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Liaisons Dangereuses, Conservation of Modern and Contemporary Art: a study of the synthetic binding media in Portugal

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Resumo

Este projecto centra-se no estudo de materiais sintéticos utilizados por artistas portugueses no século XX. O objectivo principal foi a caracterização molecular de polímeros vinílicos e acrílicos usados a partir dos anos sessenta, estudando a sua fotodegradação e evolução ao longo do tempo. Na arte contemporânea, as emulsões aquosas são utilizadas como aglutinante em pintura, nomeadamente emulsões acrílicas e vinílicas. Em países como Portugal, em que as emulsões à base de poli(acetato de vinilo) – PVAc – foram as primeiras a ser utilizadas, tanto em tintas de parede como em tintas para artistas, desde a década de 1960 por artistas como Joaquim Rodrigo e Ângelo de Sousa, o estudo dos polímeros vinílicos é particularmente importante. De modo a garantir a preservação futura das obras de arte, é essencial compreender como é que estas emulsões irão comportar-se face ao envelhecimento. Estudou-se a fotodegradação do PVAc, tendo-se investigado a presença de produtos de degradação em amostras modelo e em obras de arte datadas. Pinturas de Joaquim Rodrigo e Ângelo de Sousa, bem como um catálogo das tintas vinílicas para artistas *Sabu*, foram seleccionados como casos de estudo; tendo-se investigado a evolução real do polímero nas obras de arte. Foram realizados estudos de envelhecimento acelerado através da exposição de filmes de PVAc numa câmara equipada com uma lâmpada de xénon. O comportamento do PVAc (homopolímero) foi comparado com uma emulsão comercial e com reconstruções das tintas preparadas em laboratório. Os resultados obtidos por microespectroscopia de infravermelho (FTIR) apontam para uma estabilidade considerável destes aglutinantes, uma vez que não se obteve qualquer evidência a nível molecular no que diz respeito à formação de outros grupos carbonilo, ao desaparecimento do carbonilo do PVAc ou formação de hidroperóxidos. O processo de fotodegradação do polímero foi ainda investigado por cromatografia de exclusão molecular (SEC), seguindo a distribuição do peso molecular e pesos moleculares médios correspondentes. Concluiu-se não haver reacções da cadeia lateral e que o processo de degradação fundamental é a cisão da cadeia principal, não afectando significativamente o comportamento do polímero. Determinou-se que o rendimento quântico de cisão do homopolímero de PVAc a 313 nm é de $7,4 \times 10^{-8}$; deste modo a degradação é quantificada possibilitando a comparação entre diferentes polímeros. Foi considerada a influência de pigmentos, como o dióxido de titânio e o óxido de ferro na estabilidade do polímero, tendo-se concluído que estes não promovem a degradação, o que poderá dever-se ao encapsulamento com materiais inertes inibindo a sua actividade fotocatalítica. Seguindo uma abordagem experimental idêntica, foi efectuado um estudo paralelo para o poli(metacrilato de metilo) – PMMA – utilizado como vidro acrílico pela artista Lourdes Castro, tendo-se testado ainda a acção de um produto comercial de limpeza utilizado pela artista. Verificou-se ser bastante estável à luz, sendo o rendimento quântico de cisão de $3,85 \times 10^{-8}$.

Abstract

This project is focused on the study of synthetic materials used by Portuguese artists in the twentieth century. The aim of the study was the molecular characterization of vinyl and acrylic polymers used since the 1960s and the study of their photodegradation and evolution over time. In modern and contemporary art, water based synthetic emulsions have been widely used as painting binding media, especially acrylic and vinyl based emulsions. In some countries like Portugal where the first aqueous emulsions used as paint binders were the poly(vinyl acetate) – PVAc – ones, both as household and artist's paints, the study of vinyl polymers is of particular importance. In Portugal these emulsions were used by outstanding artists like Joaquim Rodrigo and Ângelo de Sousa since the 1960s. In order to guarantee the preservation of the artworks for the future generations it is essential to understand how these paints will behave upon ageing. The molecular photodegradation of PVAc was studied and the presence of degradation products on reference and model samples, as well as on dated artworks was investigated. Paintings by Joaquim Rodrigo and Ângelo de Sousa, and also a hand painted catalogue for the *Sabu* vinyl artists' paints, were selected as case studies. The characterization of micro-samples from the artworks provided useful information on the real evolution of the polymer binder over time. Accelerated photodegradtion studies were performed by the exposure of PVAc films on an ageing chamber equipped with a xenon-arc lamp. The behaviour of PVAc (homopolymer) was compared with a commercial emulsion (*Vulcano V7*) and paint reconstructions prepared in the laboratory. The results achieved by means of infrared microspectroscopy (FTIR) point out the considerably stable nature of these binding media as no molecular evidence was obtained concerning the formation of other carbonyl functions, the disappearance of the PVAc carbonyl or the formation of hydroperoxides. The polymer photodegradation process was further studied by means of size exclusion chromatography (SEC), following the molecular weight distribution and correspondent average molecular weights. It was concluded that no side-chain reactions are taking place and that main-chain scission is the foremost degradation mechanism, although not affecting the polymer performance significantly. The influence of pigments, such as titanium dioxide and iron oxide, on the polymer's stability was also considered and it was concluded that they do not promote degradation, which might be explained due to pigment encapsulation in inert materials inhibiting its photocatalytic behaviour. The photodegradation quantum yield was determined as 7.4×10^{-8} at 313 nm for PVAc homopolymer; therefore, degradation is quantified and comparisons may be performed for different polymers. A parallel study, according to a similar experimental approach, was undertaken on the stability of poly(methyl methacrylate) – PMMA – used as acrylic sheet by the Portuguese artist Lourdes Castro.

Symbols and Notations

ε	Molar absorptivity coefficient
δ	Bending vibration
Δ	Variation
ΔE^*	Total colour variation
Φ	Quantum yield
λ	Wavelength
μ	Micro
μ	Peak centre
ν	Stretching vibration
σ	Width at half maximum
ρ	Standard error
2-EHA	2-ethylhexyl acrylate
a	Area
A	Absorbance
APT	Associação Portuguesa de Tintas
$_{as}$	Antisymmetric vibration
ATR	Attenuated Total Reflectance
BASF	Badische Anilin & Soda Fabrik
dc	Diamond cell
CIN	Corporação Industrial do Norte, S.A.
d	Diameter
DBP	Dibutylphtalate
DCR	Departamento de Conservação e Restauro
DiBP	Diisobutylphtalate
DLS	Dynamic Light Scattering
DSM	Dutch State Mines
EDXRF	Energy Dispersive X-Ray Fluorescence
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
I_0	Intensity of the incident light
I_{abs}	Total light absorbed
ICI	Imperial Chemical Industries
IR	Infrared

kg	Kilogram
L&B	Lefranc & Bourgeois
m	Medium
M	Molar
M_n	Number average molecular weight
M_w	Weight average molecular weight
MNAC	Museu Nacional de Arte Contemporânea – Museu do Chiado
*n*BA	*n*-Butyl acrylate
nm	Nanometre
PD	Polydispersity
P(EA-MMA)	Poly(ethyl acrylate – methyl methacrylate)
PMMA	Poly(methyl methacrylate)
P*n*BMA	Poly(*n*-butyl methacrylate)
PVAc	Poly(vinyl acetate)
PVAL	Poly(vinyl alcohol)
REP	Robbialac Emulsion Paints
S	Number of scissions per chain
S’	Rate of scissions per chain
$_s$	Symmetric vibration
s	Standard deviation
s	Strong
sld	Shoulder
s_r	Relative standard deviation
SEC	Size Exclusion Chromatography
SNS	Sociedade Nacional de Sabões
T_g	Glass transition temperature
t_r	Retention time
UV-Vis	Ultraviolet-visible
VA	Vinyl acetate
VeoVa	Vinyl versatate
V_{sol}	Solution Volume
vs	Very strong
vw	Very weak
w	Weak
W&N	Winsor & Newton

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Chapter 1

Introduction

1.1 Preamble

Synthetic polymers are ubiquitous in today's daily life and are used in a variety of objects. After the three main periods of the ancient societies, classified as Stone Age, Bronze Age and Iron Age, science has evolved and, despite great discoveries throughout the centuries, the development of synthetic polymers in the early 1900s has revolutionized the life of the modern and contemporary society. In 1979 the production of steel was surpassed by the volume of plastics produced worldwide. This event was the landmark for what is now considered as the 'Plastic Age' [1]. Table 1.1 lists some of the main events marking the development of plastics, *i.e*. some of the first semi-synthetic and synthetic polymers.

Table 1.1. Important dates concerning the initial development of Plastics

Polymers	Important dates	References
Cellulose nitrate		
Parkesine	1862 (first exhibited)	[1]
Celulloid	1870 (patent date)	[2]
Phenolic polymer		
Bakelite	1909 (patent date)	[2]
Acrylics Polyethylene Polystyrene Polyamides	1930s	[2]

Poly(vinyl acetate), PVAc, was introduced in 1928 [3] and it has been widely used as household paints and adhesives in the form of aqueous emulsions [4]. The first artists' quality vinyl paint was a Polymer Tempera developed in 1946 by the American company *Borden* Co [5]. In Portugal, *Robbialac* produced a series of household PVAc based paints, REP[1], at least since 1954, and in the late 1950s *A Favrel Lisbonense* launched the production of vinyl based artists' quality products - *Sabu*, *Geo* and *Vulcano V7* (Chapter 2).

The first organic glass, poly(methyl methacrylate), PMMA, was synthesized for the first time in 1931 and its trademark was registered as *Plexiglas* by *Röhm & Hass* [6] and in 1934 as *Perspex* by ICI (*Imperial Chemical Industries*) [7]. This plastic material found worldwide applications. Its transparency made it highly suitable for aircraft canopies during World War II [7] and was also attractive for artists. Naum Gabo and other members of the Russian *avant-garde*, felt that the recently developed plastics represented modern technological materials of the industrial era [8,9]. Having a contact in ICI, it is probable that Gabo had access to *Perspex* as soon as 1937 before it was widely available [10].

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[1] Robbialac Emulsion Paints.

As mentioned above, the curiosity and experimentation practice of modern and contemporary artists, lead them to use the *new* synthetic polymers almost as soon as they became available. As a consequence, important cultural and artistic objects are made of these plastic materials, for which much is still to be learned in terms of long-term stability. In the conservation filed, synthetic polymers have been applied as consolidants and varnishes at least since the 1930s [11,12]. The concerns with the durability of these materials started with Feller who, following Thomson's work from the fifties, classified them according to their photochemical stability based on the capacity to remain soluble [3,13-16] and therefore, on their suitability to be used in conservation and restoration treatments. The awareness for the importance of correlating the phenomena at the molecular level with the material performance is recent and systematic studies have been carried out on the weathering of synthetic polymers [17-21].

In Portugal, art studies have been almost restricted to art history, with little systematic research concerning materials and techniques. PVAc based emulsions were used by Portuguese renowned artists like Joaquim Rodrigo (1912-1997) and Ângelo de Sousa (b. 1938) since the early 1960s [22,23]. Rodrigo produced some of the most important works of the Portuguese art scene in the 1960s and 1970s, with a consistent use of a vinyl binding medium until he made his last work (1990). Ângelo de Sousa, another major name of Portuguese contemporary art, has a singular work both in the national and international contexts. Using the painting media as his instrument of plastic experimentation, was also one of the first Portuguese artists to have used vinyl based paints. On the other hand, Lourdes Castro (b. 1930) has a remarkable work on the study of the shadow concept, which she has explored in multiple ways. This artist used acrylic sheet [24] in colour compositions as a painter uses paint colours and made use of the optical properties characteristic of that material.

To our knowledge this is the first systematic study of the materials used by Portuguese modern and contemporary artists. The present work is focused on the characterization of vinyl paints and acrylic sheet in artworks. The polymer photostability will be studied in models and the results compared to dated samples from selected paintings by the artists chosen as case studies – Joaquim Rodrigo, Ângelo de Sousa and Lourdes Castro. Also, the study of a catalogue made with the original *Sabu* paints will be carried out.

1.2 The advent of poly(vinyl acetate)

Hoechst had started producing polyvinyl acetate (the future Mowilith) and polyvinyl alcohol in 1928

Aftalion, 2001

Poly(vinyl acetate) was introduced in 1928 [3] and, for the first formulations, an organic solvent was used. Safer, non-toxic aqueous emulsions[2] followed very quickly and were developed in the late 40s [25]. After World War II the paints and coating industry underwent a major changeover with the lack of natural raw materials, due to the war consumption and were soon replaced by synthetic polymers [26]. In 1965 the production of poly(vinyl acetate) was estimated as being 8.6% of the total synthetic polymers world production; that is equivalent to approximately 57% if some of the largest production polymers, *i.e.* poly(ethylene), poly(vinyl chloride) and poly(styrene), are excluded [27].

In 1912 Dr. Fritz Klatte, working at the *Chemische Fabrik Griesheim-Elektron* in Frankfurt, patented the production of vinyl esters (DRP 271381 – 'Procedure for the production of ethyleneglicol esters and ethers and vinyl alcohol') and their polymerisation (DRP 281687 and DRP 281688). In the same year Klatte also patented the production of paints and varnishes and the production and utilization of poly(vinyl chloride). In 1925, *IG – Farbenindustrie AG*. was formed with the incorporation of *Farbwerke Hoechst* from *Chemische Fabrik Griesheim-Elektron*. The technical maturity achieved lead to great developments: large scale production of gas-phase vinyl acetate from acetylene and acetic acid; technical development of vinyl acetate polymerization; the introduction of vinyl acetate emulsion polymerization, with poly(vinyl alcohol) as protective colloid; among others [27,6]. Emulsion polymerization was patented by *IG – Farbenindustrie AG* in the 1930s [28]. Over the years several synthesis processes have been developed for the production of vinyl acetate and in all acetic acid is used as a raw material, Figure 1.1 [27,29,30].

$$\mathrm{HC \equiv CH + HOOC \cdot CH_3 \xrightarrow{Hg\ (liquid)} H_2C = CH \cdot OOC \cdot CH_3}$$

Figure 1.1. Example of the early synthesis process of vinyl acetate from acetylene and acetic acid. Adapted from [27].

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[2] By definition emulsion is 'a fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid' [31]. Nevertheless, here the word is used to describe a dispersion of polymer particles in water, as it is a widespread term applied to paints (emulsion paints; waterborne emulsions; aqueous emulsions) [32,33].

The polymer is formed by polymerization of its monomer, vinyl acetate. Like most polymers used as coatings, poly(vinyl acetate) is produced by free radical chain-growth polymerization, Figure 1.2 [32-34].

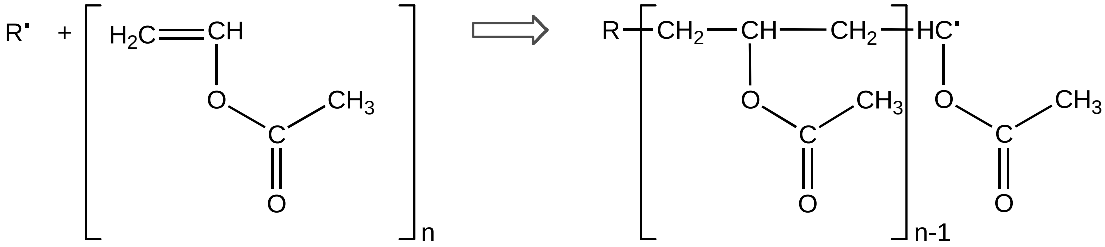

Figure 1.2. Free radical chain-growth polymerization. R$^\bullet$ - radical initiator.

A particular process of chain-growth polymerization is emulsion polymerization, Figure 1.3, in which the monomers are polymerized in water with the addition of a water soluble initiator and a surfactant [26,32-34].

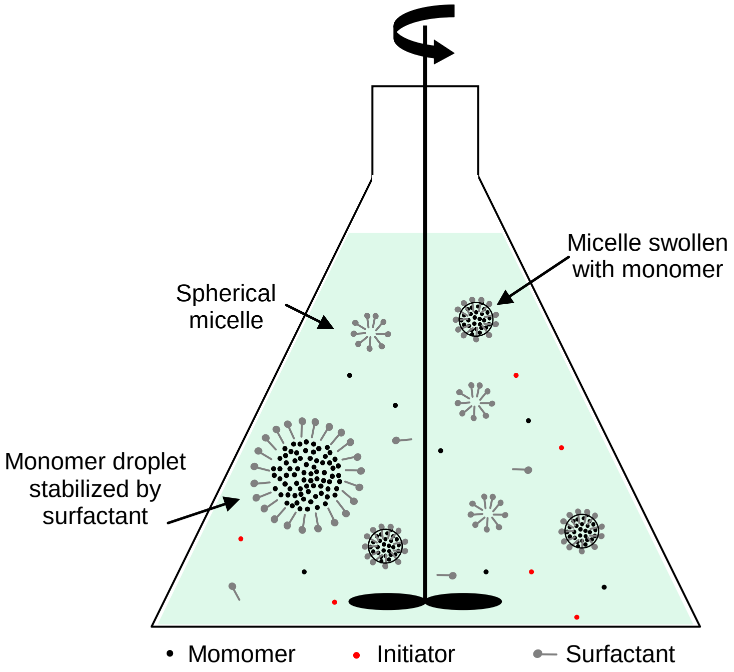

Figure 1.3. Schematic representation of emulsion polymerization. Adapted from [34].

The vinyl acetate monomers are mainly insoluble in water and are stabilized in an emulsion by the surfactant. At concentrations above the critical micelle concentration the surfactant molecules in water arrange themselves as micelles, with the polar hydrophilic head in contact with water and the non-polar hydrophobic tails in the centre of the cluster. The monomer molecules have chemical affinity to the surfactant non-polar tails. In emulsion polymerization two processes may occur; on one hand the low percentage of monomer able to dissolve in water diffuse to the interior of the micelles and, on the other hand, surfactant molecules dispersed in water are absorbed to the surface of monomer droplets. The polymerization process, which proceeds by initiation, propagation and termination steps, takes place mostly in the interior of the micelles. After circa 15% conversion of monomer, the micelles become polymer [33-35]. Further entropic stabilization can be obtained by the addition of a protective colloid (poly(vinyl alcohol), a water soluble polymer, is commonly used), creating thicker layers than the ones formed by the surfactant and increasing stability. [26,32]. An emulsion polymer is thus obtained with particle diameter of approximately 0.1μm; polymer and water typically present in a proportion of 50:50 in volume [34]. Emulsion polymers generally present high molecular weights and *Mw* values above 1×10^6 may be expected [32]. Table 1.2 summarizes some of the molecules, besides monomer and water, which may be found in an emulsion polymerization formulation.

Table 1.2. Examples of initiator, surfactant and protective colloid components in emulsion polymerization [32]

Initiator	Surfactant	Protective colloid
Persulfate salts (ammonium persulfate)	Sodium lauryl sulphate (anionic)	Poly(vinyl alcohol)
t-Butyl hydroperoxide	Nonyl phenol ethoxylates	Hydroxyethyl cellulose
Sodium formaldehyde sulfoxylate	Ethoxylates of aliphatic alcohols	

Unlike solutions, polymer emulsions dry through a complex process with several overlapping steps, still not completely understood, in which film formation occurs via coalescence of particles. For film formation to occur efficiently temperature must be above the minimum film formation temperature (MFFT); the MFFT is highly dependent on the polymer T_g and also on its structure and on the additives in the formulation [26,32,36,37].

The first step of film formation from an emulsion (Figure 1.4) is water evaporation, leading to a close packed layer of spherical polymer particles. This packaging promotes particle deformation; some authors have suggested that the water voids between the particles have a capillary force effect and that this capillary pressure will lead to particle deformation. Deformed polymer particles have a higher area of contact between them, which therefore promotes coalescence (fusion of the polymer particles) [26,32,36,37]. Figure 1.5 illustrates the film surface obtained from polymer solution (on the left) and a coating obtained from polymer emulsion (on the right). In the latter case, coalescence of the particles is not complete and a continuous film is not formed.

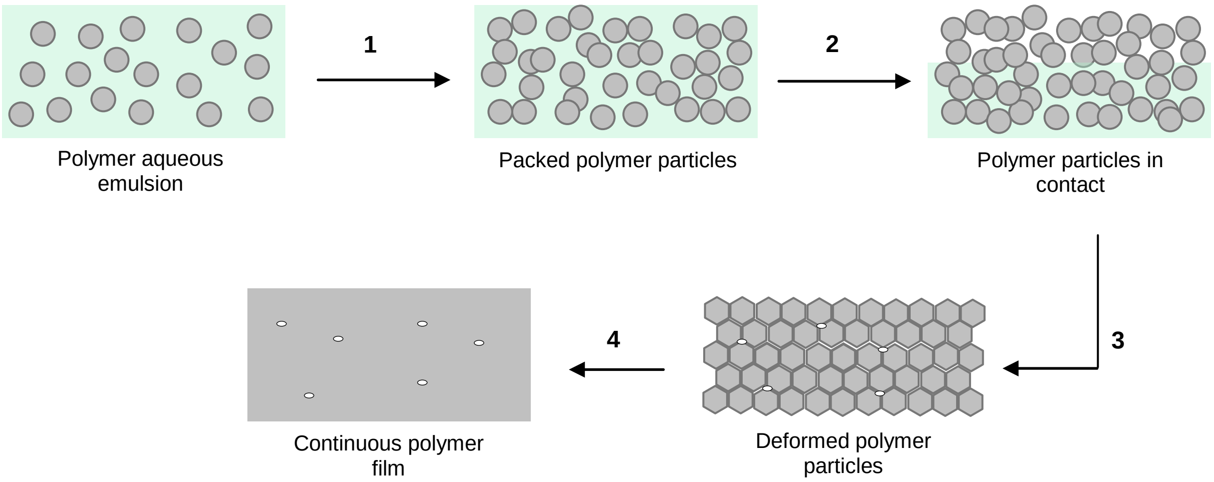

Figure 1.4. Schematic representation of film-formation from a polymer aqueous emulsion. 1 and 2 – evaporation of water; 3 – evaporation of water and deformation of polymer particles; 4 – coalescence of polymer particles. Adapted from [36].

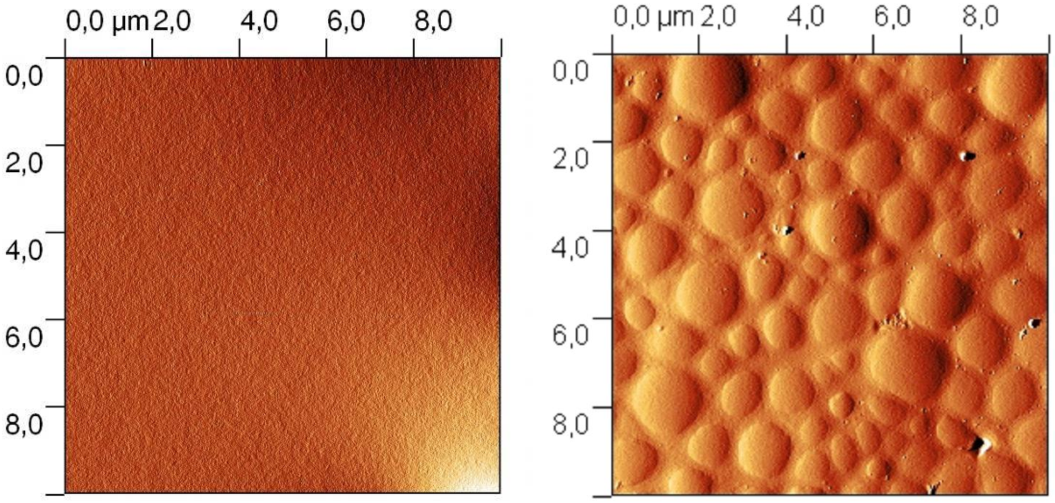

Figure 1.5. Atomic Force Microscopy (AFM) amplitude images of coating surfaces (10 x 10 µm areas): left – coating film cast from a PVAc solution in acetone; right – coating cast from a PVAc based aqueous emulsion (*Vulcano V7*). For more details please see text. Images obtained by Peter Eaton.

Emulsions of poly(vinyl acetate), PVAc, have been extensively applied as exterior and interior architectural coatings, paints and adhesives [4]. According to Stoye and Freitag PVAc binders form fine quality films: transparent, lightfast, with good hardness, gloss and adhesive strength. Nevertheless, these emulsions are known to form slightly hard[3] and brittle films [26], therefore plasticisers need to be used (sometimes up to 20% by weight) to reduce its T_g. Phthalates, namely dibutyl phthalate (DBP), are common plasticisers; being volatile they have a tendency to migrate out of the paint film. Internally plasticised PVAc emulsions with softer monomers form permanent flexible films. Some of the co-monomers used are *n*-butyl acrylate (*n*BA), 2-ethylhexyl acrylate (2-EHA), di-*n*-butyl maleate and the C_{10} branched vinyl esters (vinyl neo-decanoate), Figure 1.6 [32]. These highly branched vinyl esters are sold by *Shell* as commercial resins and named vinyl versatates (VeoVa). The PVAc/VeoVa copolymer is considered to have better hydrolytic stability and UV resistance than the homopolymer or PVAc conventional copolymers [32,36]. This higher stability has been explained by a neighbouring group steric effect due to the neo-decanoate branched structure next to the carbonyl group [38].

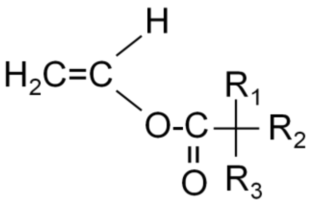

Figure 1.6. Vinyl neo-decanoate. R_1, R_2 and R_3 are alkyl groups totalling C_8H_{19}. Adapted from [32].

By definition, paint consists mainly of inorganic or organic pigment particles dispersed or dissolved in the binder (an organic matrix, the polymer when considering polymer based paints) [32]. It is in fact a complex mixture of vehicle (film-former and carrier fluid), pigments, extenders, and several additives that, applied as a thin layer and after solvent evaporation or binder crosslinking, forms a dry solid film [33,39]. Waterborne emulsion paints typically have a relatively high solids content of approximately 50-60% by weight [26]. Figure 1.7 summarizes the most common components of a paint formulation. Each component has its specific function, both in the liquid paint and in the solid film [26]. Binders, pigments and solvents or diluents are the most important components of paint and the ones which account for most material. Although additives are present in a small percentage (in some cases less than 1%), they have major influence on the paint properties [26,40]. Specific data on paint additives may be found in [28,36,40]. As shown in Figure 1.7, additives in paints are introduced to meet several purposes and it is possible to separate the ones having general functions, such as dispersants, defoamers and matting agents, and the ones with special functions, for example light stabilizers and anti-skinning agents.

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[3] The Tg of PVAc is above room temperature (*ca* 30ºC) and therefore the polymer presents a rigid behaviour.

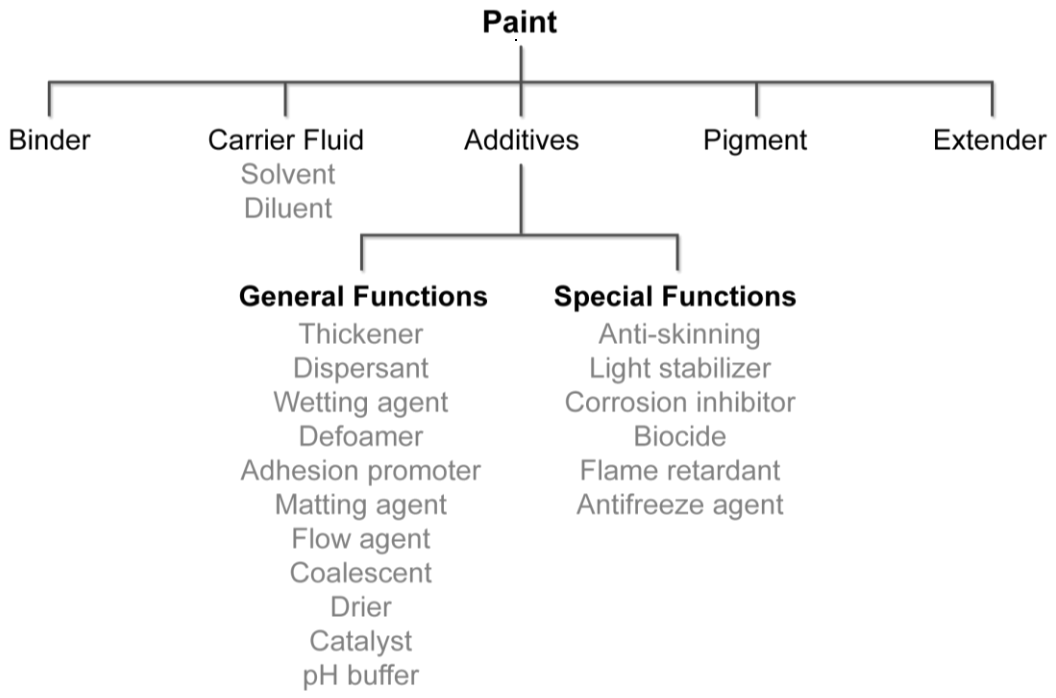

Figure 1.7. Common paint components [26,28,36,40].

The novelty of vinyl and acrylic emulsions as a paint material attracted artists and these emulsions were used in works of art probably already in the 1940s and 1950s respectively [5,36,25,41-43]. In the same decades the first artist's formulations based on these synthetic emulsions were introduced in the market [5], and have replaced the primacy of oil paints. Artists' quality paints are similar to household paints in their general formulation, although they are likely to possess higher quality pigments and higher application viscosity; these paints are thus formulated with less extender, more pigment and thickener [28]. According to Crook and Learner, the first Polymer Tempera, an artists' PVAc based emulsion paint, was developed in 1946 by the paint manufacturer *Borden* Co. with the collaboration of the American artist Alfred Duca. The first artists' quality PVAc binding medium in the UK was marketed by *Rowney* as an unpigmented binder and the same company introduced a series of PVAc colours in 1966 [5]. Other colourmen, such as *Spectrum*, *Reeves* and *New Masters*, also produced artists' quality vinyl and vinyl-acrylic paints; *Flashe* by *Lefranc & Bourgeois*, a PVAc/VeoVa emulsion based artists' paint, is still marketed [36]. In Portugal besides the household commercial paints, like *Robbialac* REP paints, which were produced at least since the 1950s, there was also an early production of artists' quality PVAc based products by *A Favrel Lisbonense* – *Sabu*, *Geo* and *Vulcano V7* (see Chapter 2.2). Vinyl paints have been used by Portuguese artists at least since the early sixties [22,23,44].

The use of vinyl resins in conservation of artworks started earlier, with Gettens and Stout reporting the application of PVAc solutions in 1932 [11,12]. In that first report, a resin produced by *Carbide and Carbon Chemicals Corporation* (New York), *Vinylite A*, was used as a consolidant for the transfer of wall paintings to new supports. PVAc solutions have also been applied in the conservation of paintings (both for lining and as surface varnish) ceramics, paper, textiles, bone and ivory [45-47]. Characteristics such as its transparency, solubility in several organic solvents, flexibility, resistance to humidity, and stability to oxidation and light have been referenced as making it suitable for this use [11,45,46]. Emulsions of PVAc have also been used in conservation, namely as adhesives for paper and paintings [47].

1.3 Poly(methyl methacrylate) – *Perspex*, *Plexiglas* or *Altuglas*

Associated with concepts such as 'modernism', 'consumerism' and 'globalization', from containers to textiles, furniture to fine art, plastics are inherently part of our cultural associations and our museum collections.

Sandra Smith, 2008

Plexiglas (*Röhm & Haas*, Germany) and *Perspex* (ICI, Britain) are worldwide known trade names for acrylic transparent sheets made from poly(methyl methacrylate), PMMA [6,7]. In the framework of new plastics discoveries and of search for transparency a new product was developed that was 'highly transparent, workable, mechanically strong' and 'unlike cellulose nitrate, did not go yellow in sunlight' [7]. The history of the development of PMMA sheets, as well as of other acrylics, goes back to 1901, when Otto Röhm 'published a thesis on the polymerization of acrylic acid, for which he took out a first patent in 1912' [6]. In 1920, the work of the chemist Walter Bauer enabled the synthesis of acrylic acid from ethylene cyanohydrin by an economic process. After that, and 'following the work that W. Chalmers had conducted at McGill University in Montreal in 1929-30, *Röhm & Haas* and ICI became interested in the esters of methacrylic acid'. In 1931 Bauer polymerized methyl methacrylate into a 'transparent thermoplastic which melted at 110ºC and which could be moulded with ease or cast in a mould to produce sheets. What turned out to be the first organic glass was called *Plexiglas*' by *Röhm & Haas*. Also in 1931, ICI patented a process to produce moulded objects from PMMA. In 1932 John Crawford, a chemist working for ICI, developed 'an elegant and economic synthesis of MMA' [6]. Methyl methacrylate was obtained in the presence of catalysts, such as cooper and sulphur, by the mixture of acetone, sodium cyanide and sulphuric acid, methanol was added to the products and the ester isolated by distillation [6,7]. The trademark was registered in 1934 by ICI under the name *Perspex*[4]. 'The working out of the process was widely recognized as a brilliant piece of chemistry and, with some modifications, Crawford's process is still the basis for large scale manufacture of acrylic plastics throughout the world' [7]. ICI sold the licenses on its production process to *Röhm* for *Plexiglas* in 1934 and to *Du Pont* (US) for *Lucite* in 1936. There was a need for a new transparent material, 'glass was suicidal and celluloid had terrible problems' [7]. 'Lighter than mineral glass, this new organic glass' [6] 'was first incorporated into the new Spitfire in 1936. (…) Its great wartime role as the material for aircraft canopies had in fact been the spur for its invention' [7].

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[4] 'From the Latin "to see through"'.

In the formulation of PMMA, as of other plastics, the incorporation of additives may significantly alter its chemical and physical properties, and also affect the appearance of the finished product. A diversity of materials is used as additives, being, antioxidants, light stabilizers and flame retardants the most common used; many others may be added depending on specific applications. Also, some overlap occurs between the functions of polymer additives. Depending on the type of additive, these materials are introduced in very different concentrations, ranging from circa 0.2% to 60%. As it was mentioned for paints, additives used to process plastics have been thorough described elsewhere [9,48]. As stated above, PMMA success relied mainly on its transparency. The transparency/opacity of polymers is either related to the presence of additives or to their degree of crystallinity. Highly crystalline polymers, if not in very thin films, are opaque, while amorphous polymers are transparent [9]. PMMA sheets, *i.e.* acrylic sheet, have been reported to be processed mainly by extrusion or cast moulding, with molecular weight of extruded PMMA being one order of magnitude lower than that of cast sheets [49-51].

The Russian artist Naum Gabo wrote in 1937 ‘our century has been enriched by the invention of many new materials’ [52]. As soon as 1910, Gabo and his brother, the artist Antoine Pevsner were the first to use plastics in sculpture [8]. Like other Russian *avant-garde* artists, they considered the recently developed plastics as modern technological materials of the industrial era [8,9]. Besides cellulose acetate and cellulose nitrate, the other plastic commonly used by Gabo was PMMA. Having a contact in ICI, it is probable that he had access to *Perspex* as soon as 1937 before it was widely available [10]. Along with Gabo other artists, like Pevsner, Archipenko and Moholy Nagy, opted for PMMA due to its better performance on ageing [8]. In the course of the 1960s the plastics industry launched a campaign intended to ‘improve the image of plastics’. BASF created a prize encouraging artists to use plastics in their works of art and in 1967 *Hoechst* invited artists of different nationalities to show their work at the Plastics Fair [8]. Despite of the large variety of colours in which acrylic sheet is processed nowadays, this material is no longer found in the colours used by Pop Art artists in the 1960s, such as fluorescent pink and bright yellow [53].

1.4 Degradation and photooxidation of polymers

Polymers, like other materials, are affected by environmental conditions, such as UV and visible light, temperature, oxygen, water and atmospheric pollution (Figure 1.8) [54]. The effect of these agents on polymer degradation is complementary and sometimes synergistic [55].

As previously stated, commercial polymers have rather complex formulations. The various additives present in the formulation will affect the durability of the polymer. Each component has its own weathering resistance; hence the interaction of the different elements will be determinant to the overall stability (Figure 1.8). The additives may have a sensitizing or stabilizing effect. Their effect may be synergistic, where for example the effect of two stabilizers will be greater than the sum of the individual effects, or it may be antagonistic. Therefore, commercial polymers are highly complex composite systems [54,56].

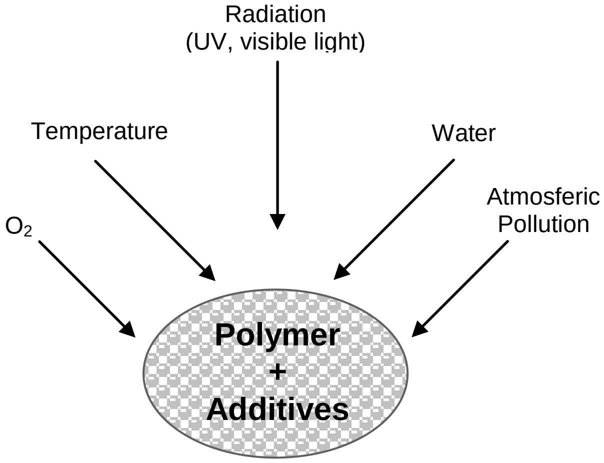

Figure 1.8. Weathering factors influencing a polymer matrix. Adapted from [54].

Photooxidation is considered to be the main factor affecting polymer weathering [17,55,56]. As Feller stated 'photochemical damage is irreversible damage'. Even the exposure under low intensity radiation levels will deteriorate sensitive objects. According to the reciprocity principle, photochemical degradation might be slowed but will not be ceased. The number of photons emitted per minute may be reduced by lowering the illumination intensity; however their damaging energy cannot be altered [57].

The UV radiation that reaches the earth (295-400 nm) is the light component responsible for initiating most degradation processes by photolysis of polymer or additive covalent bonds, photolysis of hydroperoxides and excitation of chromophores. Visible light (400-760 nm) may increase photodegradation if visible light-absorbing chromophores or additives are present in the polymeric system. Finally, infrared radiation (760-2500 nm), is responsible for thermal effects, which may be particularly important to dark pigmented polymers [55].

A basic principle in photochemistry is that for any given photochemical reaction to occur radiation must be absorbed [58,59]. The data in Table 1.3 illustrates the main transitions in some polymers and stresses that, in theory, most polymers do not absorb in the sunlight region of the electromagnetic spectrum. Nonetheless, the quantum energies associated with the near UV light that reaches the Earth (≈ 300-400 nm) are sufficient to break the chemical bonds in most polymers; therefore, photodegradation is dependent on the absorption of light by impurity chromophores [56,60]. When studying the stability of polymers an important factor is the structure of a commercial polymer, which is likely to be more complex than indicated by its molecular formula. Commercial polymers typically have structural irregularities, branches, double bonds and also carbonyl and hydroperoxide groups, introduced during polymerization and storage. These impurities may act as initiation sites for polymer degradation [56,61].

Table 1.3. Main transitions in given polymers. Adapted from [56]

Polymer	Chemical bonds	Maximum absorption
Polyolefines	C-C, C-H	140 nm ($\sigma \rightarrow \sigma^*$)
Poly(vinyl halides)	C-halogen, C-C, C-H	190 nm ($n \rightarrow \sigma^*$)
Poly(vinyl alcohol)	C-C, C-H, C-O, O-H	200 nm ($n \rightarrow \sigma^*$)
Poly(butadiene)	C-C, C-H, C=C	220 nm ($\pi \rightarrow \pi^*$)
Poly(styrene)	C-C, C-H, C=C	230-280nm ($\pi \rightarrow \pi^*$)
Aliphatic poly(amides)	C-C, C-H, N-H, C=O, C-N	220 nm ($n \rightarrow \pi^*$)

From the first time they were used, polymers have shown problems with durability, and the prediction of the long-term life of polymeric materials is still a difficult problem. Due to advances in the understanding of weathering phenomena, polymer matrixes are no longer considered black boxes but complex systems for which a consistent experimental methodology has been developed and thoroughly tested [17,54,56,62,63]. This was based in the recognition that, for polyolefin-based structures, the controlling process of aging is photooxidation, and that when a common mechanism has been observed, it is possible to correlate between weathering and accelerated artificial aging kinetics. In 1972 researchers at the Laboratory of Photochemistry from the University of Clermont-Ferrand (France) initiated fundamental research on the phenomena of polymers photodegradation in accelerated conditions [17]. These studies have demonstrated that it is possible to reproduce the natural evolution in the laboratory, controlling the chemical mechanisms at the molecular scale. In this mechanistic approach to photooxidation, the polymeric system is considered as a photochemical reactor [17], in which the formation of several functional groups will lead to chemical aging [64]. Therefore, to fully understand the photochemical mechanism it is fundamental to analyse the degradation products, as well as intermediates, at a very low reaction extent [17,59]. The degradation phenomena are thus verified at the molecular level by the identification of chemical changes occurring in the solid matrix [17]. This paved the way for the prediction of long-term behaviour and *acceleration factors* for polymers as supported by understanding of the aging mechanisms at the molecular level. The changes observed in the physical properties of the polymer are induced by chemical alterations in the matrix [17,64]. The relevance of the degradation phenomena is furthermore confirmed by the similarities found for both the physical and chemical changes occurring in natural and accelerated artificial exposures. This assessment is only possible when the nature and spatial distribution of the photoproducts are similar [17].

Because identification of the evolution mechanism is essentially based on the nature of the intermediate and final photoproducts, infrared (IR) and Raman spectroscopies have been used. Infrared spectroscopy is chemically specific and a highly sensitive technique; it is therefore suitable for the characterization of chemical changes in the polymer matrix and for the identification of photoproducts [17,64]. Derivatization reactions have been performed for an accurate identification and quantification of the photooxidation products observed in complex infrared spectra, improving its resolution [17,64,65]. The oxidized polymer is treated with reactive gases and the spectrum is thus simplified by the appearance of absorption bands assigned to the derivated products [64]. Furthermore, size exclusion chromatography is used to investigate the possible polymer chain scission as a degradation pathway [17].

