjected to an accelerated ageing with the use of a weather-ometer. For the ageing study the pigments were analysed in their dry, powder form, without any binder, to minimize the variables involved in the degradation pathways and to determine the lightfastness of the pure pigments. To our knowledge, this is the first time that synthetic pigments are tested without any binder to study their lightfastness properties.

The knowledge acquired from the study and the characterization of these organic compounds helped the research on several Contemporary Art case studies.

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Chapter 2

Oils used in modern oil-based paint media

2.1 Introduction

In this chapter the results of a survey on vegetable oils used in modern paint media are presented with the main aim to understand their behaviour under ageing and to find out molecular markers for their identification in paint media. The research herein presented has been partially published in the Journal of Chromatography A (*Core shell stationary phases for a novel separation of triglycerides in plant oils by high performance liquid chromatography with electrospray-quadrupole-time of flight mass spectrometer*) [1].

The fresh linseed, safflower, soybean, sunflower, tung and castor oils were characterized by GC/MS and HPLC-ESI-Q-ToF techniques, to obtain their fatty acids (FA) and triacylglycerols (TAGs) profiles. Moreover, both natural and artificial ageing experiments were carried out to study the curing and degradation processes underwent by these oils.

The six oils were subjected to natural ageing, achieved by exposing the oils to natural light (indoor) for 14 months, and analysed by GC/MS. The same oils, mixed with titanium white, were subjected to artificial ageing and analysed by HPLC-ESI-Q-ToF.

2.2 Materials and Methods

Reference materials. Linseed and safflower oils were purchased from Maimeri (Italy), tung oil from Kremer Pigmente (Germany), castor oil from Zeta Farmaceutici S.p.A (Italy), sunflower and soybean oils were bought on the local market. Titanium white (TiO_2) was purchased from Zecchi (Florence, Italy).

Preparation of the samples and ageing conditions. For the analysis of the fresh oils, they were sampled in liquid form, without any preparation. For the study of ageing processes, two types of reference layers were prepared: one set based on raw oils and the other on the same oils, mixed with titanium white (TiO_2), as shown in Fig. 2.1. The two types of reference layers were prepared onto glass slides as thin layers. For the natural ageing experiment the reference layers were left to dry for 14 months, while for the artificial ageing the reference layers were left to dry for three months before the insertion in the Solar Box. Then, they were subjected to an ageing kinetics, by analysing them at different times, after 0, 24, 48, 100, 200, 400 and 600 hours.

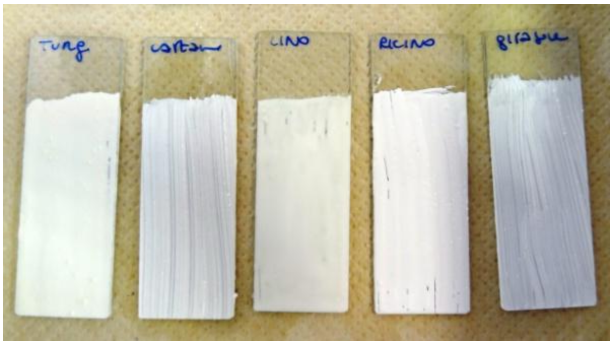

Fig. 2.1 Reference layers of the oils, mixed with titanium white (TiO_2) and subjected to artificial ageing.

The photo-ageing was performed in a Solar Box 3000e (CO.FO.ME.GRA., Italy), equipped with a Xenon lamp and a UV-IR filter that absorbs wavelengths lower than 295 nm and higher than 780 nm, corresponding to outdoor solar exposure. Irradiation was set at 700 W/m^2 and the maximum temperature on the samples was controlled with a BST, set at 30 °C.

Reagents. The derivatisation agent used for the GC/MS analyses was *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (Sigma-Aldrich, USA). Tridecanoic acid solution in *iso*-octane, 140.6 ppm, was used as acidic and neutral fraction derivatization internal standard. Hexadecane solution in *iso*-octane, 212.9 ppm, was used as injection internal standard. All acids and hexadecane, purity 99%, were purchased from Sigma-Aldrich (USA). Other reagents employed were: bi-distilled water (pesticides-grade, Carlo Erba); *iso*-octane, diethyl ether and acetone (HPLC-MS grade, Sigma Aldrich); *n*-hexane, *iso*-propanol and methanol (HPLC-MS grade, Fluka).

Apparatus. The GC/MS analyses were carried out with a Trace GC 2000 gas-chromatograph equipped with a PTV injection port and coupled to a ITQ 900 ion trap mass spectrophotometer (ThermoQuest, USA). Samples were injected in splitless mode at 280 °C. GC separation was performed on a fused silica capillary column HP-5MS, stationary phase

5% diphenyl- 95% dimethyl-polysiloxane, 30 m length, 0.25 mm i.d., 0.25 µm film thickness (J&W Scientific, Agilent Technologies, USA). The chromatographic conditions were: initial temperature 80 °C, 2 min isothermal, 10 °C/min up to 200 °C, 4 min isothermal, 6 °C/min up to 280 °C, 40 min isothermal. The helium (purity 99.9995%) gas flow was set in constant flow mode at 1.2 mL/min. MS parameters: electron impact ionization (EI, 70 eV) in positive mode; ion source temperature 230 °C; scan range 50-700 m/z; interface temperature 280 °C. The injection volume was 2 µL. The chromatograms were acquired in TIC (total ion current) mode. The semi-quantitative analysis was performed by integrating the area of each peak and expressing the result as a percentage of the sum of the areas.

The HPLC-ESI-Q-ToF analyses were carried out using a 1200 Infinity HPLC (Agilent Technologies, USA), coupled by a Jet Stream ESI interface (Agilent) to a quadrupole-time of flight tandem mass spectrometer 6530 Infinity Q-ToF detector (Agilent Technologies, USA). An Agilent Poroshell 120 EC-18 column (3.0 mm x 50 mm, 2.7 µm) with a Zorbax Eclipse Plus C-18 guard column (4.6 mm x 12.5 mm, 5µm) was used for the chromatographic separation. The injection volume was 3 µL. The separation was achieved using a gradient of methanol (eluent A) and *iso*-propanol (eluent B). The elution was programmed as follows: 90% A for 5 min, followed by a linear gradient to 90% B in 25 min, then held for 5 min. The re-equilibration time for each analysis was 10 min. The chromatographic runs were performed at a flow rate of 0.2 mL/min. The ESI operating conditions were: drying gas (N_2, purity >98%): 350 °C and 10 L/min; capillary voltage 4.5 kV; nebulizer gas 35 psig; sheath gas (N_2, purity >98%): 375 °C and 11 L/min. High resolution MS and MS/MS spectra were acquired in positive mode in the range 100-1700 m/z. The fragmentor was kept at 200 V, nozzle voltage 1000 V, skimmer 65 V, octapole RF 750 V and the voltage for the collision induced dissociation (CID) was set at 50 V. The collision gas was nitrogen (purity 99.999%). The data were collected by auto MS/MS acquisition with a MS scan rate of 1.03 spectra/s and MS/MS scan rate of 1.05 spectra/s; only one precursor was acquired per cycle (relative threshold 0.010%), active exclusion after 3 spectra and 0.50 min (selection by abundance only). The mass axis was calibrated using the Agilent tuning mix HP0321 (Agilent Technologies) in acetonitrile and water. MassHunter workstation Software (B.04.00) was used to carry out mass spectrometer control, data acquisition, and data analysis. For the fresh oils the relative abundances of the triglycerides were calculated on the integrated areas and normalized to 100% as reported in the literature [2] [3] [4]. For the ageing kinetics, instead, the integrated areas were normalized to the weight (µg) of the sample to allow a proper comparison amongst the sample sets (see Appendix B).

The saponification of lipids for the GC/MS analysis and the extraction for HPLC-ESI-Q-ToF analyses were performed using a microwave oven model ETHOS One (High Performance Microwave Digestion System), power 600 W, Milestone (Italy).

Contact angle values were determined according to the literature [5] [6]. The measurements were performed on glass slides with a NRL goniometer (Ramé-Hart Inc.) interfaced with a computer. Water droplets (5 µL) were put onto the hard material surface using 10 µl Hamilton microsyringe, and the contact angle was determined 5 s after the deposition. Contact angle measurements were carried out for each droplet and then the value at time equal to zero ϑ_0 was extrapolated.

Analytical procedures. The GC/MS analytical procedure was derived from a previously published one [7] [8], slightly modified and adapted for the analysis of the lipid-resinous fraction only. The fresh oils were sampled in liquid form (about 1 mg), whereas the reference oil layers for the natural and artificial ageing were scraped off with a lancet from the glass slides (about 1 mg) and subjected to analysis. The analytical procedure entails a saponification assisted by microwaves with 300 µL of KOH in ethanol (10% wt) at 80 °C for 60 min. After saponification, the solution was diluted in bi-distilled water, and the unsaponifiable fraction extracted in *n*-hexane (400 µL, three times). Subsequently, the residue of the *n*-hexane extraction was acidified with HCl (6 *M*) and then extracted with diethyl ether (400 µL, three times). The extract, containing both the organic acids and the neutral fraction, was subjected to derivatization with 20 µL of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 50 µL of *iso*-octane (solvent), and 5 µL of tridecanoic acid solution at 60 °C for 30 min. Finally, 100 µL of *iso*-octane and 5 µL of hexadecane solution were added and a total of 2 µL of the *iso*-octane solution of derivatized neutral and acid compounds were analysed by GC/MS. Mass spectral assignment was based on the direct match with the spectra of NIST 1.7 and Wiley 275 libraries, and a library created by the authors for fatty acids compounds. Comparisons with mass spectra of reference standards, when available, were also made. In the absence of reference spectra, the peak assignment was based on mass spectra interpretation.

The analytical procedure for the HPLC-ESI-Q-ToF analysis was the following: about 1 mg of each sample was subjected to extraction assisted by microwaves with 300 µL of a chloroform-hexane (3:2) mixture at 80 °C for 25 min. The extracts were dried under a nitrogen stream, diluted with 600 µL of elution mixture (90:10 methanol-*iso*-propanol) and filtered on a 0.45 µm PTFE filter (Grace Davison Discovery Sciences, USA) just before injection.

2.3 GC/MS results

2.3.1 Natural ageing

To highlight the different fatty acid profiles of the six oils analysed, the chromatograms of the extracts of fresh oils and of the oils aged as thin layers for 14 months - after saponification and derivatisation - are compared in Fig. 2.2 - Fig. 2.7. The compounds identified are listed in Table 2.1. The differences between the various oils are less evident in the chromatograms of the naturally aged oils. A general trend can be observed, in agreement with the literature, entailing the disappearance and/or strong decrease of unsaturated fatty acids in the aged samples, together with the appearance of di-acids (the most abundant being azelaic acid) and hydroxyacids. In particular, polyunsaturated fatty acids (e.g. linolenic and linoleic acids) completely disappear, while mono-unsaturated fatty acids - such as oleic acid - strongly decrease. The predominance of azelaic acid together with the presence of 9,10-dihydroxylated acids is a consequence of the occurrence of unsaturation mainly at position 9, consistent with the presence of large amounts of oleic acid in the un-aged oil.

Thus, we can conclude that the oxidation of unsaturated fatty acids has already extensively occurred after 14 months of natural ageing.