Although less frequently obtained, probably due to the complexity of the experimental design, reaction quantum yields (Φ_R) are a fundamental parameter when it comes to quantifying photostability [62] and to understanding the reaction mechanisms. In polymer systems, they may be defined as the ratio between the number of molecules undergoing chain scission, crosslinking, or any other relevant photodegradation aspect per photon absorbed. As such, they constitute a universal and straightforward parameter to assess and compare polymer photostability.

1.4.1 Degradation and photooxidation of vinyl polymers

In which concerns PVAc photodegradation, systematic studies for which reaction quantum yields were obtained have been carried out by several groups [66-72] in vacuum and in air under UV irradiation. Under 254 nm irradiation, PVAc undergoes both chain scission and crosslinking accompanied by the release of volatile compounds. The main product formed is acetic acid followed by other volatiles such as carbon monoxide, carbon dioxide, and methane. The quantum yield values are dependent on the presence or absence of oxygen as well as on the initial molecular weight distribution [66-72], with lower yields in air and for lower molecular weights. The values reported for chain scission and crosslinking, Tables 1.4 and 1.5, were obtained with low and medium-pressure mercury lamps, meaning that experiments were conducted with a monochromatic 254 nm source and with a continuous envelope where the 254nm band is low relative to 313 and 366 nm [73], respectively.

Table 1.4. Quantum yields of crosslinking and chain scission for PVAc photodegradation under different light sources, in vacuum and in air

	Φ	**Irradiation source**	**Air / vacuum**	**Temperature** (^{o}C)	**Polymer M_w** (10^5)	**Reference**
Crosslinking	0.0025	254 nm ^{a}	Air	Room Temp.	10.1	66
	0.0470	254 nm ^{a}	Vacuum	Room Temp.	10.1	66
	0.0760	254 nm ^{a}	Vacuum	40 ^{o}C	10.1	68
	0.0035	Medium p. Hg ^{b}	Vacuum	45 ^{o}C	1.3	70
	0.0030	Medium p. Hg ^{b}	Air	55 ^{o}C	2.2	72
Chain scission	0.0050	254 nm ^{a}	Air	Room Temp.	10.1	66
	0.0658	254 nm ^{a}	Vacuum	Room Temp.	10.1	66
	0.111	254 nm ^{a}	Vacuum	40 ^{o}C	10.1	68
	0.0037	Medium p. Hg ^{b}	Vacuum	45 ^{o}C	1.3	70
	0.0068	Medium p. Hg ^{b}	Air	55 ^{o}C	2.2	72

^{a} Low-pressure Hg lamp. ^{b} Medium-pressure Hg lamp.

Table 1.5. Quantum yields of volatiles formation for PVAc photodegradation under different light sources, in vacuum

CH_3COOH	CH_3COH	CO_2	CO	CH_4	C_2H_6	Irradiation Source	References
0.01	-	0.0065	0.0069	0.0038	-	254 nm [a]	67
0.135	0.0533	0.0241	0.0097			Medium p. Hg [b]	71

[a] Low-pressure Hg lamp; room temperature; M_w = 1010000.
[b] Medium-pressure Hg lamp; 45 ºC; M_w = 133000.

Different sources may promote different photoreactive dissipative pathways. This could explain why, when using a low pressure mercury lamp, the quantum yield for main chain scission is approximately one order of magnitude higher than for side-groups scission (and for consequent release of acetic acid and other volatile products) while using a medium-pressure lamp yields a main chain scission of approximately two orders of magnitude lower than for side-group scission. Moreover, a correlation of the quantum yield with T_g was observed; the efficiency of both processes, chain scission and crosslinking, is markedly increased above the polymer T_g [68]. The nature of the volatile products detected is in agreement with Norrish Type I and II mechanisms based on the formation of an excited carbonyl group following absorption of light [58,59,71], Figure 1.9.

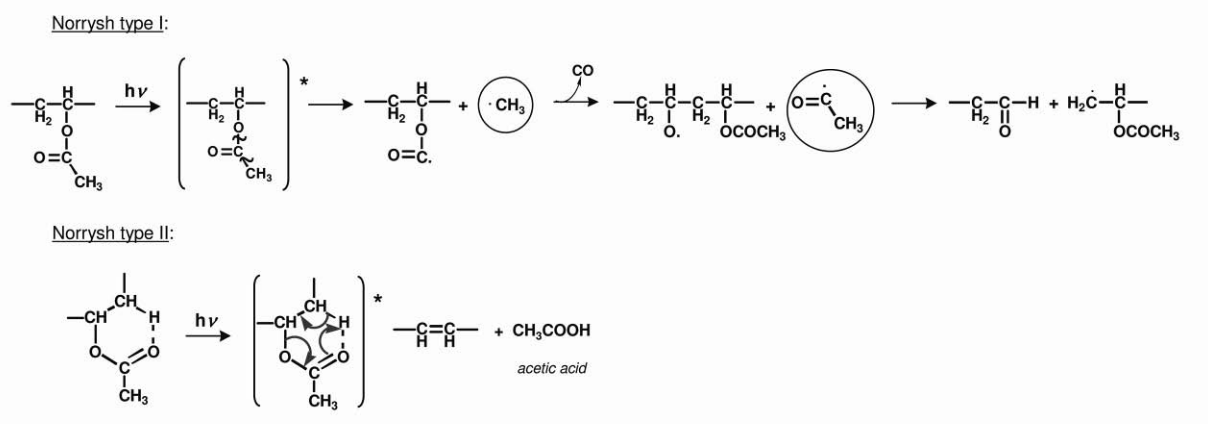

Figure 1.9. Photodegradation pathways for PVAc and proposed intermediates that lead to the formation of volatile fragments, such as CO, CH_4 and acetic acid. Adapted from [63].

More recently [74-76], PVAc and polystyrene (PS) blends were irradiated under a fluorescent lamp (λ_{irr} = 280-350 nm) and with a higher-energy polychromatic source (λ_{irr} =248 to 578 nm). Hydroxy/hydroperoxide and saturated and unsaturated ketone intermediates were predicted; a loss of methylene groups and decrease in carbonyl concentration were observed, in agreement with what was previously reported for the homopolymer. To the best of our knowledge, no photochemical studies for $\lambda \geq 300$ nm irradiation have been undertaken. Works of art made with vinyl paints will, in general, absorb radiation filtered by glass windows ($\lambda \geq 300$ nm), and consequently no direct absorption of light by the carbonyl group is expected. Radiation at $\lambda \geq 300$ nm will most probably be absorbed by chromophores existing in the PVAc matrix, such as hydroperoxide groups formed during the synthesis or processing. Even present in very low amounts, and therefore absorbing a very small fraction of light, they are likely to be the active chromophores and the key point for the understanding of the photochemistry in real systems such as the paints found in works of art. It will be important to verify if, in such conditions, side-chain reactions are still present with formation of acetic acid. The production of acetic acid during photodegradation is an important aspect in which concerns conservation, as acetic acid could promote further polymer or colorant/filler degradation with consequent loss of material and colour changes.

In the 1960s emulsions were investigated for conservation use, and the conclusion was that better materials should be found for long-term applications in conservation [12]; this was based on the study of commercial formulations that induced weakening of the support and displayed dramatic yellowing [77]. In the 1980s, the Canadian Conservation Institute started testing on vinyl adhesives [78], including 19 dispersions and eight solutions. The 27 different adhesives were irradiated[5] or naturally aged, in the dark, for three years. To assess the harmfulness of the treatment, pH and release of acetic acid (among other volatile compounds) were considered. The pH was measured in extracts of the solid films, and with two exceptions, it was already acidic at the beginning of the experiment; *most* of the studied emulsions had an initial pH close to 4. Possibly these should not have been considered for a long-term study on adhesives in conservation, as, unaged, they may be regarded as harmful materials, *e.g.*, towards cellulosic based materials as well as metals. Also, in many of the emulsions PVAL was present, possibly in the form of a co-polymer[6], and this would explain both the initial pH values as well as the fact that after a first acetic acid release it stops. From the data obtained by the authors, it is possible to conclude that for 60% of the samples tested no relevant changes in the pH over time were observed; but it was not possible to establish a correlation between the pH variation and acetic acid release. Considering that most of the samples were commercial emulsions in which, besides PVAc and PVAL, a wide range of additives may be present, one could expect that it would be difficult to find an ageing pattern and that, from such an heterogeneous set of samples, conclusions should be drawn with caution. Moreover, even for the polymers acquired as resins, the results obtained during

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[5] Under 40-watt Duro Test Vita-Lite fluorescent lamps with proportion of UV radiation in the 300-400nm range.

[6] This hypothesis is supported by reported pH values that fall in the range 4.5-7 of this kind of formulation based on PVAc plus PVAL [12].

irradiation offer no clear explanation; for the first year a decrease in pH was observed, for the second year an increase, and finally in the third year again a decrease. When compared with the initial value, the changes in pH for these resins were on the order of 4%, 8%, 16% or 25%. Again, it would be difficult to draw conclusions on the polymer stability without a clear rationale of the facts observed. On the other hand, in another study carried out during the 1980s [79] on the behaviour of polymer emulsions aged artificially, the authors obtained different results concerning the stability of vinyl dispersions, concluding that it is possible for durable vinyl emulsions to be produced. Also, following Thomson's research started in the fifties, Feller has studied the photochemical stability of PVAc and described it as highly stable (Class A), based mainly on its capacity to remain soluble [3,13-16]. More recently [36], the surface of a vinyl paint by Bridget Riley (*Fall*, 1963) was described as in good condition, velvety, and with ‘no signs of any cracks’. This state of the art, apparently contradictory, requires further clarification that may be provided by understanding the mechanisms of ageing, including the long-term stability of vinyl paints in works of art, by studying the molecular changes in the polymer matrix over time.

It is also worth to mention that acrylic paints and coating systems have been the object of detailed studies in the last decade [80-82]. Studies have particularly examined the characteristics of artists' acrylic emulsion paints and the mechanisms by which the paint films might undergo molecular changes under different aging conditions [5,78,79,83]. In contrast, less attention has been paid to vinyl artists' emulsion paints, specifically to their photostability. PVAc/VeoVa emulsion based artists’ paints by *Lefranc & Bourgeois*, *Flashe*, were included for comparison in some studies on acrylics in which accelerated ageing tests were performed under radiation above 400nm (museum conditions) [21,36]; under such conditions there were no visible changes in the FTIR spectra, nor in colour parameters.

The influence of metal ions, such as TiO_2, Fe_2O_3, PbO and ZnO, on polymer degradation has also been described and it is known that these metal oxides present in formulations may have a stabilizing or sensitizing effect on the polymer [63,82,84-90]. Recent studies show that when compared with PVC, PVAc has been considered to be mildly affected by the presence of metal oxides, in a thermal degradation procedure tested in the absence of oxygen [Sivalingam]. Titanium dioxide, especially in the anatase form, is well known for its photocatalytic properties and numerous studies have been dedicated to the subject [63, 82,85,91-94]; coating the particles has been reported to be fundamental for the pigment stability [82,85,95]. Since the 1950s the pigment industry has developed surface treatments. Specifically, titanium dioxide pigments have been produced with two coating layers. The first layer forms a barrier to the free radical production process and is typically made of silica. On the outside, a layer of hydrated alumina is then deposited to promote the separation of the pigment particles in the production process [28].

1.4.2 Degradation and photooxidation of acrylic polymers

The photodegradation of PMMA has been the subject of several systematic studies[7] [62] and different authors have found that when irradiated at room temperature it undergoes chain scission [20,63,96-99]. According to a review on the photodegradation of high polymers published in 1967 [62], crosslinking was only observed as a degradation pathway for PMMA in the presence of sensitizers. Both the presence of an hydrogen or methyl group on the α position and the nature of the alcoxy side group, influence the overall stability of the polymer. For the two types of polymers, acrylics and methacrylics, chain scission prevails over crosslinking when the alcoxy group is short, with acrylics being more sensitive to photooxidation; in the cases where the side group is long the polymer undergoes both, extensive crosslinking and fragmentation [18,20].

The main results of the studies on the photodegradation of PMMA may be summarized as follows. PMMA does not absorb the light that reaches the earth and its photodegradation results from the absorption by impurity cromophores, which may be found in the polymer matrix as a consequence of the synthesis and processing. UV-visible spectra show that PMMA absorbs essentially bellow 254 nm [50,97,99-103], absorbing for $\lambda < 320$ nm with a defined absorption band at 277nm if impurities are present in the polymer matrix [50]. Fox [97] found that when the polymer was irradiated under medium-pressure Hg lamps with a 2 mm pyrex filter[8] there was no detectable alteration, even for longer irradiation periods than those necessary for extensive scission with non-filtered radiation. Also in another study undertaken both in air and vacuum under a medium-pressure Hg light source [101], the purified polymer suffered severe chain scission but remained unaltered when wavelengths shorter than 290nm were cut off. Contrary to polyolefins, photooxidation of acrylics and methacrylics has been described as not autocatalytic [18] and the formation of degradation products is stopped with the consumption of chromophores [50].

Chain scission quantum yields were obtained by several groups for films irradiated under different conditions both in air and vacuum, with higher values for UV light with irradiation sources involving 254 nm. [96,97,100,102,103]. The data obtained for PMMA irradiated under medium and low-pressure Hg lamps showed slight higher values in vacuum than in air, but within the same order of magnitude (10^{-2}) [96,97,100]. On the other hand, the Φcs obtained for irradiations at 260 nm, 280 nm and 300 nm are two orders of magnitude lower than those presented above [102,103]. The characterization of volatile degradation products (CH_4, H_2, CO, CO_2, methyl formate, methanol and methyl methacrylate) resulting from main-chain and side-chain scission has also been performed [96-98,100,104]. Based on these

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[7] Most studies were carried out with UV irradiation sources emitting mainly at short-wavelengths and some with mono or polychromatic irradiation $\lambda > 290$ nm.

[8] Cut-off at approximately 300/320 nm.

studies it has been suggested that the photodegradation of PMMA by UV light evolves by two main degradation mechanisms, *i.e.* direct main-chain scission and main-chain scission induced by fragmentation of the side-chain [63,96,97,102]; possibly less important but also operating is the photolysis of the methyl side group [63]. Charlsby [96] observed that the ratio of the ester side chain fracture to main chain scission is close to unity, indicating that the two processes are probably related. When irradiation was undertaken at 254 nm, monomer was not found or only in very low amounts [98,100,104]. Gupta [100] obtained a low quantum yield for methyl methacrylate formation (0.01) compared to that calculated by Fox (0.5) [97]; this difference was explained by the use of different irradiation sources, low and medium-pressure Hg respectively, with the broad band lamp used by Fox inducing long wavelength absorption by the propagating radical and leading to unzipping. According to Fox [97], thermal degradation, depolymerisation or the presence of residual monomer are the three major methyl methacrylate sources. Besides the identification of the volatile products Gupta *et al* [100] also used electron spin resonance (ESR) to identify the radicals formed during PMMA degradation, namely the radicals methyl, formate, formyl, acetyl and the propagating radical.

Infrared analyses were performed in some studies in order to determine the degradation products present in the polymer matrix and the results obtained confirm the presence of different mechanisms operating [19,20,50,99,100]. According to Lemaire [50] the hydroxy groups are straightforward observed, for both accelerated ageing and natural conditions, by the formation of new bands at 3530 and 3320 cm^{-1}. The authors concluded that the formation of these degradation products is related with the presence of chromophores being stopped with their consumption. Furthermore, broadening of the carbonyl band was observed. Kaczmarec *et al* [99], in low *Mw* PMMA irradiated under low-pressure Hg lamps, detected the appearance of a new band at 3480 cm^{-1} that was assigned to free and hydrogen bonded hydroxyl/hydroperoxide groups. Formation of new carbonyl groups was also detected at lower wavenumbers (1705 cm^{-1}) on high *Mw* films irradiated with short UV monochromatic irradiation [100]. Furthermore, different results were obtained in two studies [19,20] with PMMA of *Mw* 120600 irradiated with different sources. For $\lambda > 220$ nm the chemical modifications lead to the complete fragmentation and consequent volatilization of the polymer, whereas for $\lambda > 295$ nm no changes were observed in the IR spectra.

It was confirmed by the different authors that different degradation mechanisms may occur due to different irradiation conditions. Moreover, it may be due to differences in the polymer implied by the presence of impurity chromophores working as sensitizers and inducing degradation through distinct pathways. As described, chain scission has been found to be the main degradation mechanism and PMMA is considered to be one of the most stable acrylic polymers.

1.5 Artists. Historic, artistic and material context

Joaquim Rodrigo (1912-1997), Ângelo de Sousa (b.1938) and Lourdes Castro (b.1930) are presented here as cases studies.

For all three artists the materials they have used played a central role in their artistic production. They all affirmed to have found the most suitable materials for their projects. For Joaquim Rodrigo the main material question was about the colour and he found the 'eternal palette', the palette that allowed him to create what he defined as the 'correct painting'. Also for Ângelo de Sousa colour is particularly important and throughout his career he worked mainly with primary colours; Ângelo has explored many materials and has chosen the right media at each period of his work. In the case of Lourdes Castro, while exploring the shadow concept in the 1960s, she finds the acrylic sheet and states that has finally found an appropriate material for the results she wanted.

1.5.1 Joaquim Rodrigo

One of the most important Portuguese modern artists to use a vinyl emulsion[9] to produce his own paints was Joaquim Rodrigo (1912–1997), Figure 1.10. Rodrigo was an agronomist and forest engineer who worked at the city hall in Lisbon and was one of those responsible for the construction of Monsanto Park, an important park known as the 'city's lungs' [22]. In 1950, when Rodrigo was 38 years old, he started to paint after a journey to Italy and Paris. There he had seen the works of Renaissance masters, impressionists and modernists. Rodrigo was particularly impressed by the works of Picasso and Mondrian [105,106]. Back in Lisbon, Rodrigo frequently thought of Picasso and one day asked to his friend Guilherme Filipe to help him buying paints and brushes [105].

Following a brief formal training at *Sociedade Nacional de Belas Artes*, where he attended a night course in painting, Rodrigo developed his painting skills as an autodidact [106]. His first works show a precise definition of the painting elements, not possible to learn in the academia that was still far apart from the artistic concerns of that time. Rodrigo's systematic research was 'sustained by updated information on the developments of the international modernity' [106]. After some experimental work and an important and innovative foray into geometric abstraction (Figure 1.10 on the right) mainly working with oil paints, Rodrigo entered into the Portuguese art scene in 1961 with a collection of new figurative works in a vinyl medium (Figures 1.11 and 1.12) – a new paradigm that turned him into a central figure in Portuguese painting [107-110].

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[9] Although, in his writings Rodrigo referred to the binder used as an acrylic glue [105].

Figure 1.10. Left: Joaquim Rodrigo standing in front of his painting *Rua* (1988); right: Joaquim Rodrigo painting C23 (Jardim), 1956. [22].

His strong bent toward storytelling led Rodrigo to use the paintings as a ‘diary’ in which he recounted episodes of the Portuguese political scene and the colonial war that troubled him, under titles encoded in enigmatic initials in order to escape censorship. Examples are the paintings *S. M.* (*Santa Maria*[10]) and *M. L.* (*Morte de Lumumba*, which translates to ‘Death of Lumumba’[11]), both from 1961 [106].

In formal terms, his works establish a synthesis of the primitive paintings from Lunda (a region from Angola)[12] (Figure 1.13), the orthogonal matrix that structures the paintings of Joaquim Torres-García[13] (Figure 1.14), and the colours shared by both of these influences [106,109].

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[10] Reference to the hijacking of the Portuguese liner Santa Maria (January 1961) by Henrique Galvão, planned to bring attention to the Portuguese political situation [109].

[11] Patrice Lumumba, a poet who promoted the Congolese nationalist movement of liberation, was murdered in 1961 [22,109].

[12] In 1961, Rodrigo read José Redinha’s book *Paredes Pintadas da Lunda* (Painted Walls from Lunda), which had a decisive importance on the artist’s work [22].

[13] Among Rodrigo’s belongings several references to this Uruguayan artist can be found, such as newspaper articles [22]. Joaquim Rodrigo and Joaquim Torres-García used the same colours (black, white, red, and yellow ochres) and the same orthogonal matrix, which organizes the painted forms.

Figure 1.11. *S. M.*, 1961. Vinyl on harboard; 97.3 x 146 cm. Ministry of Culture collection, deposited at the National Museum of Contemporary Art (*MNAC - Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.

Figure 1.12. *M. L.*, 1961. Vinyl on harboard; 73 x 100 cm. Private collection, deposited at the National Museum of Contemporary Art (*MNAC - Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.

From 1969 onwards, Rodrigo theorized and put into practice a ‘scientific and universal’ pictorial system that he called ‘*pintura certa*’ (*correct* painting)[14]. The system involves formal, chromatic, and compositional construction of works. Minute perceptions of banal events in his travels led to a narrative based on the distribution of graphically synthetic signs, isolated and mapped within the space of the image. Subject to the rigor of the orthogonal system and to a precise chromatic configuration, the signs function as an index to the movement (intensifying the movement suggested by the title) and inscribe a temporal value [107-109], Figure 1.15. Rodrigo will produce an extensive series of paintings that will suffer minor alterations until 1982 [106].

Figure 1.13. (Estampa 31A) *Povoação lunda-quioca do soba Tchimbango* (lunda-quioca village from soba Tchimbango); painting in the exterior wall of a house [111].

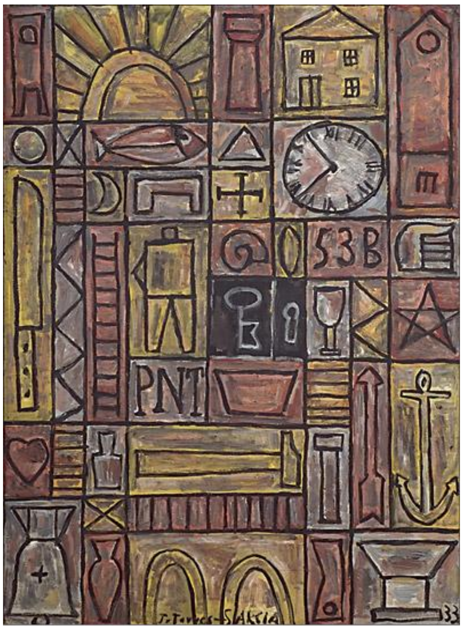

Figure 1.14. Joaquín Torres-García (1874-1949), *Composicion Universal*, 1933. Oil on masonite; 74.9 x 54.6 cm. Courtesy of the Snite Museum of Art (http://www.nd.edu/~sniteart/), Notre Dame, Indiana.

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[14] In 1982, Joaquim Rodrigo published his theories in a book called *O complementarismo em pintura: Contribuição para a ciência da arte* (The Complementarism in Painting: Contribution for the Science of Art). The book was mainly written in 1976 and part of it is the result of a talk with Rodrigo and J.A. França, F. Azevedo, F. Pernes, J.B. Portugal and J. Sasportes. Before its publication, several additions that updated the theory were included. In 1995, a new book, *Pintar Certo* (Painting Right), corresponded to an addition from 1984 with new aspects of his theory that was first published in [107,108].

Figure 1.15. *Lisboa – Oropeza*, 1969. Vinyl on plywood; 97 x 146 cm. Private collection, deposited at the National Museum of Contemporary Art (*MNAC - Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.

After 1982 Rodrigo's painting will reflect a profound alteration. He finds what he definitely considers as the *Correct Painting* (Figure 1.16), and will consider it as his only valid work [106,112]. In the theory previously developed by Rodrigo, the painting was inscribed in a *planimetric* pictorial system. After his intensive studies, the artist concluded that depth had to be added to his paintings. Rodrigo will call *telemetric* to the new form of representation. The artist now uses the expression *chiaroscruro* instead of contrast, considering that 'there is a maximum *chiaroscuro* that we all shall search for'. [113]. The figures will still not be represented with volume, but the profundity notion is given by the scale and colour relations [106].

The work of Joaquim Rodrigo has been thoroughly studied in the framework of a retrospective exhibition held at the National Museum of Contemporary Art – Museu do Chiado (MNAC[15]) and the results are published in a *Catalogue Raisonné* [22].

As mentioned above, during the first years of his artistic production, Joaquim Rodrigo worked with oil paints and also with bright colours. For his 'scientific and universal' painting system Rodrigo defined an 'eternal' pallet, restricted to the use of four colours, *i.e.* two colours (red

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[15] *Museu Nacional de Arte Contemporânea*.

and yellow ochres) and two limits (black and white) [105,112]. Since the mid 1960s, these pigments are mixed with a vinyl binding medium [22,105] within a complex set of rules that will be discussed in Chapter 4.2.

Figure 1.16. *Os quintais*, 1989. Vinyl on plywood; 89 x 130 cm. Private collection. Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.

1.5.2 Ângelo de Sousa

One of the major names of Portuguese contemporary art, Ângelo de Sousa (b. 1938), Figure 1.17 graduated from the School of Fine Arts in Porto (1955-63), where he taught from 1963 until 2000 retiring as full professor. His first solo exhibition was in 1959 (*Galeria Divulgação*)[16] [114]. In 1967-68, Ângelo spent a year in London at the St Martin's School of Fine Art with a grant from the British Council[17]. Ângelo de Sousa his known for a singularity that distinguishes his work both in the Portuguese and international art contexts [115]. About what he considers as essential in his painting [116], Ângelo says:

> *The maximum effect with minimum resources. Or: the maximum efficacy with minimum effort. Or, yet: maximum presence with minimum shouting.* [18]
>
> Ângelo de Sousa, 1985

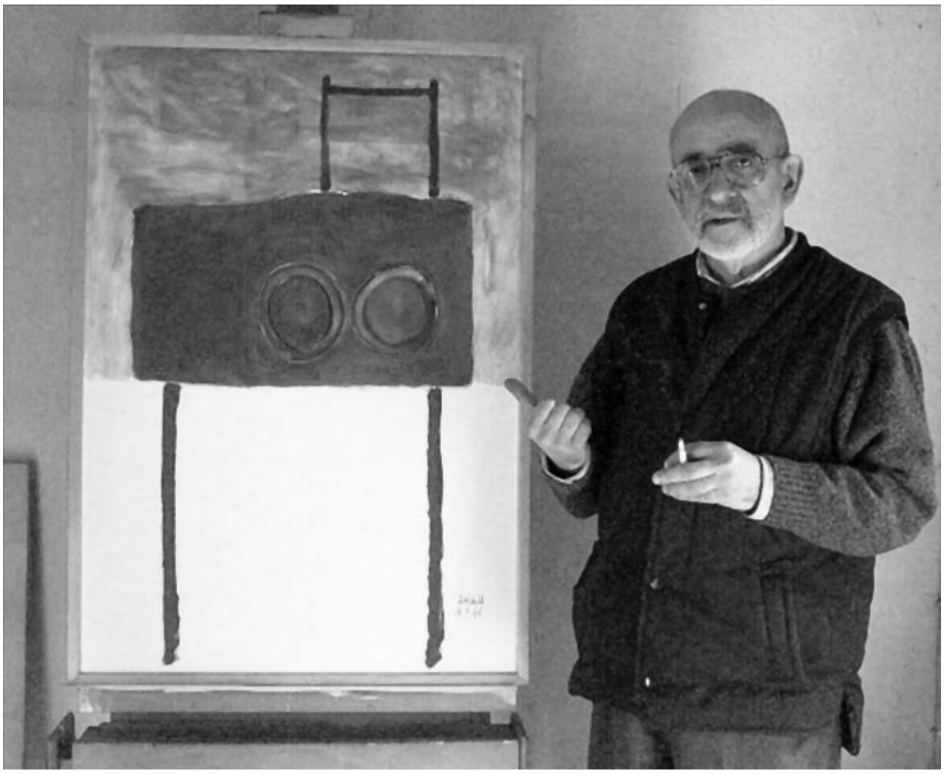

Figure 1.17. Ângelo de Sousa at his studio (Porto, December 2005), standing by his painting *Natureza Morta*, 1965.

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[16] The architect Pulido Valente had proposed a cycle of exhibitions putting together an established artist and another one starting his career. Ângelo de Sousa and José de Almada Negreiros (1893-1970) were the artists chosen for the first and only exhibition done in the framework of that project.

[17] Working also for about a month at the Slade School of Art.

[18] '*O máximo efeito com o mínimo de recursos. Ou: o máximo de eficácia como o mínimo de esforço: Ou, ainda: o máximo de presença com o mínimo de gritos*.' [116]

Despite having worked with different art forms – painting, drawing, sculpture, photography and film -, as Fernando Pernes wrote, Ângelo is essentially a painter [117].

Ângelo de Sousa, like Joaquim Rodrigo, was one of the foremost Portuguese artists of what was named as *nova-figuração* (new-figuration) by the art critique in the 1960s [118]. For Ângelo, the figure is in itself an abstraction and the problem figuration/abstraction never interested him [116,119]. His experimentation has been about the painting media, being technical, materic, semiotic or discursive issues, always exploring '*the new*, new forms, new spaces, new materials'[19] [116].

Following an initial period working with oil and exploring casein and wax (Figure 1.18) as binders, Ângelo de Sousa started using a vinyl medium and, after that, off-set inks for his paintings [23].

Figure 1.18. (Cat. 3.) *Paisagem*, 1959. Wax on hardboard, 29.5 x 40.5 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

In the paintings from the 1960s each series will be a transformation of the previous [119]. The 'plants', the 'trees', the 'bridges', the 'horses', the 'figures' or 'still-lives'. These paintings were built in intentional schematic figurations of simple outlines and vibrating colours, Figure 1.19 [117]. The sculptures (Figure 1.20) will also derive from those works, either in plans (coloured acrylic and painted metal sheets) or in straight and twisted lines in the space (steel strips) [119,120].

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[19] '(…) *explorando incessantemente "o novo", novas formas, novos materiais*.' [119]

Figure 1.19. *Plantas*, 1962. Poly(vinyl acetate) on paper glued on hardboard, 65 x 50 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

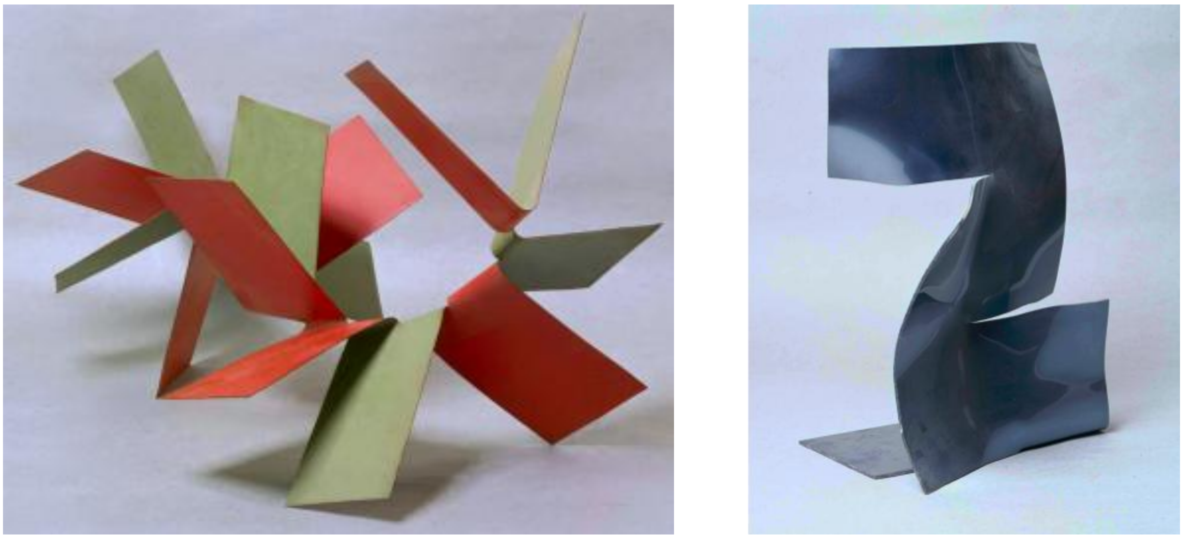

Figure 1.20. Left - (Cat. 64.) *Escultura*, 1966. Iron, 50 x 90 x 60 cm. Author's collection; right - (Cat. 61.) *Escultura*, 1966. Acrylic, 41 x 30 x 20 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Even considering the experimental films and photographs, Ângelo's artworks are developed in simple structures having its essence in the drawing, which has been a privileged field of his research expressed in the different artistic forms [120,121]. In the 1970s Ângelo starts working on what has been named the 'monochromatic' series (now in acrylic), a meticulous work of the backgrounds [117], either in *black* and white or in different *colours*, Figure 1.21. Although being perceived as monochromatic, the palette used was still composed by the three primary colours. These paintings are cut by thin lines, illusions of mathematic accuracy, a suggestion of volume, space and perspective [121]. José Gil has stated that one cannot consider an evolution in the work of Ângelo de Sousa, instead it reflects multiple transformations from one series to the other [119].

Figure 1.21. Left - (Cat. 101.) *Sem título*, 1972. Acrylic on canvas, 194 x 130 cm. Author’s collection; right - (Cat. 110.) *Sem título*, 1974. Acrylic on canvas, 200 x 125 cm. Author’s collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Acording to José-Augusto França, humor is the major dimension of Ângelo de Sousa’s art [122]. He plays with forms and colours, refusing any compliance with himself and showing his independence. As described by José Gil [119], ‘Ângelo belongs to the breed of experimenters’[20]. Being one of the consequences of the freedom/independence in that experimentation the difficulty in classifying his work:

> *it is neither abstract nor figurative, nor minimalist, nor conceptual, nor object art nor installation – or is it all of this put together? His images remain indifferent to these categories. As if they were superior to the question of representation.*[21]
>
> José Gil, 1993

---

[20] ‘*Ângelo pertence à raça dos experimentadores*.’ [119]

[21] ‘(…) *nem abstracta nem figurativa, nem minimalista nem conceptual, nem pintura-pintura nem objecto-arte ou instalação – ou tudo isto junto? As suas imagens permanecem indiferentes a estas categorias. Como se estivessem para além do problema da representação*.’ [119]

1.5.3 Lourdes Castro

About Lourdes Castro (b. 1930), Figure 1.22, one may say she is not only one of the foremost Portuguese artists, but that she has also played a major role in the European artistic scene since the early 1960s [123] showing her work in several international exhibitions [110].

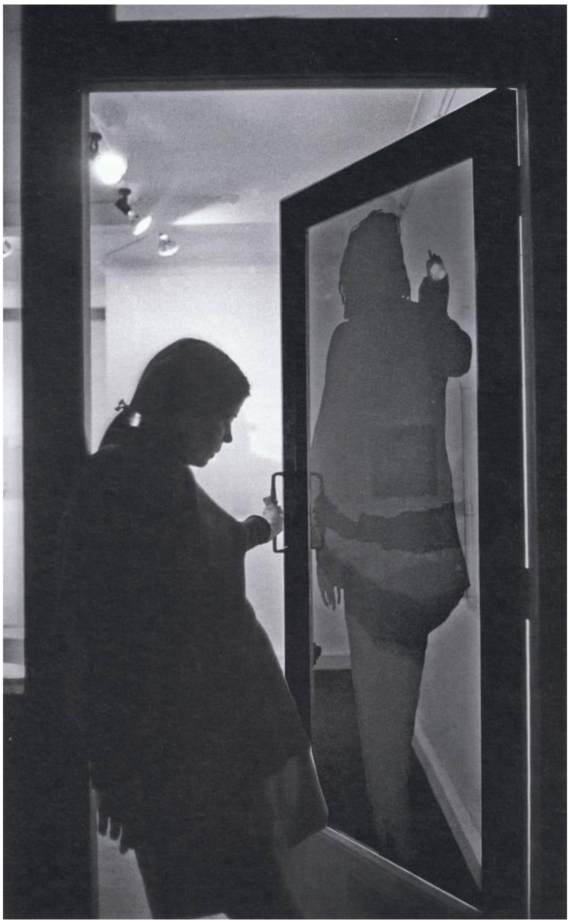

Figure 1.22. Lourdes Castro, Indica Gallery, London, 1967 [124].

The work of Lourdes Castro has surpassed the limiting boundaries of artistic categorization, leading to a profound alteration in the Portuguese twentieth century art history [125].

Born in Funchal, Madeira, Lourdes Castro left Portugal in 1957 after concluding the Painting General Course at the Fine Arts School in Lisbon, from where her paintings were excluded (Figure 1.23) due to the traditionalist character of the school. That year was spent in Munich, and in 1958 the artist moved to Paris[22] with René Bertholo, staying there until 1983 [123].

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[22] Receiving a grant from *Fundação Calouste Gulbenkian*.

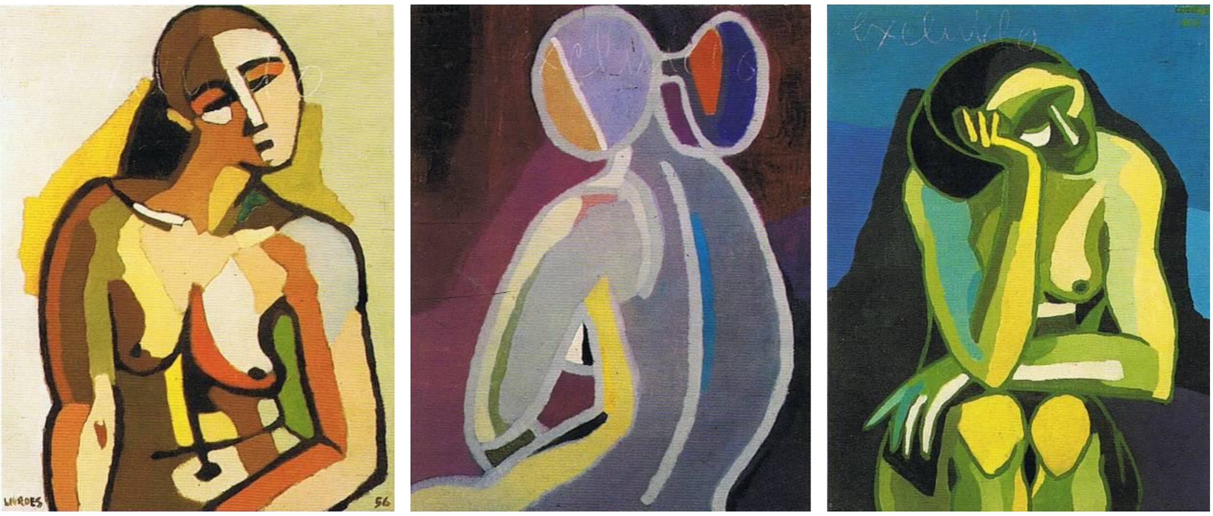

Figure 1.23. *Modelos nus*, 1956. Oil on plywood, 90 x 70 cm [24].

In Paris, Lourdes Castro and René Bertholo started the *KWY* magazine (1958-63), almost fully hand printed in serigraphy, with the artists Jan Voss and Christo, and later with Escada, Costa Pinheiro, João Vieira and Gonçalo Duarte [126]. For the different issues they would have the participation of several international artists, writers and essayists [125] and each of the twelve published issues was an autonomous artwork [127].

Between 1961 and 1963, Lourdes will work with object assemblage (Figure 1.24). Random everyday objects were assembled in boxes with a degree of unity implied by the uniform colour of the composition, obtained either by an aluminum paint[23] layer or by a meticulous selection of objects having the same initial colour [125,127].

Her painting, initially associated with the informalist abstraction, will be deeply altered [125]. In 1961 Lourdes had worked on some paintings, imprinting on the canvas pre-existing images collected from different sources, like books or magazines, where figures were outlined (Figure 1.25) [125,128].

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[23] About the aluminium paint Lourdes Castro explained that she chose it for its protective effect, the paint was industrially used for rust inhibition [128].

Figure 1.24. *Boite aluminium avec boite d’aquarelles*, 1963. Mixed media, 52 x 52 cm. Mr and Mrs Jan Voss colection [24].

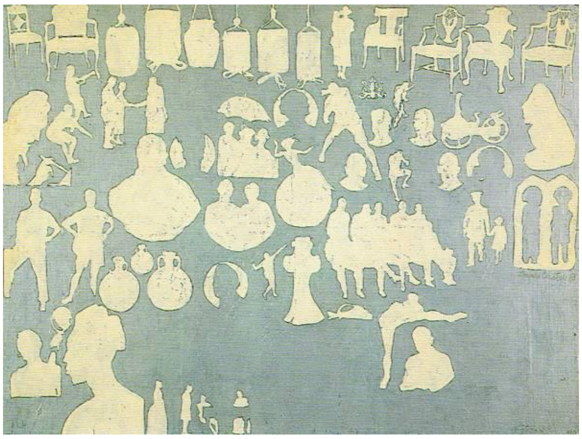

Figure 1.25. *Figuras objectos fundo prateado*, 1963. Painting on hardboard, 44 x 60 cm [24].

Assimilating the object collages with the search for graphical works, she placed those objects on the pre-sensitized silk (1962). ‘It was with the serigraphy that my first shadows came to light. (…) I obtained truly projected shadows’[24] [126]. In the words of Manuel Zimbro it was a double revelation, the shadows were revealed (Figure 1.26) by the serigraphy revelation [129]. As an annotation of the shadow, in 1963-64, Lourdes works on a series of projected shadows on canvas (Figure 1.27) and also cast on walls (Figure 1.28). These are shadows of her family and friends outlined in instantaneous poses. ‘The outline surprises me because it did not exist before I drew it (…). The outline is the Less I can have of something, of someone, saving its characteristics’[25] [130].