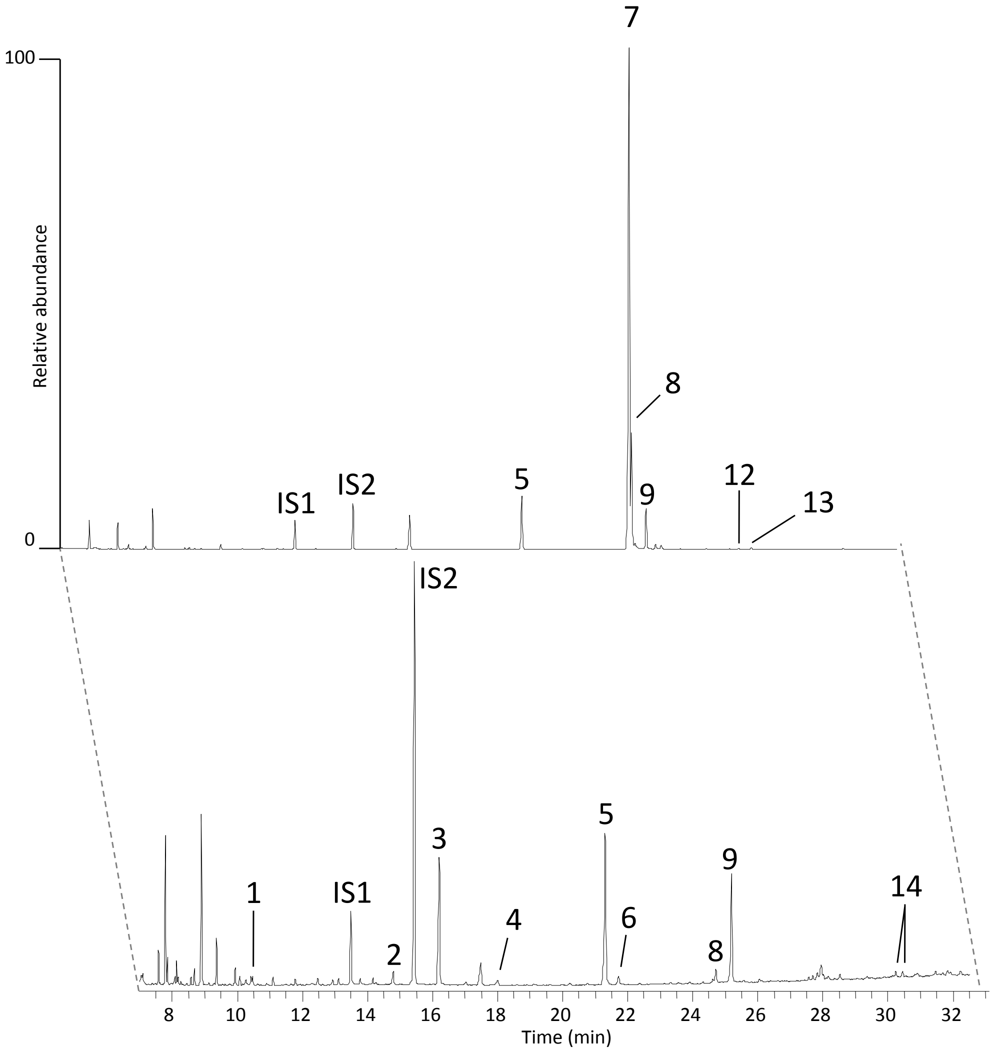

Fig. 2.2 GC/MS chromatograms of safflower oil: fresh oil (top) and naturally aged for 14 months (bottom). The identified compounds are listed in Table 2.1.

Safflower oil. The gas chromatographic profile of the fresh safflower oil is dominated by linoleic acid (peak #7), which completely disappears in the chromatogram of the aged oil; moreover, oleic acid (peak #8) strongly decreases. These unsaturated fatty acids are subjected to oxidation reactions, as discussed in Chapter 1, Section 1.3.1. The result is the formation of di-acids, such as azelaic (peak #3) and sebacic (peak #4) acids, but also the formation of hydroxyacids, e.g. the 9,10-dihydroxyoctadecanoic acids (the *cis* and *trans* isomers corresponding to the two peaks #14).

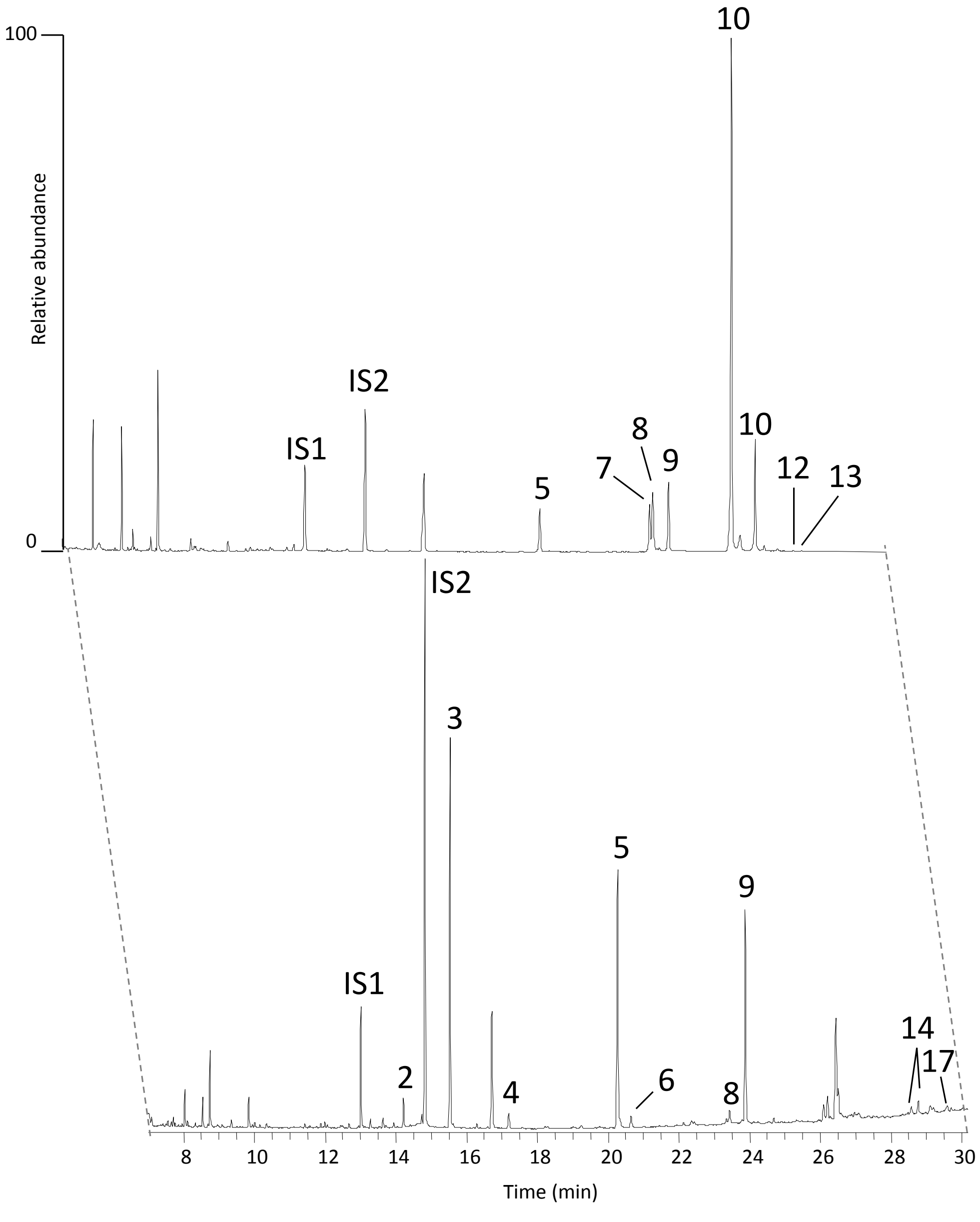

Fig. 2.3 GC/MS chromatograms of tung oil: fresh oil (top) and naturally aged for 14 months (bottom). The identified compounds are listed in Table 2.1.

Tung oil. The fresh tung oil is characterized by a high amount of α-eleostearic acid - (9Z,11E,13E)-octadeca-9,11,13-trienoic acid - which is the most abundant fatty acid in the chromatogram (peak #10, more intense). The other smaller peak #10 is the β-eleostearic acid - (9E,11E,13E)-octadeca-9,11,13-trienoic acid - a product of the isomerization of α-eleostearic acid, most probably due to the heating processes underwent by tung oil before its placing on the market. In the chromatogram of the aged oil, this triply unsaturated conjugated fatty acid completely disappears. On the other hand, azelaic acid (peak #3), a product of the oxidation of fatty acids unsaturated in position 9, is the most intense peak of the chromatogram.

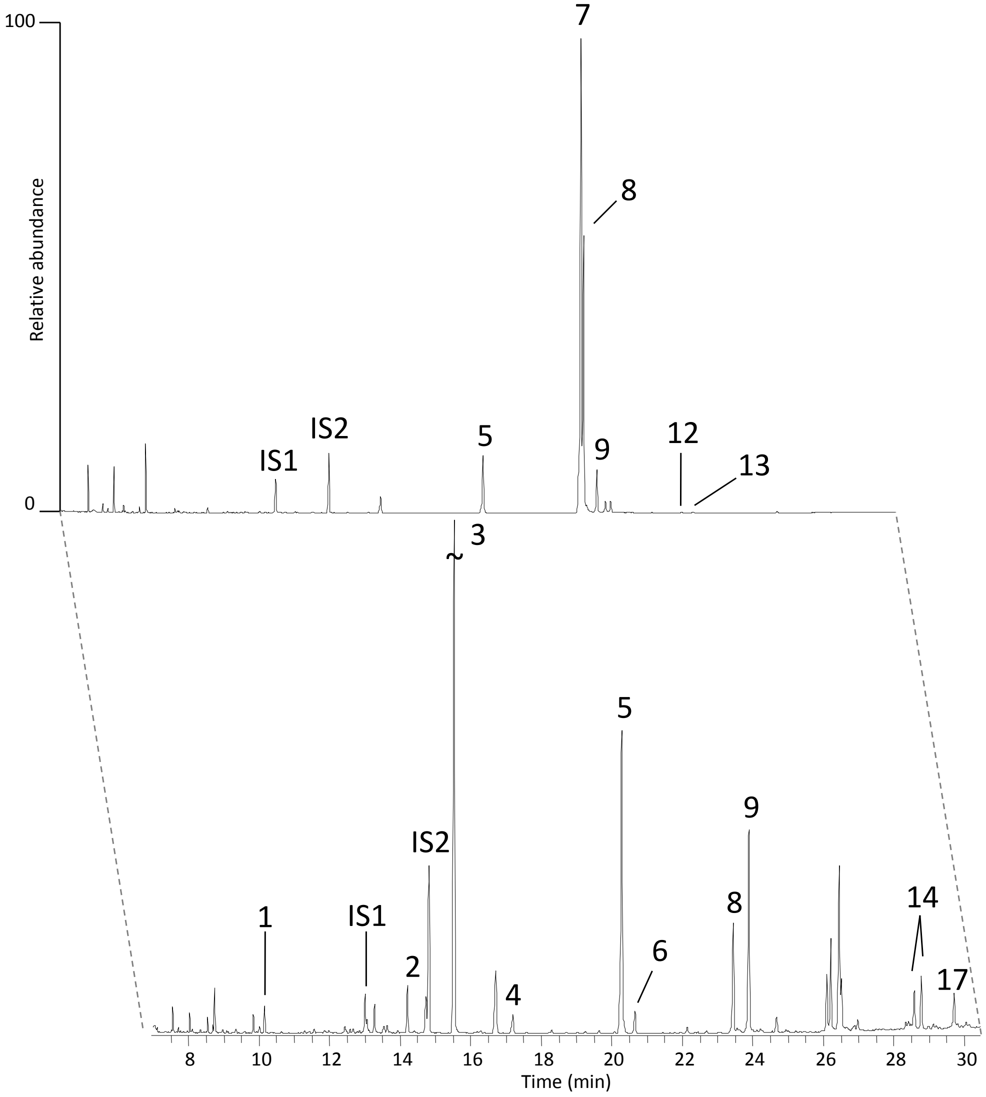

Fig. 2.4 GC/MS chromatograms of sunflower oil: fresh oil (top) and naturally aged for 14 months (bottom). The peak #3 in the chromatogram of the aged oil has been reduced for the graphic presentation. The identified compounds are listed in Table 2.1.