---

[24] ‘*Foi com a serigrafia que vieram à Luz as minhas primeiras sombras. Fazia colagens com objectos e querendo realizar obras impressas, coloquei esses mesmos objectos sobre a seda pré-sensibilizada. Obtive assim verdadeira sombras projectadas*.’ [126]

[25] ‘*O contorno surpreende-me porque não existia antes de eu o desenhar (…). O contorno é o Menos que posso ter de alguma coisa, de alguém, conservando as suas características*.’ [130]

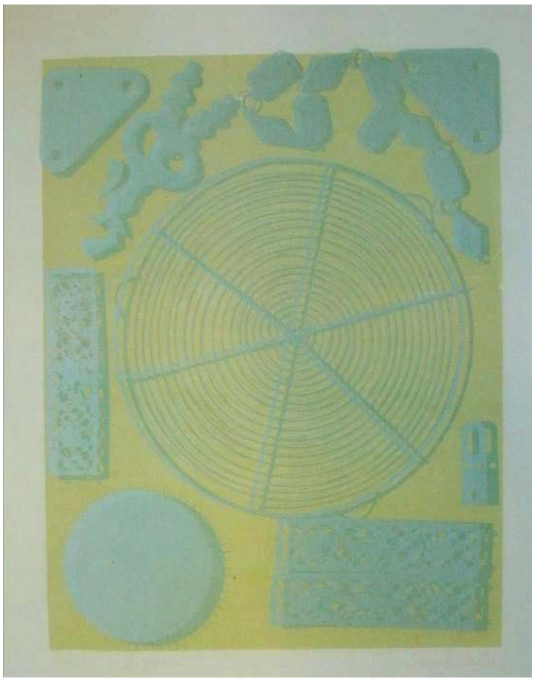

Figure 1.26. *Objectos prateados com sombras*, 1962. Serigraphy [124].

Figure 1.27. *Sombra projectada de René Bertholo*, 1964. Acrylic[26] on canvas, 100 x 81 cm. National Museum of Contemporary Art (MNAC – *Museu do Chiado*) collection [110].

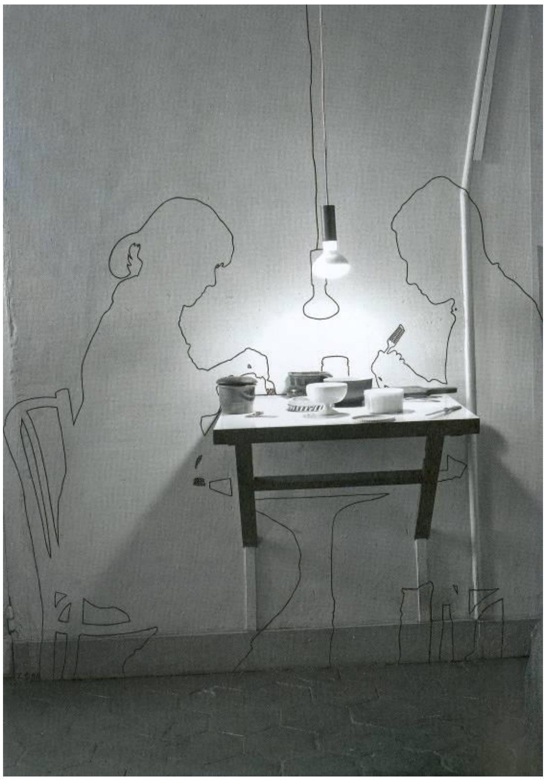

Figure 1.28. *Sombras de L. e R. projectadas na parede, Rue des Saint Pères*, Paris, 1964 [124].

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[26] Although the painting is catalogued as acrylic, the artist has referred that she painted with vinyl household paints (see Appendix III.4).

The work of Lourdes Castro is about the dichotomy presence/absence, outlining shadows not bodies. By defining these outlines, Lourdes will capture the moment, highlighting the emptiness, the absence [130,131]. The shadows outlines were painted in lines, for the shadows and background Lourdes used a paint-roller trying to make it as smooth as possible [132].

From 1964 and until 1968, Lourdes worked in acrylic sheet, a transparent and translucent material, which is in itself an 'absent presence' [133].

> *Searching for a material without texture and more in agreement with the result I wanted, I made, in 64, my first essay in plexiglas. At last, an immaterial material like the shadows.*[27]
>
> Lourdes Castro, 1966

Lourdes painted the acrylic sheets from behind or serigraphed the front surface, cut them out, and even engraved some [132]. Contrary to Ângelo de Sousa[28], Lourdes Castro never tried to mold the acrylic sheet, in her own words the volume was not her project. She brought the shadows out of the shade, 'gave them colours, an independent life'[29]. The acrylic sheet allowed Lourdes to leave the painting domain, using one or more overlaid sheets the shadows are materialized and are re-projected on the wall [125,127,132]. For a complete perception, these works require a relation of the observation angle with the space in which they are installed (Figures 1.29 and 1.30) [110].

The shadows were then (1998-99) embroidered in bed sheets, the inscription of laying bodies shifted the works of art from the vertical to an horizontal position [110,125,127]. After some experiments in 1966 and mainly during her stay in Berlin, 1972-73, Lourdes Castro will develop with Manuel Zimbro the shadows' theatre (Figure 1.31). Small everyday gestures are the arguments for a narrative. Lourdes becomes the shadow and the shadow is now in motion [125,127,134]. 'During the show I am the shadow and Manuel is the light'[30] [134].

---

[27] '*Procurando um material sem textura e mais de acordo com o resultado que pretendia obter, fiz em 1964 o meu primeiro ensaio em plexiglas. Por fim, um material imaterial como as sombras*.' [132]

[28] Ângelo de Sousa will use acrylic sheet in sculpture in the 1960s (see Chapter 4.3).

[29] '*Fiz sair as sombras da sombra, dei-lhes cores, uma vida independente*.' [132]

[30] '*Durante o espectáculo, eu sou a sombra e o Manuel é a luz*.' [134]

Figure 1.29. *La place en marche*, 1965. Acrylic sheet, 28.5 x 282 cm. National Museum of Contemporary Art (MNAC – *Museu do Chiado*) collection [110].

Figure 1.30. *Rosa fluo*, 1968. Serigraphy/acrylic sheet (2 sheets) 36 x 31 cm [135].

Figure 1.31. *As cinco estações*, 1976 [124].

Chapter 2

Historical framework

The Vinyl Paints used by Portuguese Artists

Part of the results presented in this chapter were published in peer reviewed proceedings.

Ferreira JL, Melo MJ, Ramos AM, Ávila, MJ. *'Eternity Is in Love with the Productions of Time': Joaquim Rodrigo's Classical Palette in a Vinyl Synthetic Medium.* In: Learner TJS, Smithen P, Krueger JW, Schilling MR, editors. Proceedings from the Symposium Modern Paints Uncovered; 2006 May 16-19; Tate Modern, London. Los Angeles: Getty Publications; 2007 p. 43-52.

2.1 From chemical industry to the paints' manufacturers

> *In the last thirty years, the paint industry and technology have made such a progress and the number of painting methods and materials has increased so much, (…).*
>
> Robbialac Portuguesa, 1958

2.1.1 Overview

When considering the paints used by Portuguese artists one question that becomes obvious is: which paints were our artists using? What was available in Portugal? The so called synthetic paints are made of synthetic resins, *i.e.* synthetic polymers. Is there a national history or do we need to call upon the international history of polymers production?

To answer these questions we prepared some interviews and collected archival information from paint manufacturers, of both industrial and artists' quality paints. We also counted on the help of Engineer Raul Morgado Costa[31] to build a time line that could drive us through the main events influencing the development of aqueous emulsions in Portugal and of our paint and coatings industry. An informal interview was held at DCR FCT/UNL in May 2005[32].

After a period of initial development, the world chemical industry was involved in a profound evolution since the 1920s along with the effects of the two World Wars. Despite the small number of giant industries that emerged during that period in Germany, *IG Farben Industrie AG*[33], in Great Britain, *Imperial Chemical Industries* (*ICI*), and in the United States, *Allied Chemical & Dyes* and *Du Pont*, as well as the Anglo-Dutch *Royal Dutch Shell* and *Unilever*, 'each national industry developed in its own natural, economic, and political environment' [6].

In Portugal the most important chemical industries producing synthetic resins in the late 1950s and 1960s were probably what became *Indústrias Químicas Synres Portuguesa*, Lda. and *Resiquímica – Resínas Químicas*, Lda. Through the years other industrial units working with these materials were established (*E. Brunner*[34]; *Companhia União Fabril* (*CUF*); Resipez[35]; Probos/Proadec[36]). At that time there were already several paint manufacturers in Portugal, such as *Robbialac*, *CIN* and *Dyrup*. Raw materials were either produced at their own plants or imported from foreign countries.

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[31] Former head of *Indústrias Químicas Synres Portuguesa*, Lda [136].

[32] All data concerning the chemical industry in Portugal that is not referenced in the text was provided as oral information by Engineer Morgado Costa.

[33] *Hoechst* was one of the eight associated companies that in 1925 merged to form *IG Farben Industrie AG* [6].

[34] An industry established in Porto that produced aqueous emulsions using technology of the English *Vinyl Products* (*i.e. Vinamul*).

[35] Today *Respol – Resinas Sintéticas*, SA.

[36] Initially it belonged to the group *Sonae – Sociedade Nacional de Estratificados*, SA.

Sociedade Nacional de Sabões (*SNS*)[37] was founded in 1919 as a merge of three soap makers [137]. In the 1950s Caetano Beirão da Veiga ran *SNS* with the help of an engineer who had previously worked for the paint industry. *SNS* main business was in the production of soaps, vegetable oils and glycerol. In 1957/58 the heads for *SNS* considered expanding their business to include the production of synthetic resins, in which the surplus oils, glycerol and fatty acids could be used. According to Engineer Morgado Costa [136], in 1959 an agreement was negotiated with the German *Chemische Werke Albert*, which provided the know-how to what became the *SNS* new division, the Synthetic Resins Industrial Unit. The production started in January 1960 with a plant working with five reactors. Five different resins, (Figure 2.1) were then produced for the paint and coatings industry: alkyd, colophony modified phenolic, maleic, colophy esters and butylated urea-formaldehyde resins, in a total of twelve different formulations.

It soon became apparent that the royalties plan with *Albert* was profitable for the Germans but not for the Portuguese. The evolution was slow due to the restricted range of resins and the limited background of the technical and sales staff in the polymers business [136]. According to Morgado Costa, *JC Andrade*[38] suggested a joint venture between the *SNS* Synthetic Resins division and the Dutch company *Chemische Industrie Synres*[39]. In 1962 *Indústrias Químicas Synres Portuguesa*, Lda.[40] became the fifth *Synres*' plant outside the Netherlands. *JC Andrade* sold polymers from both, the Portuguese and the Dutch *Synres*. At that time the Dutch *Synres* was producing aqueous emulsions and *Hoechst* supplied them to the Portuguese market. The Portuguese considered the emulsions to be an important share of the polymers market and launched their production (see Chapter 2.1.2.1). In the same year (1962) *Synres Portugal* was producing a PVAc based emulsion (Figure 2.1) [136].

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[37] Soaps National Society.

[38] The representative in Portugal of the company *Chemische Industrie Synres.*

[39] *Synres* was founded in 1947 [138] and was a subsidiary from *Chemische Werke Albert*.

[40] 50% *Sociedade Nacional de Sabões* (Synthetic Resins Industrial Unit) and 50% *Chemische Industrie Synres*.

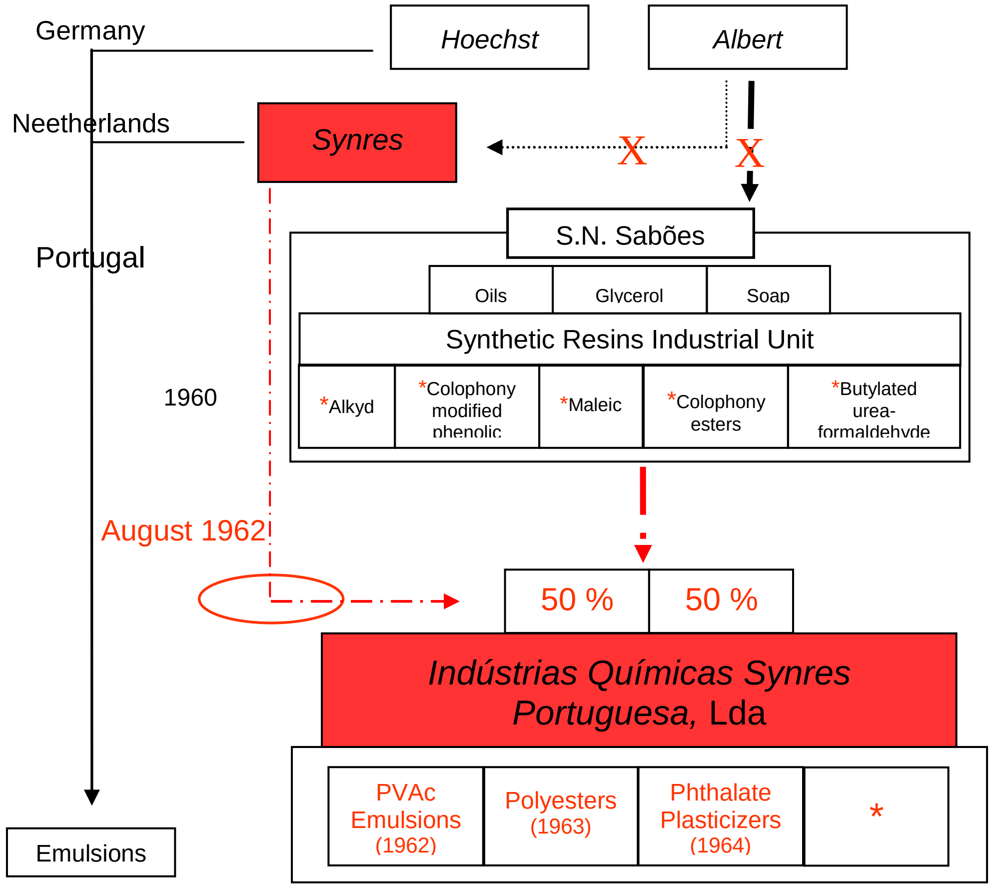

Figure 2.1. Schematic representation of the industrial structure of the main suppliers of synthetic resins acting in the Portuguese market in the early 1960s. The resins produced in Portugal by the *Synthetic Resins Industrial Unit* of *Sociedade Nacional de Sabões* (1960) and by *Indústrias Química Synres Portuguesa*, Lda. (after 1962) are represented.

The plant was well equipped and it was concluded that they should target other markets beyond resins for the paints industry. In the following years the product range became wider. While the production of resins expanded to other markets they also began producing additives for the paint and reinforced plastics industries. The plant was enlarged to ten reactors [136].

According to Aftalion [6], the Anglo-Dutch giant *Unilever* purchased *Synres* in 1960 accessing a range of synthetic resins and vinyl emulsions. In 1971 *Synres*, which had plants in the Netherlands, Portugal, Spain, France and Mexico, was sold to *DSM* (Dutch State Mines)[41]. Later, in 1983 *DSM Resins* is formed by the merge of *Synres* and *Unilever*'s *Unichema/Scado* (unsaturated polyester and coating resins) [138,139]. Still in partnership with *SNS*, the Portuguese company becomes *DSM Resinas de Portugal* [139]. Less than a decade later it was decided to halt the production and maintain the commercial activity. *DSM Resinas de Portugal*, which had become 100% Dutch, closed in the early 1990s.

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[41] Dutch company, 100% public since 1902 [140].

As the pioneers in the Portuguese production of synthetic resins, the emphasis of this chapter is on the company *Indústrias Químicas Synres Portuguesa*, Lda. Nevertheless, it is considered important to mention here the most significant steps on the evolution of *Resiquímica – Resinas Químicas*, Lda.

Resiquímica is a Portuguese chemical industry still in business that developed in a parallel line to that of *Synres*. It was first formed in 1957 under the name *Resintela - Resinas Sintéticas*, Lda. and it was a partnership between *Socer – Sociedade Central de Resinas*, SARL, *Sepulchre*, Lda. and *Reichhold Chemie* AG. In 1961 it became *Resiquímica – Resinas Químicas*, Lda.[42] [141]. Through the years, it has undergone multiple transformations and companies like the American *Hercules Powder Company*, LTD, the German *Chemische Werke Albert* and *Hoechst* AG were involved in the business [142]. *Resiquímica* had started by producing colophony, alkyd and some polyester resins but in 1966, with *Hoechst* holding 50% of the business[43], began to produce and commercialize PVAc emulsions[44] [141]. The giant *Hoechst* AG held two thirds of *Resiquímica* for more than thirty years [143]. This strong connection to world leading industries allowed the company to become the most important in the field of synthetic resins in Portugal [141]. *Resiquímica* was also founding partner of *Bresfor*, Lda. (1973)[45] and, in 1990, bought *E. Brunner* & Cª Lda., a Portuguese producer of emulsions. Today *Resiquímica* is 100% Portuguese[46] [143].

According to the Portuguese Association of Paints (APT) [144] the market of paint and coatings industry is comprised mainly of small and medium-sized companies. In 2002 there were 148 companies in this market sector, of which 10 represented 70% of the business. *CIN* (*Corporação Industrial do Norte,* S.A.) is the leader in the Portuguese and Iberian markets since 1992 and 1995, respectively [145]. In 2005 *CIN* held a 29% share of the Portuguese market and *Robbialac* was second with a 20% share[47] [146].

---

[42] With *Socer – Sociedade Central de Resinas*, SARL and *GEDIN – Gestora de Investimentos*, SARL as partners.

[43] *Hoeschst*, *Socer* and *Hercules* holding 50%, 25% and 25% of the business, respectively.

[44] Four years after *Synres* Portugal was constituted and started the production of emulsions.

[45] Production of urea-formaldehyde resins.

[46] With the founding partner *Socer* being the only holder of the business.

[47] *Robbialac* data referes to 2006.

2.1.2 Polymers and paint industry

2.1.2.1 Synres

Synres Portugal was a subsidiary of the Dutch company *Chemische Industrie Synres*, which had already businesses with the Portuguese industry, as referred in 2.1.1, and had its plant in Lisbon[48]. This Portuguese company was both producer and distributer.

For *Synres* the paint industry was the most important market followed by reinforced plastics. The technical phenolic resins were marketed for several industries, e.g., cork industry, sandpaper and sand casting. Depending on the type of polymer it would be produced as an emulsion or in solution. *Synres* production was mainly limited to polymers, but they produced and commercialized a small percentage of other products such as additives for paints. Regarding raw materials, *Synres* worked with more than 100 compounds and most of them were purchased from foreign companies. Colophony, glycerol, formaldehyde (*Bresfor*), urea (*CUF*), white-spirit, xylene and toluene (solvents produced by the petrochemical industry) were national products.

The first vinyl emulsion produced at *Indústria Química Synres Portugal* was a homopolymer of vinyl acetate and after that, probably already in the 1960s, VA/VeoVa copolymers. VeoVa (Shell) was cheaper than the acrylics and allowed a good quality VA copolymerization. Later they produced PVAc copolymers with acrylates and also styrene/acrylates. All emulsions had a cellulosic emulsifier. Aqueous emulsions were about 70% of the business.

Synresil LM15 was the first vinyl emulsion produced by *Synres* Portugal in 1962, which included 15% of 2,2-ethylhexyl phthalate as plasticizer and a cellulose ether as emulsifier. According to the records of *A Favrel Lisbonense* it was the emulsion used in the *Vulcano V7* glue (Chapter 2.2). Also in *Favrel*'s records there is a reference to another resin by *Synres*: *Synresol M80*, which was a colophony resin modified with maleic anhydride.

Indústrias Químicas Synres Portuguesa developed and produced products, specifically for certain companies, with special characteristics and costs. Examples of such agreements were with *Robbialac* (which for a while produced its own resins) and *Tinco*[49]. *Tinco* was founded by CUF and was an important producer of special paints for the automobile and ship industries; in this context they made a deal with *ICI* and *Synres* produced *ICI* resins. *Synres* only produced polymers but *DSM* produced monomers also. Styrene-acrylic emulsions were produced by *DSM* and were considered to be better than *Hoechst*'s corresponding product (a world leader in aqueous emulsions). For a while they produced them, as well as some other products, at *Resiquímica*.

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[48] Head quarters of Sociedade Nacional de Sabões at Beato, Lisbon.

[49] *Sotinco – Sociedade Fabril de Tintas de Construção Tinco*, SA. Today is part of the group *CIN* [147].

2.1.2.2 CIN

The history of CIN goes back to 1917. *Companhia Industrial do Norte*, SARL, produced oils, soaps, paints and varnishes among other products and had 3 plants. In 1926 *Corporação Industrial do Norte*, Lda., was established within a new partnership. The business was then focused on the paints and coatings industry sector and had its headquarters and plant in Porto[50]. With a lack of suppliers at that time CIN was practically self-sufficient. They purchased base raw materials, natural or slightly modified, and produced theirs own resins, packages and pigments[51]. In 1950 CIN had already created a laboratory for a research centre that became the Research & Development Department [148-149].

Since the 1970s CIN has undertaken an internationalization plan. New plants were established in Africa and later CIN bought a large share of a Spanish company, *Barnices Valentine*, keeping an investment position in the international market.

A meeting with Dr. José Alberto Alves[52] and Engineer José Luís Nogueira[53], held at CIN facilities (Maia, Porto) in March 2005, provided some details on the development of aqueous emulsion paints.

Historically, aqueous based paints have been a substantial component of CIN's business. In which concerns household paints, the proportion of aqueous and solvent based is about 70% and 30%, respectively; in industrial paints there is a greater equilibrium. While CIN-Portugal is strong in the aqueous based paints market, CIN-Spain is strong in the market of solvent based products.

CIN paints are mainly produced in Portugal and a small percentage at the CIN plants in Spain. The polymers are purchased from *Resiquímica* and most additives from foreign companies.

In the mid 1960s CIN worked with vinyl copolymers based paints. According to Eng. José Nogueira, in 1969 CIN was using a copolymer of vinyl acetate and acrylates; it was probably *Mowilith DM5*[54] sold by *Resiquímica*. After that, in the early 1970s, styrene-acrylic polymers were introduced and the resin used was *Acronal 290D* (BASF). Having some problems with the styrene-acrylic resin, CIN changed to an ethylene based emulsion. Since then, they changed to VA/VeoVa for the production of high quality interior paints, styrene/acrylates for low cost interior paints and pure acrylics for high quality exterior paints.

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[50] Rua Bento Júnior.

[51] Since the sixties these products are purchased from specialty companies.

[52] CIN Technical Director, Decorative Products (PhD).

[53] CIN R&D and Quality Director.

[54] Vinyl acetate + *n*butyl acrylate (35%) [154].

The **pigments** initially used were natural, like Umbria and Sienna, and were purchased in Italy. Nowadays they are essentially synthetic metal oxides and synthetic organic pigments, such as: titanium dioxide (white); red and yellow iron oxides; chromium oxide (green); bismuth vanadate (yellow); lamp black; phthalocyanine blue and green; DPP[55] red and orange; dioxazine purple[56] and hansa yellow. As **fillers**, CIN paints include calcium carbonate, kaolin, talc, mica and silica (for special applications, like textured paints, in which sand and silica flower are used). Other additives used by CIN in emulsion paints include: **surfactants** (acrylic acid sodium salt [BASF]); **wetting agents** (sodium hexametaphosphate was primarily used, but not anymore[57]); **biocides** (until 1975, when they became prohibited, mercury based products were used; then iodine, chlorine and formaldehyde compounds); **thickeners** (cellulose derivatives[58] and later acrylic and polyurethane based associative thickeners[59]); **matting agents** (wax).

2.1.2.3 Robbialac

Robbialac, a paint manufacturer since 1760, was established in Portugal in 1931 as *Sociedade Robbialac*, Lda. [150]. Its name comes from the 19th century when the English paint manufacturer *Jensen & Nicholson* developed a new lacquer under the name *Della Robbia White*[60]. Today the Portuguese company is registered as *Tintas Robbialac,* S.A. [151]. *Robbialac* was the first company to introduce aqueous emulsion paints in Portugal, under the trade name *REP*, which stands for Robbialac Emulsion Paint [152].

In 1958 *Robbialac* launched a Painting Manual [153] with the main objective of educating the consumers about fundamental painting procedures. The progress in the paint industry and technology is stressed, and also the increasing number of painting methods and materials. The manual contains about 200 pages, presenting both painting materials and painting systems. The first chapter of the manual is dedicated to the raw materials, the properties of the painting products and paint films, and the different types of paints and their purposes. The four subsequent chapters present a thorough description of all specialty *Robbialac* paints and auxiliary products.

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[55] The previously used monoazo pigments from *Hoechst* were substituted by diketo-pyrrolo-pyrrole pigments from *Ciba-Geigy*.

[56] Carbazole dioxazine.

[57] Information on the compound used nowadays was not provided.

[58] Methylhydroxyethylcellulose and ethylhydroxyethylcellulose.

[59] The current tendency is to produce associative cellulosic products with hydrophobic properties.

[60] A ‘lacquer capable of matching 'the brilliance and purity of the enamels of Della Robbia”’ [150].

Being conscious of the importance pigments have in a paint formulation, the manual started the chapter dedicated to raw material and paint components with a complete explanation about them. Pigments were known to 'influence several other paint properties [besides colour], such as hiding power, durability, consistency, etc. (...) almost all paint properties are more or less affected by the type and amount of pigments it contains' [153]. The pigments were classified as mineral extenders and opaque pigments (organic or inorganic). The extenders listed as being the most usual were: *blanc* fix (precipitated barium sulphate); Paris white (calcium carbonate); diatomaceous silica; magnesium silicate; mica; and kaolin. On the other hand opaque pigments were listed by colour. White pigments: titanium white (titanium dioxide, in its two crystalline forms rutile and anatase); lead white (basic led carbonate); zinc oxide and lithopone (mixture of zinc sulfide and barium sulfate). Coloured inorganic pigments: chrome yellow and orange; Prussian blue; chrome green; red and yellow iron oxides; and carbon black. The organic pigments considered to be of practical importance were: toluidine red; hansa yellow; and phthalocyanine blue and green.

The chapter dedicated to household paints comprises: anti-alkali primaries; oil paints[61]; synthetic based aqueous paints[62]; and oil based aqueous paints[63]. The reader of the manual is elucidated about the difference in the type of emulsion used as binder in synthetic paints and oil temperas. The latter were resin-oil based and were usually produced by the paint manufacturer. The synthetic emulsions, very different in nature, had a different production process that was technically more complex and were therefore bought from specialty industry. The synthetic aqueous emulsions were described as having had a growing popularity in the last 4 or 5 years due to their very desirable properties (fast drying; odourless; ease of applicability; excellent appearance; washability; good permanence; mixes with water). It is also explained that when first developed the styrene-butadiene based emulsions were the most used, being replaced by the 'better poly(vinyl acetate) ones'. According to the manual, PVAc based emulsions had better general properties and possessed a higher exterior durability. These resins were thought to be highly durable, resistant to alkalis and non-oxidizing (only undergoing through a very slow degrading process induced by UV light). The acrylics, which were more expensive, had not proven to be advantageous.

Robbialac **REP Paints**

Robbialac manual presents *REP* as 'synthetic aqueous paints', 'latex paints' or 'plastic paints'. *REP* was a poly(vinyl acetate) based emulsion, formulated with an emphasis on high

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[61] *Pintamur* – series 26.

[62] *REP* – series 24-100; *Interep* – series 25; *Murep* – series 24-600; *REP Cores Fortes* (REP Strong Colours) - series 24-400.

[63] *Aquatinta* – series 27.

permanence, outdoor durability, water resistance, excellent hiding power and opacity [153]. The paint was formulated in 16 colours with a velvet like gloss and good adhesion to a number of surfaces. Its concentration allowed a dilution of 15% to 25%. With the same binding media, *Robbialac* also produced and commercialized *Interep*, *Murep* and *REP Cores Fortes*. In the same 16 colours and described as having the same properties, *Interep* was suited for mate and *Murep* for textured surfaces. *REP Cores Fortes* was the forth product of the PVAc based line and was produced in 11 colours: black, 2 yellows, 3 greens, 1 blue, 1 red, 1 orange and 2 browns. Although these paints were similar to *REP* in their properties, *Robbialac* had to formulate them as a less viscous product in order to obtain stable intense colours. Therefore, *REP Cores Fortes* could only be diluted by a maximum of 10% water [153].

As previously mentioned, this Painting Manual referred to *Robbialac* products in 1958. Fortunately it was also possible to access a collection of original *Robbialac* paint catalogues (Figure 2.2), including printed and hand-painted samples.

Figure 2.2. Folders containing the original *Robbialac* paint catalogues.

This collection contains paint series dated back to April 1947, *Pintamur* – series 26, April 1949, *Membranite* – series 25, and October 1953, *Aquantinta* – series 27 (Figure 2.3). With the exception of *Membranite*, which may have been discontinued, the other two series were mentioned in the painting manual from 1958 and were described as oil *(Pintamur)* and oil based aqueous paint *(Aquatinta)*.

Figure. 2.3. Hand-painted catalogues from *Robbialac* paints. From left to right: *Pintamur* (1947), *Membranite* (1949), *Aquatinta* (1953), REP *Cores Fortes* (1954).

Also in the collection, the first REP – series 24-100 catalogue of paint colours found is dated January 1954 (Figures 2.4 and 2.5) and REP *Cores Fortes*[64] – series 24-400 dates July 1954 (Figure 2.3).

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[64] Intense Colours.

SÉRIE 24

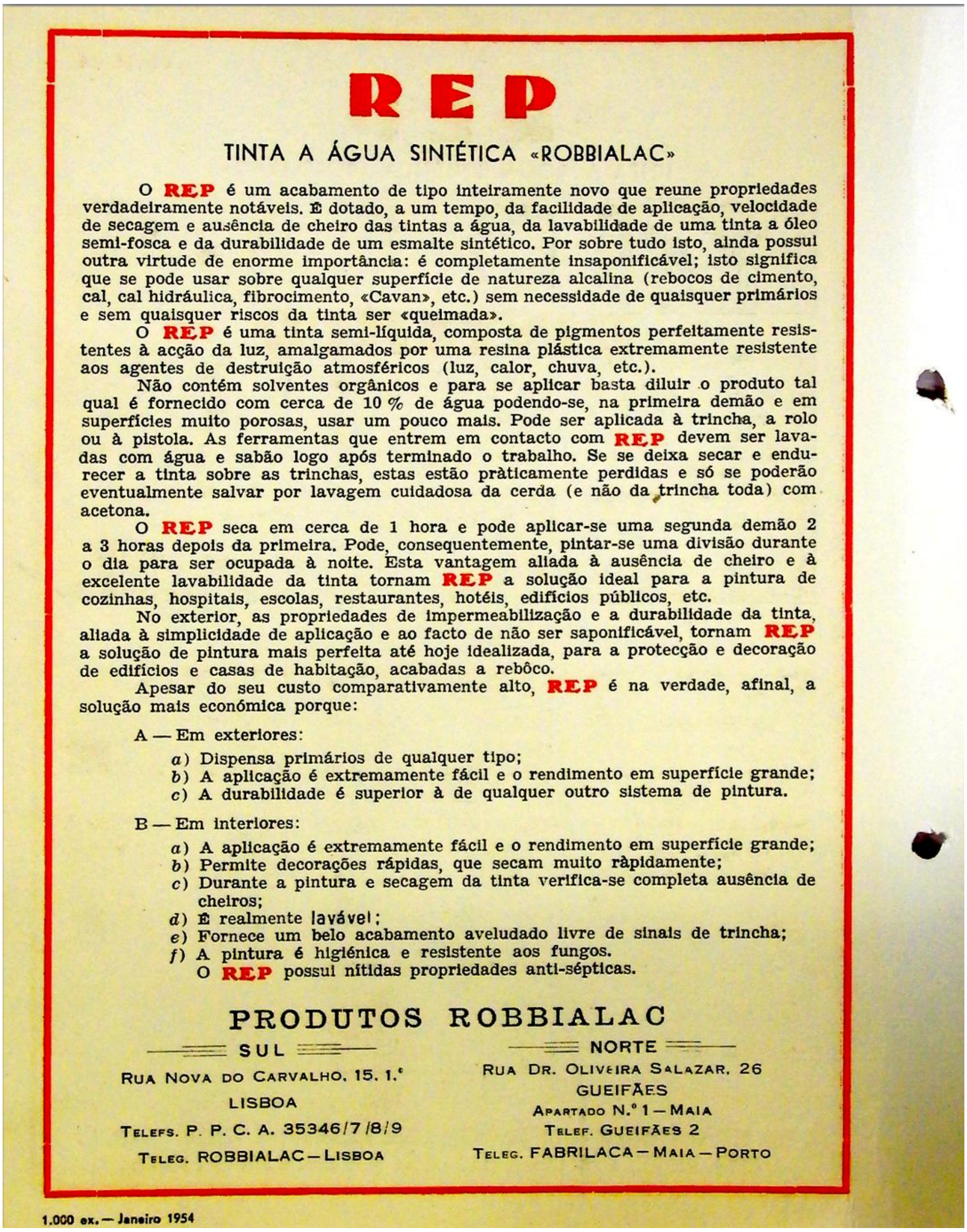
REP

TINTA A ÁGUA SINTÉTICA «ROBBIALAC»

24-102	24-103	24-104
24-105	24-106	24-110
24-112	24-113	24-115
24-114	24-117	24-116
24-108	24-109	24-107
BRANCO 24-101	24-111	BRANCO 24-101

As cores exibidas obedecem aos nossos padrões com a maior precisão possível. Pequenas variações são contudo inevitáveis e deve fazer-se pois um exame da cor antes de proceder à pintura.

Figure 2.4. Front of a hand-painted catalogue from *Robbialac* REP – series 24-100 dated January 1954, where it is described as ‘*Robbialac* Synthetic Water Paint’.



REP

TINTA A ÁGUA SINTÉTICA «ROBBIALAC»

O **REP** é um acabamento de tipo inteiramente novo que reune propriedades verdadeiramente notáveis. É dotado, a um tempo, da facilidade de aplicação, velocidade de secagem e ausência de cheiro das tintas a água, da lavabilidade de uma tinta a óleo semi-fosca e da durabilidade de um esmalte sintético. Por sobre tudo isto, ainda possui outra virtude de enorme importância: é completamente insaponificável; isto significa que se pode usar sobre qualquer superfície de natureza alcalina (rebocos de cimento, cal, cal hidráulica, fibrocimento, «Cavan», etc.) sem necessidade de quaisquer primários e sem quaisquer riscos da tinta ser «queimada».

O **REP** é uma tinta semi-líquida, composta de pigmentos perfeitamente resistentes à acção da luz, amalgamados por uma resina plástica extremamente resistente aos agentes de destruição atmosféricos (luz, calor, chuva, etc.).

Não contém solventes orgânicos e para se aplicar basta diluir o produto tal qual é fornecido com cerca de 10 % de água podendo-se, na primeira demão e em superfícies muito porosas, usar um pouco mais. Pode ser aplicada à trincha, a rolo ou à pistola. As ferramentas que entrem em contacto com **REP** devem ser lavadas com água e sabão logo após terminado o trabalho. Se se deixa secar e endurecer a tinta sobre as trinchas, estas estão pràticamente perdidas e só se poderão eventualmente salvar por lavagem cuidadosa da cerda (e não da trincha toda) com acetona.

O **REP** seca em cerca de 1 hora e pode aplicar-se uma segunda demão 2 a 3 horas depois da primeira. Pode, consequentemente, pintar-se uma divisão durante o dia para ser ocupada à noite. Esta vantagem aliada à ausência de cheiro e à excelente lavabilidade da tinta tornam **REP** a solução ideal para a pintura de cozinhas, hospitais, escolas, restaurantes, hotéis, edifícios públicos, etc.

No exterior, as propriedades de impermeabilização e a durabilidade da tinta, aliada à simplicidade de aplicação e ao facto de não ser saponificável, tornam **REP** a solução de pintura mais perfeita até hoje idealizada, para a protecção e decoração de edifícios e casas de habitação, acabadas a rebôco.

Apesar do seu custo comparativamente alto, **REP** é na verdade, afinal, a solução mais económica porque:

A — Em exteriores:

- *a*) Dispensa primários de qualquer tipo;
- *b*) A aplicação é extremamente fácil e o rendimento em superfície grande;
- *c*) A durabilidade é superior à de qualquer outro sistema de pintura.

B — Em interiores:

- *a*) A aplicação é extremamente fácil e o rendimento em superfície grande;
- *b*) Permite decorações rápidas, que secam muito ràpidamente;
- *c*) Durante a pintura e secagem da tinta verifica-se completa ausência de cheiros;
- *d*) É realmente lavável;
- *e*) Fornece um belo acabamento aveludado livre de sinais de trincha;
- *f*) A pintura é higiénica e resistente aos fungos.
  O **REP** possui nítidas propriedades anti-sépticas.

PRODUTOS ROBBIALAC

SUL
Rua Nova do Carvalho, 15. 1.°
LISBOA
Telefs. P. P. C. A. 35346/7/8/9
Teleg. ROBBIALAC — Lisboa

NORTE
Rua Dr. Oliveira Salazar, 26
GUEIFÃES
Apartado N.° 1 — Maia
Telef. Gueifães 2
Teleg. FABRILACA — Maia — Porto

1.000 ex. — Janeiro 1954

Figure 2.5. Back of the catalogue from *Robbialac* REP – series 24-100. In the bottom left corner it reads ‘January 1954’.

It was possible to confirm by μFTIR analysis that REP was already a PVAc emulsion (Figure 2.6) (please see Appendix I for experimental details). However, REP *Cores Fortes* was not assigned to PVAc, but to a nitrocellulose based paint[65] (Figure 2.7). As mentioned above, for a good quality paint, in 1958, REP *Cores Fortes* was formulated with a less viscous PVAc emulsion, compared to that used in the other synthetic based aqueous paints [153]. It is possible that the paint formulators were not satisfied with the paint resulting from the mixture of the pigments used to obtain these intense colours with PVAc and employed another polymer in the first formulations. However, It is not clear why nitrocellulose paint would be marketed under the name REP, which stands for *Robbialac Emulsion Paint*, the same used for a synthetic aqueous based line. Another possibility is that the catalogue was painted with a different binding media than that used in the actual paint formulation or that a nitrocellulose based varnish was applied over the paint.

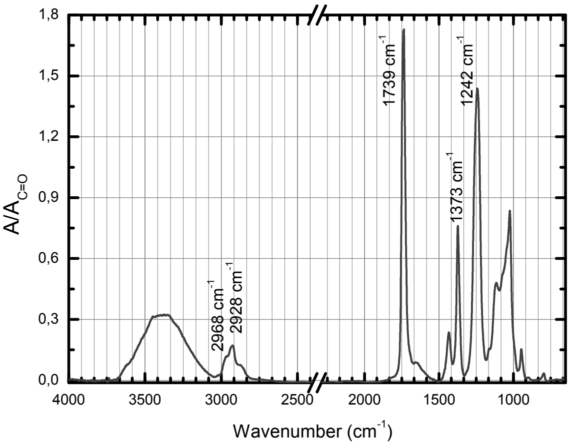


Figure 2.6. Infrared spectrum of *Robbialac* REP 24-114 paint sample. Spectrum assigned to poly(vinyl acetate) paint collected from a μ-sample (transmittance).

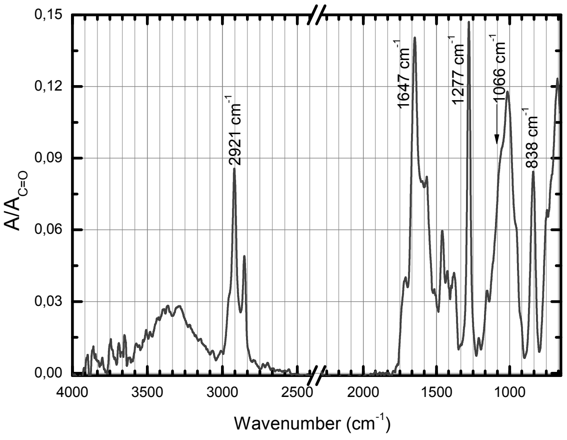


Figure 2.7. Infrared spectrum of *Robbialac* REP 24-405 paint. Spectrum assigned to a nitrocellulose based paint collected directly from the surface (reflectance).

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[65] Nitrocellulose paints are based on the blend of cellulose nitrate with other resin [155].

2.2 *A Favrel Lisbonense*[66]

2.2.1 The history of *A Favrel*

A *Favrel Lisbonense*[67] was the oldest Portuguese Fine Arts Materials Company in business until December 2006 and it had a long tradition. It was the first to introduce vinyl paints for artistic use in Portugal. The first reference to this company, *Favrel Portuense*[68], was in the eighteenth century[69] and, according to the family it prepared paints for the naval industry. Information from written records, such as catalogues, begins with José Netto Varella, who was *Favrel*'s manager from 1869 to 1891 in Porto. He was also responsible for the company's branch in Lisbon, to where the business was transferred in 1891*.* *Favrel* also ran a shop known as *Casa Varela* (Figure 2.8).

Varella went to Paris to learn about the art of gilding and, when he returned, introduced some new techniques to Portugal such as working with aluminium-based products. After this trip, *Favrel* advertised the production of gold, silver, platinum, and aluminium leaf and powder (Figure. 2.9). This information can be found in *Favrel*'s first catalogues from the early twentieth century, which list a diversity of materials, such as gold and other metal leafs, powders, and liquid paints; metal powders for pyrotechnics; crystal tears and blood for religious sculpture; glass and crystal eyes; brushes and all kinds of artists' tools; oil paints, watercolours, pastels, pigments, varnishes and essences; and enamel paints (as early as 1904). Favrel produced its own metal leafs and varnishes and was also the representative in Portugal for many international companies: *Reeves & Sons*, *Lefranc*, *Winsor & Newton*, *Paillard*, *Talens*, *Pelikan*, *Nelis*, *Shemink*, *Whatman*, *Nipon*, *Molin*, *Colorin*, and *Pearlin*.

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[66] All data that is not referenced in the text was provided as oral information during the interviews with former managers from *A Favrel Lisbonense*, Ricardo Caido and Mário Varela Gomes (Appendix II).

[67] Although the name of the company is *A Favrel Lisbonense* (*Favrel* from Lisbon), throughout the text it will be referred to simply as *Favrel*. According to official documents, it was registered as a trademark in 1906.