Sunflower oil. The fresh sunflower oil is characterized by a high amount of linoleic acid (peak #7), which, being a polyunsaturated acid, completely disappears in the chromatogram of the aged oil. Like tung oil, the aged sunflower oil shows azelaic acid (peak #3) as the most abundant compound.

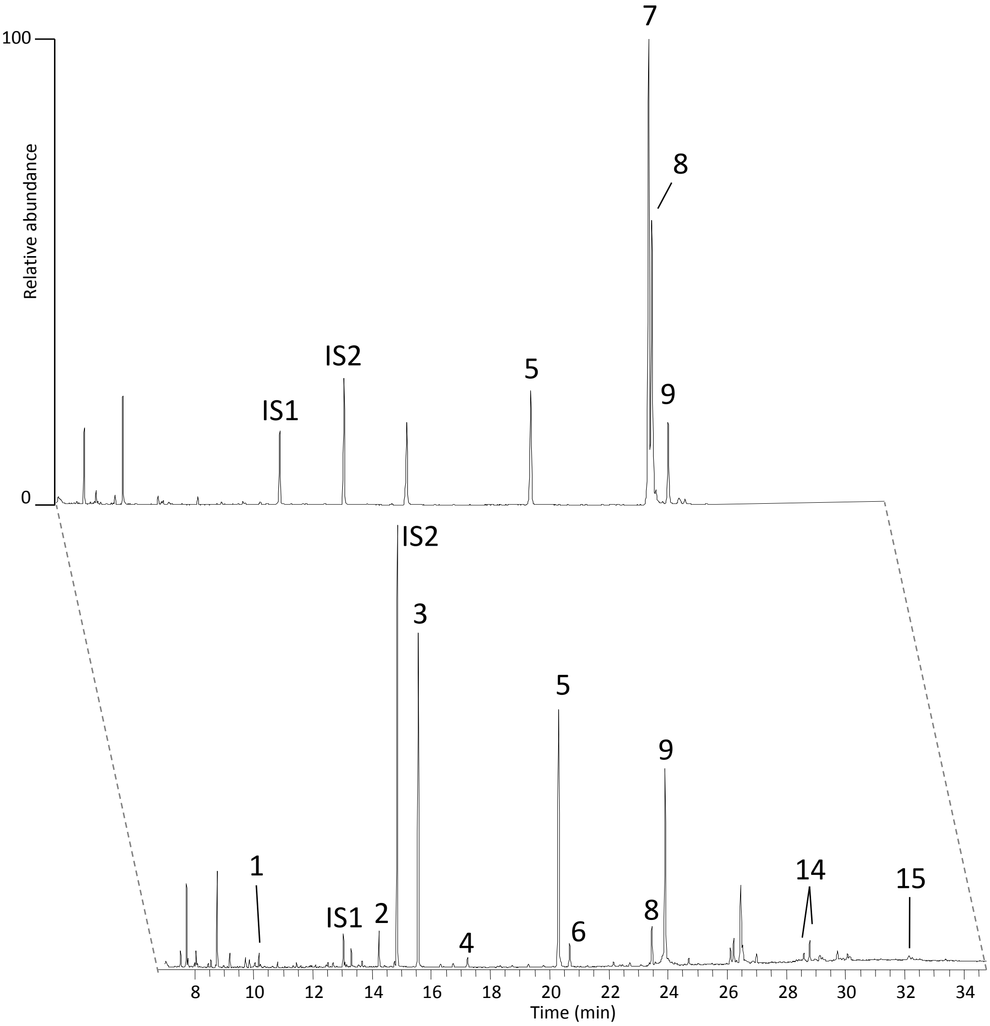

Fig. 2.5 GC/MS chromatograms of soybean oil: fresh oil (top) and naturally aged for 14 months (bottom). The identified compounds are listed in Table 2.1.

<u>Soybean oil</u>. Fresh soybean oil has a fatty acids profile similar to fresh sunflower oil, being linoleic acid (#7) the most intense peak of the chromatogram. In the aged soybean oil, instead, azelaic acid is the most abundant, followed by palmitic and stearic acids.

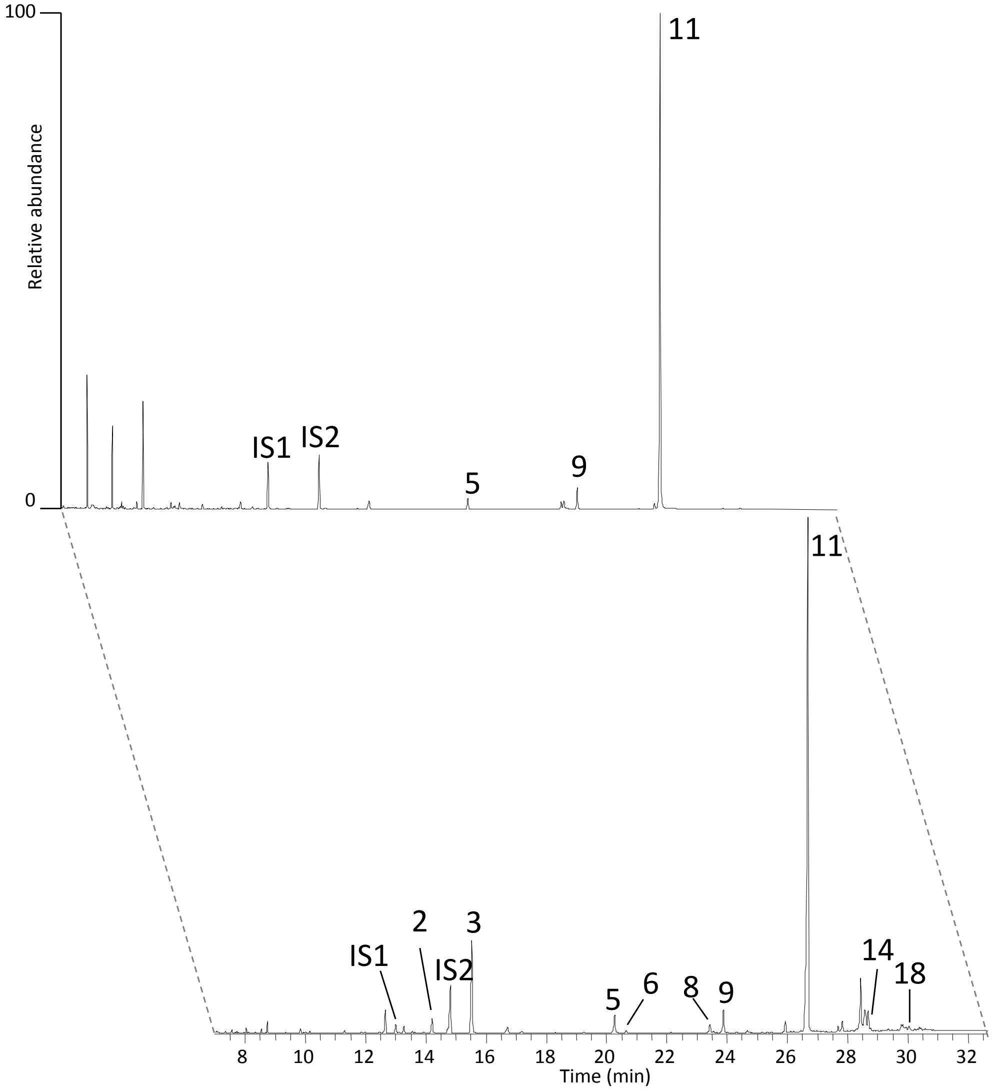

Fig. 2.6 GC/MS chromatograms of castor oil: fresh oil (top) and naturally aged for 14 months (bottom). The identified compounds are listed in Table 2.1.

Castor oil. Fresh castor oil is characterized by a high amount of ricinoleic acid (peak #11), which is the most intense peak also in the chromatogram of the naturally aged oil, but with a lower relative abundance. Castor oil, in fact, is a non-siccative oil, because it does not contain high amounts of polyunsaturated fatty acids, ricinoleic acid being a mono-unsaturated fatty acid. Thus, the fatty acid profile of the fresh castor oil is not very different from that of the oil aged for 14 months in natural conditions. Nonetheless, the chromatogram of the aged oil contains 9,12-dihydroxyoctadecanoic acid (peak #18), which is an extremely characteristic acid, its formation being related to the oxidation reactions of the double bond of ricinoleic acid [9] [10].

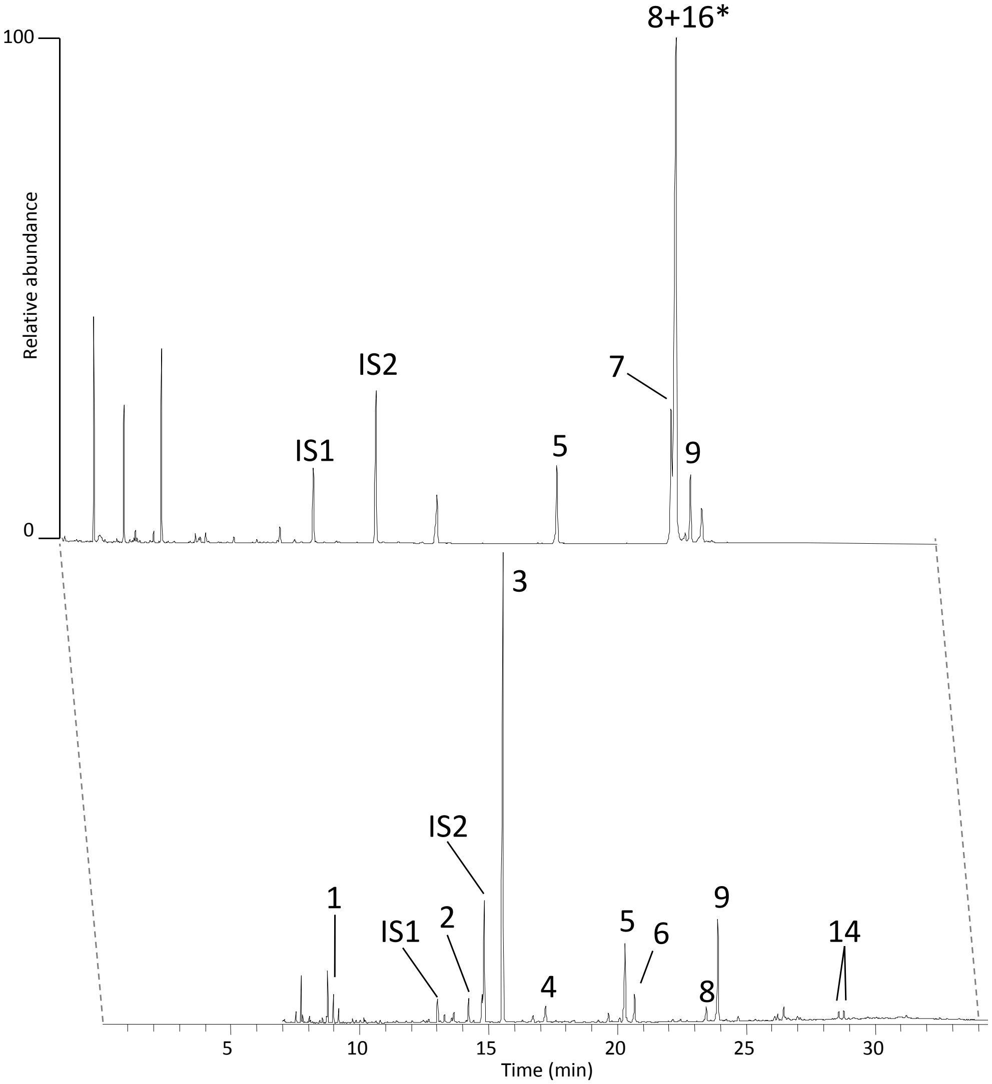

Fig. 2.7 GC/MS chromatograms of linseed oil: fresh oil (top) and naturally aged for 14 months (bottom). *Peak #8+16 in the fresh oil chromatogram corresponds to both oleic (#8) and linolenic (#16) acids, which almost co-elute in the conditions adopted. The identified compounds are listed in Table 2.1.