[68] Favrel from Porto.

[69] A 1952 catalogue reads, '*Favrel Lisbonense* was founded in 1891 in Lisbon, and its founder, José Netto Varella, had already worked at his grandparents' company (*Favrel Portuense*), dated from 1752.'

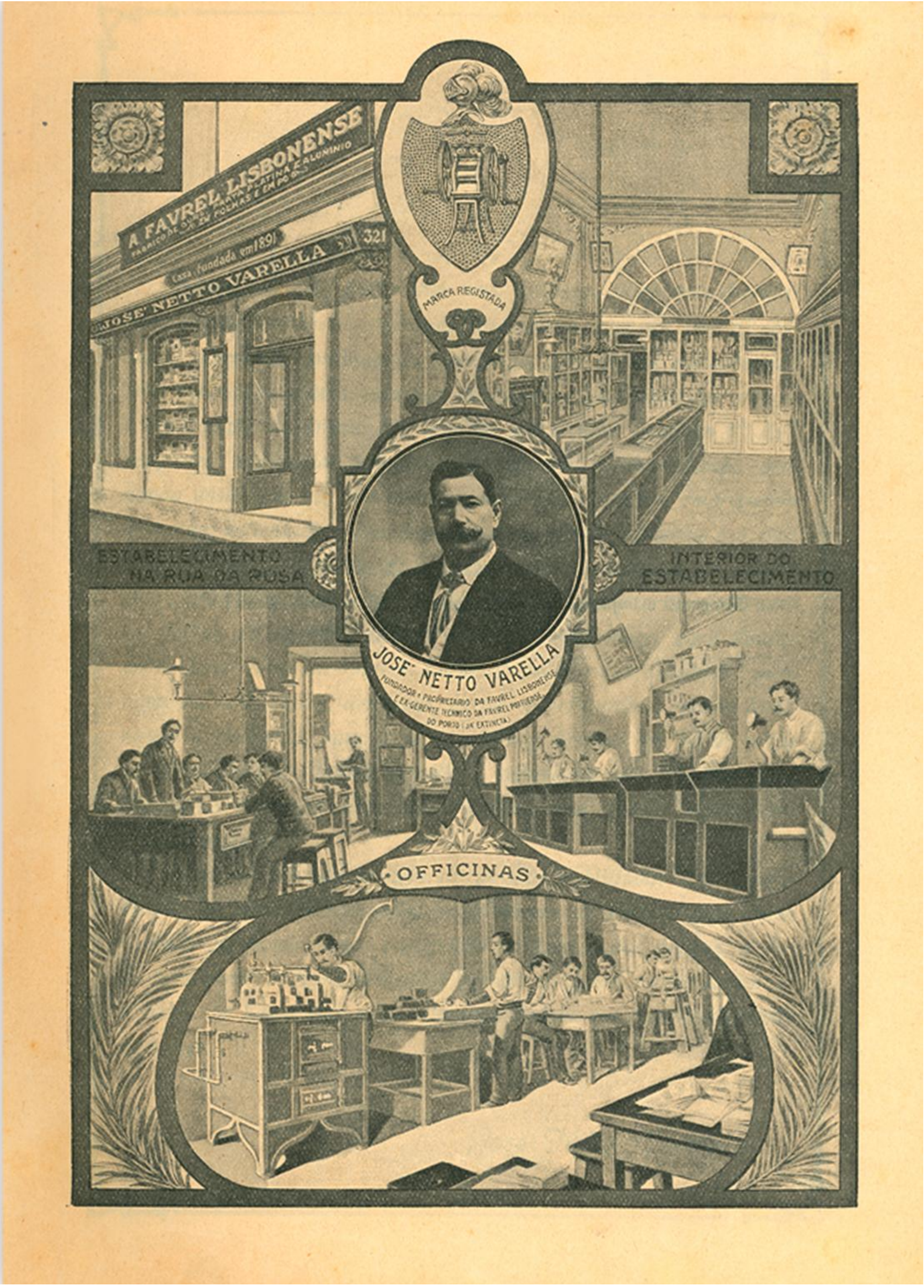

Figure 2.8. First page of a *Favrel* catalogue from the early twentieth century. Top – the shop as it still is nowadays; bottom – the factory with men working; centre – the company founder, José Netto Varella.

Titulo Privilegiado

A FAVREL LISBONENSE

Fabrica de
Ouro, Prata, Platina e
Aluminio em folhas e em pó

MARCA REGISTADA

JOSÉ NETTO VARELLA

UNICA NO PAIZ

FUNDADA EM 1891·

LISBOA
321·A-RUA DA ROSA-321-B·

ARTIGOS E FERRAMENTAS
PARA PINTORES, DOURADORES,
SANTEIROS, ENCADERNADORES
E PIROTECHNICOS

Telephone nº 1150

DEPOSITO NO PORTO
R. dos Martires da Liberdade - 199 a 201

Figure 2.9. *Favrel* catalogue from the early twentieth century; main advertisements include ‘Gold, Silver, Platinum and Aluminum leaf and powder factory. Materials and Tools for Painters, Gilders, *Santeiros* (saint-image makers), Bookbinders and Pyrotechnists’.

From 1925 to 1949, the family business was owned by José Netto Varella's daughter, Arminda Pereira Varela and, after her death, by her sister Maria Pereira Varela Gomes. They maintained the company but did not introduce relevant changes. After about 1935 the business was managed by António Varela Gomes, Maria P. Varela Gomes' son.

In a 1939 catalogue, a few entries for new materials produced by *Favrel* were introduced: paint, fixative, and white glue, as well as some kind of powder glue named *Vulcano*, but no reference was made to the materials used in their formulation. Over a decade later things began to change. In the 1950s *Favrel* was already advertising a selection of new modern products, such as the 'New, Plastic, Modern - opaque tempera colours' *Sabu* (Figures 2.10 and 2.11), described as a 'waterproof product',[70] *Omar* synthetic enamels, synthetic dyes, and *Radex* 'atomic age paints', which were fluorescent colours.

SABU, é uma tinta de medium plástico Palivy-nile. Solúvel com água, insolúvel depois de seca. Apresenta-se em estado pastoso e de grande rendimento.

SABU é fixa, aderente sobre todos os materiais, cartão, cortiça, cimento, gesso, madeira, metais, vidro, papel, cerâmica, etc. NÃO TEM ODOR.

SABU não tem cheiro e as suas cores são manipuladas com pigmentos fixos (frescos) e monolites.

SABU, pode-se dizer, é o expoente máximo das tintas murais, a pintura do fresco séc. XX.

SABU é diferente das vulgares tintas plásticas porque a sua maior cencentração e garantia de pigmentos sólidos torna-a um material especial para ser usado pelos artistas e decoradores.

SABU tem grande rendimento e cobre só com uma pincelada, seca com rapidez e o seu medium (Liam) dá tempo a misturar composições e manobra pictorial de paleta ou emendas de fundo.

SABU não mancha. Uniforme, resiste aos ácidos, alkalis, sol, chuva, calor, humidade, etc.

	EMBALAGENS				LATAS	
	1/16 kg.	1/4 kg.	1/2 kg.	1 kg.	5 kg.	10 kg.
Branco:	5$00	15$00	27$50	50$00	47$50	45$00
Cores:	6$00	17$50	32$50	60$00	57$50	55$00

FAVREL - VARELA
R. da Rosa, 321-A, 321-B (Esquina da R. D. Pedro V)
Telefs. 2 82 05-3 42 75 — LISBOA

Figure 2.10. Cover of a *Sabu* hand-painted catalogue from the 1960s, where the paint is advertised in English as being 'New, Plastic, Modern. Opaque tempera colours. Water proof product'.

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[70] 'Water mixable, unmixable after drying'.

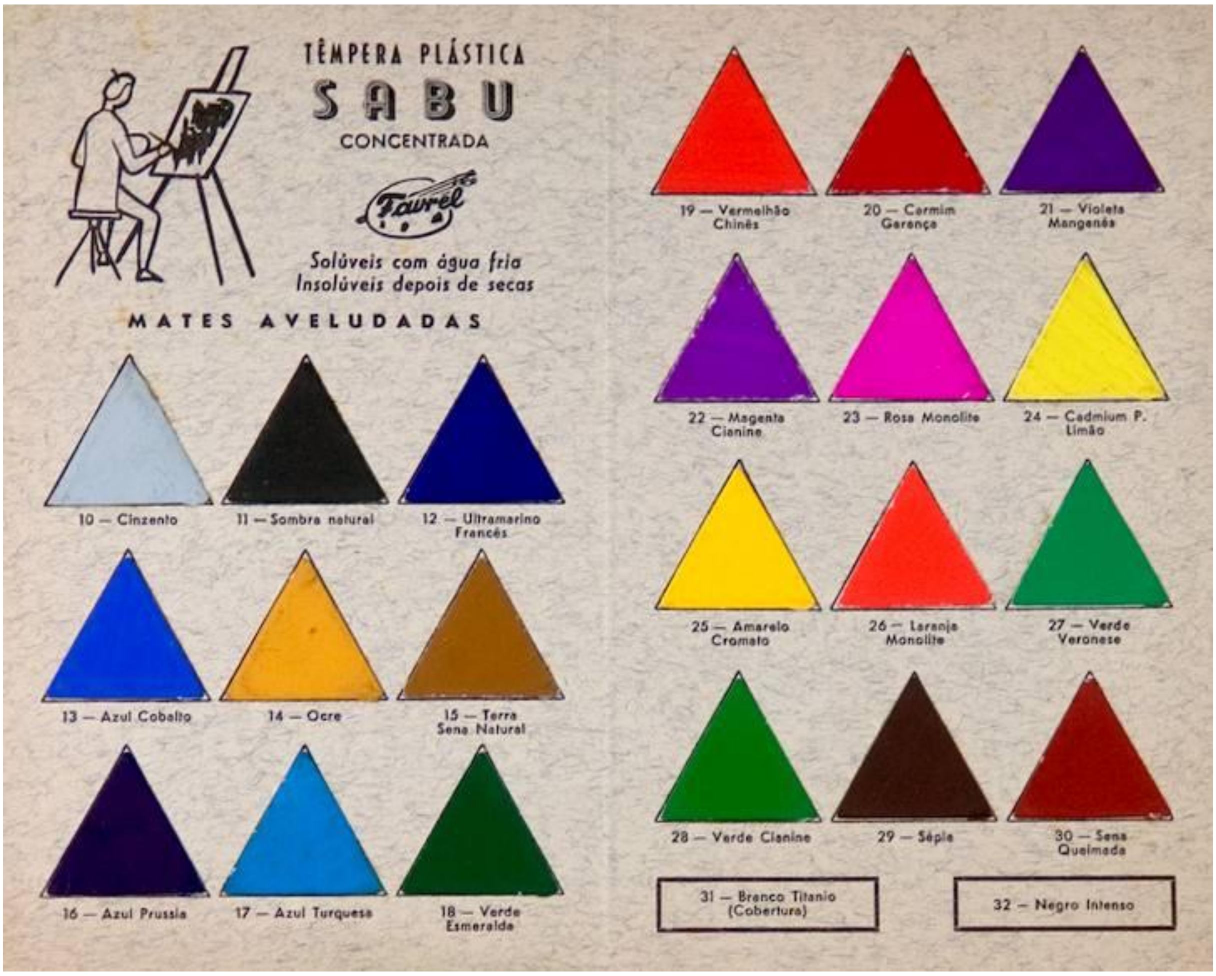

Figure 2.11. Inside of a *Sabu* catalogue from the 1960s, where the twenty-one *Sabu* colours are hand-painted in cardboard triangles.

António Varela Gomes, who became the owner in 1952, was responsible during the 1950s for the company's development and for the production of modern plastic paints[71]. In particular, he developed a series of vinyl aqueous paints with trade names such as *Vulcano V7* white glue, *Sabu* tempera colours, and *Geo* fluorescent paints, Figure 2.12. Varela Gomes was a cultured person with an eclectic upbringing and an inquisitive mind. He owned an art gallery and was close friends with many Portuguese artists. He was also a persistent man, an 'entrepreneur', who was able to run a successful business in a time when this was very difficult in Portugal [156], as António Oliveira Salazar (President of the Ministers' Council from 1932 to 1968) did not approve of industry. The *Sabu* paints and *Vulcano V7* glue became *Favrel*'s most popular materials[72]. The development of these modern artists' paints was especially important during the 1960s and the 1970s, when imports were restricted in Portugal, with new materials being made accessible to Portuguese artists at acceptable

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[71] There is a reference to an art fair, '*Feira de Artes da Estrela*', in 1957/58 (Lisbon), where *Sabu* paints were already used (Interview with Mário Varela Gomes, Appendix II.2).

[72] Interview with Ricardo Caiado, Appendix II.1.

prices[73]. Their availability and price were key reasons why Portuguese artists, such as Joaquim Rodrigo (1912–1997), Julião Sarmento (b. 1948), Eduardo Batarda (b. 1943) and Eduardo Nery (b. 1938) (according to the questionnaires sent to Portuguese artists, please see Chapter 2.3), used *Favrel* vinyl paints or the *Vulcano V7* glue to prepare their own paint during this period.

Figure 2.12. *Sabu* tempera colours, *Geo* fluorescent colours and *Vulcano V7* white glue (2006).

Varela Gomes died in 1970, but the business continued to be managed by his family (Figure 2.13). After 1970, the family business was owned and managed by his daughter and two sons: Maria Helena dos Santos Varela Gomes F. Caiado, Mário Augusto dos Santos Varela Gomes, and João António dos Santos Varela Gomes. In 1985, it was decided to separate the factory and the materials shop, which was then registered under the name of *Varela Gomes—Artes Plásticas*. From that year until 2002, the factory was managed by Maria Helena’s husband, António Micael Franco Caiado. More recently, from 2002 to January 2006, it was managed by their son, Ricardo Varela F. Caiado, and since then by their daughter, Maria Varela F. Caiado until it closed in December 31st 2006. The shop is still managed by António Varela Gomes’ sons and daughter.

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[73] Under Salazar’s authoritarian government (1932–68) and up until 1974, imports were extremely restricted and imported products were very expensive. Imported products only became more readily available and affordable in the 1980s.

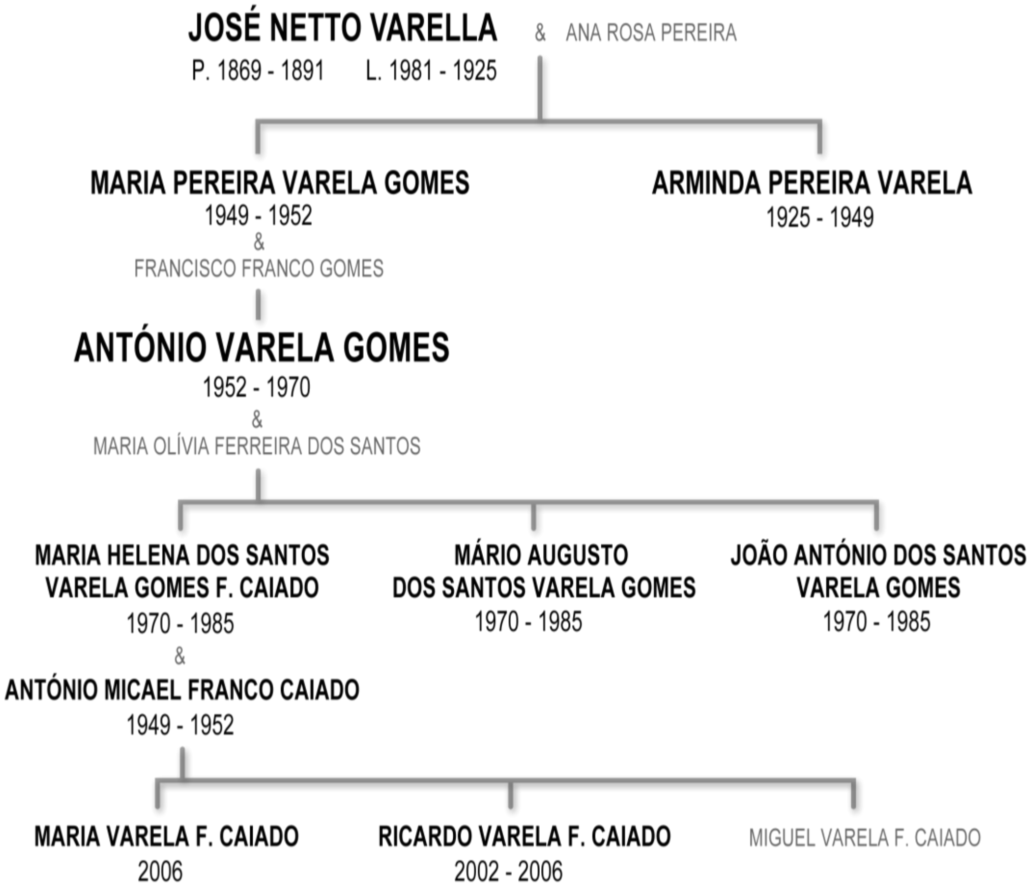

Figure 2.13. Varela family's genealogy, where *Favrel's* managers from 1869 to 2006 are represented.

2.2.2 *Favrel* vinyl emulsions

According to *Favrel*'s written records, two different polymer brands were usually used for the *Vulcano V7* glue and the *Sabu* line. Since 1962, *Indústrias Químicas Synres Portuguesa*, a chemical company in Portugal, produced a polyvinyl acetate (PVAc) emulsion, *Synresil LM15* (Chapter 2.1.2.1). This company was one of *Favrel*'s suppliers[74]; therefore, it is possible that António Varela Gomes prepared the emulsions in the early sixties using a vinyl emulsion from *Synres* for *V7* white glue. Furthermore, according to the company's formulation notebooks[75], until 1987 the polymer used in *Vulcano V7* formulation was *Synresil LM15*. More recently, it changed to a PVAc emulsion that was first distributed in Portugal by *Sarcol* under the name of *Imofan,* and afterwards by *Globalcor* as *Albucol 25 P*.

On the other hand, for the *Sabu* line (PVAc based aqueous paints), the binding medium was *Vinamul*. There is a reference in a 1978 notebook to *Vinamul* as the binder used, and a 1985 notebook refers to *Vinamul 6975*, vinyl acetate–vinyl versatate copolymer. In the paint

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[74] Confirmed by *Favrel*'s written records and by Engineer Morgado Costa.

[75] Examined in February 2005 with the manager's permission.

formulation used in the last years, the polymer was *Vinamul 3469*, a vinyl acetate–*co*-vinyl chloride–*co*-ethylene terpolymer. The films formed with this terpolymer have been considered to be more resistant to hydrolysis than PVAc homopolymer and copolymer dispersions and to have a higher mechanical strength [26]. Furthermore, at least since 1978, the pigments were first encapsulated in a cellulose ether and only afterwards mixed with the vinyl emulsion.

Geo was another aqueous paint formulation by *Favrel*, for fluorescent colours, and it was first produced as a casein tempera. However, its formulation changed and the binding medium became the same as that used for *Sabu*.

Finally, since the early 1990s *Favrel* also produced an acrylic series. In these paints the binder was a copolymer P(EA-MMA) produced by *Marl Polymer Latex* and distributed in Portugal by *Sarcol*. According to the literature, P(EA-MMA) is also the acrylic polymer used in *Grumbacher* [155] and *Liquitex* [157] paints from the early 1990s. An acrylic varnish was also available, in which a blend of P*n*BMA and PMMA was used[76].

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[76] This resin was also distributed in Portugal by *Sarcol*.

2.3 Overview of the materials used by Portuguese contemporary artists

In the framework of the present thesis, a written questionnaire (Figure 2.14) with general questions about the materials used was prepared and sent to 47 Portuguese artists who started their careers between the 1940s and 1970s (Appendix III). The questionnaire was aimed at understanding which were the classes of synthetic materials, and more specifically of synthetic polymer based paints, most used by Portuguese artists; which were the most used paint brands; when were they used; and which artists used them the most. To our knowledge, this was the first of its kind to be held in Portugal and was a starting point towards data collection on the synthetic materials used by our artists.

From the 47 artists inquired 28 returned the questionnaires, Figure 2.15. Twenty two artists affirmed to having used what we called ‘new materials’[77]. Of the 22 all have used synthetic paints and 13 used acrylic glass. Some artists listed other polymeric materials such as polyester, epoxy resins, synthetic fibres and silicone. Also, other non traditional materials were mentioned, such as photosensitive canvasses, video, audio, etc. While most of the returned questionnaires were carefully completed, in some cases precise questions, like ‘which brands of paints were used?’, were not answered. From these questionnaires it became evident that even when artists recall the brand names, in some cases, they categorize the paints incorrectly. For example, Paula Rego claims to have used acrylic emulsions but not vinyls, yet when asked about ‘other’ materials used, she mentions PVAc. Ana Hatherly, when asked about brand names referred to *Robbialac* (household paints) for acrylic emulsions; to our knowledge the first formulations of *Robbialac* aqueous emulsions were poly(vinyl acetate) based (Chapter 2.1.2.3) and some still are [151]. When considering modern paints, acrylic is probably the most familiar chemical designation for the majority of the artists and it is possible that when discussing synthetic paints they refer to them generally as being acrylics. From the 22 artists, 21 recall having used acrylic emulsions while only 12 refer to vinyl emulsions, 5 to alkyds and 3 to nitrocellulose paints. According to the information collected, most acrylic paints used were foreign brands (eighteen artists mentioned several foreign brands; 7 referred Portuguese brands[78]). As for vinyls, 5 artists named foreign brands[79] and 5 named national brands – Ângelo de Sousa referred to

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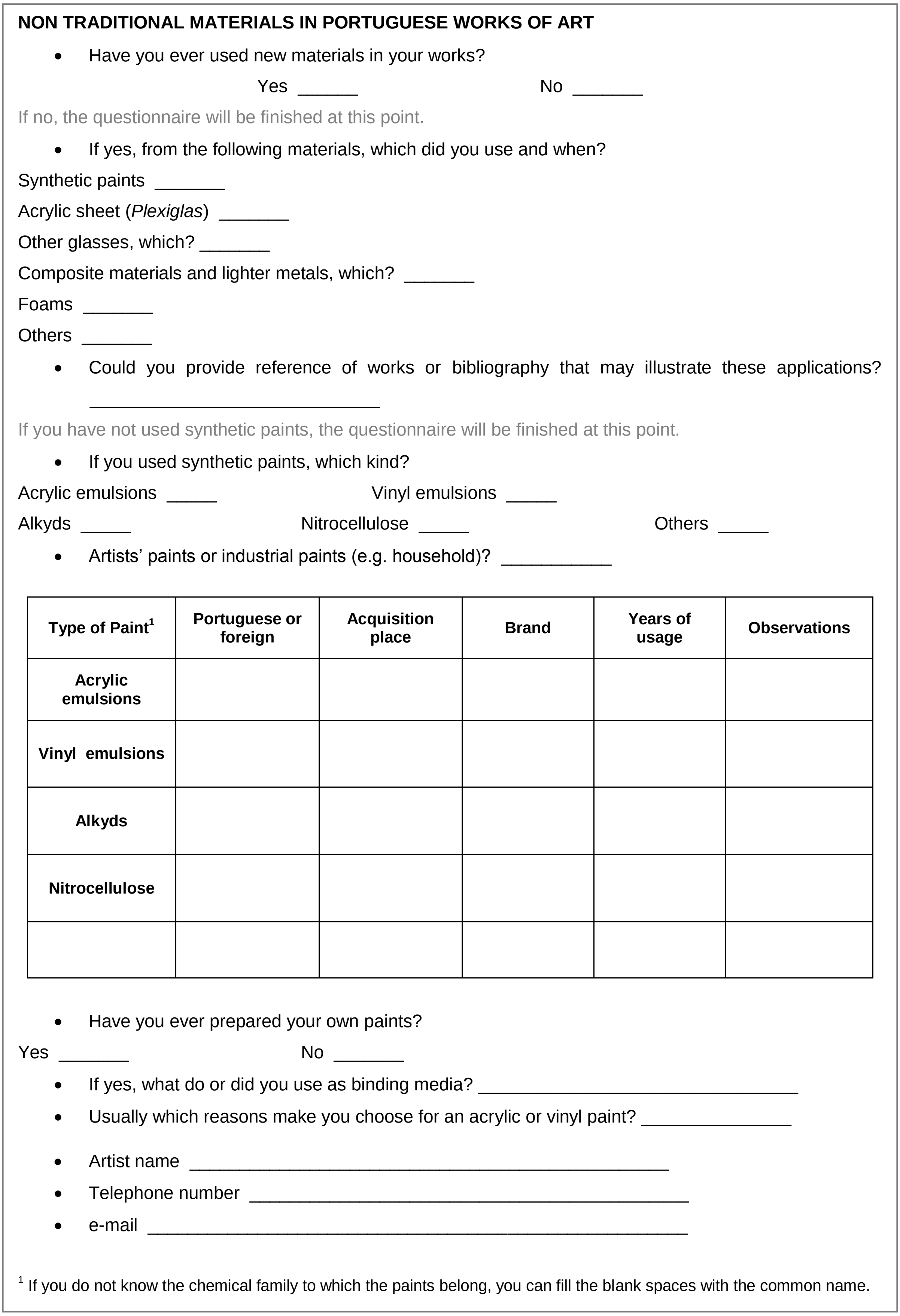
[77] In this context ‘new materials’ are intended to be associated with non traditional, ‘art-unknown’ materials [8], *i.e.* mainly synthetic materials developed in the twentieth century.

[78] *Robbialac* (and again it shall be stressed that it might have been a vinyl emulsion) and *Hitt* by *Dyrup* (described as aqueous acrylic enamel).

[79] *Pébéo*, *Flashe* by *L&B*, and also a French brand.



NON TRADITIONAL MATERIALS IN PORTUGUESE WORKS OF ART

- Have you ever used new materials in your works?

Yes ______ No _______

If no, the questionnaire will be finished at this point.

- If yes, from the following materials, which did you use and when?

Synthetic paints _______
Acrylic sheet (*Plexiglas*) _______
Other glasses, which? _______
Composite materials and lighter metals, which? _______
Foams _______
Others _______

- Could you provide reference of works or bibliography that may illustrate these applications? _____________________________

If you have not used synthetic paints, the questionnaire will be finished at this point.

- If you used synthetic paints, which kind?

Acrylic emulsions _____ Vinyl emulsions _____
Alkyds _____ Nitrocellulose _____ Others _____

- Artists' paints or industrial paints (e.g. household)? ___________

Type of Paint[1]	Portuguese or foreign	Acquisition place	Brand	Years of usage	Observations
Acrylic emulsions					
Vinyl emulsions					
Alkyds					
Nitrocellulose					

- Have you ever prepared your own paints?

Yes _______ No _______

- If yes, what do or did you use as binding media? ________________________________
- Usually which reasons make you choose for an acrylic or vinyl paint? _______________
- Artist name ____
- Telephone number ____
- e-mail ____

[1] If you do not know the chemical family to which the paints belong, you can fill the blank spaces with the common name.

Figure 2.14. English version of the questionnaire sent to Portuguese artists (2005).

Soberana industrial paints and Eduardo Batarda, Eduardo Nery and Pires Vieira to *Sabu* vinyl artists' paints by *Favrel*. The answers to a question about whether artists have used industrial (e.g. household) or artists' quality paints were surprising. We would expect that most artists had used the accessible and economical industrial paints, specially considering that the decades under study are from the 1950s forward. In reality 12 artists claim to have only used artists' quality paints, 6 affirm to have used both, 2 answered that they have just used industrial paints and 2 did not answer this question.

At this point it is important to discuss the accuracy of the results obtained. Although one of the privileges of contemporary art conservation is to be able to collect information directly from the artists or their assistants, it is necessary to scrutinize the information as it may not be accurate. For several reasons, artists do not always have a thorough knowledge of the materials they used. This may be caused either by the passage of time or by a misunderstanding about the nature of the materials [128,158]. Also the information provided by the manufacturers and/or material suppliers is not always accurate or complete [158]. Joaquim Rodrigo (Chapter 4.2), for example, wrote in his books [105,112] that he used acrylic glue as binding medium, whereas infrared analyses have proven that he was using PVAc.

Furthermore, when asked about the reasons why they opted for acrylic or vinyl paints, artists in general pointed out that they are easy to use, have good plasticity and are fast drying. Also, these aqueous paints are non-toxic, have good quality and durability. Experimental and economical reasons were also given. Eduardo Nery did compare the acrylic to the vinyl paints, which he considers to be more opaque than the former (allowing smooth and homogeneous colours). Furthermore, Eduardo Batarda recalls being at the store when the first acrylic paint tubes came out and believes he was the first Portuguese artist to have used them regularly.

Ângelo de Sousa showed a particular care answering the questionnaire. It is important to state here that he has a special interest in the material issues of his work. This interest, and curiosity about the possible results, led Ângelo to a cooperative attitude towards our research project. Joaquim Rodrigo and Ângelo de Sousa [22,23] were two of the first Portuguese artists to have systematically used PVAc based paints (since 1961), and where therefore selected as case studies for the present study (see Chapters 4.2 and 4.3.). On the other hand, Lourdes Castro selected the acrylic sheet as the ideal material for her shadow works from the 1960s and was also selected as a case study for the studies of PMMA (Chapter 4.5).

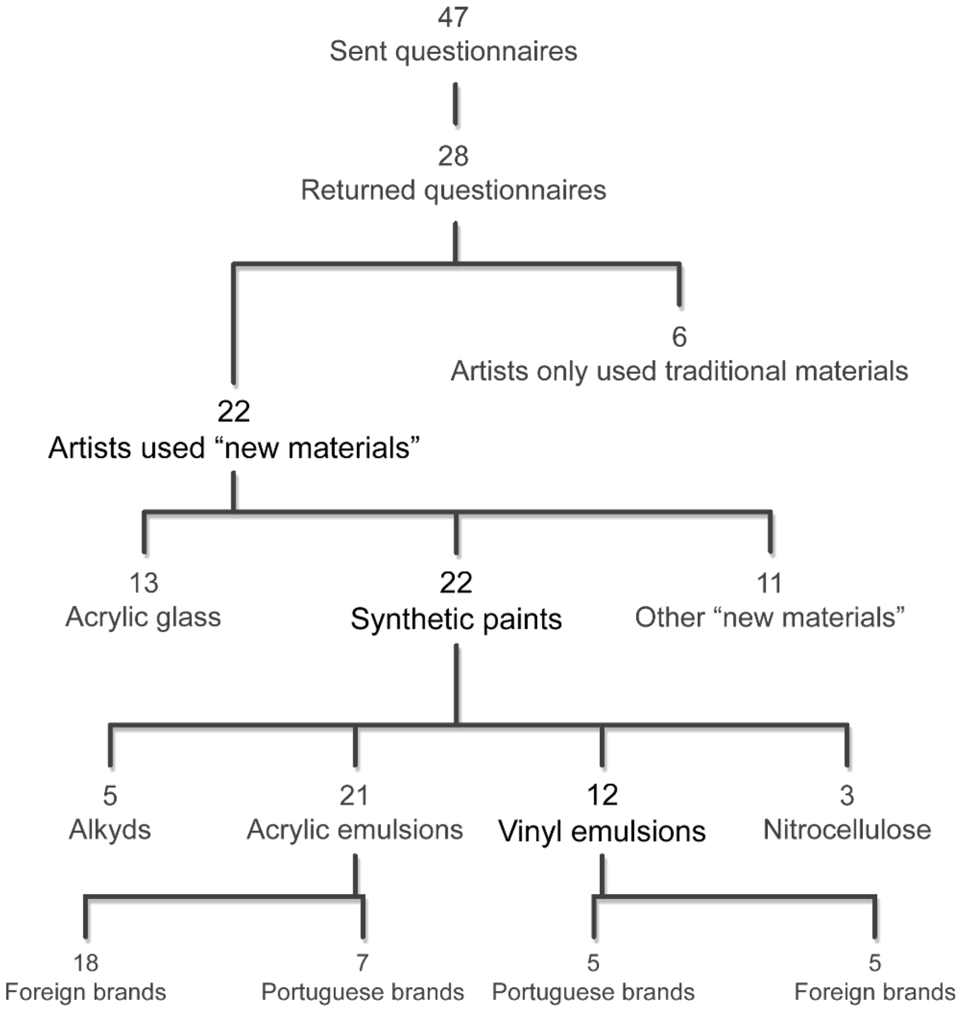


Figure 2.15. Schematic output from the questionnaires sent to Portuguese artists (2005).

2.4 Conclusion

The major premise for the present work was that Portuguese artists, like Joaquim Rodrigo and Ângelo de Sousa, used vinyl emulsion paints in their works since the early 1960s. Therefore, the first questions for which an answer was needed were concerned with the production of such paints and their raw materials and also with the extension of their use.

It was concluded that vinyl emulsions have been used in Portugal for the production of both household and artists quality paints since the 1950s, by *Robbialac* and *A Favrel Lisbonense*, respectively. The analysis of a hand painted catalogue for the REP paints by *Robbilac* showed that at least since 1954 PVAc was used as the binding medium in their production. Also in the fifties, *Favrel* was already advertising the *Sabu* paints as ‘New, Plastic, Modern – opaque tempera colours’. Although not being possible to confirm which was the polymer used at that time, the paints analysed from a catalogue dated from the sixties allowed to identify PVAc as the binder in *Sabu* paints. Besides these tempera colours, *Favrel* also produced *Geo*, a line of fluorescent vinyl paints and a vinyl based glue, *Vulcano V7*. At the same time the Portuguese chemical industry launched the polymer production, first with *Indústrias Químicas Synres Portuguesa* followed by *Resiquímica – Resinas Químicas*, using the technology of leading international companies. Prior to this, companies like *JC Andrade* supplied the national market with resins produced in other countries. *Synresil* LM15 was found to be the first emulsion produced in Portugal by *Synres* in 1962 and a vinyl acetate homopolymer was used. Four years after that *Resiquímica* also introduced the production of PVAc emulsions.

From the questionnaire sent to Portuguese artists about the synthetic materials used, some interesting issues were raised. One of the issues that became evident from the answers is that even when artists recall the brand names, in some cases they categorize the paints incorrectly. While all artists who have used what we called ‘new materials’ (*i.e.* mainly synthetic materials developed in the twentieth century) mentioned the usage of acrylic paints, only half referred to vinyls. It was also interesting to find that most brands of acrylic paints used were foreign and in which concerns the vinyl ones, foreign and national brands were even. Another remarkable finding was about the question whether industrial or artists’ paints were used. Over half of the artists claimed to have only used artists’ quality paints, one artist affirmed to have only worked with industrial paints and six (out of twenty two) answered that have used both. The answers given by Ângelo de Sousa were precise and correct, and it was possible to conclude that he would have been one of the first Portuguese artists to use vinyl based paints (since 1961/62).

Chapter 3

Molecular framework

Photodegradation on model samples

Part of the results presented in this chapter were published in international scientific journals.

Ferreira JL, Melo MJ, Ramos AM. *PVAc paints in works of art: a photochemical approach - Part 1*. Polymer Degradation and Stability 2010;95:453-461.

de Sá MH, Eaton P, Ferreira JL, Melo MJ, Ramos AM. *Ageing of vinyl emulsion paints – an atomic force microscopy study*. Surface and Interface Analysis (DOI 10.1002/sia.3664).

de Sá MH, Ferreira JL, Melo MJ, Ramos AM. *An AFM contribution to the understanding of surface effects caused by ageing and cleaning on acrylic glass. The Shadows by Lourdes Castro, a case study.* Surface and Interface Analysis (DOI 10.1002/sia.3663).

3.1 Preamble

Science is spectral analysis. Art is light synthesis.
Karl Kraus

As first mentioned in the introduction, in most cases contemporary works of art have been acquired by museums and private collections without undergoing a time proof in which concerns their stability. Materials based in synthetic polymers have often been used by artists in the twentieth and twenty first centuries. Photooxidation has been considered the main factor affecting their weathering [17,55,56] and therefore, a study of the molecular photo-oxidative mechanisms on synthetic paints used by Portuguese artists like Joaquim Rodrigo (Chapter 4.2) and Ângelo de Sousa (Chapter 4.3), as well as on the acrylic glasses used by Lourdes Castro (Chapter 4.5), is proposed.

Photodegradation studies on model samples are undertaken under both, polychromatic and monochromatic irradiation. Natural ageing conditions are simulated using a Xenon-arc lamp apparatus with $\lambda \geq 300$ nm (*Solarbox*, technical details are depicted in Appendix I), where the illuminance conditions are ensured by a set of reflectors which allow even irradiation, with all samples being irradiated at constant light. The molecular evolution upon photodegradation is followed by infrared spectroscopy (FTIR) and size exclusion chromatography (SEC) and the surface condition is evaluated by atomic force microscopy. Furthermore, colour variations were determined.

In which concerns the material performance, mechanical tests are a useful tool to access the evolution of film properties such as its cohesion and adhesion to the support. Stress-strain curves were obtained to evaluate the adhesion of the paint films placed on glass slides, however no reproducible results were obtained. On the other hand, from the data obtained at the molecular level it is possible to affirm that at our irradiations times the polymer is still in the first degradation steps. To estimate the physical evolution of the paint films upon ageing, a new experimental design would be required for a longer irradiation period and samples with adequate size.

The polymers studied in the present thesis, when used in artworks, are exposed mainly in the interior, protected from sunlight either by ordinary glass windows or in ideal museum conditions where UV light may be cut-off [36]. For an accurate comparison between the accelerated degradation conditions used and real time exposure, it would be necessary to measure the radiation in the interior of selected exhibition rooms and perform the experiments under radiation of the same energies. Another problem that should be taken into account when calculating correlation factors is the non-linear rate of photooxidation, due to factors such as the radicalar character of the degradation mechanism or, on the other hand, chromophore consumption. Therefore, only a merely indicative correlation factor may be calculated based on Feller's statement that the annual radiation in a museum in London is approximately 1.55% of the exterior [57]. If one considers that the average annual solar irradiation in London is 3240 MJ, in the interior of a museum it will be 50.22 MJ. The polymer films studied have been exposed for a maximum period of 5000h, with total irradiance being 13 762 MJ/m2, which would correspond to *ca* 275 years if exposed in museum conditions. Thus, a correlation factor of approximately 500 X could be considered.

The photodegradation of *Vulcano V7* vinyl glue (set 1) or PVAc (set 2) homopolymer, and PMMA (acrylic sheet) is studied. Accurate paint reconstructions (Figure 3.1) are based on real paint samples from dated case studies[80]: paints prepared by the Portuguese artist Joaquim Rodrigo (please see Chapter 4.2) and the vinyl aqueous emulsion paints, *Sabu*, produced by the company *A Favrel Lisbonense* (Chapter 4.4). These mock-ups were prepared with the pigments titanium white, iron oxide, ultramarine blue and the extender calcium carbonate, widely used in paint formulations (see Appendix I.7.1 for more details). Furthermore, the photochemical reactivity of the emulsion based reconstruction paints is compared with that of PVAc homopolymer. The latter is, in turn, compared with the reactivity of PMMA, considered one of the most stable polymers [19,20]. Two sets of commercial cast transparent samples, colourless and blue, are included. Furthermore, the influence on the polymer photodegradation of a commercial product used by Lourdes Castro for acrylic sheet cleaning will be considered.

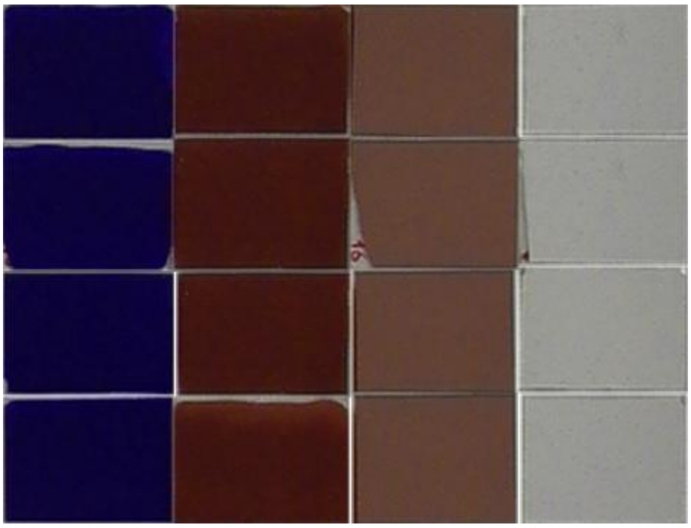


Figure 3.1. Paint reconstructions with *Vulcano V7* as binding medium. From left to right: ultramarine, iron oxide, iron oxide + titanium white and titanium white.

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[80] Although it is not possible to guarantee that the emulsion formulation used for the paint reconstructions is the same of what had been used in the real paints studied (the surfactant and other additives possibly present in low percentage were not identified), these are considered accurate as in both cases the emulsion is based on a vinyl acetate homopolymer, the plasticizer is a phthalate, and pigment mixtures reproduce what was found in paints from selected case studies.

3.2 Poly(vinyl acetate)

PVAc and its mixtures with pigments (set 2) did not suffer relevant weight loss (bellow 5% for all samples, including reference samples kept in the dark). With the exception of two mixtures (presenting losses of 1.4 mg and 2.4 mg in 35 mg), *Vulcano V7* irradiated samples (set 1) suffered 3 mg weight loss after irradiation, representing an average of 7% for paint mixtures and 14% for the emulsion, which may be related to plasticizer release from the film surface. Weight loss data are presented in Appendix IV.1.1 for the different irradiation times and control samples.

3.2.1 Solubility and molecular weight distribution

PVAc remains soluble after 5000h under Xenon irradiation with no gel formation being observed (Appendix IV.1.2). This is in agreement with the dynamic light scattering results, which show that for unfiltered PVAc solutions in acetone, the particle diameter decreases from 23 nm to 7 nm after 3500h irradiation (Figure 3.2). Although the results are presented here for the solutions in acetone, the same trend was observed for PVAc solutions in chloroform.