Linseed oil. Fresh linseed oil is characterized by a high amount of linolenic acid. In the chromatogram in Fig. 2.7 linolenic acid almost co-elutes with oleic acid to form the most intense peak (#8+16). In the chromatogram of the naturally aged oil, linolenic acid completely disappears, and oleic acid strongly decreases. Moreover, as in the case of tung, sunflower and soybean oils, azelaic acid is the most abundant fatty acid.

Table 2.1 Compounds identified in the chromatograms reported in Fig. 2.2 - Fig. 2.7.

Number	Compound (TMS derivates)	Main m/z
IS1	hexadecane (internal standard 1)	71-85
IS2	tridecanoic acid (internal standard 2)	117-271
1	2-hydroxyheptanoic acid	73-247
2	octanedioic acid (suberic acid)	169-303
3	nonanedioic acid (azelaic acid)	149-317
4	decanedioic acid (sebacic acid)	149-331
5	hexadecanoic acid (palmitic acid)	117-313
6	2-hydroxydecanedioic acid	317-391
7	(9Z,12Z)-9,12-octadecadienoic acid (linoleic acid)	117-337
8	(9Z)-octadec-9-enoic acid (oleic acid)	117-339
9	octadecanoic acid (stearic acid)	117-341
10	(9Z,11E,13E)-octadeca-9,11,13-trienoic acid (α-eleostearic acid)	117-335
11	(9Z,12R)-12-hydroxyoctadec-9-enoic acid (ricinoleic acid)	187-328
12	eicosanoic acid (arachidic acid)	117-367
13	11-eicosenoic acid (gondoic acid)	117-369
14	9,10-dihydroxyoctadecanoic acid	317-390
15	24-hydroxytetracosanoic acid	149-497
16	(9Z,12Z,15Z)-9,12,15-octadecatrienoic acid (linolenic acid)	117-335
17	docosanoic acid (behenic acid)	117-397
18	9,12-dihydroxyoctadecanoic acid	187-390

A semi-quantitative analysis of the compounds identified in the oils was performed. The fatty acid composition for both the fresh and the naturally aged oils is shown in Table 2.2 and Table 2.3, respectively. The relative standard deviation (RSD%) was lower than 2% for all the oils analysed. For the fresh oils the results are in agreement with the literature [11] (see Chapter 1, Table 1.3).

Table 2.2 Percentage composition in terms of fatty acids % of the fresh oils (only the main peaks are reported). *Linolenic and oleic acids in linseed oil co-eluted, thus it was not possible to quantify them individually.

	Safflower oil	**Tung oil**	**Soybean oil**	**Sunflower oil**	**Linseed oil**	**Castor oil**
lauric acid	0	0.1	0.5	0	0.3	0.2
myristic acid	0	0	0.4	0	0.1	0.1
palmitoleic acid	0	0.2	0	0	0	0
palmitic acid	8	2	5	3	6	1.7
linoleic acid	59	4	51	55	9	1.4
oleic acid	9	6	22	26	*	2
stearic acid	4	2	4	2	5	3.2
α-eleostearic acid	0	63	0	0	0	0
11-eicosenoic acid	< 0.1	0	0	< 0.3	0	0
eicosanoic acid	< 0.1	< 0.3	< 0.3	< 0.3	0	0
behenic acid	< 0.1	0	0	< 0.3	0	0
ricinoleic acid	0	0	0	0	0	71
linolenic acid	0	0	0	0	56.6*	0

Table 2.3 Percentage composition in terms of fatty acids % of the naturally aged oils (only the main peaks are reported).

	Safflower oil	**Tung oil**	**Soybean oil**	**Sun-flower oil**	**Linseed oil**	**Castor oil**
2-hydroxy-hexanoic acid	0	0	0	0	1.2	0
2-hydroxy-heptanoic acid	0.9	0.6	0.6	0.7	0.4	0.2
suberic acid	1.1	1.2	1.4	1.3	1.9	0.9
azelaic acid	10.1	15.1	15.3	18.3	39.8	7.4

sebacic acid	0.6	0.8	0.6	0.9	1.6	0.3
palmitic acid	12.6	15.2	15.9	13.4	6.7	2.2
hydroxy-sebacic acid	0.8	0.6	1.4	0.6	2.4	0.1
oleic acid	1.4	1.3	2.3	4.5	1.3	1.1
stearic acid	8.6	11.9	13.1	8.5	7.5	2.3
ricinoleic acid	0	0	0	0	0	50.6
9,10-dihydroxy-octadecanoic acid	1.7	2.4	1.8	4.4	1.2	0
24-hydroxy-tetracosanoic acid	0	0	0.9	0	0	0

The ratios between specific fatty acids are largely employed for the analysis of the binders in Ancient Art, to distinguish between different triglycerides sources (i.e. drying oils or egg) and to determine the kind of drying oil used as paint binder on the basis of characteristic parameters: P/S (palmitic over stearic acid ratio), A/P (azelaic over palmitic acid ratio), Σdic (sum of dicarboxylic acids) [7] [12] (Table 2.4).

Table 2.4 Values of the fatty acids* ratios used to characterize the binders employed in Ancient Art.

	Linseed oil	**Walnut oil**	**Poppyseed oil**	**Egg**	**Tempera grassa**
P/S	< 2	2.2-3.0	> 3	2.7-3.2	
A/P	> 1	> 1	> 1	< 0.1	0.5-1
Σdic	> 40%	> 40%	> 40%	< 25%	20-40%
cholesterol	no	no	no	yes	yes

*P = palmitic acid; S = stearic acid; A = azelaic acid; Σdic = sum of the dicarboxylic acids.

In detail, the botanical source of a lipid material in a work of art is conventionally determined on the basis of the ratio between palmitic and stearic acids (P/S) [13]. This evaluation is based on the hypothesis that saturated fatty acids, such as palmitic and stearic, do not undergo relevant modifications during the drying, curing or ageing of an oil film and on the fact that traditionally employed drying oils, namely linseed, walnut and poppyseed, have different average values of P/S (see Table 2.4). In particular, linseed oil is characterized by a P/S < 2.

We aimed at verifying if these characteristic ratios were reliable also for the identification of the oils used in modern paint media. Thus, the characteristic parameters were evaluated for the fresh and naturally aged oils. The results are summarized in Table 2.5 and each parameter is commented separately.

Table 2.5 Comparison of the characteristic fatty acids* values between the fresh and the aged oils.

	Safflower oil	**Tung oil**	**Soybean oil**	**Sun-flower oil**	**Linseed oil**	**Castor oil**
P/S fresh oil	2.0	0.9	1.3	1.5	1.3	0.5
P/S cured oil	1.5	1.3	1.2	1.6	0.9	0.9
A/P cured oil	0.8	1	1	1.4	6	3.4
O/S fresh oil	2.3	2.5	6.1	11.8	*	0.6
O/S cured oil	0.2	0.1	0.2	0.5	0.2	0.5
Σdic	11.8	17.1	17.3	20.5	43.3	8.6

*P = palmitic acid; S = stearic acid; A = azelaic acid; O = oleic acid; Σdic = sum of the dicarboxylic acids.

All the "modern" oils analysed in this survey have a P/S value lower than 2, whether fresh or aged (see Table 2.5). Thus, the identification of linseed oil on the basis of the P/S value is not valid for modern paintings, by taking in consideration the possibility of the presence of a "modern oil" or of a mixture of linseed oil with a different siccative or semi-siccative oil.

Moreover, the P/S value shows a relevant change in the curing process of the "modern" oils. Safflower oil, for example, has a P/S value which decreases from a 2.0 to 1.5.

Recent studies [14] [15] have shown that the P/S ratio may decrease with ageing; this phenomenon has been explained with the preferential loss from the paint layer of palmitic with respect to stearic acid, due to their different volatilities. In our case, however, the P/S ratio decreases for linseed, safflower and soybean oils, while it increases for tung, castor and sunflower oils.

The occurrence of a drying oil in a paint sample is often determined on the basis of the azelaic over palmitic ratio (A/P), together with its dicarboxylic acids content (see Table 2.4). High amounts of dicarboxylic acids, and azelaic in particular, are registered in aged drying oils as they are formed during the auto-oxidation of the unsaturated fatty acids. All the chromatograms of the six oils analysed contained azelaic acid, even castor oil, which is a non-siccative oil. For the most aged oils, azelaic acid was the highest peak of the chromatograms.

The A/P ratio can be also used to discriminate between a drying oil and an egg binder, as shown in Table 2.4, being A/P > 1 for oils and A/P < 0.3 for egg [7] [12]. All the oils analysed after 14 months of curing, except for safflower oil, have an A/P > 1, thus they cannot be confused with egg. Safflower oil has an A/P of 0.8, which is still higher than the upper limit for an egg binder (0.3). This result is relevant because it confirms the validity of the A/P ratio as a reliable discrimination parameter between egg and aged lipids deriving form plant oils, also for the binders in modern paints.

The ratio between oleic and stearic acids (O/S) is an index of oxidation, since the unsaturated oleic acid is particularly reactive to oxygen. Generally, for aged films of traditional siccative oils, O/S is around 0.1-0.2 [12]. The decrease in oleic acid as a consequence of oxidation reactions entails a decrease of the O/S ratio: e.g. the O/S ratio of sunflower oil decreases from a value of 11.8 for the fresh oil to a value of 0.5 for the naturally aged oil.

Another index of oxidation is the sum of the relative content of dicarboxylic acids (Σdic), which is usually above 40% for siccative oils after curing [7] [12]. Amongst the investigated oils, only linseed shows the expected Σdic. This results is most probably due to the semi-siccative or non-siccative nature of the other five oils analysed. Tung, soybean and sunflower oils all have a Σdic value of about 20%, being semi-siccative. Castor oil has the lowest value, being a non-siccative oil. Safflower oil has a Σdic value lower than 20%, but higher than castor oil.

2.4 HPLC-ESI-Q-ToF results

We developed and optimized a new method for the characterization of triglycerides (TAGs), which represents the first application of core-shell stationary phases in reverse phase HPLC coupled with a high resolution ESI-Q-ToF analyser [1]. The developed method was applied to the oils selected for the study to evaluate their TAGs profiles. The use of high resolution tandem mass spectrometry as detection system allowed us to obtain a method with a high selectivity toward TAGs, to separate 40 TAGs in a 25 min run, and to identify them on the basis of their CID (Collision Induced Dissociation) tandem mass spectra. The triglycerides are named according to the fatty acids abbreviations listed in Table 2.6.

Table 2.6 Nomenclature used for the acylic chains in triglycerides.

Abbreviation	Fatty acid
Li	Lignoceryl $C_{24:0}$
Er	Erucyl $C_{22:1}$
B	Behenyl $C_{22:0}$
G	Gadolenyl $C_{20:1}$
A	Arachidyl $C_{20:0}$
Rn	Ricinoleyl $C_{18:1,OH}$
Ln	Linolenyl $C_{18:3}$
E	Eleostearyl $C_{18:3}$
L	Linoleyl $C_{18:2}$
O	Oleyl $C_{18:1}$
S	Stearyl $C_{18:0}$
Po	Palmitoleyl $C_{16:1}$
P	Palmityl $C_{16:0}$
M	Myristyl $C_{14:0}$

2.4.1 Fresh oils

The TAGs profiles obtained in this study for the fresh oils are consistent with those reported in the literature [3] [16] [17]. As expected, for each oil, palmitate was absent in the sn-2 position, which is a characteristic feature of plant TAGs: palmitic acid in vegetable oils is preferentially incorporated into the sn-1 and sn-3 positions.