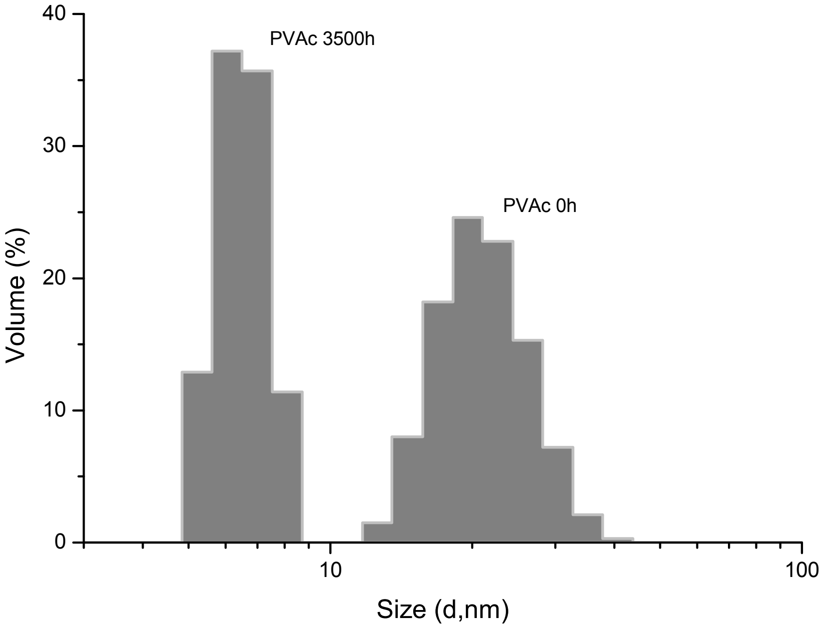


Figure 3.2. Size distribution by solution volume, statistics graph, of PVAc samples in acetone before and after 3500 h irradiation.

A reduction in the particle size distribution is possibly explained by chain restructuring following main chain scission, with the particles packing more closely together [56]. Also, Allen stresses that these compact structures may cause an increase in the polymer density; in fact, some embrittlement was verified on manipulation of the aged films for sample preparation (both PVAc and *Vulcano V7* based).

Changes in molecular weight distribution are already present, for *Vucalno V7* and PVAc homopolymer, after 500h under irradiation. Molecular weight distributions, weight average molecular weight (M_W), and respective polydispersity (PD) were determined and are presented in Tables 3.1 and 3.2. The sequential decrease in M_W values and the slight increase in PD indicate that PVAc as well as its mixtures with pigments (Table 3.1) undergo chain scission from the beginning of irradiation. The results obtained for the *V7* set (Table 3.2) are less straightforward; during the first 1500h, it is possible to detect an increase in the molecular weight distribution, and only afterwards chain scission is observed. The increase of *V7*'s M_W and PD points to the occurrence of branching, by chain transfer reactions to polymer, as an initial pathway to crosslinking. It is worth mentioning that the initial molecular weights of the paint reconstructions (set 1), when compared with the binder used, *V7*, display about twice its value; this suggests that the formation of aggregates may occur promoted by interactions between the polymer chains and pigments.

Table 3.1. Average molecular weight (M_W) and Polydispersity (PD) for PVAc homopolymer and reference paint samples over irradiation time

Sample	**0h**		**500h**		**1500h**		**2500h**		**3500h**	
	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***
PVAc	8.5	*2.0*	7.4	*2.1*	6.7	*2.1*	5.7	*2.4*	4.7	*2.4*
+TiO_2	8.4	*2.0*	8.4	*2.0*	8.0	*1.9*	7.9	*2.0*	7.3	*2.1*
+Fe_2O_3	8.4	*2.0*	8.1	*2.1*	8.1	*2.1*	7.8	*2.2*	7.5	*2.2*
+Ultramarine	8.4	*2.0*	7.8	*1.9*	6.2	*2.2*	4.3	*2.4*	3.9	*2.2*
+$CaCO_3$	8.5	*1.9*	5.8	*2.2*	4.3	*2.3*	3.5	*2.5*	3.0	*2.5*
+$CaCO_3$+TiO_2	8.5	*1.9*	8.5	*2.0*	8.0	*2.0*	7.6	*2.2*	7.5	*2.1*
+$CaCO_3$+Fe_2O_3	8.3	*2.0*	8.0	*2.0*	7.0	*2.1*	7.0	*2.2*	6.7	*2.2*
+$CaCO_3$+Ultramarine	8.5	*2.0*	7.4	*2.0*	6.2	*2.0*	4.9	*2.3*	3.9	*2.2*
+TiO_2+Fe_2O_3	8.4	*2.0*	8.1	*2.1*	8.1	*2.1*	7.9	*2.2*	7.6	*2.2*

Table 3.2. Average molecular weight (M_W) and Polydispersity (PD) for *V7* vinyl glue and paint reconstruction samples over irradiation time

Sample	**0h**		**500h**		**1500h**		**2500h**		**3500h**	
	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***	M_w (x 10^4)	***PD***
V7	15	*2.0*	25	*2.6*	34	*3.1*	26	*5.0*	22	*5.1*
+TiO_2	40	*2.0*	39	*2.3*	38	*2.4*	33	*3.6*	30	*4.3*
+Fe_2O_3	38	*2.3*	39	*2.4*	34	*3.4*	33	*3.3*	35	*3.3*
+Ultramarine	39	*2.4*	38	*3.0*	37	*3.0*	32	*4.4*	32	*3.6*
+$CaCO_3$	31	*2.5*	33	*3.1*	36	*2.9*	26	*4.6*	11	*5.1*
+$CaCO_3$+TiO_2	38	*2.4*	37	*2.8*	38	*2.8*	32	*3.9*	33	*3.5*
+$CaCO_3$+Fe_2O_3	40	*2.1*	39	*2.5*	37	*2.9*	35	*3.6*	36	*3.4*
+$CaCO_3$+Ultramarine	39	*2.3*	41	*2.4*	37	*3.1*	29	*4.4*	31	*3.9*
+TiO_2+Fe_2O_3	38	*2.3*	39	*2.4*	37	*2.8*	33	*3.9*	33	*3.6*

It is also important to consider the polymer T_g. While the PVAc value of T_g is approximately 30 ^{0}C, the polymer from the emulsion has a T_g of approximately 10 ^{0}C; during irradiation *V7* samples were above their T_g (the temperature was maintained at *ca* 24 ºC inside the ageing chamber), having a higher chain mobility than the pure polymer, which favours polymer/polymer and polymer/additive interactions.

In all chromatograms obtained for the *V7*-based samples (set 1), another peak was observed, corresponding to a low molecular weight substance, Figure 3.3, (chromatograms obtained for *V7* and PVAc mixtures with pigments are presented in Appendix IV.1.4), attributed to an additive in the formulation which tends to disappear during irradiation.

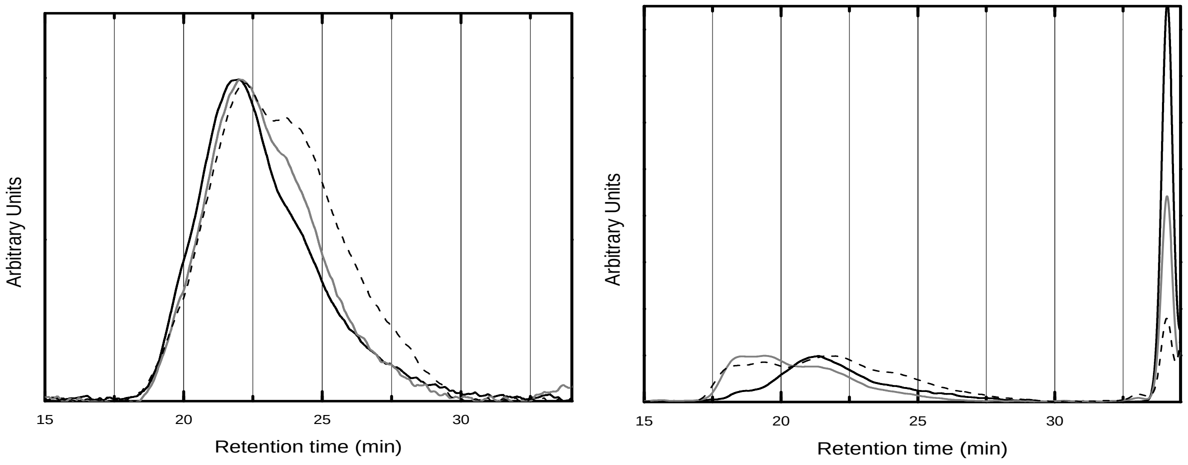


Figure 3.3. SEC chromatograms of PVAc (left) and *Vulcano V7* emulsion (right) before and after irradiation: black line – 0h; grey line – 1500h; dashed line – 3500h. The peaks appearing at t_R>30 min on the *V7* chromatogram are from an additive.

Analyzing in more detail the scission process, namely the effect of pigments on it, the number of scissions per chain may be considered according to $S = M_{n0}(1-x) / M_{nt} - 1$, where x is the fraction of volatilized polymer [18]. As mentioned above, no relevant weight losses were found relating to the release of volatiles and therefore S was calculated through the simplified expression $S = M_{n0} / M_{nt} - 1$.

Figure 3.4 compares the rate of scissions per chain for PVAc, *V7* and PMMA. It can be observed that PMMA displays the lowest rate, followed by PVAc (*ca* one scission per polymer molecular chain) and *V7*.

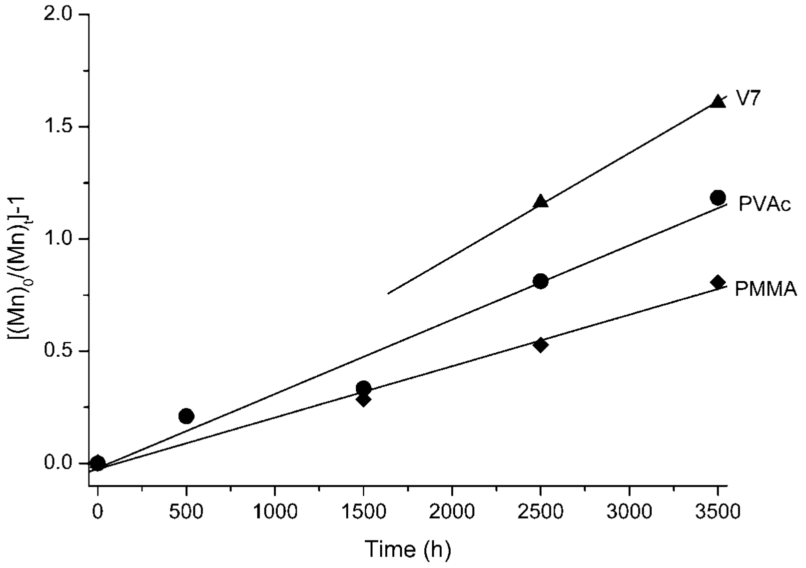


Figure 3.4. Scissions per chain as a function of irradiation time for PVAc, *V7* and PMMA. Where M_{n0}= original number average molecular weight; M_{nt}=number average molecular weight after irradiation.

Considering the effect of pigments on the photodegradation of PVAc, Figure 3.5, it is possible to separate the pigments into two groups, stabilizing and sensitizing. Titanium dioxide and iron oxide display a protective effect on paint films shown by a decrease in the scission rate when compared to PVAc. On the other hand, calcium carbonate and ultramarine blue promote an increase in the polymer scission rate.

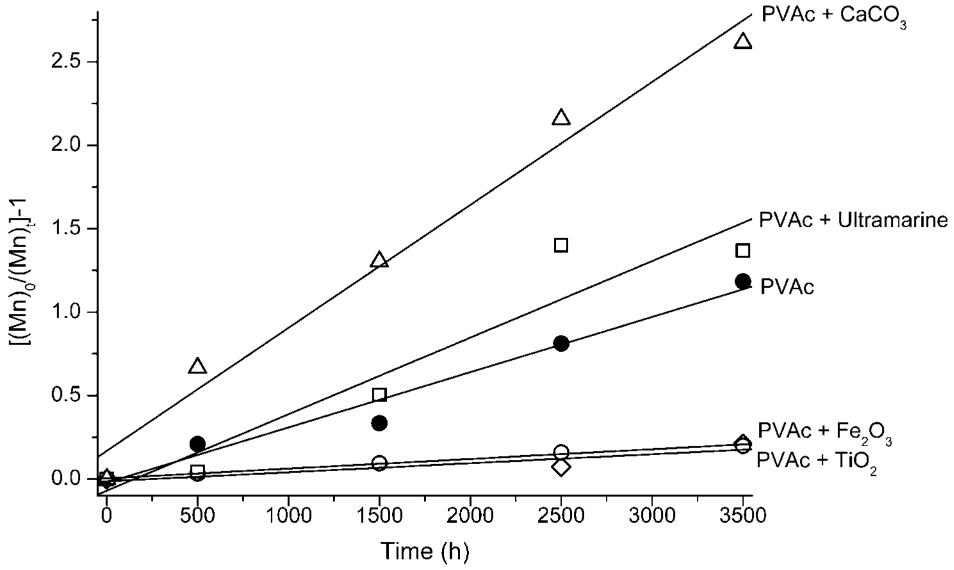


Figure 3.5. Scission per chain as a function of irradiation time for PVAc and its mixtures with pigments. Where M_{n0}= original number average molecular weight; M_{nt}=number average molecular weight after irradiation.

These results cannot be explained based on the photocatalytic properties of the pure pigments, where both Fe^{2+} and Ti^{4+} are well-known photosensitizers; most probably TiO_2 and Fe_2O_3 are commercialized with a protective coating, *i.e.* encapsulated with inert materials. This hypothesis was not confirmed by other techniques, such as μRaman and SEM-EDX. The ultramarine pigment is an aluminosilicate matrix where colour is provided by S_3^- groups entrapped in the lattice. Therefore it is a pigment where no photocatylitic activity is predicted. For a discussion of the results obtained it is necessary to take into account the partition of light absorption by the composite system, *i.e.,* between pigment and polymer. If the pigment is able to compete for light absorption, without promoting any secondary photochemical reactions, it will display a protective effect; the larger the fraction of light absorbed, especially for lower wavelengths, the more efficient this effect will be. Both iron oxide and titanium dioxide absorb completely (cut off) radiation below 400 nm (Figure 3.6.A and 3.6.B) and are possibly encapsulated. Therefore a protective effect is observed. The results for calcium carbonate and ultramarine blue do not present an immediate explanation. The scission rate for ultramarine blue is not very far from that observed for PVAc, so the slight increase could be explained by impurities or as the result of pigment degradation. On the other hand, the rate increase in the presence of calcium carbonate is high. Calcium carbonate does not display a sharp cut-off, and between 300 and 350 nm (Figure 3.6.C) both reflects and scatters light. In this region, both the scattered and reflected light could be re-absorbed by the polymer (internal scattering), intensifying the light absorption [60]. A similar reasoning could explain the observation for ultramarine (Figure 3.6.D) but, in this case, due to the presence of kaolin as an impurity (Table IV.4 in Appendix IV).

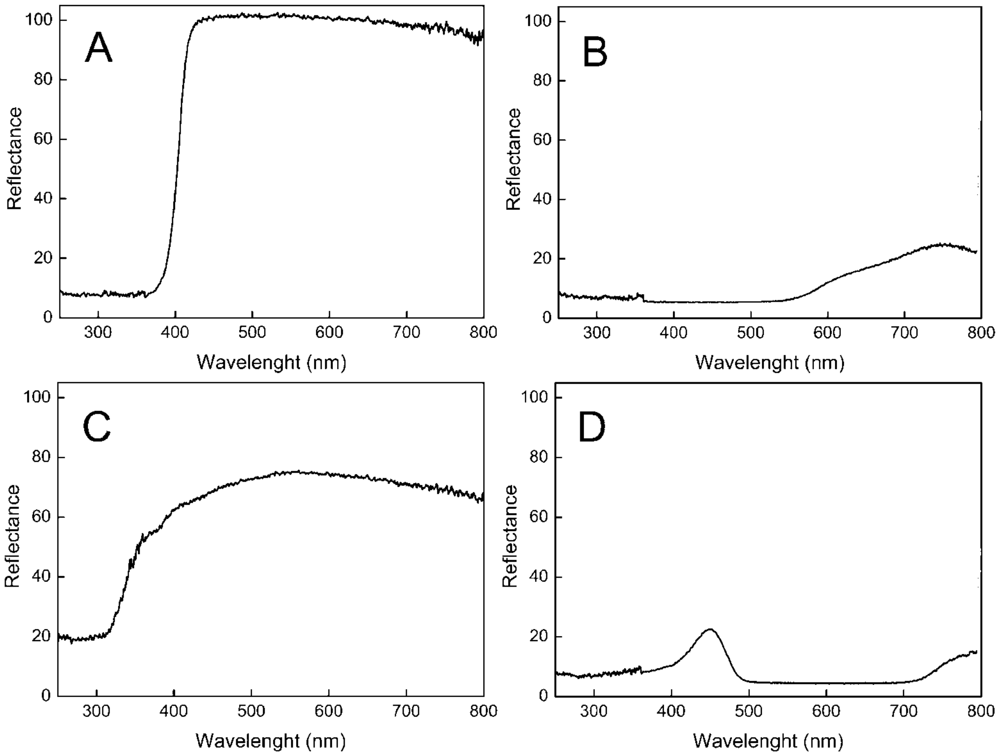


Figure 3.6. Reflectance spectra for (A) titanium dioxide, (B) iron oxide, (C) calcium carbonate and (D) ultramarine blue.

Results obtained for the *V7* mixtures, Table 3.3, require a more complex analysis. As described above, *V7* alone initially undergoes a molecular weight increase followed by chain scission. The existence of two competitive pathways may mask the results interpretation. The *V7* rate of scissions per chain was calculated for comparison, with M_{n0} based on the values obtained for t=1500h. Nevertheless, the paint reconstructions produced by mixing the vinyl emulsion with several pigments have a virtually linear chain scission behaviour as shown for set 2. Calcium carbonate and iron oxide follow the same trend, whereas titanium dioxide does not protect the polymer obtained from the emulsion, and ultramarine blue has a stabilizing effect.

Table 3.3. Rate of scissions per chain for PVAc and *V7*. Where *S'* is the curve slope and *R* the correlation coefficient

Sample	**PVAc**		***V7***	
	S' ($x10^{-4}$)	***R***	***S'*** ($x10^{-4}$)	***R***
Polymer	3.31	*0.985*	4.60[a]	*0.999*
+TiO$_2$	0.54	*0.917*	5.23	*0.958*
+Fe$_2$O$_3$	0.58	*0.996*	1.98	*0.831*
+Ultramarine	4.60	*0.956*	2.80	*0.832*
+CaCO$_3$	7.40	*0.991*	13.00	*0.853*
+CaCO$_3$+TiO$_2$	0.62	*0.894*	2.10	*0.854*
+CaCO$_3$+Fe$_2$O$_3$	1.13	*0.966*	2.55	*0.913*
+CaCO$_3$+Ultramarine	4.05	*0.991*	4.00	*0.855*
+TiO$_2$+Fe$_2$O$_3$	0.56	*0.978*	2.80	*0.893*
PVAc[b]	0.0200	*0.957*	-	-

[a] Calculated considering the values obtained for 1500h as M_{n0}.
[b] Irradiation carried out at 313 nm over 1850h (for more details see experimental section).

Possible synergetic effects, either protective or sensitizing as a result of pigment mixtures, were also investigated for calcium carbonate with titanium white, iron oxide, ultramarine blue, and also titanium white with iron oxide, Table 3.3. It was not possible to observe any synergetic effect. Nevertheless, in the paint mixtures of calcium carbonate with the three pigments, the sensitizing effect of calcium carbonate is eliminated.

The correlation coefficients obtained for *V7* are, in general, lower than the corresponding values for PVAc. The difference may be due to a higher experimental error on the polymer extraction, explained by the complexity of *V7* formulation and the interactions between its components.

3.2.2 FT-IR studies

The main conclusions to be drawn from the infrared monitoring are that, concerning PVAc and *V7*, the loss of material as well as molecular changes in the polymer are small, almost negligible, Figures 3.7 and 3.8. It is possible to observe that after 5000h irradiation the intensity of the PVAc spectrum is lowered by a maximum of 10%, and its shape is maintained when compared to non-irradiated samples. The lower absorption could also be explained by a physical parameter, such as different distribution of the film layer over the silicon disks, after 5000 h irradiation.

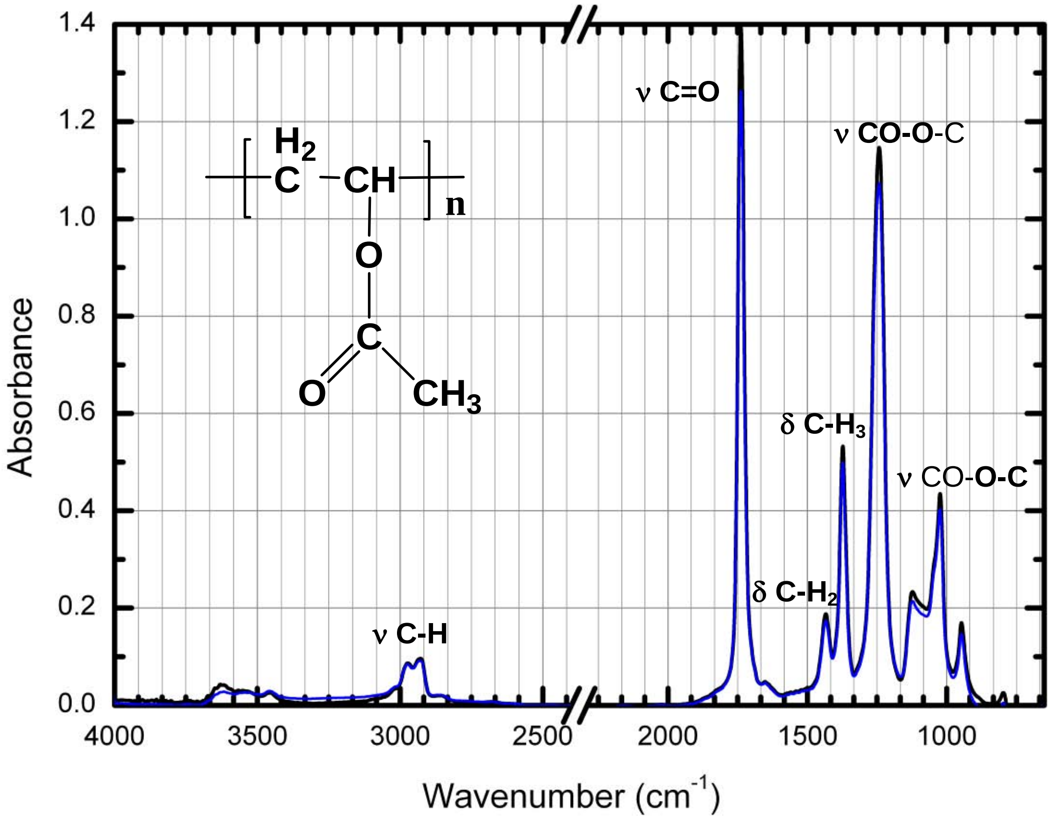


Figure 3.7. Infrared spectra of PVAc homopolymer: black line – t=0h; blue line - 5000h of irradiation.

On the other hand, and in agreement with conclusions from the M_W determinations, it is also possible to detect the presence of the plasticizer in the *V7* formulation and its loss during the irradiation. The plasticizer is identified by its infrared spectrum as di-iso-butyl phthalate (DiBP), Figure 3.9. The loss of the plasticizer is easily seen by the desapearence of the (peaks at approximately 980 and 1073 cm^{-1}, by the shift and change in the C-H stretching peaks profile, and by decrease, a small shift and straightening of the C=O and C-O peaks.

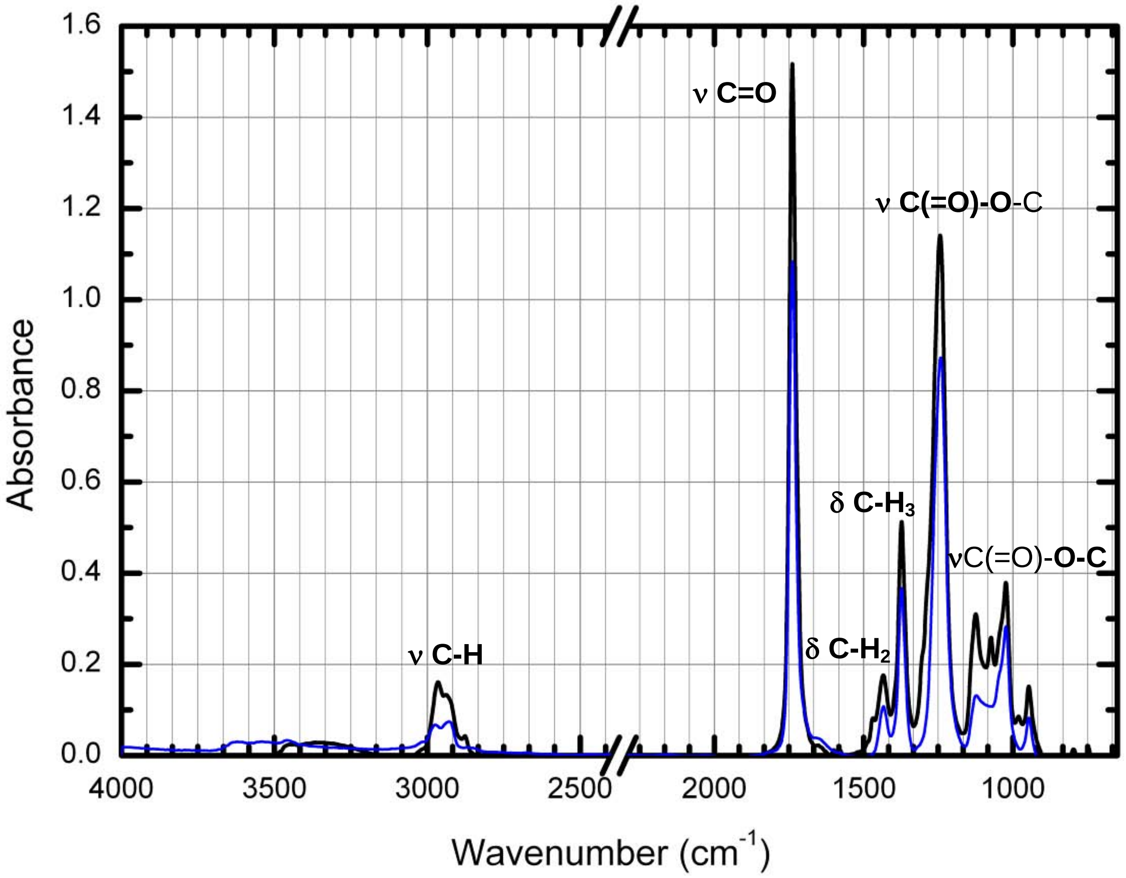


Figure 3.8. Infrared spectra of *Vulcano V7*: black line – t=0h; blue line - 5000h of irradiation.

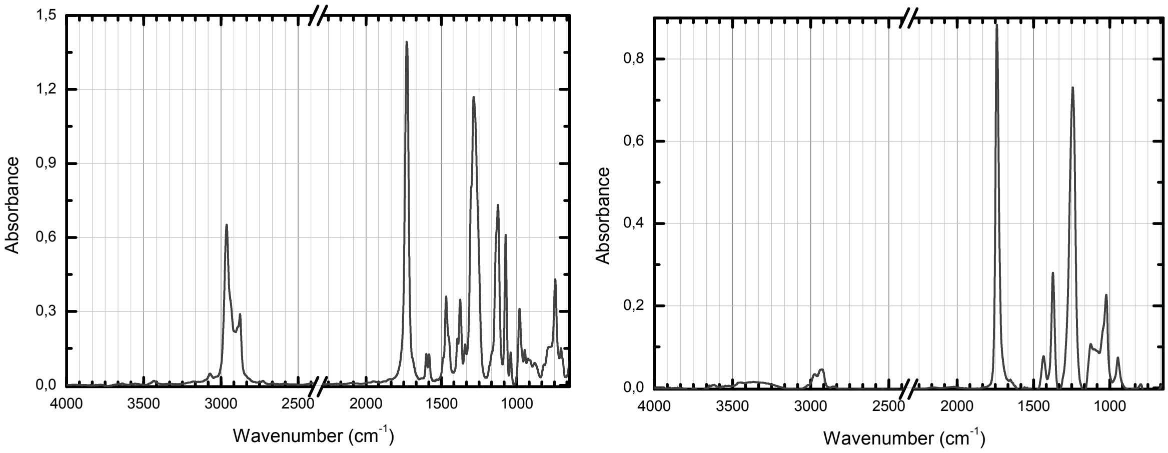


Figure 3.9. Infrared spectra: left – DiBP plasticizer; right – *Vulcano V7* after subtraction of 13% DiBP.

Before discussing in detail what was observed, we will summarize what we might have expected to detect in the infrared spectrum as a result of irradiation and photodegradation. The evolution of the infrared spectrum may enable us to assess the presence of chain scission due to ester cleavage or fragmentation (see Figure 1.9) and the appearance of other functional groups such as ketones, peracids, and carbon-carbon double bonds. Acetic acid, described in literature as the main volatile product formed during irradiation by a Norrish Type II mechanism, may be produced accompanied by the formation of a double bond in the main chain. Due to its low ε, the formation of these double bonds may not be detected in the infrared spectrum, but the extensive production of acetic acid would be reflected in loss of polymer; this would result in a loss of intensity in infrared absorption as well as broadening of the ester absorption band as a result of the appearance of other carbonyl functions. Side chain reactions would also be readily detected in the infrared spectrum; the loss of a CH_3 group would be detected both in the C=O/C-H ratios and in alteration of the C-H_3 stretching and CH_3 bending, at approximately 2970 cm^{-1} and 1373 cm^{-1}, respectively. Acetic acid release may also be a consequence of heterolytic (non-photochemical) acidic hydrolysis, resulting in the formation of PVAL which could be detected in the IR spectrum for a concentration of PVAL greater than 10% (Appendix IV.1.6) [159]. The appearance of an O-H stretching from the alcohol group present in PVAL together with the ratios νCH_3/C=O, νCH_2/C=O, δCH_3/C=O and νC-O/C=O may provide relevant information on the extent and type of the ester fragmentation. For monitoring the evolution of the methyl and methylene groups present in PVAc, the C-H asymmetric stretching absorptions at approximately 2972 cm^{-1} for the tertiary C-H and at approximately 2930 cm^{-1} for the methylene hydrogens can be used [160-162]. In the colour paints, the C-H bending vibrations are less useful as they may be masked by the pigment or the calcium carbonate extender.

As discussed above, the spectra of unaged PVAc and *V7* present some differences due to the presence of the plasticizer in the formulation of *V7* glue. If DiBP spectrum is subtracted from *V7*, the resulting spectrum corresponds to the PVAc homopolymer (Figure 3.9).

The spectra of both PVAc and *V7* (Figures 3.7 and 3.8), as well as of their mixtures with the four selected pigments (Appendix IV.1.5), were recorded before and after irradiation (approximately 5000h for PVAc and *V7* and 3500h for the paints). Peak ratios were calculated (Tables 3.4 and Table 3.5), and it was concluded that there were no significant changes except for that already described as corresponding to DiBP release from *V7* films. For all samples the differences found for the δCH_3/C=O and νC-O/C=O ratios (absorption and peak area) are below 5.5%. Only small changes were observed for νCH_3/C=O and νCH_2/C=O, but they were not considered relevant as the PVAc CH_3 and CH_2 stretching peaks correspond to weak vibrations, and a higher error in the calculation of both peak intensity and area is expected.

Table 3.4. Main infrared absorptions normalized for the C=O stretching for PVAc homopolymer, *V7* vinyl glue and paint reconstructions. Before and after 3500h accelerated ageing

Sample	ν_{CH_3} 2974 cm^{-1}		ν_{CH_2} 2927 cm^{-1}		δ_{CH_3} 1373 cm^{-1}		$\nu_{C=O}$ 1738 cm^{-1}		$\nu_{C(=O)-O-C}$ 1242 cm^{-1}	
	0h	**3500h**	**0h**	**3500h**	**0h**	**3500h**	**0h**	**3500h**	**0h**	**3500h**
PVAc	0.038	0.034	0.042	0.038	0.29	0.31	1.00		0.79	0.80
+ TiO_2	0.032	0.030	0.037	0.035	0.28	0.28	1.00		0.74	0.74
+ Fe_2O_3	0.035	0.032	0.039	0.037	0.31	0.32	1.00		0.81	0.81
+ Ultramarine	0.040	0.039	0.045	0.046	0.35	0.35	1.00		0.86	0.86
+ $CaCO_3$	0.039	0.038	0.044	0.043	0.58	0.59	1.00		0.95	0.97
V7	[a]		[a]		0.32	0.32	1.00		0.76	0.78
+ TiO_2	[a]		[a]		0.33	0.32	1.00		0.76	0.75
+ Fe_2O_3	[a]		[a]		0.33	0.33	1.00		0.81	0.81
+ Ultramarine	[a]		[a]		0.38	0.38	1.00		0.83	0.86
+ $CaCO_3$	[a]		[a]		0.72	0.76	1.00		0.91	0.96

[a] These peaks are not considered: at time 0 they are shifted in relation to PVAc due to the presence of the phthalate plasticizer, which disappears during irradiation.

Table 3.5. Main infrared peak areas normalized for the C=O stretching for PVAc homopolymer [a] and its mixtures with pigments. Before and after 3500h accelerated ageing

Sample	ν_{CH_3} 2974 cm^{-1}		ν_{CH_2} 2927 cm^{-1}		δ_{CH_3} 1373 cm^{-1}		$\nu_{C=O}$ 1738 cm^{-1}		$\nu_{C(=O)-O-C}$ 1242 cm^{-1}	
	0h	**3500h**	**0h**	**3500h**	**0h**	**3500h**	**0h**	**3500h**	**0h**	**3500h**
PVAc	0.14	0.10	0.02	0.02	0.27	0.26	1.00		1.41	1.40
+ TiO_2	0.09	0.08	0.04	0.04	0.26	0.26	1.00		1.39	1.38
+ Fe_2O_3	0.11	0.08	0.02	0.04	0.27	0.27	1.00		1.45	1.41
+ Ultramarine	0.09	0.10	0.04	0.04	0.29	0.29	1.00		1.44	1.43
+ $CaCO_3$	0.09	0.07	0.04	0.05	0.37	0.35	1.00		1.51	1.49

[a] The peak areas were calculated only for PVAc; the error inferred on the emulsion peak areas is high due to plasticizer loss.

Regarding the PVAc carbonyl band, no relevant shifts are detected in the carbonyl position after irradiation, and when broadening is observed, it falls below 5% (Table 3.6). The heterogeneity of the values found for the different samples already at t=0h may be related to differences in paint films thickness [63]. The three parameters calculated for the *Vulcano V7* set again illustrate the plasticizer release, *i.e.*, carbonyl shift to higher wavenumbers and a decrease of both, peak width and peak area; even when fitting was performed after 13% DiBP subtraction on the samples spectra a decrease is verified, showing that even if in low concentration the plasticizer is still present for the samples at t=0h.

Also, no PVAL formation could be detected. Similar trends are observed for the films containing metal ions. From the results, no trend relating to the presence of titanium and iron oxides with band broadening over irradiation time could be consistently observed. Overall, it is possible to conclude that the photochemical reactions involving the carbonyl group, if present, are still not relevant as detected by IR.

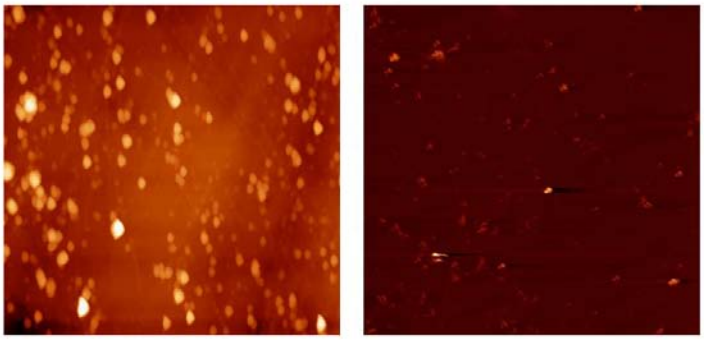
Table 3.6. Values of peak centre (μ), peak width at half maximum (σ) and peak area (A) for the carbonyl stretching absorption (Gaussian function) for PVAc homopolymer, *V7* vinyl glue and paint reconstructions. Before and after 3500h accelerated ageing

Sample	**μ**		**σ**		**A**	
	0h	**3500h**	**0h**	**3500h**	**0h**	**3500h**
PVAc	1738.2	1738.0	20.59	21.19	24.84	25.43
+ TiO_2	1738.2	1738.2	19.98	19.94	23.12	23.18
+ Fe_2O_3	1737.8	1737.3	20.98	21.45	25.41	25.95
+ Ultramarine	1737.3	1737.2	22.71	22.59	27.37	27.31
+ $CaCO_3$	1738.5	1737.6	21.25	21.23	25.80	25.97
V7	1737.0	1738.1	23.48	21.90	27.97	26.24
+ TiO_2	1736.6	1737.6	24.03	22.36	28.80	26.85
+ Fe_2O_3	1736.7	1737.7	23.81	21.99	29.08	27.11
+ Ultramarine	1736.1	1737.2	26.33	24.21	31.30	28.92
+ $CaCO_3$	1736.7	1737.7	25.13	23.25	30.41	28.35
V7 - DiBP [a]	1738.0	1738.1	22.03	21.90	26.14	26.24
+ TiO_2 [a]	1737.6	1737.6	22.75	22.36	27.05	26.85
+ Fe_2O_3 [a]	1737.7	1737.7	22.58	21.99	27.40	27.11
+ Ultramarine [a]	1737.1	1737.2	25.40	24.21	29.74	28.92
+ $CaCO_3$ [a]	1737.7	1737.7	24.04	23.25	28.81	28.35

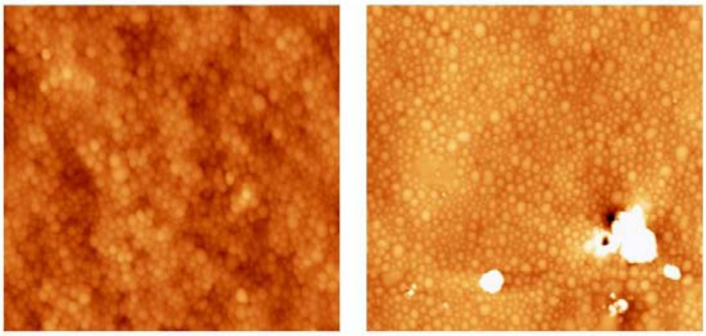
[a] Before fitting 13% of DiBP was subtracted to the spectra of the samples (0h).

3.2.3 Surface studies

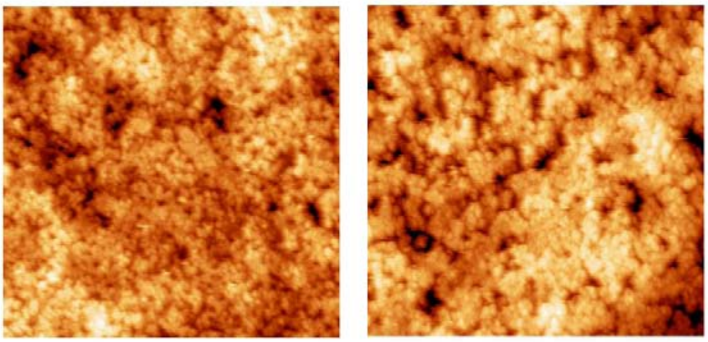
The surface changes on PVAc, *Vulcano V7* and *V7* with TiO_2 films were evaluated by atomic force microscopy [163], Figure 3.10. From the data obtained, Table 3.7, it is possible to conclude that the irradiated films have suffered only minor surface changes. The decrease in the roughness values of the PVAc film may be related with the film formation process and also with particle packing following chain scission (please see discussion in Chapter 3.2.1). The AFM images show that the main changes occurring are probably related with the release of additives from the films cast from the *V7* emulsion. Furthermore, in the case of the paint films (*V7* + TiO_2), the surface parameters remained unaltered.



PVAc 0h PVAc 3500h



Vulcano V7 0h *Vulcano V7* 3500h



Vulcano V7 + TiO_2 0h *Vulcano V7* + TiO_2 3500h

Figure 3.10. AFM height images of 50x50 μm^2 scan areas of the film surfaces before and after irradiation. Z (height) scales are 500 nm for PVAc and *V7*, and 2000 nm for *V7* + TiO_2. Images obtained by M.H. Sá [163].

Table 3.7 AFM surface average parameters measured in 50x50 μm^2 scan areas

Sample		**Arithmetic mean surface roughness (*Ra*, nm)**	**Mean height ($\overline{Z}$, nm)**	**Maximum height (Z_{MAX} , nm)**
PVAc	0h *(15)*[a]	29 ± 10	169 ± 164	713 ± 397
	3500h *(12)*	15 ± 4	168 ± 141	571 ± 502
Vulcano V7	0h *(5)*	30 ± 2	150 ± 23	331 ± 40
	3500h *(10)*	35 ± 8	339 ± 123	1224 ± 334
Vulcano V7 + TiO_2	0h *(4)*	247 ± 40	1309 ± 369	2404 ± 476
	3500h *(4)*	265 ± 11	1443 ± 109	2559 ± 153

[a] In brackets *()* is the number of averaged scans for each sample.

3.2.4 Colourimetry

Colour variations were determined as a measure of the polymer/paint performance over exposure. The results obtained for PVAc, *V7*, and their mixtures with the whites, TiO_2, and $CaCO_3$ are presented in Table 3.8. Concerning PVAc and *V7*, it is concluded that no colour changes occurred for PVAc, whereas *V7* presents a low degree of yellowing (ΔE^* = 3.37). For the white paints, the variations were negligible with the exception of PVAc + $CaCO_3$, where the b* coordinate decreases from 6.8 to 4.2 ($\Delta E^* < 3$). It is worth to mention that the measurements for t=0h and t=3500h were performed on different samples, *i.e.* control samples (un-irradiated) and irradiated samples. Therefore, variations on the values obtained may be due to experimental error related to possible differences in sample thickness.