Castor oil has a distinctive profile with RnRnRn, RnRnL, RnRnO and RnRnS as the main triglycerides. It is the only oil to contain a ricinoleyl substituent. The tung oil profile shows EEE, EEL and ELL as the main TAGs and it is the only oil containing an eleostearyl substituent. LnLnLn, LnLnL and LnLL are specific for linseed and soybean oils. Safflower oil shows LLL, LLP, LLO and OOL as the main TAGs. For sunflower oil the most abundant triglycerides are LLL, LLP, LOP and OOP. The results of the HPLC analyses on the fresh oils are shown in Table 2.7 as percentage profiles of identified TAGs, determined on the basis of peak areas in extract ion chromatograms corresponding to the pseudomolecular ions of the TAGs species.

Table 2.7 Relative abundances (%) for the main identified triglycerides in the analysed oils.

TAG	Tung oil	Soybean oil	Safflower oil	Linseed oil	Sunflower oil	Castor oil
RnRnRn	-	-	-	-	-	49.5

RnRnL	-	-	-	-	-	20.2
RnRnO	-	-	-	-	-	17.1
RnRnS	-	-	-	-	-	10.2
RnLL	-	-	-	-	-	0.3
RnLO	-	-	-	-	-	2.6
RnLS	-	-	-	-	-	0.1
LnLnLn	-	0.8	-	15.0	-	-
EEE	52.0	-	-	-	-	-
LnLnL	-	1.9	1.2	12.5	0.9	-
EEL	15.0	-	-	--	-	-
LnLnP	-	-	-	7.2	-	-
ELL	19.8	-	-	-	-	-
LnLL	-	7.2	1.0	14.4	0.8	-
PoLnL	3.9	-	-	-	-	-
MLL	-	0.6	-	-	-	-
LLnP	-	-	1.0	14.4	0.8	-
PoLL	2.2	-	-	-	-	-
LLL	3.4	16.9	26.9	5.4	20.3	-
LLP	-	16.9	21.2	-	16.7	-
PLnP	-	-	-	2.7	-	-
GLL	1.6	-	-	-	-	-
LLO	1.0	21.3	19.4	-	-	-
PLP	-	1.9	-	10.8	-	-
LOP	-	-	4.7	-	20.6	-
MLO	-	-	-	1.6	-	-
OOL	0.9	15.7	4.8	-	5.5	-
OOP	-	-	2.0	2.0	16.8	-
POP	-	7.2	-	10.2	-	-
OOO	-	1.3	4.4	-	4.8	-
ALL	-	-	2.2	1.6	2.7	-
ErLO	-	1.9	-	-	-	-
OSP	-	0.7	-	0.4	1.7	-
OOS	0.1	4.4	2.3	-	-	-
ALO	-	-	2.1	1.6	-	-
BLL	-	-	2.4	-	1.7	-
BLO	-	-	2.1	-	1.6	-
AOO	-	-	-	-	1.8	-
LiLLn	-	0.4	1.7	-	-	-
LiLL	-	0.7	-	-	1.6	-
BOO	-		-	-	1.3	-

2.4.2 Artificial ageing

We performed an ageing kinetics by analysing linseed, sunflower, safflower, soybean, tung and castor oils as thin layers at different ageing times, after 0, 24, 48, 100, 200, 400 and 600 hours of artificial ageing in a Solar Box.

Table 2.8 Normalized abundances (integrated areas normalized with respect to the weight of the sample) of the sum of the TAGs present in the oils analysed.

	0 h (t_0)	**24 h (t_1)**	**48 h (t_2)**	**100 h (t_3)**	**200 h (t_4)**	**400 h (t_5)**	**600 h (t_6)**
Linseed oil	96357	29116	25103	18530	9629	4929	-
Sunflower oil	61407	39398	27273	34924	17597	1560	6507
Safflower oil	38046	25382	24071	31108	22362	7106	1059
Soybean oil	693359	281137	120618	43109	40887	23630	4472
Tung oil	8150	9541	8516	10419	710	1456	2948
Castor oil	1246836	-	993181	545161	209108	151891	12265

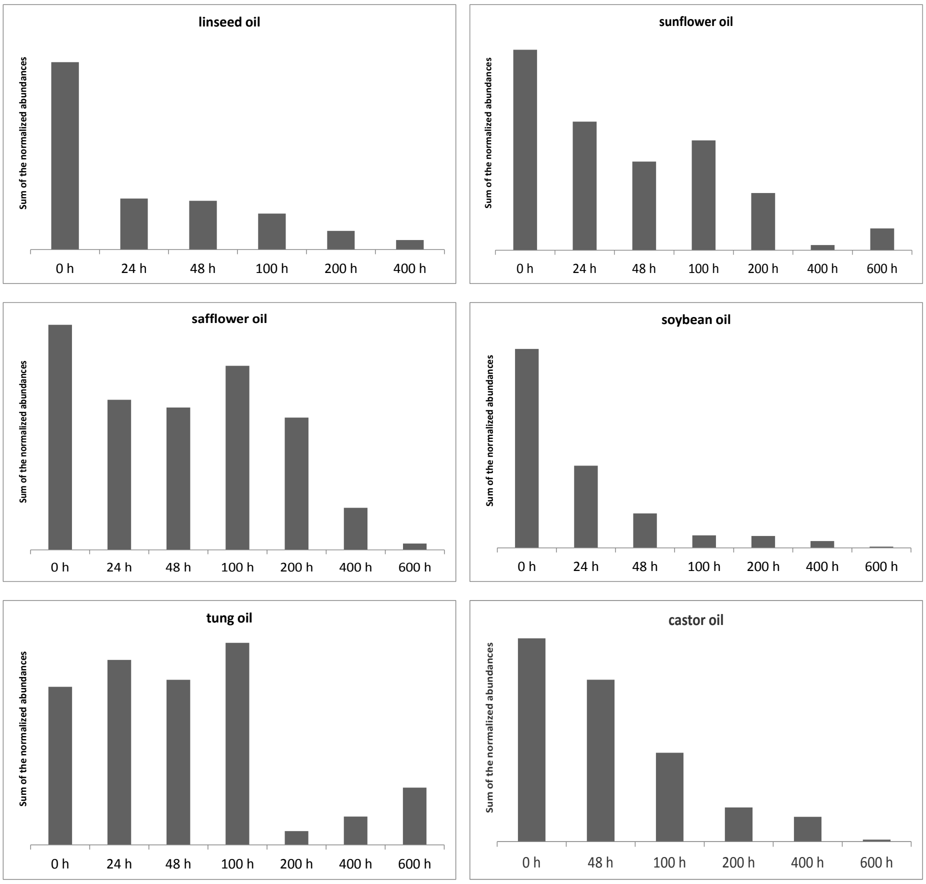

Fig. 2.8 Sum of the normalized abundances of each TAGs detected in the oils analysed. From top left to right: linseed oil, sunflower oil, safflower oil, soybean oil, tung oil, castor oil.

For the ageing conditions, see Section 2.2, Materials and methods.

To our knowledge, this is the first time a survey with HPLC-ESI-Q-ToF on the ageing kinetics of these oils is performed.

For all the oils analysed the amount of TAGs detected in the extracts decreased with the increase of the ageing time (Table 2.8 and Fig. 2.8). This phenomenon is due to the crosslinking reactions taking place during the curing of the oils, which prevent the extraction of the TAGs and the consequent detection.

The oils were compared at the seven different ageing times, and the results are shown, for each oil, as histograms, which highlight the variation of the normalized abundances of the different TAGs. Moreover, for each oil, the chromatograms of the less aged oil (0 h of artificial ageing) and of the most aged (400 or 600 h of artificial ageing) are shown. The chromatograms were obtained by overlapping the extract ion chromatograms of the identified TAGs species. It must be noted that in the extract ion chromatograms more than one peak is present for each extracted molecular ion due to the occurrence of isobaric species.

A general trend can be observed comparing the extracts of the thin layers of the oils at different ageing times: the decrease of the TAGs containing unsaturated fatty acids in the aged ones, with the increase in oxidised TAGs.

Linseed oil. In linseed oil POP, OOP, OOO, OSP, OOS, SOS, $C_{18:2,OH}$OP, S$C_{18:1,OH}$O strongly decrease during irradiation (Fig. 2.9). An intermediate oxidation product, S$C_{18:1,OH}$P, increases in abundance and then decreases, until it disappears completely at 400 h of artificial ageing. The TAG $C_{18:1,OH}C_{18:1,OH}$P appears only after 100 h of ageing. Interestingly, in linseed oil none of the TAGs containing polyunsaturated fatty acids (linolenic and linoleic acids) was detected, not even in the less aged oil (t_0). It must be noted, however, that the hours of ageing are referred exclusively to the hours of artificial ageing, thus the oils labelled as t_0 or “0 hours” were not fresh, but they were left to cure for three months before the insertion in the Solar Box. Therefore, after three months of natural drying, the polyunsaturated fatty acids of the TAGs in linseed oil were already oxidised. The amount of TAGs extracted after 600 h of irradiation was very low, thus the results were not reported in Fig. 2.9 and the chromatogram of the extract after 400 h of irradiation is shown instead.

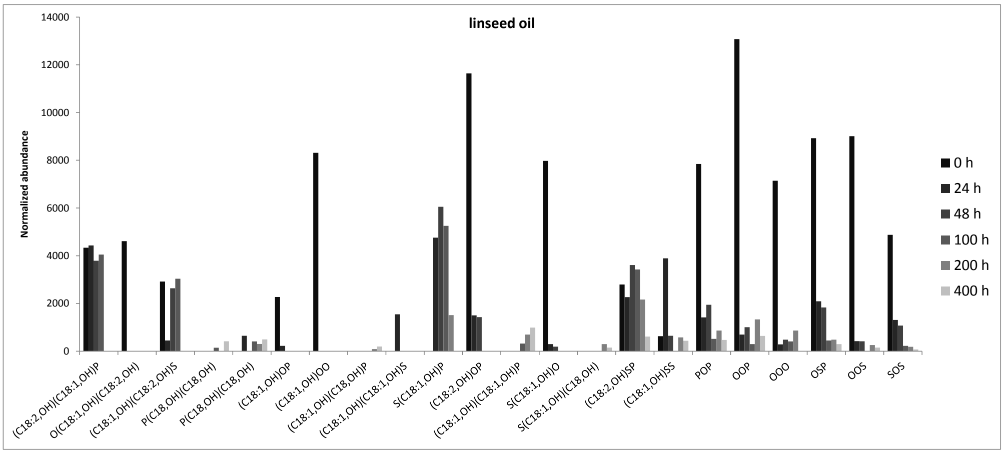

Fig. 2.9 TAGs present in linseed oil at different artificial ageing times.