Table 3.8. $L^*a^*b^*$ and ΔE^* for PVAc, *V7*, and their mixtures with white pigments for t=0h and after 3500h irradiation

Sample	L^*	a^*	b^*	ΔE^*
PVA	91.50	-0.96	4.01	**0.68**
	90.82	-0.93	4.00	
+TiO2	93.32	-1.00	1.14	**1.47**
	94.30	-0.83	2.23	
+$CaCO_3$	83.24	-0.78	6.79	**2.63**
	83.50	-0.76	4.18	
V7	88.65	-0.65	5.11	**3.37**
	89.24	-0.89	8.42	
+TiO_2	96.48	-0.45	1.58	**1.84**
	96.65	-0.39	3.41	
+$CaCO_3$	82.16	-0.61	6.17	**1.11**
	82.62	-0.87	7.14	

3.2.5 Quantum yield determination

For an accurate determination of reaction quantum yields, we should ensure measurement accuracy for the phenomenon as well as for the light absorbed. Also, thin films where radiation penetrates into all parts, with no attenuation, must be used. From what has been already discussed, for PVAc photodegradation, chain scission is the predominant mechanism, and for our irradiation times, no cross-linking is observed. Therefore the reaction quantum yield for PVAc photodegradation can be considered as the rate of scissions per chain, S', per mole of photons absorbed, I_A (eq 4). Considering that the polymer absorption is low, I_A will be the parameter that must be considered more carefully. To minimize experimental error involved in using all the absorption spectra for $\lambda \geq$300nm, it was chosen to calculate the reaction quantum yield for a selected wavelength, 313 nm. In this way, both I_0 and absorbance were calculated for 313 nm, a wavelength in which it is still possible to measure the polymer matrix absorption with acceptable accuracy, Figure 3.11. As Φ_R is dimensionless, the unities for both S' and I_A should be the same as detailed bellow. The Φ_R was determined for PVAc homopolymer for 1850 h irradiation at 313 nm as 7.40x10^{-8}.

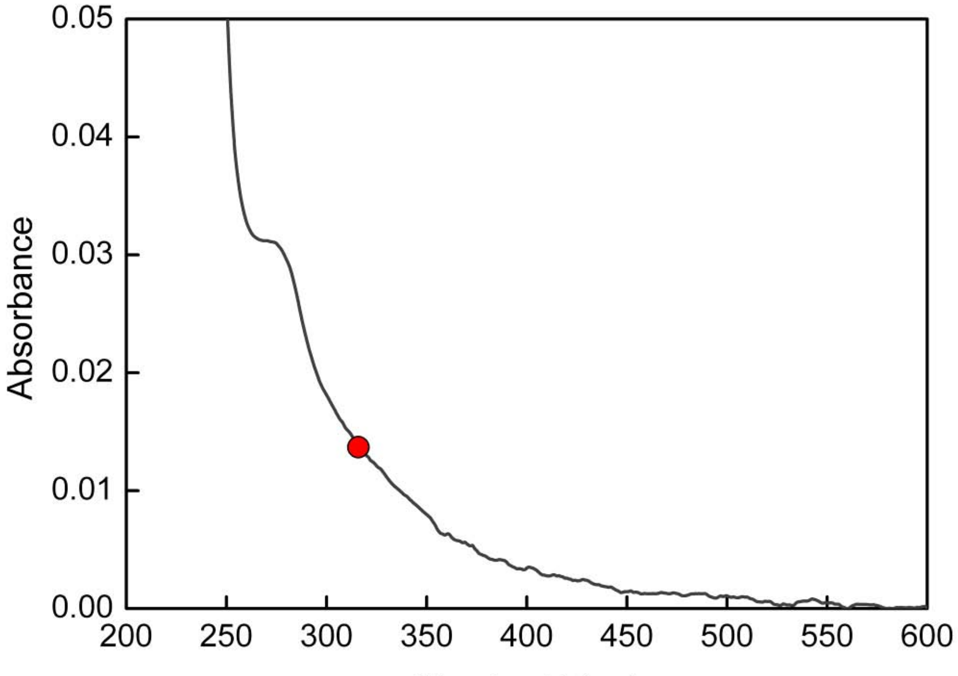


Figure 3.11. Absorption spectrum for PVAc, where the red circle indicates the polymer absorption at 313nm (0.0155).

3.2.5.1 I_0 and I_A

I_0 at 313 nm was obtained using potassium hexacyanocobaltate(III) as actinometer ($K_3[Co(CN)_6]$) (Appendix I.7.15) and equation 1; I_0 is expressed as $mol.cm^{-2}.min^{-1}$, *i.e.*, the mole of photons per unit area per unit time.

$$I_0 = \frac{V_{sol} \times \left(\frac{\Delta A}{\Delta \varepsilon} \right)}{1000 \times \Phi_R \times \Delta t} = 1.16 x 10^{-7} \text{ mol.L}^{-1}\text{.cm.min}^{-1} = 1.16 x 10^{-7} x 10^{3} \text{ mol.cm}^{-2}\text{.min}^{-1} \quad (1)$$

Where, V_{sol} is the volume of irradiated solution in ml (3 ml); ΔA is the change in absorbance at the monitoring wavelength (380 nm) over the irradiation time period, corrected by the light absorption of the reagent at 313; $\Delta\varepsilon$ is the difference between the molar absorption coefficients of reagent (ε(R)=10 $M^{-1}cm^{-1}$) and product (ε(P)=280 $M^{-1}cm^{-1}$) at the monitoring wavelength, in $L.mol^{-1}.cm^{-1}$; 1000 corresponds to ml; Δt to irradiation period in min; and Φ_R is the quantum yield of the reaction (Φ_R=0.31) [164].

The number of photons absorbed is:

$$I_A \text{ (PVAc)} = I_0 \text{ x } (1-10^{-A}) = 1.16 x 10^{-4} \text{ x } (1-10^{-0,0155}) = 4.1 x 10^{-6} \text{ mol.cm}^{-2}\text{.min}^{-1} \quad (2)$$

3.2.5.2 Rate of scissions per chain

The number of scissions per chain per unit time (S') is presented in Table 3.3. To be used in the reaction quantum yield this number must refer to the moles irradiated per area, *i.e.*, it must be multiplied by the weight of polymer irradiated (*w*, g) and divided by M_{n0} and irradiated area (*a*, cm^2), as indicated below:

Nº of moles undergoing chain scission per unit time per area (PVAc) =

$$\frac{S' \times w}{Mn_0 \times a} = \frac{2.0 \times 10^{-6} \times 0.01981}{39982 \times 3.3} = 3.0 \times 10^{-13} \text{ mol.cm}^{-2}\text{.min}^{-1} \quad (3)$$

3.2.5.3 Quantum yield

The quantum yield of reaction may now be obtained by dividing the moles of polymer undergoing chain scission (equation 3) by the moles of photons absorbed, both by unit area and unit time:

$$\Phi_R(PVAc) = \frac{3.0\times10^{-13}}{4.1\times10^{-6}} = 7.40\text{x}10^{-8} \tag{4}$$

3.2.5.4 Discussion

The Φ_R determined this way for PVAc homopolymer for 1850h irradiation at 313 nm is 7.40x10^{-8}. When compared with the values published in literature for irradiation involving 254 nm, the Φ_R for PVAc is five orders of magnitude lower, which indicates that a different photochemical mechanism is involved. Further supporting this conclusion is the fact that Vaidergorin, *et al* [72], using a medium-pressure mercury lamp and a set-up similar to Buchanan, *et al* [70], observed relevant changes in the infrared carbonyl peaks without modification in the molecular weight distribution for a low M_W PVAc, *i.e.*, without observing chain scission. The data discussed here support the hypothesis that no relevant side chain cleavage is taking place and that the photodegradation evolves essentially by main chain scission.

Taking into account that it was not possible to detect any change in the infrared spectra, the discussion that follows brings up a hypothesis that only further experimental testing can answer. Main chain scission may be the result of excitation of the hydroperoxide groups, present in very low amounts in the polymer matrix and not detected in the infrared spectrum ($\leq$ 3%). The absorption of light by these groups will result in main chain scission and possibly the formation of other functional groups, namely double bonds and carbonyl groups, and the release of volatile moieties. These would still be in very low concentrations and therefore not detected in the infrared spectrum. Another possibility is that the first cleavage is accompanied by a certain degree of depolymerization, and this could explain both the unchanged infrared spectra even after 5000h of irradiation as well as the slight decrease in intensity by loss of polymer. Quantitative measurements of possible volatile products will be necessary to get further insight into this aspect.

3.3 Poly(methyl methacrylate)

The photodegradation of PMMA was studied both in thin films (Mw ~ 1 x 10^5) and in 3 mm thick sheets (Mw ~ 10 x 10^5). Two sets of acrylic sheet were included, transparent colourless and transparent blue. Besides the pure photooxidative mechanisms, also the effect of a commercial cleaning product (*Altuglas cleaner*) on degradation was evaluated on samples which were cleaned at regular intervals during the experiment (see experimental details in Appendix I.7.1).

The samples did not suffer relevant weight variations, *i.e.* maximum loss of approximately 0.5% for the PMMA sheets. In the last 1250h period both PMMA sheet sets re-gained 0.2%, this could be explained by a small incorporation of oxygen or increase in hygroscopicity with ageing [50].

3.3.1. Solubility and molecular weight distribution

PMMA films remain totally soluble after 4250h irradiation and no gel fraction was observed. Due to the presence of additives in the acrylic sheets it was not possible to the investigate the gel formation in this case. A decrease in *Mw*, for thin films and sheets, was already present at the first 500h under irradiation, Table 3.9 (chromatograms are presented in Appendix IV.2.3).

Table 3.9. Average molecular weight (M_W) and Polydispersity (PD) for PMMA thin film and for transparent and blue sheets over irradiation time

Sample	**0h**		**1750h**		**3000h**		**4250h**	
	M_w (x 10^5)	*PD*	M_w (x 10^5)	*PD*	M_w (x 10^5)	*PD*	M_w (x 10^5)	*PD*
PMMA Transparent	10.5	*1.6*	5.9	*1.8*	3.5	*1.9*	3.2	*1.9*
+ Cleaner	10.5	*1.6*	4.2	*1.8*	3.1	*2.4*	3.0	*2.3*
PMMA Blue	11.1	*1.9*	5.4	*2.0*	5.4	*2.4*	4.3	*2.3*
+ Cleaner	11.1	*1.9*	6.8	*2.0*	5.6	*2.2*	3.7	*2.4*
PMMA film	0.86	*1.6*	0.76	*1.8*	0.75	*2.2*	0.7	*2.4*

This trend will be the same throughout the experiment accompanied by a slight increase in PD. Nevertheless, polydispersity remains circa 2 for all samples from 0h to 4250h irradiation. It is possible to conclude that chain scission is the major degradation mechanism taking place, with no higher molecular weight fraction formation. This results are in agreement with the publish data showing that this methacrylic polymer undergoes chain scission when irradiated under UV [20,63,96-99]. The number of scissions per chain ($S = M_{n0}/M_{nt} - 1$) was calculated and is presented in Figure 3.12 for the acrylic sheets. From the values presented in Table 3.10 it is possible to observe that the film displays the lowest scission rate, but within the same order of magnitude of those presented by the sheets (10^{-4}). UV-visible spectra for the PMMA film and sheets are presented in Figure 3.13. In which concerns the PMMA sheets, the rates of scission per chain are slightly lower in blue samples. Although the blue colourant was not characterized, it is possible that due to the total absorption of UV light below 370 nm (cut-off), Figure 3.13, by the transparent blue sheet, the dye is competing for light absorption and protecting the polymer. In both, blue and transparent samples, an increase is observed for the cleaned samples. Although more pronounced for the transparent sheets, this scission rate increase is not considered to be relevant when the *Mw* values (Table 3.9) are compared and only a small decrease is found.

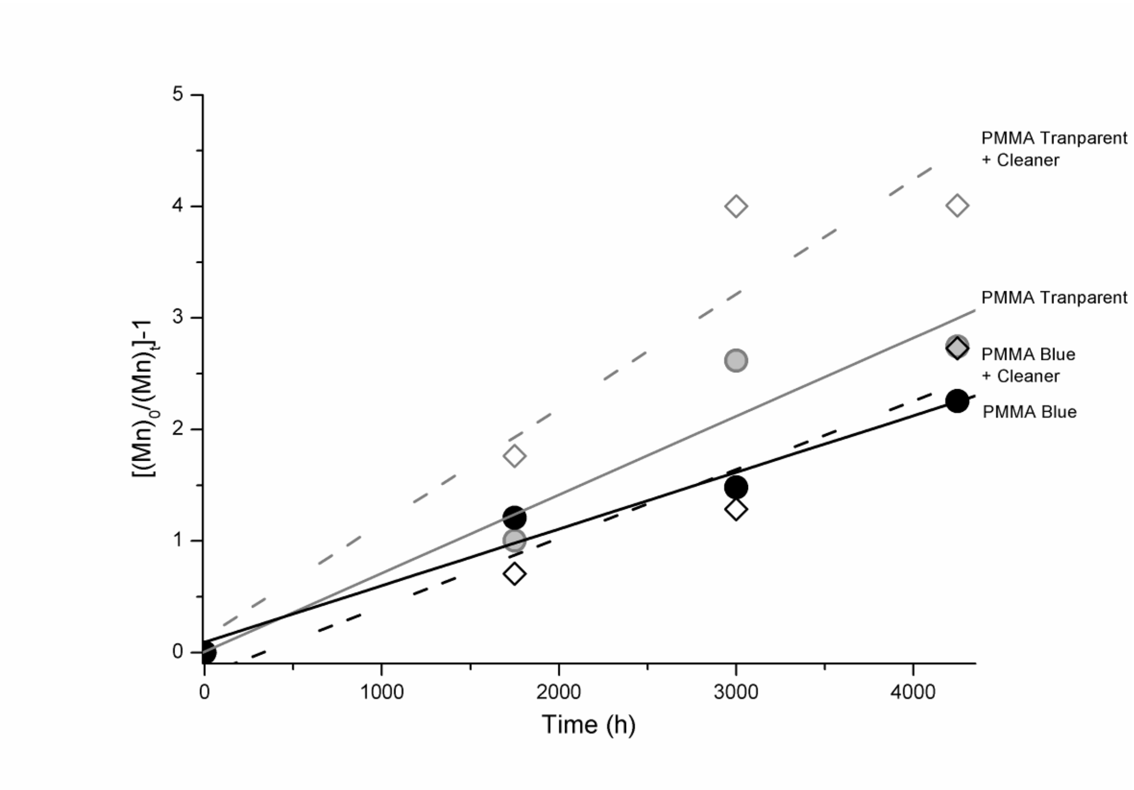


Figure 3.12. Scission per chain as a function of irradiation time for PMMA transparent and blue sheets. Where M_{n0}= original number average molecular weight; M_{nt}=number average molecular weight after irradiation.

Table 3.10. Rate of scissions per chain for PMMA sheets and PMMA homopolymer film. Where *S'* is the curve slope and *R* the correlation coefficient

Sample	***S'*** ($x10^{-4}$)	***R***
PMMA Transparent	7.0	*0.959*
+ Cleaner	10.3	*0.960*
PMMA Blue	5.1	*0.985*
+ Cleaner	6.1	*0.963*
PMMA film	2.3	*0.996*
PMMA film [a]	0.0193	*0.976*

[a] Irradiation carried out at 313 nm over 1850h (for more details see experimental section).

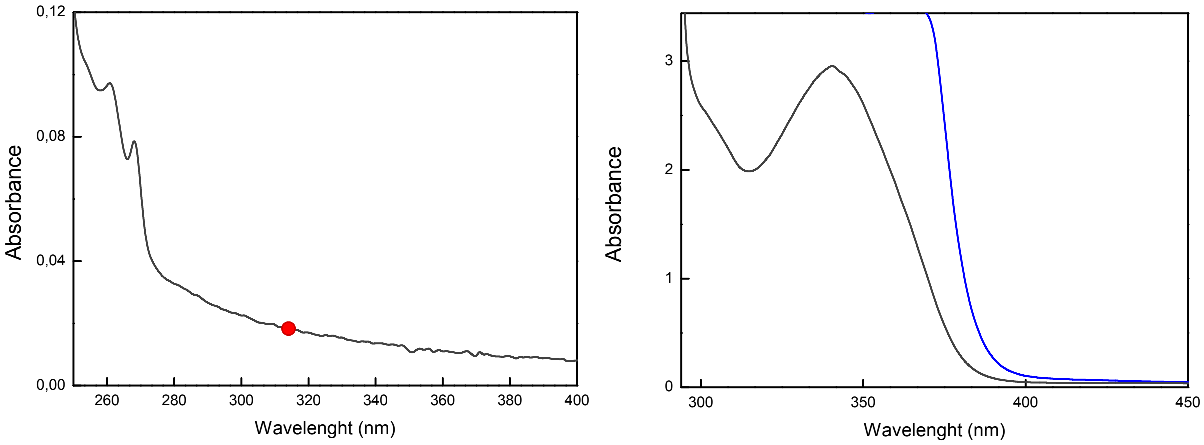


Figure 3.13. Absorption spectra for PMMA: left – PMMA film; right – PMMA sheet, transparent colourless (black line) and transparent blue (blue line). The red circle indicates the absorption (0.0193) at 313 nm for the film.

3.3.2. FTIR studies

The IR spectra of the PMMA film before and after irradiation are presented in Figure 3.14 and no visible changes are detected. In the same way, no changes are observed on the infrared spectra of the PMMA sheets (Appendix IV.2.4).

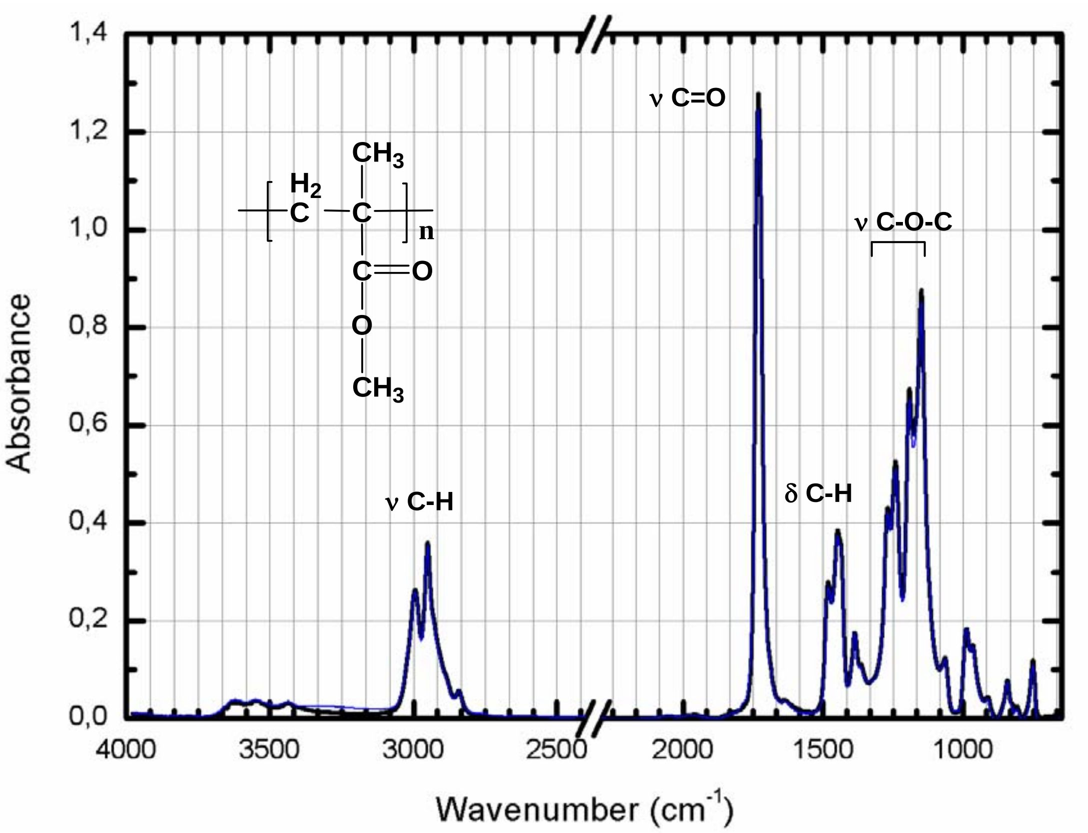


Figure 3.14. Infrared spectra of PMMA homopolymer: black line – t=0h; blue line – 5000h of irradiation.

A closer observation of the carbonyl band was performed, for polymer films and sheets, by fitting with a Gaussian function. No relevant shifts were found and broadening, when observed, falls below 6% (Table 3.11). The differences found for the several νC-O/C=O peak ratios (absorptions and peak areas) are below 10% for all aged samples when compared with the unaged ones, Tables 3.12 and 3.13. On the other hand, small changes are observed for νC-H/C=O ratios, but considered as not relevant due to their relative low intensity where a higher error is expected. Thereby, no degradation products or intermediates are detected, indicating that for our irradiation times there are no side-chain reactions taking place, or only in a very low percentage and not detected by infrared spectroscopy.

Table 3.11. Values of peak centre (μ), peak width at half maximum (σ) and peak area (A) for the carbonyl stretching absorption (Gaussian function) for PMMA samples. Before and after 3500h accelerated ageing

Sample	$\nu_{C=O}$ μ	σ	A	ρ
PMMA film (Mw 86 000) 0h [a]	1730.2	23.92	29.23	*0.990*
PMMA film (Mw 86 000) 2500h [a]	1730.4	24.03	29.19	*0,991*
PMMA film (Mw 86 000) 5000h [a]	1730.4	24.88	30.32	*0.991*
PMMA Transparent 0h [b]	1726.2	21.74	26.41	*0.992*
PMMA Transparent 4250h [b]	1726.0	23.14	27.63	*0.990*
+ Cleaner 4250h [b]	1726.0	22.98	27.60	*0.992*
PMMA Blue 0h [b]	1726.2	22.59	27.36	*0.989*
PMMA Blue 4250h [b]	1726.1	23.30	27.81	*0.988*
+ Cleaner 4250h [b]	1726.2	22.72	27.27	*0.991*

[a] Spectra acquired from films deposited on Si discs (transmittance FTIR).

[b] Spectra acquired directly from the sample surface using ATR accessory (reflectance μ-FTIR).

Table 3.12. Main infrared peak absorptions normalized for the C=O stretching for PMMA film samples, before and after 4250h accelerated ageing. Spectra acquired from films deposited on Si discs (transmittance FTIR)

Sample	ν_{CH3} 2995 cm^{-1}	ν_{CH2} 2950 cm^{-1}	$\nu_{C=O}$ 1731 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ [a] 1270 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ [a] 1242 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ [b] 1192 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ [b] 1150 cm^{-1}
PMMA film (Mw 86 000) 0h	0.20	0.28	1	0.33	0.40	0.52	0.68
PMMA film (Mw 86 000) 4250h	0.21	0.28	1	0.34	0.41	0.52	0.68

[a] Absorption bands possibly assigned to antisymmetric C-O-C stretching [164a].

[b] Absorption bands possibly assigned to symmetric C-O-C stretching [164a].

Table 3.13. Main infrared peak areas normalized for the C=O stretching for standard transparent colourless and transparent blue PMMA samples, before and after 4250h accelerated ageing. Spectra acquired directly on sample surface using ATR accessory (reflection μ-FTIR)

Sample	ν_{CH_3} 2995 cm^{-1}	ν_{CH_2} 2952 cm^{-1}	$\nu_{C=O}$ 1725 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1270 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1242 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1191 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1146 cm^{-1}
PMMA Transparent 0h	0.08	0.12	1	0.30	0.39	0.55	0.99
PMMA Transparent 4250h	0.08	0.13	1	0.31	0.39	0.54	0.97
+ Cleaner 4250h	0.08	0.13	1	0.32	0.40	0.55	0.98
PMMA Blue 0h	0.07	0.12	1	0.27	0.37	0.53	0.98
PMMA Blue 4250h	0.08	0.13	1	0.28	0.37	0.53	0.95
+ Cleaner 4250h	0.08	0.13	1	0.29	0.38	0.53	0.96

[a] Absorption bands possibly assigned to antisymmetric C-O-C stretching [164a].

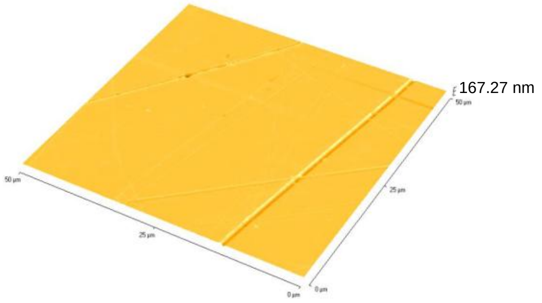
[b] Absorption bands possibly assigned to symmetric C-O-C stretching [164a].

3.3.3 Surface studies

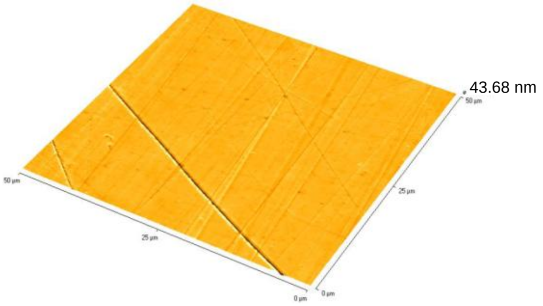
Before any further experiment, the PMMA sheets were analyzed by atomic force microscopy (AFM) and revealed relatively flat surfaces with few features, Figure 3.15 [165].

Altuglas Cleaner (current name for *Altunet*) was applied by Lourdes Castro as a final treatment and maintenance of her PMMA shadows. This commercial product was applied for surface cleaning and mainly for its antistatic properties. Although the artist stated (Chapter 4.5) she would use a smooth cotton cloth for product application, in this study lens tissues were used. Being commercialized for lens cleaning they were considered to be harmless for the surfaces and its applicability was tested. The cleaning action prior to light exposure increased the number of scratches, which led to a small increase of the surface roughness (Table 3.14). Such increase is possibly related with the cleaning mechanical action [165]. Further experiments will be performed in order to test other procedures, namely the application of the cleaning product with smooth clothes similar to those used by the artist.

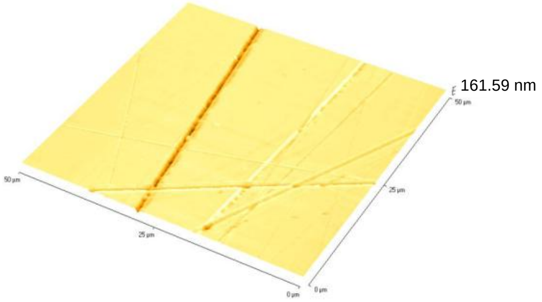
PMMA Transparent untreated



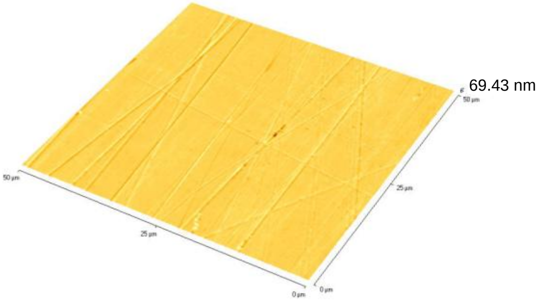
PMMA Blue untreated



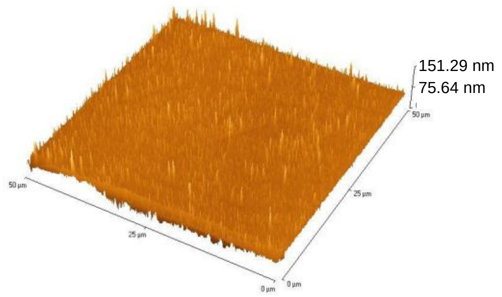
PMMA Transparent 0h



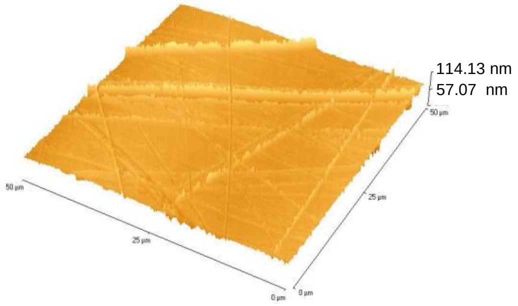
PMMA Blue 0h



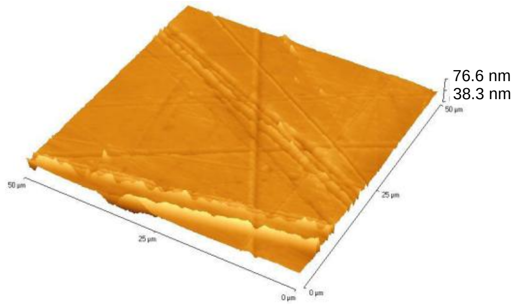
PMMA Transparent 4250h



PMMA Blue 4250h



PMMA Transparent + Cleaner 4250h



PMMA Blue + Cleaner 4250h

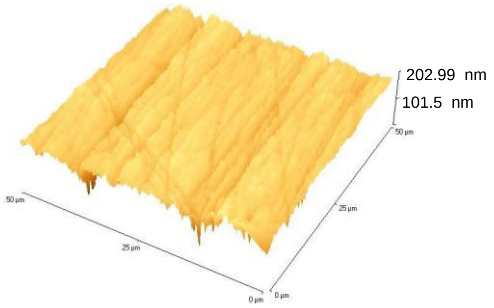


Figure 3.15. AFM height images of transparent and blue PMMA sheet surfaces before and after irradiation following a cleaning treatment (50x50 µm^2 scan areas). Images obtained by M.H. Sá [165].

Table 3.14. AFM surface average parameters measured in 50x50 μm^2 scan areas for all samples and procedures

Sample	**Number of averaged scans**	**Arithmetic mean surface roughness (*Ra*, nm)**	**Mean height ($\overline{Z}$, nm)**	**Maximum height (Z_{MAX}, nm)**
PMMA Transparent untreated	(5)	1.0 ± 0.2	64.1 ± 29.2	108.4 ± 36.8
PMMA Transparent 0h	(5)	2.5 ± 1.8	117.7 ± 41.3	148.8 ± 51.5
PMMA Transparent 4250h	(7)	5.1 ± 0.9	82.1 ± 44.9	310.0 ± 145.0
+ Cleaner 4250h	(13)	4.8 ± 2.8	87.1 ± 56.6	154.2 ± 97.0
PMMA Blue untreated	(4)	1.4 ± 0.3	98.6 ± 59.3	145.3 ± 91.2
PMMA Blue 0h	(5)	2.2 ± 0.9	98.7 ± 45.6	148.5 ± 70.1
PMMA Blue 4250h	(8)	5.1 ± 1.2	75.8 ± 16.9	151.0 ± 32.5
+ Cleaner 4250h	(7)	9.6 ± 1.8	109.3 ± 45.0	164.8 ± 54.0

The AFM images (Figure 3.15) of the irradiated samples reveal significant surface disruption with an increase in surface roughness and masking the scratches profile. The formation of spike features might be caused by an evolution of volatile products of the photolytic degradation of the polymer, migration of additives towards the surface, or even an alteration of the protective coating left by the cleaner applied before the ageing experiment. Due to their homogeneity this features do not seem to be related to dust accumulation. Infrared spectra were acquired on the surface of the aged samples but all peaks were assigned to the polymer; the low concentration of the deposited material does not allow its identification by infrared (< 3%). The images (Figure 3.15) obtained for the aged samples after cleaning show that this process is able to remove the surface protrusions without significant additional surface alterations on the transparent sheet. Nevertheless, the surface roughness of the blue sample is considerably increased (Table 3.14) with deeper scratches visible on its surface [165]. As the transparency of acrylic glass is a primary characteristic of this material and therefore of its use by artists, the pristine state of the surface is fundamental for the preservation of the work of art. The application of *Altuglas Cleaner* proved its efficiency in removal of surface protrusions. On the other hand, the results obtained for the blue samples were not satisfactory and further testing is still needed to insure the safety of the cleaning procedures; as mentioned above, different application methods will be tested.

3.3.4. Colourimetry

*L*a*b** coordinates are presented in Table 3.15 for transparent and blue samples. As it had been previously observed for thin films [166], no colour changes are observed for transparent colourless PMMA, which does not undergo yellowing and it maintains its transparency. On the other hand, the transparent blue samples become almost colourless after 4250h irradiation at λ >300 nm (ΔE^* = 25). Also, the cleaning procedure did not cause any colour changes.

Table 3.15. *L*a*b** and ΔE^* for PMMA transparent and blue sheets for t=0h and after 4250h irradiation

Sample	***L****	***a****	***b****	ΔE^*
PMMA Transparent	90.35	-0.28	4.73	**1.16**
	89.38	-0.33	5.35	
PMMA Transparent + Cleaner	90.35	-0.28	4.73	**1.19**
	90.07	0.42	5.64	
PMMA Blue	70.47	-11.15	-25.34	**25.00**
	81.56	-4.12	-4.06	
PMMA Blue + Cleaner	70.47	-11.15	-25.34	**24.05**
	81.52	-4.49	-5.04	

3.3.5. Quantum yields determination

As discussed in 3.2.5, the PMMA photodegradation reaction quantum yield (Φ_R) may be described as the rate of scissions per chain (S') per moles of photons absorbed. PMMA thin films were irradiated under monochromatic irradiation at 313 nm (Figure 3.13); the scission quantum yield obtained is very low (3.85×10^{-8}) and therefore PMMA is considered stable to light when irradiated under the current conditions.

3.3.5.1 I_0 and I_A

I_0 was calculated as described in 3.3.5.1

The number of photons absorbed is:

$$I_A = I_0 \times (1\text{-}10^{-A}) = 1.16\times10^{-4} \times (1\text{-}10^{-0,0193}) = 5.0\times10^{-6}\ \text{mol.cm}^{-2}.\text{min}^{-1} \quad (5)$$

3.3.5.2 Rate of scissions per chain

The number of scissions per chain per unit time (S') is presented in Table 3.10. To be used in the reaction quantum yield this number must refer to the moles irradiated per area, *i.e.*, it must be multiplied by the weight of polymer irradiated (w, g) and divided by M_{n0} and irradiated area (a, cm^2), as indicated below:

Number of moles undergoing chain scission per unit time per area =

$$\frac{S'\times w}{Mn_0 \times a} = \frac{1.93\times 10^{-6}\times 0.0159}{51859\times 3.06} = 1.93\times 10^{-13}\,\text{mol.cm}^{-2}.\text{min}^{-1} \qquad (6)$$

3.3.5.3. Quantum yield

The quantum yield of reaction may now be obtained by dividing the moles of polymer undergoing chain scission by the moles of photons absorbed, both by unit area and unit time. For the irradiation of 0.01981 g and 3.3 cm^2 we obtain:

$$\Phi_R(PMMA) = \frac{1.93\times 10^{-13}}{5.0\times 10^{-6}} = 3.85\text{x}10^{-8} \qquad (7)$$

3.3.5.4. Discussion

The scission Φ_R calculated for PMMA is approximately six orders of magnitude lower than those published in the literature for irradiation in air involving 254 nm [96,97]. In the mentioned studies, the degradation mechanism is described as side-chain scission followed by scission of the main-chain. As it had been concluded for poly(vinyl acetate), this differences indicate that different photochemical mechanisms are involved. It is also worth to mention another study [102] where quantum yields were obtained at 300 nm, irradiation with energy closer to that used in the present study, for which the values published are still 4 orders of magnitude higher than ours. On the other hand, in the same study it was proved that PMMA does not photodegrade at $\lambda \geq 320$ nm, which may explain the differences found for the quantum yield obtained at 300 nm [102] and our results for 313 nm.

3.4 Conclusion

PVAc as pure homopolymer or as an emulsion paint proved to be very stable to light when irradiated at $\lambda \geq 300$ nm. After 5000h irradiation with a 1000 W Xe-arc lamp, no gel fraction was obtained, and the Φ_R for chain scission was determined to be 7.40×10^{-8} at 313 nm for PVAc homopolymer. This value indicates that the mechanism/s operating when irradiating at $\lambda \geq 300$ nm are different from those studied with irradiation involving 254 nm [66-72]. No molecular evidence was obtained concerning the formation of other carbonyl functions, the disappearance of the PVAc ester carbonyl, or the formation of hydroperoxides; the only observation is the slight decrease in intensity of the entire spectrum. Based on these results, it is possible to suggest that, for the irradiated films, no side-group scission is taking place and that main chain scission is the foremost photodegradation mechanism. Taking into account the very low Φ_R, it would be important to consider continuing this study for even longer times. Also, the metal ions present in the pigments do not affect the photochemical stability of the polymer. Even well-known photocatalysts as TiO_2 (present in the rutile form) and Fe_2O_3 proved to be harmless. Both these compounds compete for light absorption and, being encapsulated in inert materials, present a protective effect. Concerning the colouring performance of the vinyl emulsions, no relevant yellowing was observed for the white paints. The results obtained for the PVAc homopolymer present a more straightforward interpretation than those observed for the *V7* formulation which was actually used by Portuguese artists. However, the general trend and main conclusions may be applied to both systems, PVAc and *V7* glue. Finally, based on the results obtained, it is possible to conclude that PVAc homopolymer displays high photostability, constituting a good choice as a material for artists.

Also PMMA, both as thin films or thick sheets, proved to be stable to light when irradiated at these irradiation wavelengths. For the used irradiation times, no gel formation was detected and the chain scission quantum yield obtained for the films is very low (3.85×10^{-8}). As for the PVAc, no degradation products or intermediates were detected by infrared spectroscopy, indicating that possibly there are no side-chain reactions taking place. When a comparison is made between the photochemical stability of the transparent colourless and transparent blue sheets, the colourant seems to have a protective effect as a smaller scission rate was obtained for the blue sample. On the other hand, the colourant used (probably present in a low concentration as it is a transparent sheet) showed to be extremely fugitive and after 4250h irradiation, under the present irradiation conditions, the samples became almost colourless. The cleaning procedure used for surface treatment did not seem to alter the acrylic glass degradation mechanisms, with only a small increase in the scission rate for the colourless samples. This product proved to fulfil its role, with the advantage of leaving an anti-static film that prevents dust accumulation, avoiding a constant need for cleaning.

Nevertheless, the overall safety of the cleaning procedure still needs further insight allowing it to be recommended for the cleaning of acrylic glass used in works of art. Further work will include the determination of scission quantum yields for PMMA sheets and photodegradation studies on the PMMA samples provided by the artist, allowing a more precise prediction of her artworks' long term stability.

Chapter 4

Case Studies

Tracing degradation on naturally aged works of art

Part of the results presented in this chapter were published in peer reviewed proceedings and submitted for publication in an international scientific journal.

Ferreira JL, Melo MJ, Ramos AM, Ávila, MJ. ‘*Eternity Is in Love with the Productions of Time’: Joaquim Rodrigo’s Classical Palette in a Vinyl Synthetic Medium.* In: TJS Learner, P Smithen, JW Krueger, MR Schilling, editors. Proceedings from the Symposium Modern Paints Uncovered; 2006 May 16-19; Tate Modern, London. Los Angeles: Getty Publications; 2007 p. 43-52.

Ferreira JL, Ávila MJ, Melo MJ, Ramos AM. *Poly(vinyl acetate) paints in works of art: Joaquim Rodrigo and Ângelo de Sousa. Part 2*. Submitted.

4.1 Preamble

After having investigated in accelerated conditions the molecular evolution of the polymers under study upon photooxidation, the results are compared with those obtained for naturally aged samples from dated works of art. If a common degradation pattern is found between accelerated and natural ageing conditions, this approach will allow a validation of the results discussed in the previous chapter. The main objective of the work presented in this chapter is to assess the conservation condition of artworks by important Portuguese artists made with poly(vinyl acetate) based paints and also with poly(methyl methacrylate) sheets.

In the former case, paintings made with vinyl media by Joaquim Rodrigo and Ângelo de Sousa were selected as case studies. As a first step, the materials and techniques of these artists were studied, mainly based on interviews. We interviewed the artist, in the case of Ângelo, with the purpose of understanding his choices concerning the materials used. For Rodrigo, we spoke with Sofia Agrela, his companion and assistant who helped him in the preparation of his paints since 1968, and his books were also an invaluable source. To get a deeper insight into Rodrigo’s technique, his paints as well as complete works have also been reproduced, with the participation of Sofia Agrela. In a second step, information from the interviews is compared with that obtained from analysis of the works themselves. Finally, the conservation condition of the binder is evaluated in the framework of the results obtained from the accelerated ageing studies.

Also, the opportunity to study and collect data from a catalogue of twenty one vinyl colours from a Portuguese brand, *Sabu*, especially designed as an artist's formulation by *A Favrel Lisbonense*, may provide information on the materials used and on the real evolution of the polymer binder over time, as well as on the effect of the pigments upon it. Being a catalogue it is probable that these paints have not been exposed to light on a regular basis. Therefore, the results obtained allow a correlation with those from the artworks studied that have actually been exposed, availing to find a trend concerning the stability of vinyl paints.

On the other hand, the construction process of the PMMA shadows by Lourdes Castro was documented. A PMMA sample collection belonging to the artist, as well as her work from 1965 *La place en marche*, are studied following a similar approach.

The relevance of the collected data for photodegradation studies and life-time predictions is discussed.

4.2 Joaquim Rodrigo

And why eternal painting?(...), for now, because time has proven so.[81]

Joaquim Rodrigo, 1982

4.2.1 The artist, his theory and materials

4.2.1.1 Documentary evidence and interviews

To the best of our knowledge, the first painting made by Rodrigo with a vinyl medium dates from 1961, possibly with the vinyl emulsion *Vulcano V7*, a brand name commercialized by the Portuguese fine art company, *A Favrel Lisbonense* (Chapater 2.2). He prepared his own paints[82] by mixing the vinyl emulsion with a restricted palette. This would become Rodrigo's technique, and his last paintings were made/finished during 1990 [22]. Detailed information on all paintings from 1961 until 1990 concerning the binder, support, dimensions and date, as described in *Joaquim Rodrigo Catalogue Raisonné* [22], is presented in Tables V.1-V.8 (Appendix V). Sofia Agrela, who assisted Joaquim Rodrigo in his studio for about thirty years, has collaborated in this project providing information, materials and leading several workshops on Rodrigo's technique at DCR (Appendix I.3).