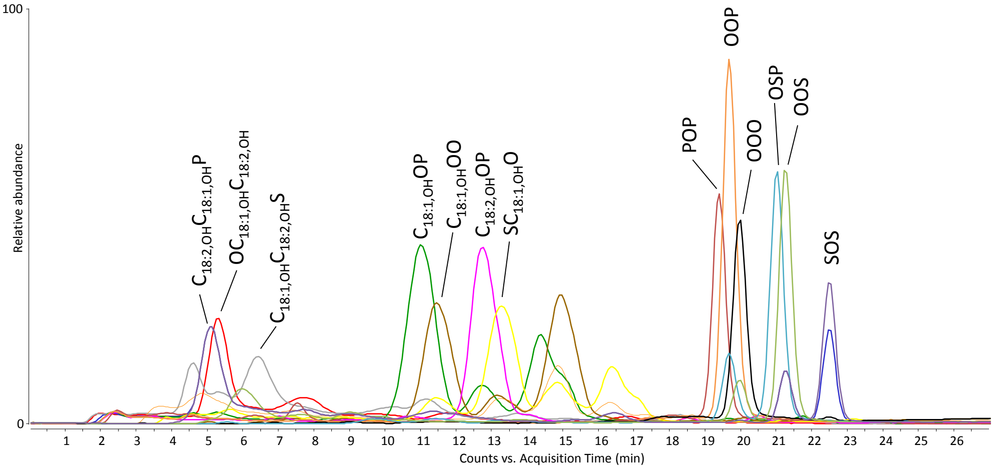

Fig. 2.10 HPLC-ESI-Q-ToF extract ion chromatogram of linseed oil artificially aged for 0 h (t_0).

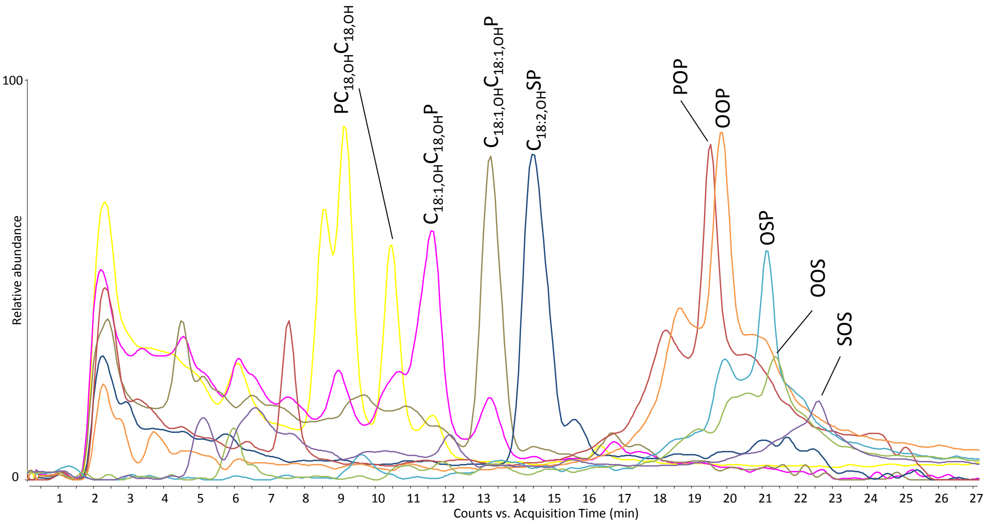

Fig. 2.11 HPLC-ESI-Q-ToF extract ion chromatogram of linseed oil artificially aged for 400 h (t_5).

Sunflower oil. Sunflower oil (Fig. 2.12) shows a very similar ageing behaviour to linseed oil, with the decrease of the TAGs containing unsaturated fatty acids (POP, OOP, OOO, OSP, OOS, SOS, $C_{18:1,OH}$OO). Like linseed oil, also in sunflower oil none of the TAGs containing polyunsaturated fatty acids was detected, although the main component of the fresh sunflower is linoleic acid.

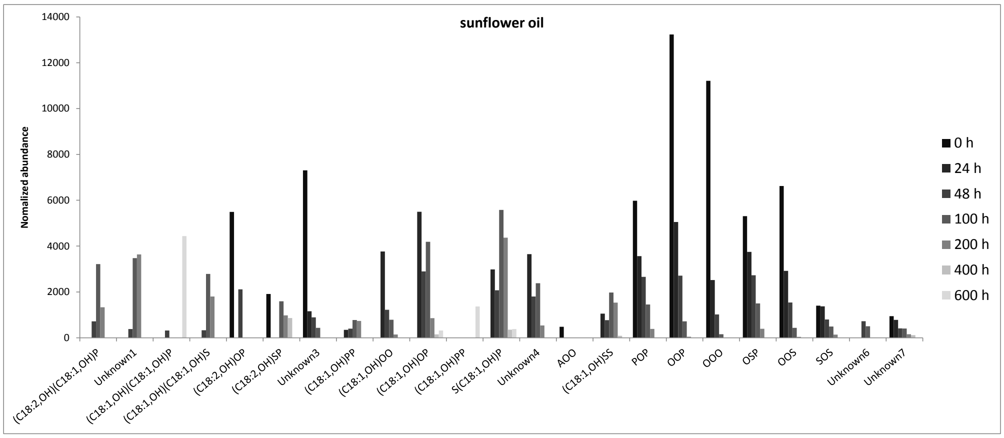

Fig. 2.12 TAGs present in sunflower oil at different artificial ageing times.

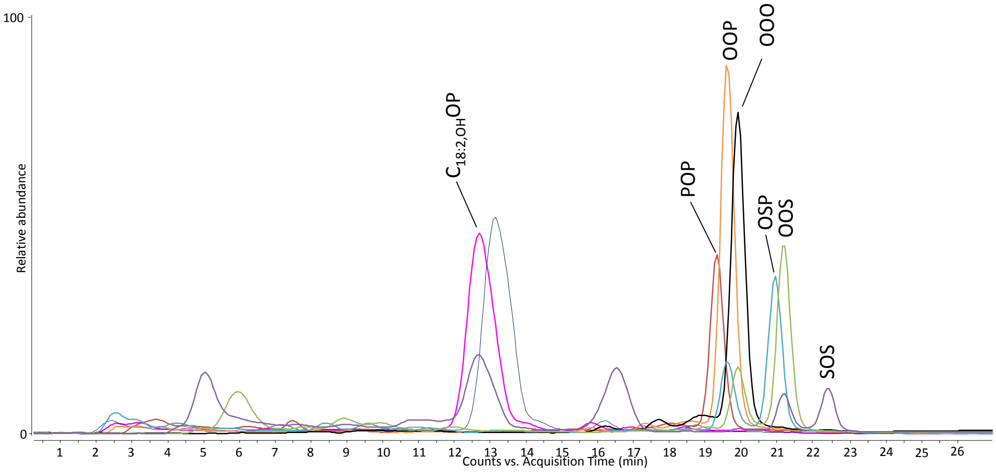

Fig. 2.13 HPLC-ESI-Q-ToF extract ion chromatogram of sunflower oil artificially aged for 0 h (t_0).

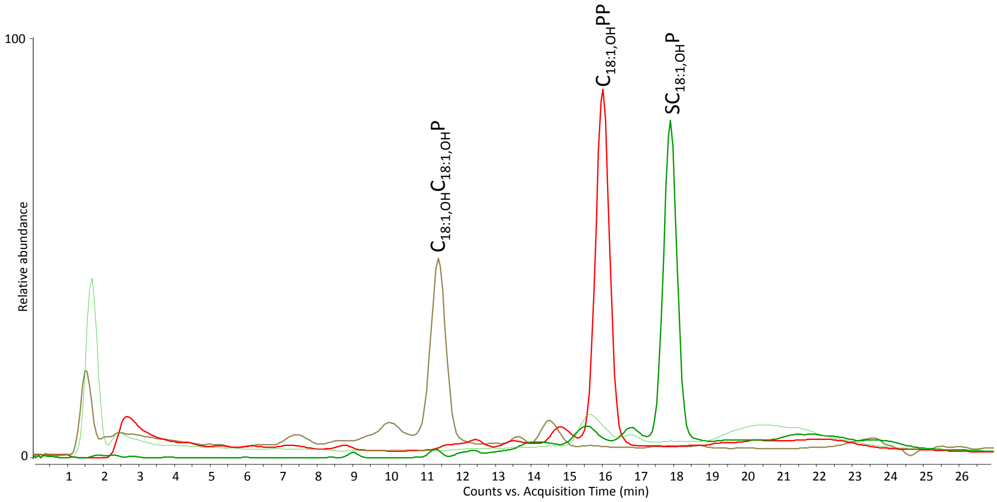

Fig. 2.14 HPLC-ESI-Q-ToF extract ion chromatogram of sunflower oil artificially aged for 600 h (t_6).

<u>Safflower oil</u>. The HPLC-ESI-Q-ToF analysis of safflower oil shows the decrease of the TAGs containing unsaturated fatty acids, with the presence of two intermediate oxidation products: $SC_{18:1,OH}P$ and $C_{18:1,OH}SS$ (Fig. 2.15). Unlike linseed and sunflower oils, safflower oil after 24 h of artificial ageing still shows un-oxidized TAGs (LnLnP, LLnP).

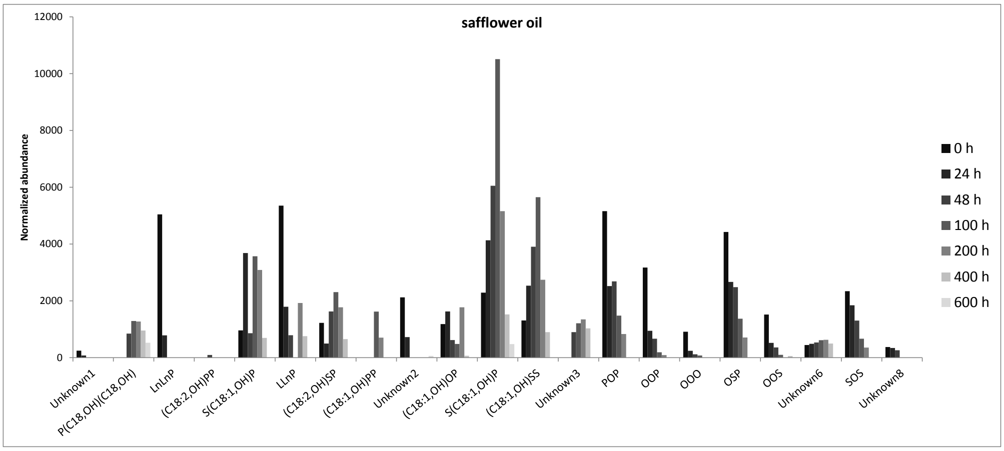

Fig. 2.15 TAGs present in safflower oil at different artificial ageing times.

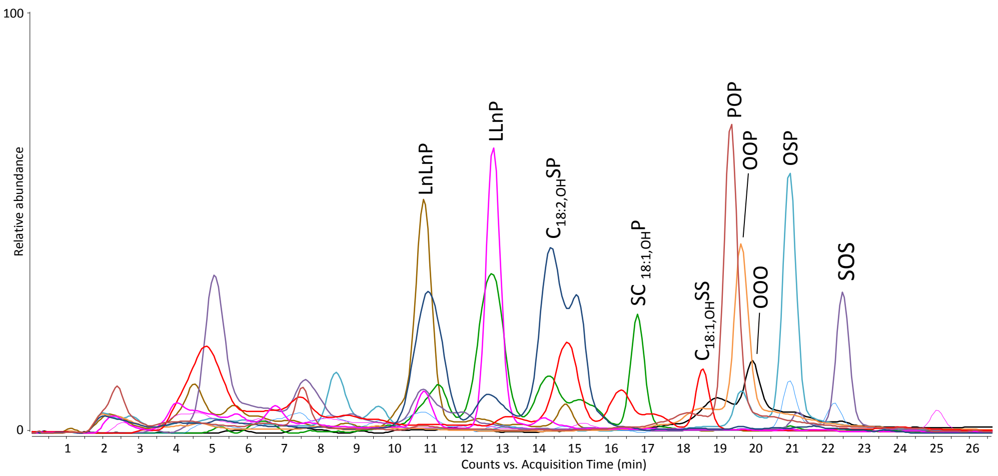

Fig. 2.16 HPLC-ESI-Q-ToF extract ion chromatogram of safflower oil artificially aged for 0 h (t_0).

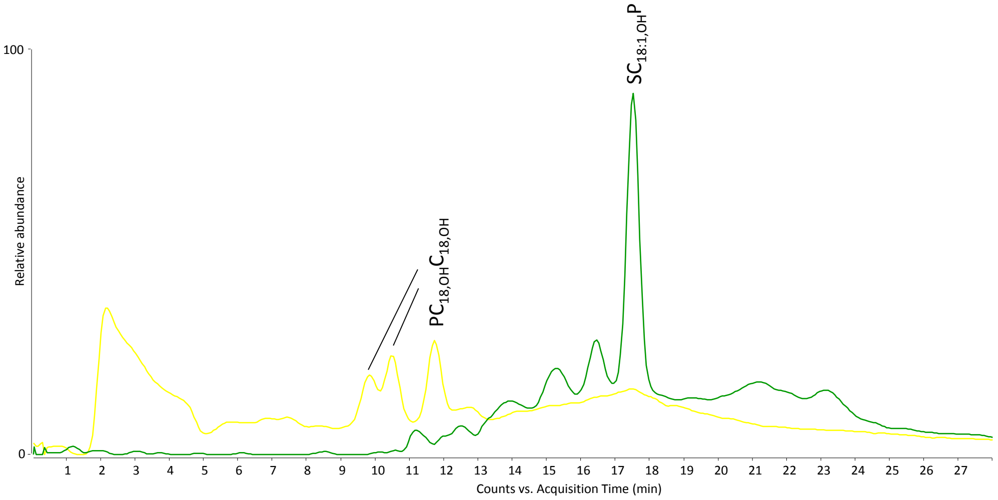

Fig. 2.17 HPLC-ESI-Q-ToF extract ion chromatogram of safflower oil artificially aged for 600 h (t_6).

Soybean oil. In soybean oil the TAGs containing unsaturated fatty acids, such as LnLnP, LLnP, $C_{18:2,OH}$OP, $C_{18:1,OH}$OP, POP, OOP, OOO, OSP, OOS, SOS, strongly decrease during the ageing process (Fig. 2.18). Moreover, soybean oil, like safflower oil, shows TAGs containing linolenic and linoleic acids (LnLnP, LLnP), pointing out the semi-siccative nature of the oil. Most probably, the lower concentration of unsaturated alkyl chains subjected to oxidation reactions in soybean and safflower oils compared to linseed oil entails that the crosslinking reactions occur at a slower rate. Thus, the reactions required to form a cross-linked polymeric network are not completed, not even after 400 h of artificial ageing. On the contrary, in linseed oil the higher concentration of linolenyl (Ln) chains implies a higher speed of reticulation and a complete depletion of unreached linoleyl chains.

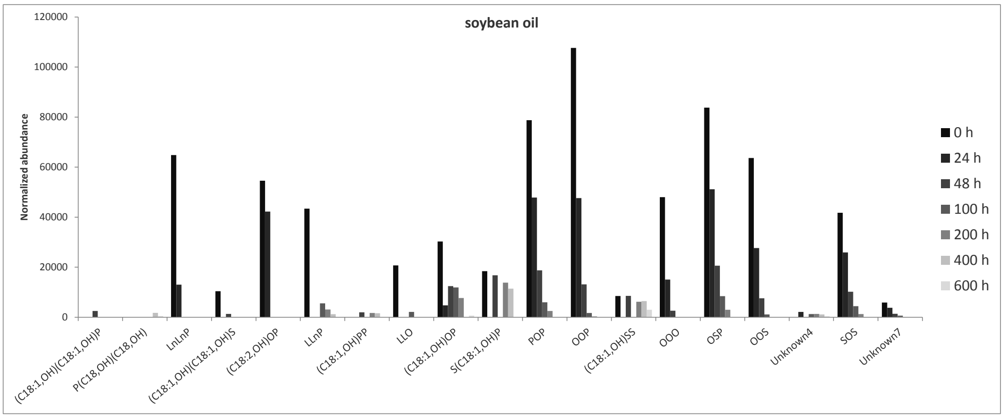

Fig. 2.18 TAGs present in soybean oil at different artificial ageing times.

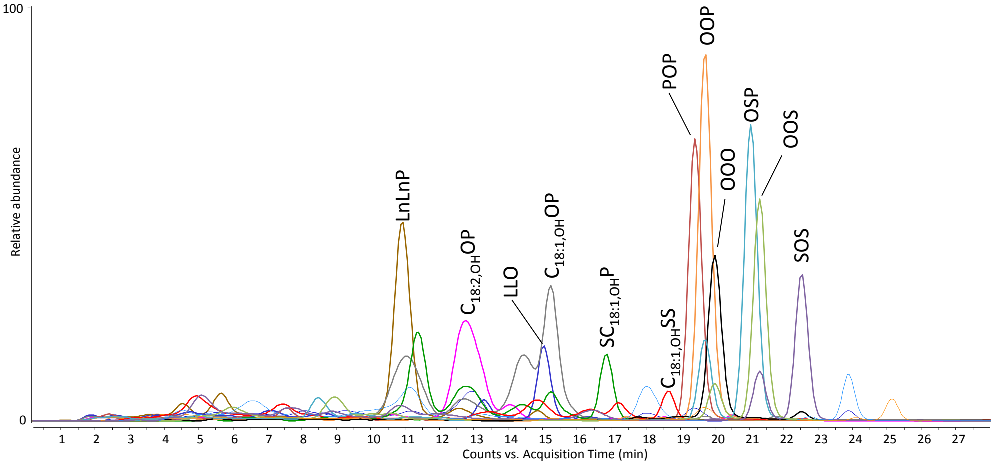

Fig. 2.19 HPLC-ESI-Q-ToF extract ion chromatogram of soybean oil artificially aged for 0 h (t_0).

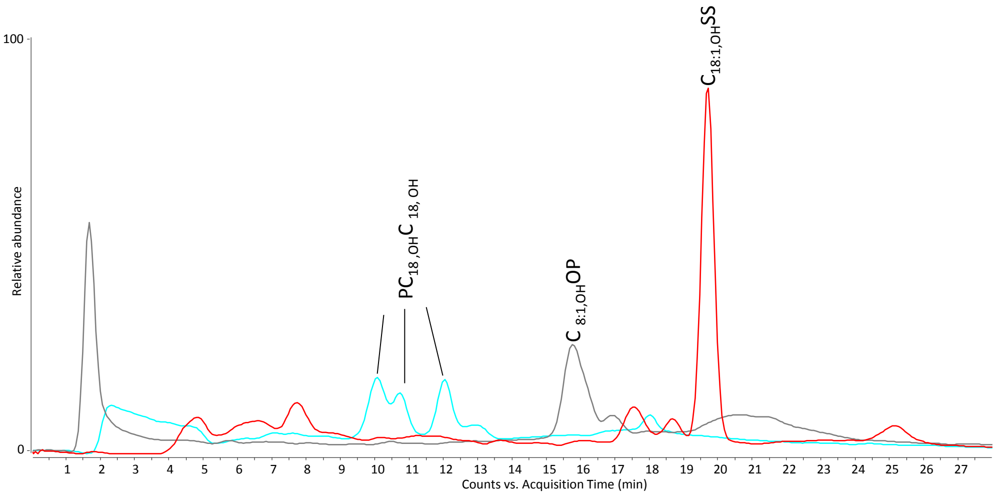

Fig. 2.20 HPLC-ESI-Q-ToF extract ion chromatogram of soybean oil artificially aged for 600 h (t_6).

Tung oil. For tung oil, the TAGs detected and identified were fewer, compared to the other five oils analysed (Fig. 2.21). Moreover, α-eleostearic acid, the main component of fresh tung oil (see Table 2.7) disappears completely even at t_0, corresponding to three months of curing in indoor conditions before the artificial ageing experiment. Three new TAGs species were identified in the oil after 600 h of artificial ageing: $C_{18:1,OH}OP$, $C_{18:1,OH}OO$, $SC_{18:1,OH}P$.

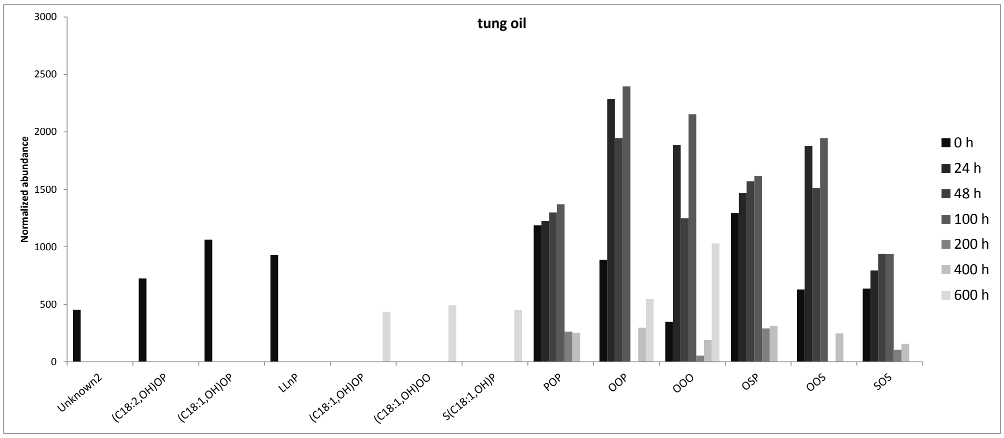

Fig. 2.21 TAGs present in tung oil at different artificial ageing times.

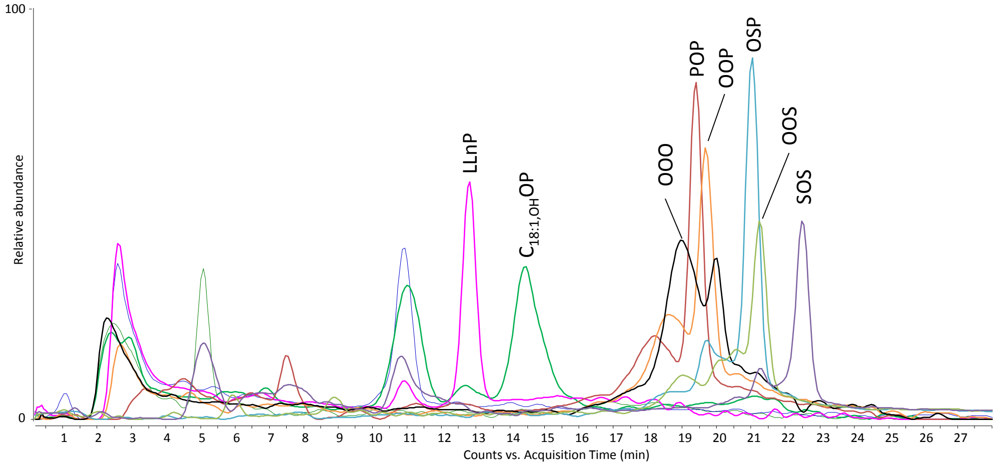

Fig. 2.22 HPLC-ESI-Q-ToF extract ion chromatogram of tung oil artificially aged 0 h (t_0).