Colour system

In 1961, Rodrigo was still using a full colour palette that included bright cadmium yellows and reds[83] as well as greens and blues, as in the case of *S. M.* (1961), Figure 1.11. At the same time, he was already experimenting, as in the paintings *M. L.* (1961), Figure 1.12, *Kultur – 1962* (1962), Figure V.4, *Mondo Cane I* (1963), Figure V.5, and *Liberté* (1963), Figure V.6, with what he defined later as the 'eternal palette' made with earth colours. By 1969, with *Lisboa-Oropeza* (Figure 1.15), he finally arrived at both the correct colours and pigments. *i.e.*, he built up a restricted palette based on red and yellow iron oxides, titanium dioxide and a suitable black, which he described as two colours, red and yellow, and two limits, black and white.

---

[81] '*E porquê pintura eterna? Que mais não fosse, e por agora, porque no tempo tem dado provas disso*.' [105]

[82] Sofia Agrela, his companion and assistant since 1968, can confirm that in that period he was already preparing his own paints by mixing a PVAc emulsion with pigments.

[83] Later Rodrigo will say about the cadmium pigments that they are 'very decorative'('*E também conheço os cádmios. Muito decorativos*!...) [105].

> *I prefer:*
> *As white – the titanium dioxide (as there is not a more convenient natural white);*
> *As yellow – the yellow ochre or earth (the most-hydrated iron oxide);*
> *As red – the red ochre or earth (the least-hydrated iron oxide);*
> *As black – the iron oxide (dehydrated) or the vine black (as there is not a more convenient natural black).*[84]
>
> Joaquim Rodrigo, 1982

These were the colours that Rodrigo considered to have been used in 'eternal paintings'.

> *And what is the eternal painting? (...) the prehistoric painting, some Egyptian painting, Chinese and Japanese, most of the Greek painting, Etruscan, pre-Colombian, romanic Catalan, aboriginal African, Australian, and Amazonian.*[85]
>
> Joaquim Rodrigo, 1982

Other reasons given by Rodrigo for his pigment choices were that these were the most natural and ubiquitous ones, with better hiding power and durability, and also that they were economical. Moreover, he considered the earth colours to be 'fertile' colours.

The pigments would be mixed and contours would be applied in the search for the maximum colour contrast. This colour system evolved over time to a complex and precise set of rules that would be fully expressed in Rodrigo's final book, *Pintar Certo* (*Painting Right*) [112]. In the meantime he had published *O Complementarismo em Pintura* [105], where he discussed and proposed a 'scientific and universal' pictorial system that he will call '*pintura certa*' (correct painting). As stated in the introduction, the system defines the formal, chromatic, and compositional construction of the works. For this chromatic system (Figure 4.1) the background colours were obtained either by mixing the two colours alone or the two colours with one or both limits; the red was always *corrected* with yellow[86], and the colours were built by the mixture of the *corrected* red with titanium white (pink or light yellow) or black (brown or green)[87]. The black and white colours were used as single pigments. Grey, prepared with black and white, could exceptionally be applied.

---

[84] '*Pois eu prefiro: Como branco – o óxido de titânio (à falta de um branco natural mais conveniente); Como amarelo – o ocre ou terra amarela (pelo óxido de ferro mais hidratado); Como vermelho – o ocre ou terra vermelha (pelo óxido de ferro menos hidratado); Como preto o óxido de ferro (já desidratado) ou o preto de vinha (à falta de um preto natural mais conveniente)*.' [105]

[85] '*E qual é a pintura eterna? Dentre a que tive oportunidade de observar, e de uma maneira geral, é designadamente a pintura pré-histórica, certa pintura egípcia, chinesa e japonesa, e uma grande parte da pintura grega, etrusca, pré-colombiana, românica catalã, aborígene africana, australiana e amazónica*.' [105]

[86] Rodrigo explained in his writings [105] that the red pigment was not used pure, it had to be corrected with yellow. In order to guarantee the colour equidistance between the background and the limits.

[87] Light yellow and green would result from the preparation of a *corrected* red with a higher concentration of yellow (*i.e.* from a *corrected* yellow)

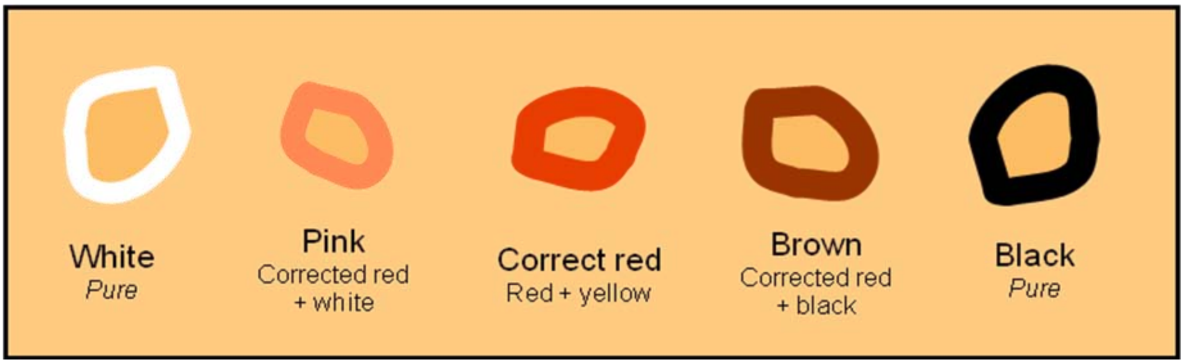


Figure 4.1. Schematic representation of Rodrigo's palette as described in '*O Complementarismo em Pintura*' [105].

As the paints were prepared, Rodrigo tested them on phone book pages (Figure 4.2); the composition studies were sometimes painted with extra water, or with pastel pencils[88], over a colour layer or on coloured paper, Figure 4.3.

Figure 4.2. Example of colour studies painted on phone book pages; 5.3 x 10.2 cm. Private collection.

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[88] *Schwan-Stabilo Carb-Othello* pastel pencils were found in his studio.

Figure 4.3. Study for the painting *San Esteban de Gormaz – Soria*, 1971; 24.5 x 31.7 cm. Private collection.

In the paintings that Rodrigo ultimately considered as the 'correct paintings' (painted after 1982) [107,108,112], such as the painting *Os quintais* (1989) represented in Figure 1.16, he was using not only a different narrative system but creating less colourful and bright paintings[89]. This can be seen as a consequence of a more extensive colour mixing, as indicated in his final colour theory. For these final 'correct paintings' (Figure 4.4), the background was always obtained by mixing all four colours; what Joaquim Rodrigo considered then as white (off-white) was a mixture of the background paint with titanium white, and grey was produced by mixing this white with black. The red, after being *corrected* with yellow, was mixed with black. Finally, black was applied as a pure colour.

> *I consider the final result insuperable in economy, formal and chromatic equilibrium, contrast, chiaroscuro or legibility and harmony, which is everything the observatory wishes, as a smaller effort is thus required (almost always unconsciously).* [90]
>
> Joaquim Rodrigo, 1995

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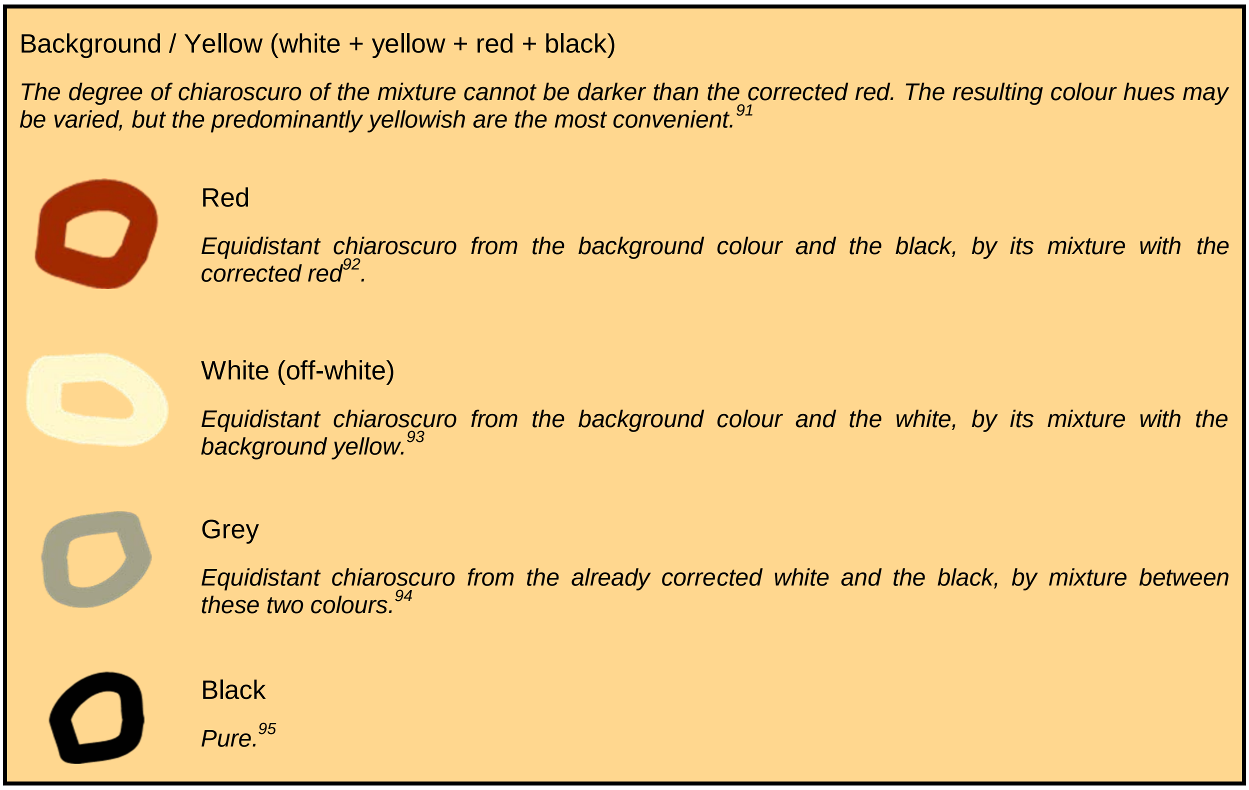
[89] More mixture implies higher absorption and lower reflexion of light; fewer photons will stimulate our vision and the colour paint will be perceived as more dim.

[90] '*O resultado final, considero-o insuperável de economia, equilíbrio formal e cromático, contraste, claro-escuro ou legibilidade e harmonia, que é tudo aquilo que o observador deseja, por assim (inconscientemente quase sempre) lhe ser exigido um menor esforço*.' [112]



Background / Yellow (white + yellow + red + black)

The degree of chiaroscuro of the mixture cannot be darker than the corrected red. The resulting colour hues may be varied, but the predominantly yellowish are the most convenient.[91]

Red

Equidistant chiaroscuro from the background colour and the black, by its mixture with the corrected red[92]*.*

White (off-white)

Equidistant chiaroscuro from the background colour and the white, by its mixture with the background yellow.[93]

Grey

Equidistant chiaroscuro from the already corrected white and the black, by mixture between these two colours.[94]

Black

Pure.[95]

Figure 4.4. Schematic representation of Rodrigo's final palette as described in '*Pintar Certo*' [112].

Pigments

The iron based pigments used by Rodrigo, in a wide palette of shades, were mainly the colours by *Lefranc & Bourgeois* sold for mural paintings (*Couleur pour la fresque*) but the black and white pigments were usually acquired in drugstores[96]. Nevertheless, some paints were also prepared with iron oxide pigments from drugstores and titanium dioxide could also be purchased at *Casa Varela* (see Chapter 4.2.2.1). Rodrigo spoke about producing his own pigments with stones from Monsanto Park. As Sofia Agrela recalls, he tried to grind some at home and once even asked António Varela Gomes (interview with Mário Varela Gomes, Appendix II.2) to use *Favrel*'s mills. To our knowledge these attempts did not succeed and to the moment we have no evidence that Rodrigo actually used pigments ground from stones in his paintings. Joaquim Rodrigo was meticulous in his working process as he was in his

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[91] '*Fundo franco (B+A+E+P)* o grau de claro-escuro da mistura não poderá ser mais escuro do que o do encarnado corrigido (Ec)**. As tonalidades da cor resultante são variáveis, mas as predominantemente amareladas são as mais convenientes (chamemos-lhe amarelo para facilitar a exposição)'. * 'B (branco), A (amarelo), E (encarnado), P (preto).' ** 'Ec – Vermelho com claro-escuro equidistante do preto e do branco. Se necessário para o efeito, utilizar o amarelo*.' [112]

[92] '*Encarnado (claro-escuro equidistante entre a cor do fundo e o preto, por mistura deste com o encarnado corrigido*.'

[93] '*Branco (claro-escuro equidistante entre a cor do fundo e o preto, por mistura deste com o amarelo do fundo)*.' [112]

[94] '*Cinzento (claro escuro entre o branco já corrigido e o preto, por mistura destas duas cores)*.' [112]

[95] '*Preto (puro)*.' [112]

[96] Drugstores in Lisbon at Praça da Alegria, Bairro Alto, Príncipe Real, Belém, among others.

theories. The pigments were kept in glass containers and aligned in a wooden shelf, that he called ‘piano’ (Figure 4.5).

Figure 4.5. The pigments used by Joaquim Rodrigo aligned on the ‘piano’. Red and yellow iron oxides, titanium dioxide and a black pigment.

Binding medium

The colours were prepared with vinyl white glue, *Vulcano V7*, usually purchased in 5 L containers. In the technical analysis that accompanies the catalogue *Raisonné* [167], it has been stated that Joaquim Rodrigo used *V2*, which is a vinyl emulsion commercialized by another Portuguese fine arts company, *Casa Ferreira*[97]. In the informal interviews carried out with Sofia Agrela and Mário Varela Gomes it was only possible confirm that Joaquim Rodrigo used *V7* (commercialized by *Casa Varela* / *A Favrel Lisbonense*).

The PVAc emulsion was first diluted in water, initially in a proportion of 1:1 (v:v) and some extra water from a plastic bottle was eventually added to a final proportion of 1:1.5. The water was thoroughly mixed with the vinyl emulsion, using a wooden stick and both hands, until a certain viscosity – ‘measured’ by touch – was obtained (Figure 4.6). The emulsion

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[97] In the above mentioned technical contribution, it is also mentioned that Joaquim Rodrigo experimented with a mixture of oil and gum arabic (1955-1960) and casein (1960-61), both described as ‘tempera’ [167]. The author mentions that the oil and gum arabic mixture was revealed by infrared spectroscopy (the results were not published, and it was not possible to have access to them although the author has been contacted). Based on that data there are several paintings described as tempera and others as vinyl in the *Catalogue Raisonné*. From the research work carried out in the framework of the present thesis, it was not possible confirm the use by Rodrigo of these ‘temperas’. On the contrary, the results now obtained point to the existence of an aged oil in *Directrizes* (1958) and to the use of a PVAc binder in *S. M.* (1961), *Kultur - 1962* (1962), *Mondo Cane I* (1963) and *Liberté* (1963). All these works are described, in the catalogue, as temperas (meaning the mixture oil/gum arabic or casein), where they coexist with the description of oils and vinyls in the period ranging from 1955 to 1964. Vinyl appears as the only medium from 1965 onwards (see Tables V.1 and V.3, Appendix V), whereas the present results indicate a consistent use of PVAc since 1961. Based on these experimental data, it is proposed that some of the binding media attributions in the catalogue, in works dated form 1955-1964, should be reviewed.

thus prepared was conserved in a glass bottle (Figure 4.6) and used to prepare the paints by mixing in the pigment with the aid of a brush. The paints were prepared and kept in white translucent *Tupperware* containers (Figure 4.6), then they were settled to rest overnight. This allowed some of the water that would separate out to be removed before the paint was used. On the other hand, if the paint was too thick or too glossy, extra water could be added. As Rodrigo stated, he prepared his paints with 'more or less water (more or less glue)', the necessary amount to produce an adherent continuous film, but that would not alter the pigments' colour and appearance, *i.e.* the natural characteristics of the pigments [105].

Figure 4.6. From left to right: *Vulcano V7* glue mixed with water, prepared by Sofia Agrela; the bottle where Joaquim Rodrigo kept the emulsion; emulsion and red ochre; paint prepared by Sofia Agrela.

Support

Rodrigo also prepared his supports, mainly large hardboard[98] panels (see Tables V.4-V.8, Appendix V) that he considered to be less vulnerable than canvas[99], following a regular procedure illustrated in Figure 4.7. Wood bars were applied in the back (screen pattern side) of the hardboard to reinforce the structure; these bars were attached with nails hammered from the board front surface[100] (Figure 4.8); furthermore, a linear white painted wood frame was attached to the side of the bars.

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[98] Hardboard is 'a high-density fiberboard building material first made by Masonite Corporation in 1926. Hardboard is composed of 100% wood fibers obtained from wood chips, sawdust, and board trimmings. They are broken into fine particles by grinding (dry process) or by steam (wet process). The interfelted fibers are consolidated with heat and pressure (at least 31 pounds per cubic foot) to form a dense, rigid sheet that is held together by naturally occurring lignin with no additional adhesive. Hardboards range from a dark brown to a light tan in color and have one very smooth surface; the reverse side has a wire screen impression. Some hardboards contain a small amount of oil on the surface either as a residual lubricant or as an additive to increase weather resistance (such as Tempered Presdwood®). These oils may hinder the adherence of paint or gesso and may be removed with acetone' [168].

[99] '*The background is applied over the support. For that I prefer hardboard, which is much more resistant or less vulnerable than canvas.' ('O fundo é feito sobre o suporte. Prefiro, para tal, o aglomerado de madeira, que é muito mais resistente ou menos vulnerável do que a tela*.')[105]

[100] First built at home, this structure was then ordered from a carpentry in *Rua Dona Estefânia*, Lisbon.

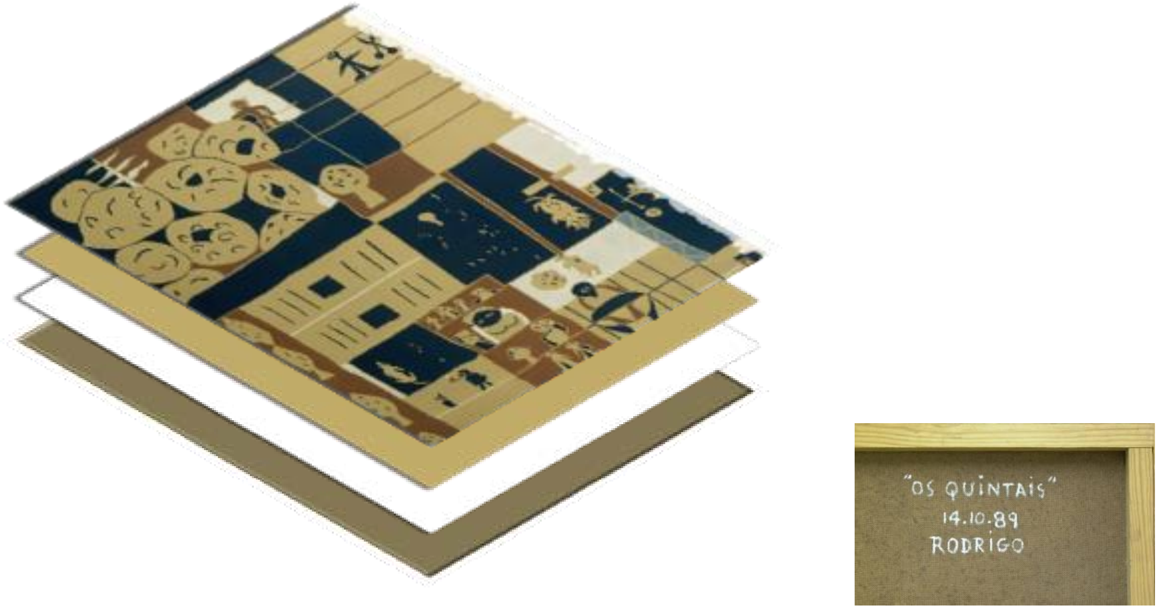

Figure 4.7. Schematic representation of the structure in the final ‘correct painting’ by Joaquim Rodrigo. Left (from bottom to top): hardboard; white preparation layer; coloured background layer; finished painting (detail from the painting *Os quintais*, 1989). Right: detail from the back, in which wood bars are applied to reinforce the structure, and also the identification of the painting, date and signature.

Figure 4.8. Detail of the painting *Os quintais* (1989) photographed in ranking light, where it is possible to observe the black, red and off-white applied over the background and two protrusions (top) revealing the nails’ heads on the surface.

Paint layers

A white preparation layer of titanium white PVAc paint was applied on the smoth surface of the hardboard and left to dry. Rodrigo called *subcapa* (undercoating) to this first white layer and explained [105] that it would reveal any support heterogeneity easier, which could then be removed; offer a better bonding with the background colour and diminish its vulnerability; allow an improved ‘freshness, vibration or purity’ of the background colour; and it would also allow a better transparency/opacity control of the subsequent coloured layers. Over this preparation a layer of coloured PVAc paint, the background, was applied in one ‘irregular’, although ‘rhythmic’, coat[101] with a flat brush[102], with the concern of not diverging (‘by excessive transparency’) from the original colour value[16]. Over the background, Rodrigo would first draw using charcoal sticks[103], and finally he would finish his painting with the ‘positive forms’[104] [105]. To create less control of the forms, Rodrigo would draw with his left hand and the painting upside-down and sometimes even with the paint brush attached to a long stick. No varnish was ever used by the artist, and the texture and fullness of his brushstroke is evident at a closer look, Figure 4.8.

4.2.1.2 Colour Reproduction

Within the scope of the present work, several workshops were organized at the DCR with the participation of Sofia Agrela since 2005 (Figure 4.9). Together with the students from the department, we had the opportunity to get a deeper insight on Rodrigo’s painting technique. The process was followed from the preparation of the support, including applying the wood bars to reinforce the hardboard structure, preparation of the paints and painting. The help of Sofia in the course of these workshops was fundamental for a better understanding of the paints preparation, specifically on the colour mixtures, binder/water and binder/pigment proportions, *i.e*. to find the ‘correct painting’ in which concerns colour and texture. After systematic experimentation and selecting the painting *Os quintais* (1989) as representative, the colours of one of the final ‘correct paintings’ were reproduced. For the paints preparation *Vulcano V7* was used as the binding medium; the ochre colours chosen for the reproduction were *ocre rouge* 2202 and o*cre jaune* 2202 from *Lefranc & Bourgeois*, both belonging to the pigment collection found at Rodrigo’s studio; titanium white from *Casa Varela* and *nero di marte* from *Zecchi* were the limits used. As described by Joaquim Rodrigo each of the colours were prepared individually in separate containers and were mixed as paints following the rules explained above (Chapter 4.2.1.1) in order to reproduce the colours from *Os quintais* (Figure 4.10).

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[101] ‘*Ao fim de vários anos acabei por preferir executá-lo com uma só de mão, em pincelada (trincha) naturalmente irregular, embora naturalmente ritmada* e apenas com a preocupação de não me afastar, por excessiva transparência, do valor que serviu de medida-aferição à preparação de todas as cores que vão participar no quadro, por sobreposição.’ [105]

[102] A paint-brush that would allow a stroke thickness proportional or appropriate to the board size [105].

[103] This is described by the artist in [112] and can be easily observed in the painting *Os quintais* (1989), but it was not confirmed for his earlier works; after the painting was finished, Rodrigo would remove the charcoal with a brush.

[104] Also the brushes used to paint the forms should allow a stroke thickness proportional or appropriate to the board size.

Figure 4.9. Workshop held in May 2008 at DCR – reproduction of the painting *Port-Ligat – Granada* from 1980. From top to bottom: Sofia Agrela and one student applying the white preparation layer; students applying the background; background colour; bottle containing the binder; painting the forms. Photos: Joana Lima da Silva.

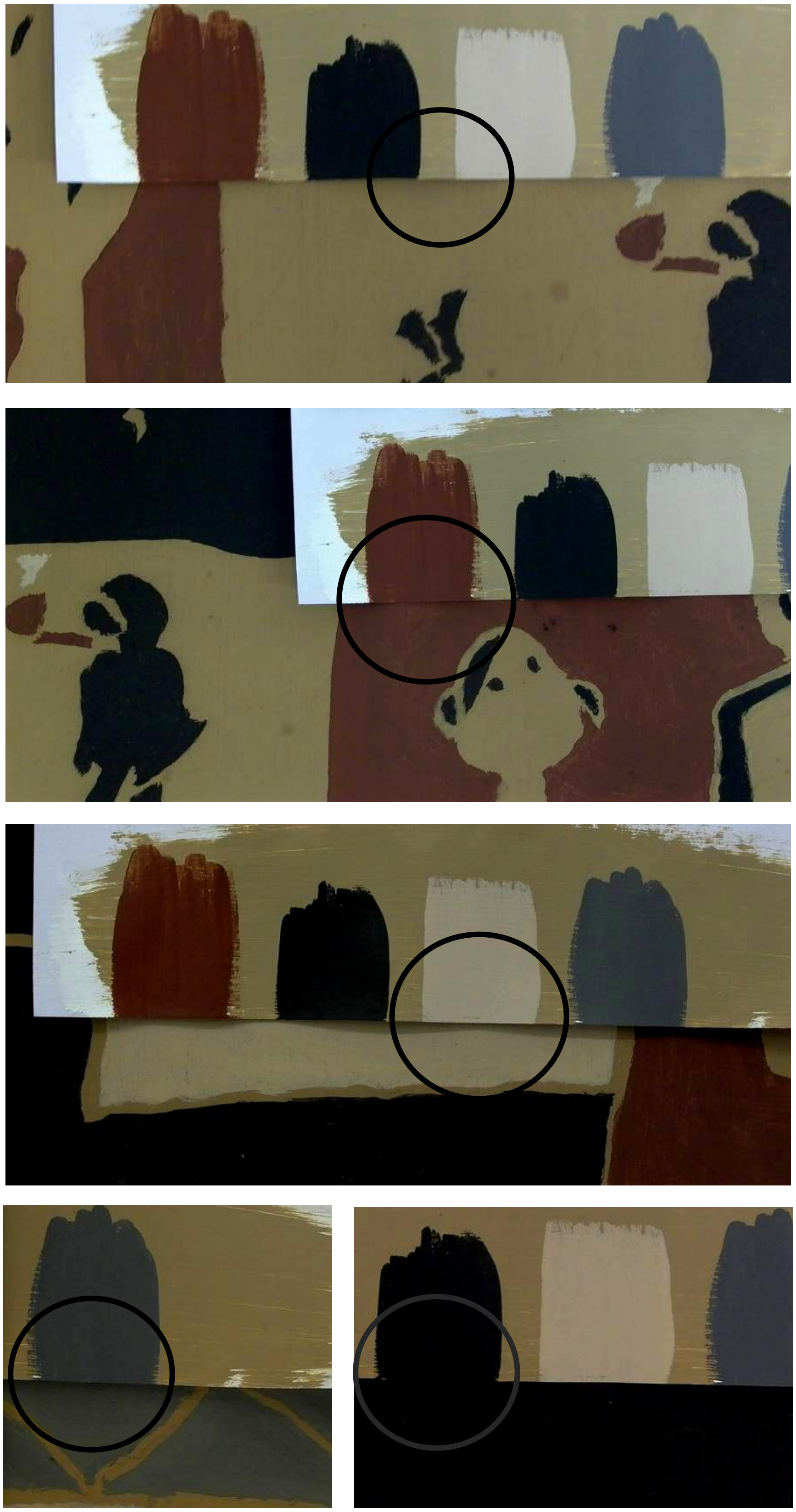

Figure 4.10. Reproductions of the colours in one of the final ‘correct paintings’ – *Os quintais* – from 1989. From top to bottom: background yellow (red ochre + yellow ochre + titanium white + black), red (red ochre + yellow ochre), off-white (background + titanium white), grey (off-white + black) and black.

4.2.2 Characterization – materials and conservation condition

For the present study, nine representative paintings dated from 1961 to 1989 were selected as case studies (Appendix V.3). A sample of white paint left by the artist in his studio (possibly the last one he produced) was also included. In addition to the characterization of the paints, Rodrigo's palette is also studied.

4.2.2.1 Pigment palette: molecular characterization

Twenty pigments were collected from Joaquim Rodrigo's studio, including 16 different shades of iron oxides, two whites, and two blacks, Figure 4.11. Ten of the iron oxide based colours and one black are from *Lefranc & Bourgeois*, one iron oxide had been purchased at a drugstore, one white was supplied by *Casa Varela* (Chapter 2.2), and seven pigments (yellow and green iron oxides, black, and white) are from unknown suppliers.

Figure 4.11. The colour palette used by Joaquim Rodrigo: yellow and red ochres, black and white. The pigments were collected from his studio.

The iron oxide pigment samples were characterized [169] in a previous work by μ-Raman and infrared. In that study, the pigments were identified according to the different iron oxides chromophores and matrixes. From the 16 iron oxide samples, 14 were fully characterized (spectra are presented in Appendix V.2). In eight of these, the colour centres are found within a matrix (e.g., kaolin, talc, gypsum), in five only hematite and/or goethite was identified, and one could be classified as an umber due to the presence of MnO_2. It is possible that eight are natural ochres and five are synthetic iron oxides.

Concerning the blacks and whites, the black from *L&B* is a bone black pigment, identified by the infrared fingerprint of the phosphate matrix at 874, 962, 1040, 1090, and 2014 cm^{-1} [160] and the presence of carbon in the Raman spectra (broad bands at 1328 and 1596 cm^{-1}) [170], Figure 4.12 A and B; the other black pigment, purchased from an unknown drugstore, is a carbon black (Raman) with gypsum (IR absorptions at 669, 1133, 1620, 1685, 3407, 3493 and 3550 cm^{-1} [171]), Figure 4.12 C and D. Both white pigments are titanium dioxides, and it was possible to identify rutile as the main crystalline form present (Raman: 142, 236, 447 and 609 cm^{-1} [170]), Figure 4.13.

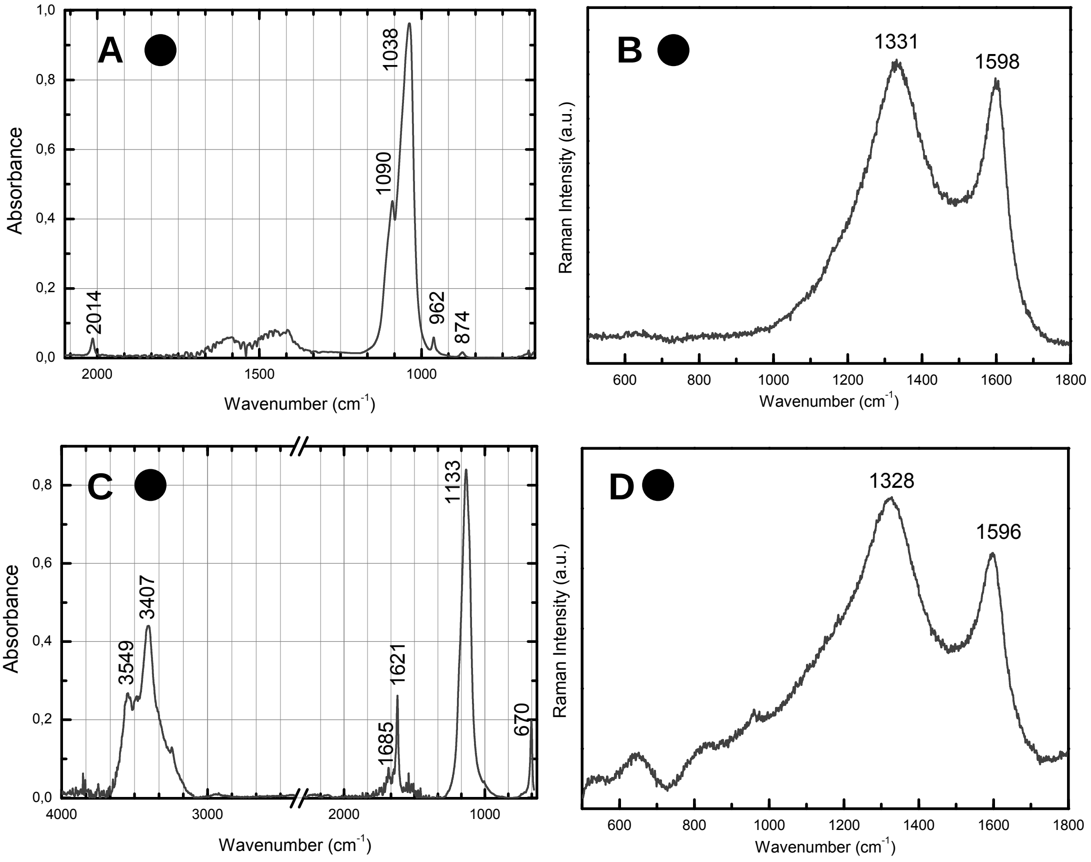

Figure 4.12. Spectra of the black pigments from Rodrigo's palette: A – infrared spectrum of *L&B* black pigment; B – Raman spectrum of *L&B* black pigment; C – infrared spectrum of black pigment from a drugstore; D – Raman spectrum of black pigment from a drugstore.

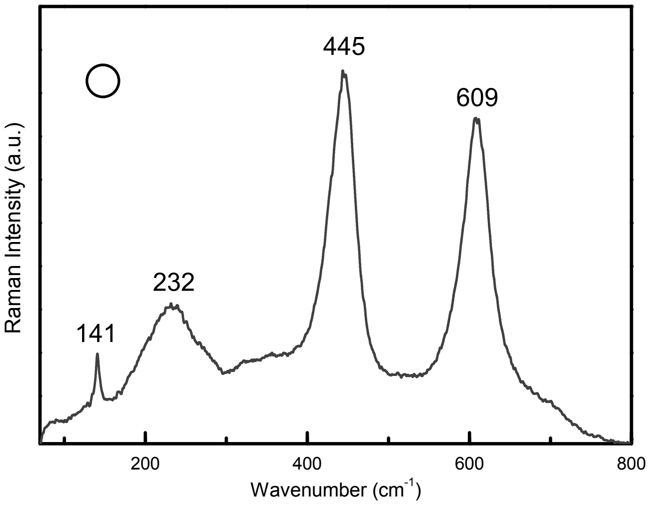

Figure 4.13. Raman spectrum of a white pigment (drugstore) from Rodrigo's palette.

4.2.2.1 Painting materials and techniques: molecular approach

Table 4.1 presents the paint samples collected from Rodrigo's works and summarizes the main results concerning the colourants and fillers characterization. A PVAc homopolymer was identified as the binder in all paint samples, as confirmed by the infrared carbonyl stretching absorption peak at 1738 cm^{-1} and the relative intensities of the other diagnostic peaks, namely the C-O stretching at 1242 cm^{-1} and C-H_3 bending at 1373 cm^{-1} [160], Figure 3.7. In at least one of the paintings (*Lisboa – Oropeza*, 1969), the plasticizer was still present in low amounts, infrared analysis points to a phthalate evidenced by the small peak at approximately 1073 cm^{-1} [160], Figure 4.14, and the presence of di-iso-butyl-phthalate (DiBP) in the "final white paint" was confirmed by pyrolysis-gas chromatography-mass spectrometry (PY-GC-MS). A more detailed discussion on the conservation condition of PVAc will be presented below. Pigment identification was based on the results obtained by infrared and Raman microspectroscopies (infrared and Raman peaks assignment is depicted in Tables 4.2 and 4.3 for the pigments identified) as well as μ-EDXRF. Spectra are presented in Appendix V.4 for all paintings.

Table 4.1. Colourants and fillers found in Joaquim Rodrigo's paintings

Sample			**µ–FTIR**	**µ–EDXRF**	**µ–Raman**
 *M.L.*, 1961	White	○	[a]	**Ti**	TiO_2
	Red (background)	●	$BaSO_4$	**Ba**, **Ca**, **Cd**, **Se**, S, Fe	CdS, *x*CdSe
	Brown	●	Fosfate matrix	**Ca**, Cd, Se, Zn, Ti, S, P, Fe	C [b]
	Black	●	Fosfate matrix	**Ca**, P, S	C [b]
 *S.M.*, 1961	Red	●	**-**	**Ti**, **Cd**, **Se**, Cr, Zn	CdS, *x*CdSe
	Yellow	●	-	**Ti**, **Cd**, Se, S	CdS [c]
 *Kultur- 1962*, 1962	White	○	[a]	**Ti**	TiO_2
	Dark Red	●	$CaSO_4.2H_2O$	**Ca**, **Cd**, **Se**, **Ba**, S, Fe	CdS, *x*CdSe
	Yellow (background)	●	FeOOH	**Fe**, **Ti**	FeOOH
 *Mondo Cane I*, 1963	White	○	[a]	**Ti**	TiO_2
	Yellow	●	$BaSO_4$	**Ti** [d], **Cd**, S, Zn	CdS [c]
 *Liberté*, 1963	White	○	[a]	**Fe**, **Ti**, Mn, Ca	TiO_2
	Light Brown	●	FeOOH	**Fe**, **Mn**, Ca	FeOOH
 *Lisboa – Oropeza*, 1969	White	○	[a]	**Ti**, Fe	TiO_2
	Pink	●	FeOOH [a]	**Ti**, **Fe**	Fe_2O_3, TiO_2
	Red	●	FeOOH [a]	**Fe**, **Ti**, Ca, Zn	Fe_2O_3
 *Alassio – Nice*, 1971	White	○	[a]	**Ti**, Zn	TiO_2
	Red Ochre	●	$Al_2Si_2O_5(OH)_4$, SiO_2 [e]	**Fe**, Ti	Fe_2O_3
	Black	●	-	**Fe**, Ca, Ti, K, S, Si	C [f], Fe_2O_3
 *Port-Ligat – Granada*, 1980	White	○	[a]	**Ti**, Zn	TiO_2
	Pink	●	FeOOH [a]	**Ti**, **Fe**, Zn	Fe_2O_3, TiO_2
	Dark Brown (background)	●	FeOOH	**Fe**, **Ti**, Zn	Fe_2O_3, C [f]
 *Os quintais*, 1989	Off-White	○	$Al_2Si_2O_5(OH)_4$, SiO_2 [a]	**Ti**, **Fe**, K, Si, Zn	TiO_2, C [f]
	Yellow (background)	●	$Al_2Si_2O_5(OH)_4$, SiO_2	**Fe**, **Ti**, K, Zn, Si, Ca	FeOOH, Fe_2O_3, TiO_2, C [f]
	Red ochre	●	$Al_2Si_2O_5(OH)_4$, SiO_2	**Fe**, Ti, Si, K, Mn	Fe_2O_3, FeOOH, C [f]
	Grey	●	$Al_2Si_2O_5(OH)_4$, SiO_2	**Fe**, Ti	Fe_2O_3, FeOOH, TiO_2, C [f]
	Black	●	-	**Fe**, Mn	C [f]

[a] A shoulder at the right end of the spectrum indicates the presence of titanium dioxide, which peak centre is below 650 cm^{-1}. [b] Bone black. [c] Analysed with the 532 nm laser. [d] Due to the strong emission of Ti it was not possible to confirm the presence of Ba. [e] FeOOH present in low amounts. [f] Carbon black

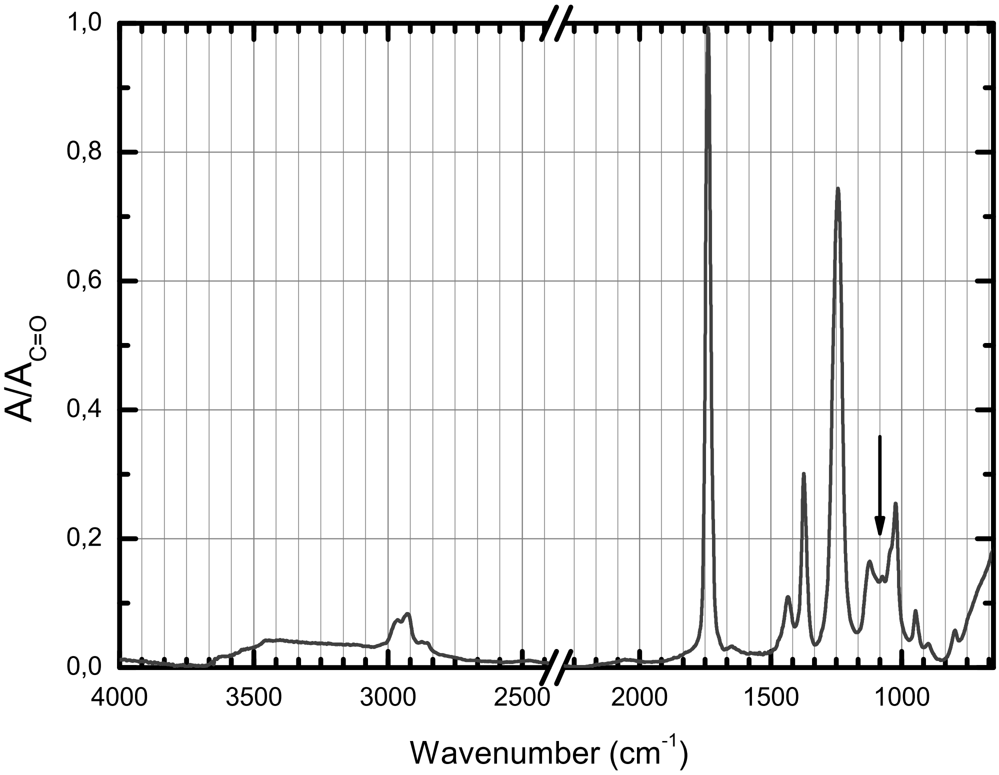

Figure 4.14. Infrared spectrum of a brown sample from *Lisboa – Oropeza*, 1969, with absorptions normalized for the C=O stretching. The arrow indicates a characteristic absorption of the plasticizer (phthalate).