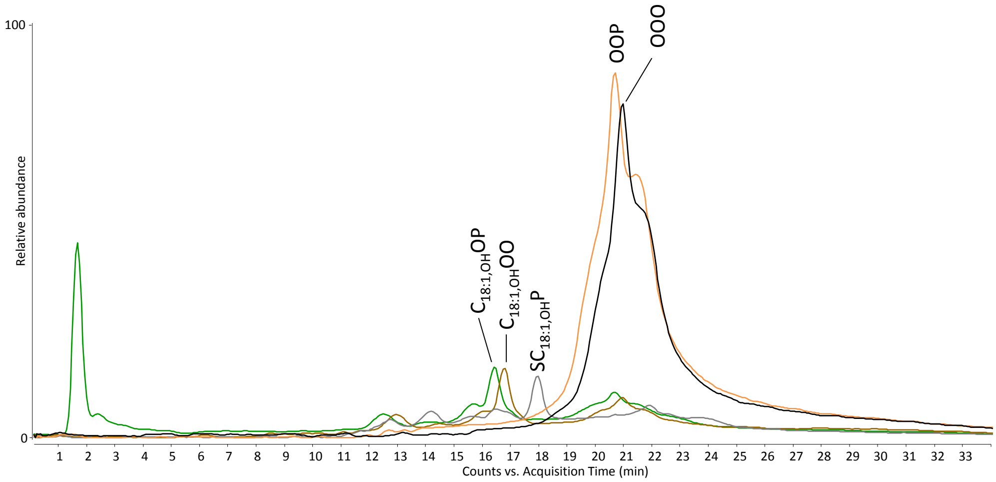

Fig. 2.23 HPLC-ESI-Q-ToF extract ion chromatogram of tung oil artificially aged for 600 h (t_6).

Castor oil. In castor oil, the TAGs containing ricinoleic acid (Rn) decrease until disappearing in the oil aged for 600 h (Fig. 2.24). The amount of TAGs extracted after 200 h of irradiation onward is very low.

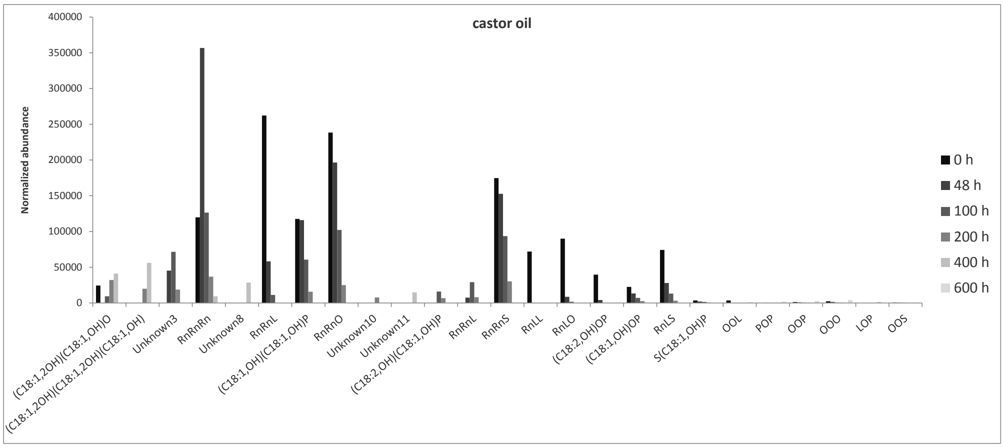

Fig. 2.24 TAGs present in castor oil at different artificial ageing times.

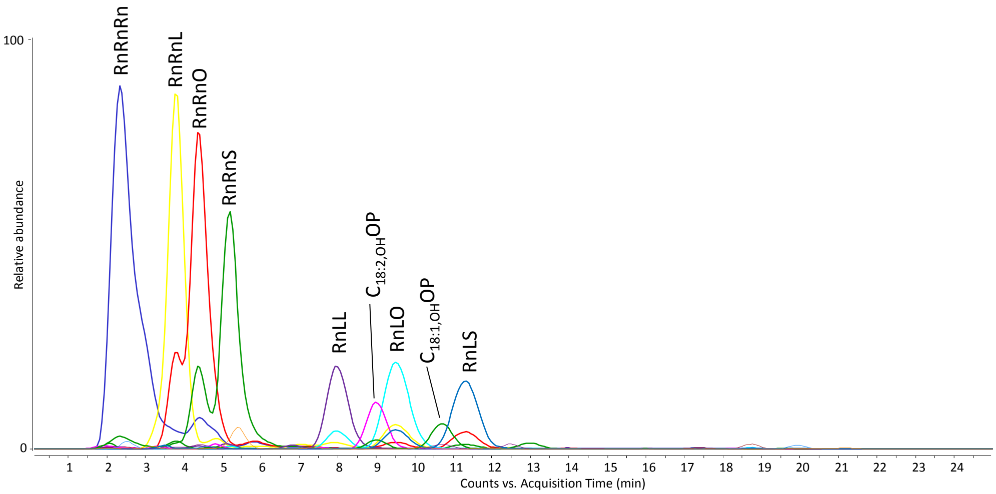

Fig. 2.25 HPLC-ESI-Q-ToF extract ion chromatogram of castor oil artificially aged for 0 h (t_0).

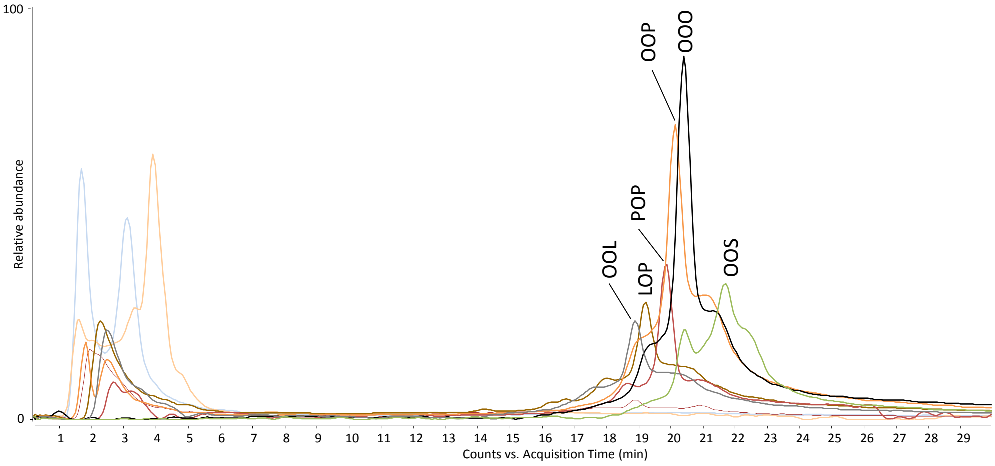

Fig. 2.26 HPLC-ESI-Q-ToF extract ion chromatogram of castor oil artificially aged for 600 h (t_6).

2.5 Contact angle measurements

The contact angle is the angle, conventionally measured through the liquid, where a liquid/vapour interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid via the Young equation. A given system of solid, liquid, and vapor at a given temperature and pressure has a unique equilibrium contact angle. If the liquid molecules are strongly attracted to the solid molecules, then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0°. Generally, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic [18].

2.5.1 Results and discussion

The contact angle measurements were carried out on the oils after 3 months of drying (t_0). The contact angles are reported with their standard deviations as the average of 10 measurements. The results are shown in Fig. 2.27.

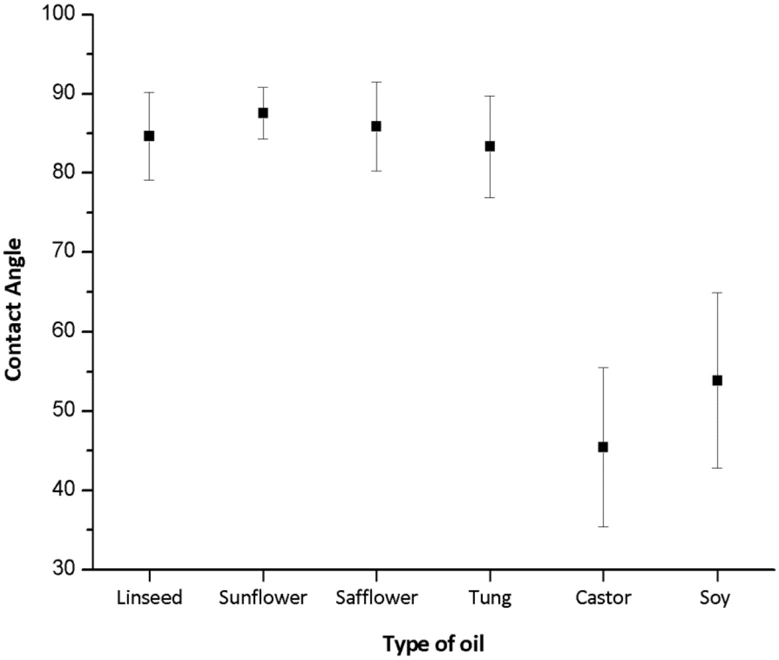

Fig. 2.27 Contact angle measurements for the six oils analysed.

Castor and soybean oils have a similar contact angle, of about 50, while the other four oils have an average contact angle value of about 85. Castor and soybean oils appear to be more hydrophilic than the other oils. For castor oil a possible explanation is that, containing about 90% of ricinoleic acid, which has a hydroxyl functional group on the 12th carbon, it is more polar than the other oils. For soybean oil, instead, the explanation is not so obvious, because it has a fatty acids profile very similar to that of sunflower oil, with linoleic acid as the most abundant compound. However, it shows a very different contact angle from sunflower oil.

It must be noted that the variance of the measures is higher for castor and soybean oils with respect to the other oils, pointing out a greater uncertainty of the measure, which may depend on the semi-siccative nature of these two lipid materials.

It was not possible to perform contact angle measurements on the naturally aged (14 months) and artificially aged oils because the surface of these aged oil layers was too rough and irregular to obtain significant results.

2.6 Conclusions

The application of analytical GC/MS and HPLC-ESI-Q-ToF methodologies enabled the characterization of the oils selected for the study. The fatty acids profile was determined with GC/MS, for both the fresh oils and the naturally aged (14 months) oils. Unfortunately, although the fresh oils showed in some cases a characteristic fatty acids profile, the aged oils were difficult to differentiate with GC/MS. With the exception of castor oil, they all showed very similar profiles, characterized by the same di-acids and hydroxy-acids, with azelaic acid being the most abundant for tung, sunflower, soybean and linseed oils. Thus, we decided to employ HPLC-ESI-Q-ToF to study the triglycerides profiles. An innovative HPLC-mass spectrometric method to perform analyses on lipids was developed, optimized and in particular applied to the study of the target oils. The HPLC-MS^2 analyses led to the characterization of the majority of the triglycerides constituting the oils and of several oxidized triglycerides, some of them being intermediate oxidation products.

The HPLC-ESI-Q-ToF technique proved to be more reliable for the identification and differentiation of the “modern” oils, compared to GC/MS. We found that some TAGs are characteristic of specific oils, e.g. LnLnLn, LnLnL and LnLL are specific for linseed and soybean oils, LLO is specific for safflower and soybean oils, castor oil is the only oil to contain a ricinoleyl substituent, while tung oil a eleostearyl substituent.

Moreover, some oxidized TAGs are characteristic of a certain oil: $SC_{18:1,OH}O$, $SC_{18:1,OH}C_{18,OH}$ and $OC_{18:1,OH}C_{18:2,OH}$ are oxidized TAGs specific for linseed oil; $C_{18:2,OH}PP$ is specific for safflower oil, $C_{18:2,OH}OP$ is characteristic of tung oil and $C_{18:1,2OH}C_{18:1,OH}O$, $C_{18:1,OH}C_{18:1,2OH}C_{18:1,OH}$ are TAGs specific for castor oil.

However, in the presence of mixtures of different oils, the identification is still challenging, even with HPLC-ESI-Q-ToF.

The results obtained from this survey have given an insight on the ageing processes underwent by the oils, highlighting:

- a decrease of TAGs containing unsaturated fatty acids;
- the fast disappearance of polyunsaturated chains in linseed and sunflower oils, because of quick crosslinking reactions, in opposition to the detection of these chains in soybean and safflower oils even after 48 h of artificial ageing;
- an increase in oxidized TAGs;
- a decrease of the total amount of TAGs extracted due to crosslinking reactions;
- a deeper knowledge on the TAGs constituting the oils used in modern paints and of their evolution over the time with respect to the curing.

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