Table 4.2. Infrared assignment for the pigments in the paint samples from Joaquim Rodrigo

Compound identified	**Band** (wavenumber/cm^{-1})	**Reference**
Barium sulfate ($BaSO_4$)	~1180(sld), 1120(sld), 1079(vs), 984(w)	[160]
Calcium carbonate ($CaCO_3$)	~1430(vs) , 877(m)	[160]
Calcium Phosphate ($Ca_3(PO_4)_2$)	2014(m), 1090(sld), 1045(vs), 962(w), 874(w)	[160]
Gypsum ($CaSO_4.2H_2O$)	3555(s), 3405(s),1685(vw), 1620(m), 1145(vs), 1115(vs), 669(w)	[160]
Goethite (FeOOH)	798(m), 904(m), 3138(m)	[160]
Kaolin ($Al_4(OH)_2Si_4O_{10}$)	3700(m), 3653(w), 3624(m), 1100(s), 1032(vs), 1009(s), 914(s)	[162]
Quartz (SiO_2)	1165(sld), 1110(vs), 798(m), 780(m), 698(w)	[160]

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very week; w – week.

Table 4.3. Raman assignment for the pigments in the paint samples from Joaquim Rodrigo

Compound identified	**Band** (wavenumber/cm^{-1})	**Reference**
Cadmium red (CdS, *x*CdSe)	195(m), 289(s), 489(w), 590(m)	[172]
Cadmium yellow (CdS)	301(w), 600(w)	[172]
Carbon (C)	1328(vs), 1580(vs)	[173]
Goethie (FeOOH)	247(m), 300(m), 387(vs), 485(w), 552(m)	[174]
Hematite (Fe_2O_3)	224(s), 245(w), 291(vs), 411(m), 611(m), 1330(m)	[174]
Titanium dioxide (TiO_2)[a]	141(w), 233(m), 445(vs), 610(vs)	[174]

[a] Rutile crystalline form.
m – medium; s – strong; vs – very strong; w – week.

Cadmium colours

In the first four paintings analysed (from 1961, 1962 and 1963) cadmium sulfide (yellow) and cadmium sulfoselenide (red) were identified by Raman microespectroscopy (Figure 4.15 A and B), namely by the peaks at 301 and 603 cm^{-1} for the sulfide and at 194, 289, 482, 580 cm^{-1} for the sulfoselenide. This is in agreement with the fact that, in the 1960s, as already described, Joaquim Rodrigo was using bright colours besides experimenting with an ochre based palette. In three of the five cadmium colours, it was possible to identify the presence of extenders by infrared (Figure 4.16). In the dark red sample from *Kultur - 1962* (1962), gypsum ($CaSO_4.2H_2O$) was identified by its characteristic IR fingerprint (Figure 4.16 A). In the red sample from *M. L.* (1961) and the yellow from *Mondo Cane I* (1963), the identification of barium sulfate by infrared (984, 1079, 1120 and ~1180 cm^{-1}), Figure 4.16 B, together with the presence of barium[105], zinc, and sulphur (μ-EDXRF, Figure 4.16 C) suggest that lithopone (coprecipitate of barium sulfate (71%) and zinc sulfide (29%) [95]) was the extender used.

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[105] It was not possible to confirm the presence of Ba in the yellow sample from *Mondo Cane I*, as it may be masked due to the intense emissions of Cd and Ti.

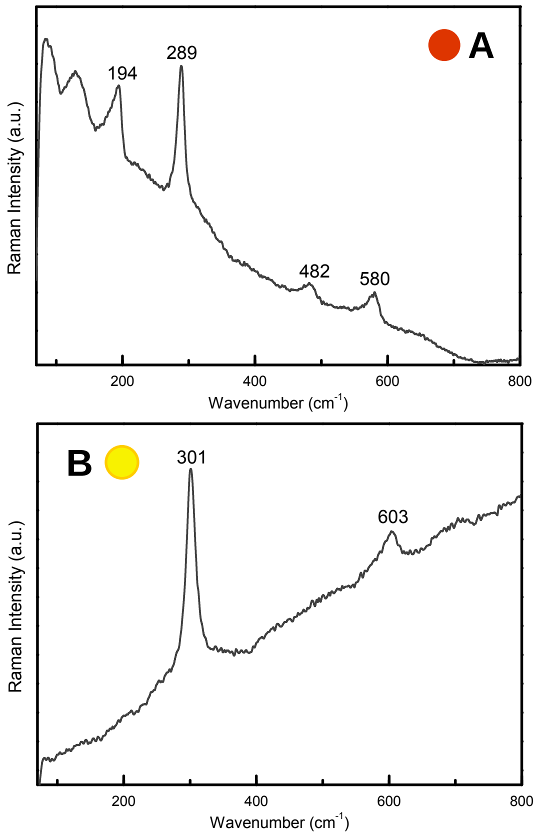

Figure 4.15. Representative Raman spectra of pigments found in the cadmium colours of paint samples from the works by Joaquim Rodrigo: A – Raman spectrum (cadmium red) of a red sample from *M. L.*, 1961; B – Raman spectrum (cadmium yellow) of a yellow sample from *S. M.*, 1961.

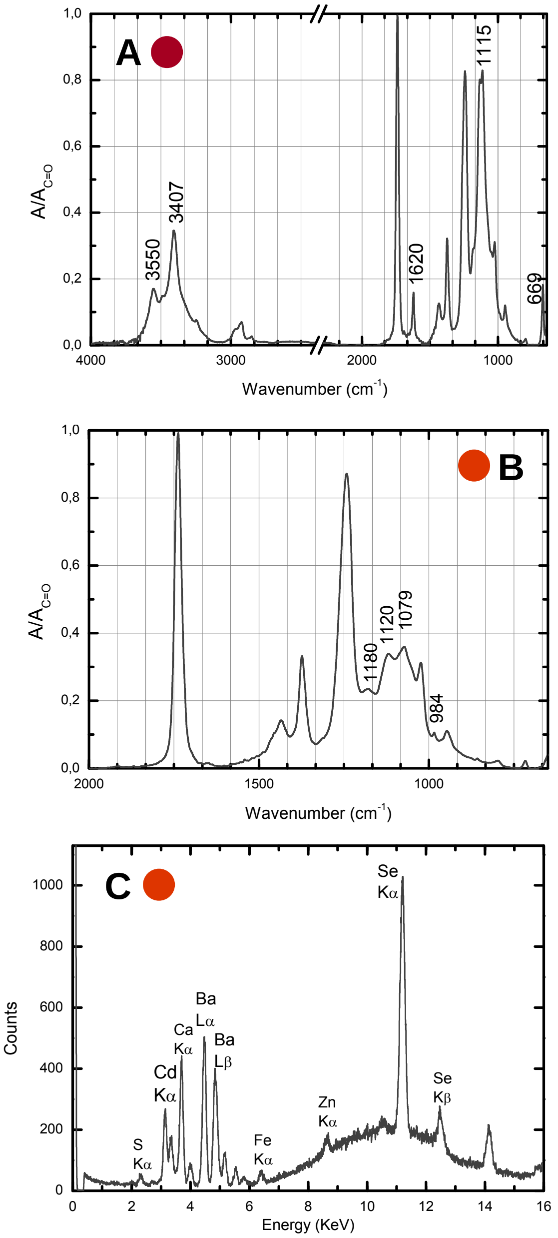

Figure 4.16. Representative spectra of extenders found in the cadmium colours of paint samples from the works by Joaquim Rodrigo: A – infrared spectrum (gypsum) of a red sample from *Kultur - 1962*, 1962; B – infrared spectrum (barium sulfate) of a red sample from *M. L.*, 1961; C – EDXRF spectrum (with Ba and Zn) of a red sample from *M. L.*, 1961.

Iron oxide colours

As expected, iron oxide pigments were identified in the studied paintings from 1962 onwards. In the iron oxides found in the paintings from 1962, 1963, 1969, and 1980, only the colour centres were characterized and no matrix was detected by infrared spectroscopy, suggesting that synthetic pigments were used. Only in the paintings from 1971 and 1989 could the identified pigments be assigned to natural ochres displaying a kaolin (914, 1032, 3620 and 3699 cm^{-1}) / quartz (695, 781, 798, 1116 and 1164 cm^{-1}, Figure 4.17 A) matrix [169] in agreement with the infrared fingerprint of the *L&B* natural earth colours. The iron oxide chromophores were identified mainly by μ-Raman as hematite (224, 242, 290, 407, 496, 610 and 1310 cm^{-1} (Figure 4.18 A) and goethite (240, 299, 387, 416, 484 and 550 cm^{-1}, Figure 4.18 B). For goethite, it was also possible to clearly fingerprint its presence in the infrared spectra (3136, 907 and 801 cm^{-1}, Figure 4.18 C) except for the work *Os quintais* (1989) where it was only possible to detect the colour centers by μ-Raman. This could be explained by the greater mixing of colours and, as a consequence, a lower pigment concentration in comparison to the clay minerals present. It could also be explained by a more extensive use of natural ochres and, again, a lower goethite concentration relative to the matrix. The presence of manganese (μ-EDXRF, Figure 4.17 B) together with quartz in the red and black samples from *Os quintais* (1989) suggests that umber was used in this painting [169,175], which could be a pigment from *L&B*. On the other hand, in the light brown sample from *Liberté* (1963), manganese was also detected, but neither quartz nor other inorganic matrix was observed in the infrared spectra, pointing to the presence of a synthetic brown.

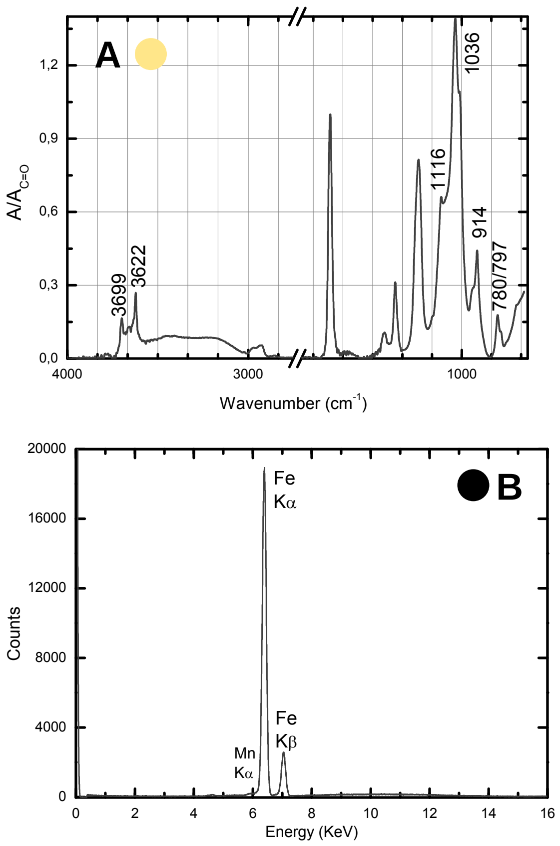

Figure 4.17. Representative spectra of pigment matrixes found in the iron oxide colours of paint samples from the works by Joaquim Rodrigo: A – infrared spectrum (kaolin and quartz) of a background sample from *Os quintais*, 1989; B – EDXRF spectrum (with Mn) of a black sample from *Os quintais*, 1989.

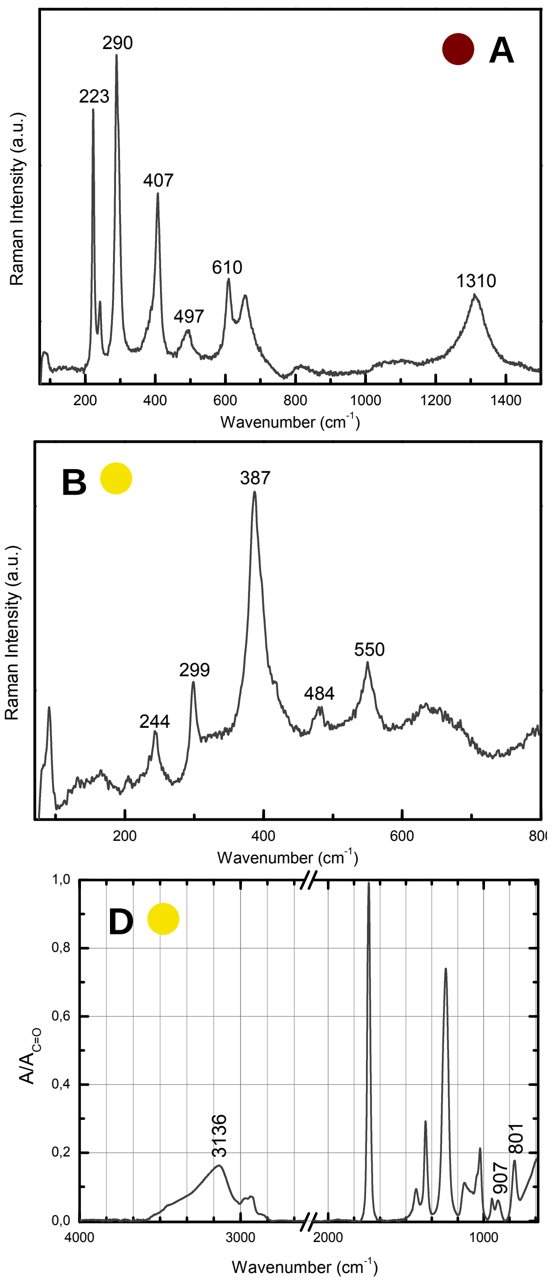

Figure 4.18. Representative spectra of colour centers found in the iron oxide colours of paint samples from the works by Joaquim Rodrigo: A – Raman spectrum (hematite) of a red sample from *Lisboa - Oropeza*, 1969; B – Raman spectrum (goethite) of a yellow sample from *Kultur - 1962*, 1962; C – infrared spectrum (goethite) of a yellow sample from *Kultur - 1962*, 1962.

Blacks and whites

In *M. L.* (1961), a bone black pigment was identified by the infrared phosphate matrix absorption, Figure 4.19 A, and the carbon Raman spectrum (as discussed above). The other black samples analysed from *Alassio – Nice* (1971) and *Os quintais* (1989), Table 4.1, were carbon blacks (Raman), Figure 4.19 B. In all paintings, the white pigment was identified by μ-Raman as titanium dioxide, mainly in the rutile crystalline form, Figure 4.20 (in the infrared spectra only the tail of its peak was observed starting at about 670 cm^{-1}).

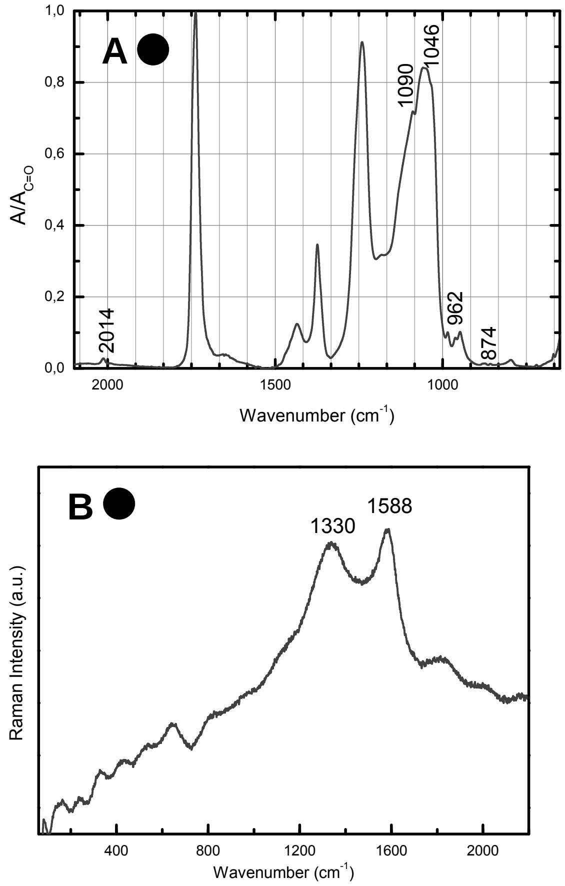

Figure 4.19. Representative spectra of colourants found in the black colours of paint samples from the works by Joaquim Rodrigo: A – infrared spectrum (calcium phosfate) of a black sample from *M. L.*, 1961; B – Raman spectrum (carbon black) of a black sample from *M. L.*, 1961; C – Raman spectrum (titanium dioxide - rutile) of a white sample from *M. L.*, 1961.

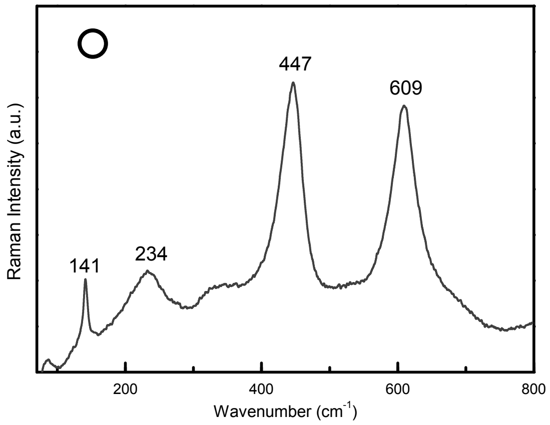

Figure 4.20. Representative spectra of the colourant found in the white colours of paint samples from the works by Joaquim Rodrigo: A – Raman spectrum (titanium dioxide - rutile) of a white sample from *M. L.*, 1961.

Colour Mixtures

The paintings *Lisboa – Oropeza* (1969) and *Port-Ligat – Granada* (1980) are representative of Rodrigo's colour theory [105], in which the pigment palette is limited to the four colours already described, and only some pigment mixtures were used in order to achieve maximum contrast. From these two paintings, two pinks, a dark red, and a dark brown were analyzed (Table 4.1). The pink colour could have been produced by mixing a 'corrected' red with white, *i.e.*, by mixing titanium white with both yellow and red iron oxides, goethite and hematite, respectively. For these pinks, the iron oxides were probably synthetic as no matrix could be found in the infrared spectra. Also, both dark red and brown could have been produced by mixing, in different proportions, yellow and red iron oxides.

Concerning *Os quintais*, one of the final 'correct paintings', the results obtained (Table 4.1) corroborate the theory presented by Rodrigo in his last publication [112]. The yellow (from the background) and grey were prepared as a mixture of the four colours: titanium white, carbon black and possibly two iron oxides, red and yellow. As already described, one or both of them were natural ochres, due to the presence of the kaolin/quartz matrix. Although the white was described as being composed of the same four pigments, the higher content of titanium white did not allow the identification of the ochre colour centres by Raman, but the presence of at least one natural ochre could be deduced by the kaolin/quartz signature in the infrared spectra and the presence of iron (μ-EDXRF). The red is the result of a mixture of red and yellow ochres with carbon black, and the black colour was possibly used pure (please see discussion for blacks & white, above).

It is worth to further mention that the white paint found at the artist's studio and possibly one of the last paints he prepared in the 1990s, might be also the result of some pigment mixture (spectra in Appendix V.4). Besides the titanium dioxide found in all white paint samples, calcium carbonate (which could be present as the matrix for an iron oxide or as an extender), bone black and quartz (in low amounts) were also detected by infrared.

Colour measurements were also performed for all paintings, and with the exception of some cases in which the layers were particularly thin, the paint chroma was found to be very homogeneous when comparing different areas of the same colour. In Table 4.4 average $L^*a^*b^*$ and maximum colour variations (ΔE^*) are presented for each of the studied paintings, complete colour measurements and mapping may be found in Appendix V.5.

Table 4.4. *L*a*b** (average) and maximum colour variations (*ΔE**) determined for each colour in Joaquim Rodrigo's paintings

Sample			***L****	***a****	***b****	ΔE^*_{max}
M. L. 1961	White	○	80.44	0.70	12.62	3.20
	Red	●	38.25	28.35	20.37	0.42
	Brown	●	27.76	7.28	5.34	5.98
	Black	●	24.56	0.58	-0.07	1.86
S. M. 1961	Red	●	40.24	32.65	21.35	4.59
	Yellow	●	74.39	10.58	76.05	2.72
Kultur- 1962 1962	White	○	84.51	0.24	5.78	2.38
	Dark Red	●	30.10	8.56	7.61	0.79
	Yellow (background)	●	54.32	10.50	41.77	1.80
Mondo Cane I 1963	White	○	89.21	-1.04	5.12	1.68
	Yellow	●	76.75	10.48	83.41	4.01
Liberté 1963	White	○	85.64	-0.10	5.88	4.59
	Light Brown	●	49.72	7.77	36.37	3.59
Lisboa – Oropeza 1969	White	○	84.47	-0.45	2.39	4.78
	Pink	●	53.27	17.59	16.79	0.96
	Red	●	36.55	17.84	18.40	0.84
Alassio – Nice 1971	White	○	83.79	-0.60	-1.67	4.24
	Red Ochre	●	37.95	17.79	20.63	0.72
	Black	●	21.67	0.14	0.19	0.49
Port-Ligat – Granada 1980	White	○	75.01	-0.57	-3.10	3.34
	Pink	●	59.03	12.15	15.78	2.82
	Dark Brown (background)	●	31.61	1.47	2.76	0.46
Os quintais 1989	White (off-White)	○	68.22	6.86	15.57	1.39
	Yellow (background)	●	56.32	10.20	21.89	2.81
	Red ochre	●	33.78	13.47	11.37	1.63
	Grey	●	45.85	0.84	1.60	2.01
	Black	●	25.26	0.99	0.38	1.83

Binding medium

One of the main goals of this work is to assess the molecular ageing of the binder. As previously described (Chapter 3.2.2), infrared spectra may unveil important information on degradation mechanisms, namely detecting if the ester bond is being broken with the consequent release of acetic acid.

In most samples from the studied paintings, it was possible to have a clear window for the main diagnostic PVAc absorptions. In some of the paint samples, the C-H stretching absorptions were masked by absorptions due to other compounds present in the formulation, and therefore these absorptions were not considered. The $\delta CH_3/\nu C{=}O$ and $\nu C\text{-}O/\nu C{=}O$ ratios are in agreement with those displayed by unaged PVAc, Table 4.5. Maximum broadening of the carbonyl band was below 8% for all analysed samples, also in agreement with a standard PVAc (see Table 4.5). Dated paint samples, ranging from 1961 to the 1990s, were analyzed, and no evolution trend could be detected. Furthermore, no signs of degradation catalyzed by the presence of metal ions from the pigments was found. Based on these results, it is possible to conclude that no relevant molecular degradation is observed in the binder, namely concerning hydrolysis and the formation of oxidized degradation products.

In the systematic studies undertaken on the photodegradation of PVAc, Chapter 3.2, it was found that the first molecular changes are observed for the polymer weight distribution as detected by SEC. For this reason, the last white paint prepared by the artist in the 1990s was further analysed by SEC, presenting a *Mw* of *ca* of 2.2×10^4 and a PD of 2.5 (Figure 4.21). It is possible to discuss this result taking into consideration that the *Mw* value found is within the values expected for a vinyl emulsion based paint (Chapter 3.2). Also, the polydispersity is consistent with that determined for unaged paints or for the first steps of degradation. An accurate evaluation of the naturally aged polymer molecular weight distribution will only be possible after future measurements in order to characterize the evolution trend. It was not possible to carry out this analysis in samples from paintings due to the minimum amount required (in the order of several mg).

Table 4.5. Paint samples from Joaquim Rodrigo works: infrared absorptions at 1373 ($\delta_{C\text{-}H3}$) and 1242 cm^{-1} ($\nu_{C(=O)\text{-}O\text{-}C}$), normalized for ($\nu_{C=O}$), at ~1738 cm^{-1}; and fitting parameters for the C=O absorption, peak centre (μ), full width at half maximum (σ) and correlation coefficient (ρ), with a Gaussian function

Sample		$\delta_{C\text{-}H3}$	$\nu_{C(=O)\text{-}O\text{-}C}$	$\nu_{C=O}$		
				μ	σ	ρ
M. L.	White	0.28	0.72	1739.3	19.35	0.992
1961	Red	0.33	[a]	1737.8	20.77	0.994
	Brown	0.34	[a]	1738.6	20.86	0.992
	Black	0.34	[a]	1738.1	21.34	0.989
S. M.	Red	0.33	0.77	1738.8	20.12	0.997
1961	Yellow	0.33	0.76	1738.8	20.57	0.995
Kultur - 1962	White	0.30	0.70	1739.0	19.96	0.984
1962	Dark Red	0.32	[a]	1739.2	20.02	0.998
	Yellow Ochre	0.29	0.71	1739.0	16.64	0.996
Mondo Cane I	White	0.28	0.71	1739.2	19.48	0.994
1963	Yellow	0.33	[a]	1738.5	20.50	0.994
Liberté	White	0.30	0.73	1738.9	20.33	0.997
1963	Light Brown	0.31	0.78	1738.6	19.96	0.992
Lisboa – Oropeza	White	0.29	0.74	1738.6	19.66	0.992
1969	Pink	0.30	0.74	1738.4	19.78	0.992
	Brown	0.30	0.75	1738.7	19.57	0.996
Alassio – Nice	White	0.30	0.74	1738.9	19.11	0.990
1971	Red Ochre	0.31	[a]	1738.7	19.34	0.994
	Black	[a]	[a]	1739.1	20.80	0.997
Port-Ligat – Granada	White	0.29	0.70	1739.5	19.98	0.997
1980	Pink	0.31	0.74	1739.1	19.70	0.997
	Dark Brown	0.30	0.74	1738.7	19.31	0.993
Os quintais	Off-White	0.32	[a]	1738.3	20.59	0.993
1989	Yellow Ochre	0.31	[a]	1738.4	20.28	0.995
	Red Ochre	0.30	[a]	1738.2	20.72	0.990
	Grey	0.29	0.71	1738.8	20.02	0.990
	Black	0.33	[a]	1737.9	19.97	0.98
Final white 1990s	Acetone extract	0.32	0.77	1737.4	20.22	0.981
PVAc standard		0.31	0.77	1738.5	19.72	0.933
Vulcano V7		0.28	0.72	1737.6	20.68	0.988

[a] Absorption masked by the pigment.

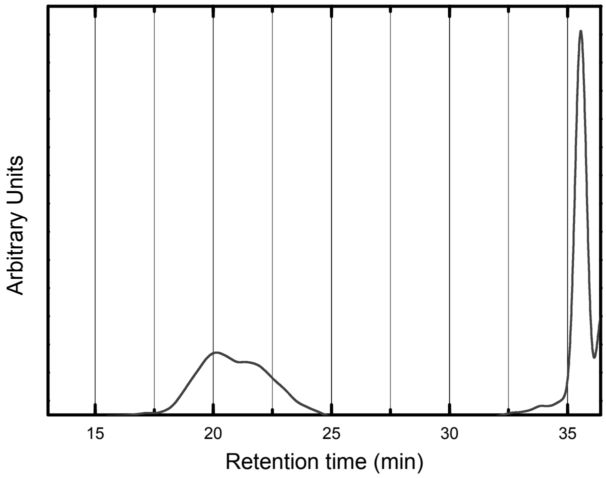

Figure 4.21. SEC chromatogram of the final white paint left by Rodrigo in his studio (Mw ~2.2 x 10^4; PD, 2.5). The peak appearing at t_R>35 min is attributed to an additive.

Paint condition

For all studied paintings by Joaquim Rodrigo, it was possible to assess the good conservation condition of the paint film, with no signs of loss of cohesion or adhesion to the support. The only failure observed is related with the structure of the support (see Chapter 4.2.1.1). The wood bars applied for reinforcement turn out to be the weakness of Rodrigo's works on hardboard. Due to the fact that these wood bars are hammered from the front surface, with repeated movements through the years, the nails become loose implying the fracture of the paint film that eventually detaches from the support (Figure 4.22).

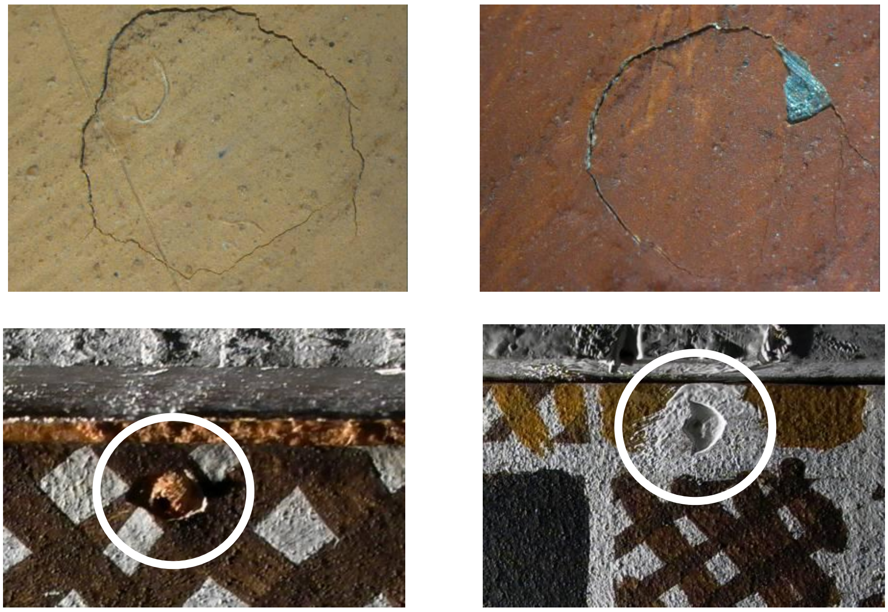

Figure 4.22. Paint film failure due to nail movements. Top: *Os quintais*, 1989 – left, area with paint fracture; right area with paint fracture and detachment (amp. 40x). Bottom: *Liberté*, 1963 - left, area where the paint has detached; right, area with retouch covering the paint detachment.

The colourimetric studies undertaken on the white areas of the paintings show that no yellowing has occurred. The values for the yellow coordinate (*b** maximum ≈ 6), Table 4.6, are in agreement with those measured in white paint reproductions, Figure 4.23. The exception is the white from *M. L.* (1961) with a *b** value of *ca* 13, for which an explanation is not clear at present. These results are in agreement with PVAc being considered a very stable binder, presenting extremely low degradation quantum yields as concluded in Chapter 3.2.

Table 4.6. *L*a*b** coordinates determined for the white colours on Joaquim Rodrigo's paintings and white paint reproductions applied with paint brush and film applicator

Painting	***L****	***a****	***b****
M. L., 1961	80.44	0.70	12.62
Kultur- 1962, 1962	84.51	0.24	5.78
Mondo Cane I, 1963	89.21	-1.04	5.12
Liberté, 1963	85.64	-0.10	5.88
Lisboa – Oropeza, 1969	84.47	-0.45	2.39
Alassio – Nice 1971	83.79	-0.60	-1.67
Port-Ligat – Granada, 1980	75.01	-0.57	-3.10
Os quintais, 1989	68.22	6.86	15.57 [a]
White paint reproduction applied with brush (thin layer)	81.65	0.81	0.74
White paint reproduction applied with film applicator (thicker layer)	93.57	-0.95	5.06

[a] Value not comparable, as in this painting the white (off-white) results from the mixture of all colours.

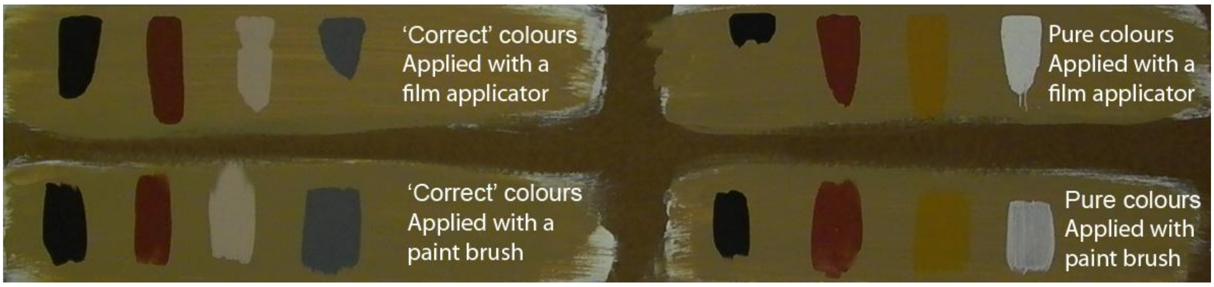

Figure 4.23 Colour reproductions, from the painting *Os quintais*, 1969, for which colour measurements were preformed. The pure and 'corrected' colours were applied, both with paint brush and film applicator, on hardboard over a white preparation layer and background, reproducing Rodrigo's technique.

4.3 Ângelo de Sousa

(...) *a painter, deeply and essentially a painter*[106]

Fernando Pernes, 1993

4.3.1 The artist and his selection of materials

This chapter is focused on the interviews (Appendix VI.1 and VI.2) conducted within the scope of the present thesis and intends to summarize the main ideas discussed with the artist[107].

The first interview (October 2005) with Ângelo de Sousa took place at his home; in this first conversation we tried to understand his choices and concerns about the materials. In a second meeting (June 2008), we incorporated our knowledge about Ângelo's work and also what art historians and critics have written about it. Questions were aimed at understanding the possible relationship between the technical issues raised by the use of certain materials in each period and the merely aesthetic aims.

Ângelo de Sousa describes himself as a technology enthusiast. Ever since Ângelo started painting, in the fifties, he has experimented with many materials and feels that such a research is part of his character. Ângelo stated, 'since I was a little boy, whenever I do something I need to understand how it works'[108].

In his early years as a painter, right after he arrived from Mozambique in 1955[109], he bought Dörner's book *The materials of the artist and their use in painting* which for 300 Escudos was a major investment at that time (a fifth of his monthly income). He also purchased *The Artist's Handbook of Materials and Techniques* by Ralph Mayer in 1959 (Figure 4.24). This interest goes beyond traditional painting materials and Ângelo also collected books about plastics (Figure 4.25). Unlike other artists, Ângelo shows an extreme care in giving the precise names of the materials he uses to provide correct information to anyone who may need to restore his works; each painting has a label (Figure 4.26) describing the support, preparation, paint and protection layers.

---

[106] '*Contudo, pintor, profunda e essencialmente pintor, foi sobretudo no desafio havido perante as telas virgens que o artista trilho e logrou plena maturidade,* (…)' [117].

[107] Unless stated, Ângelo's quotations derive from the oral interviews conducted by the authors.

[108] '*Quando faço qualquer coisa tento sempre saber como é que ela funciona, desde pequenino*.' (Interview with Ângelo de Sousa, 2005; Appendix VI.1)

[109] Ângelo was born in Mozambique in 1938 where he lived until 1955, when he moved to Porto to study.

Angelo de Sousa Porto 11.55

MAX DOERNER
PROFESOR DE LA ACADEMIA DE BELLAS ARTES, DE MUNICH

LOS
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DE PINTURA
y su empleo en el Arte

Materiales y técnica de las pinturas al óleo, temple, acuarela, fresco, pastel. Técnica de los antiguos maestros. Técnica en el siglo XIX. Conservación de monumentos y cuadros

2.ª edición, traducida de la novena alemana, revisada ésta por Toni Roth, pintor y conservador en Munich, con la colaboración técnica del Dr. Ricardo Jacobi.
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Figure 4.24. First pages of the Spanish editions of: top – *The materials of the artist and their use in painting* by Max Dörner; bottom – *The Artist's Handbook of Materials and Techniques* by Ralph Mayer, bought by Ângelo de Sousa in 1955 and 1959.

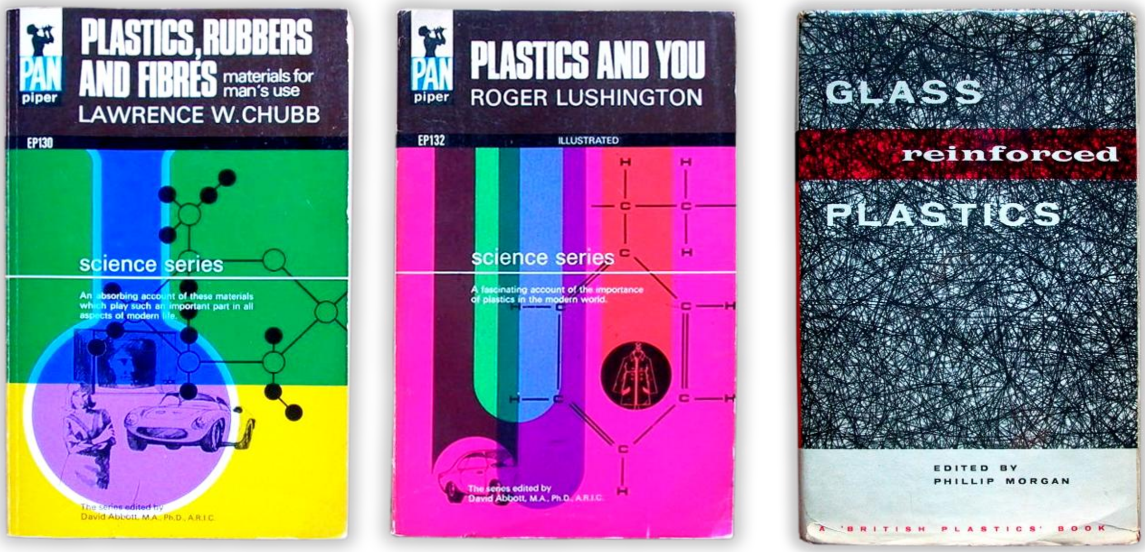
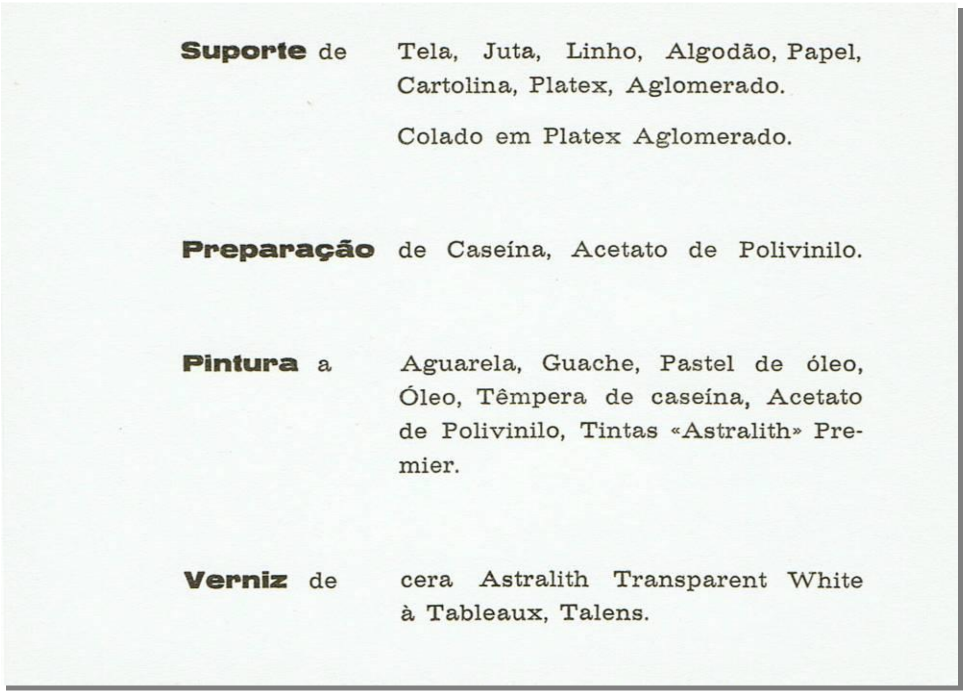


Figure 4.25. Examples of books collected by Ângelo de Sousa about plastics.



Suporte de	Tela, Juta, Linho, Algodão, Papel, Cartolina, Platex, Aglomerado. Colado em Platex Aglomerado.
Preparação	de Caseína, Acetato de Polivinilo.
Pintura a	Aguarela, Guache, Pastel de óleo, Óleo, Têmpera de caseína, Acetato de Polivinilo, Tintas «Astralith» Premier.
Verniz de	cera Astralith Transparent White à Tableaux, Talens.

Figure 4.26. Label used by Ângelo de Sousa to identify the materials used in the support, preparation, paint and protection layers. The labels are placed in the back of the paintings.

Moreover, being interested in verifying the stability of the materials he uses, Ângelo has read several books about their properties and has performed his own tests (Figure 4.27) behind a glass, with a precise inclination in relation to the sun during the summer months.

Figures 4.27. Lightfast tests performed by Ângelo de Sousa. Top: on the left A – tests on paints prepared by Ângelo with PVAc and pigments supplied by Joaquim Simões, magenta is the only colour which shows a small loss of coloration; on the right B – tests performed on *Talens* acrylic paints, again magenta is the colour showing some discolouration. Bottom: several colouring materials, such as paints, crayons, pencils and pens.

When asked about how he finds and selects new materials for his work, Ângelo says ‘that is a matter of luck’[110]; he has an idea in his head and sooner or later something will come up.

After an initial period working with oil, casein and wax (encaustic), Ângelo de Sousa started using a vinyl medium for his paintings (Table 4.7). Later he used offset inks, acrylic paints and numerous drawing materials. He also made use of acrylic sheet (PMMA) and metals, like iron and steel, for sculpture, photographs and films [117,121].

Like other artists, as a painting student, Ângelo lived on a limited grant[111]. He experimented with oil but commercially available paints were very expensive. Therefore, he often made his own with boiled oil and lead or zinc white. The pigments he used depended on what was available at the drugstore. The long drying time of oils frustrated Ângelo so he began to explore other materials[112]. From 1956 to 1958 Ângelo used casein as his main painting medium and he would also prepare his canvasses with casein mixed with cheap pigments. At that time Ângelo found it hard to acquire prepared canvas in Portugal, at least in Porto where he lived. Also, he occasionally painted with household paints like *Ripolin*[113]. From 1958 until about 61 he experimented with encaustic; beeswax was warmed in a water-bath that was placed on sand to maintain the heat which would keep it soft longer. Ângelo would mix wax with the limited pigment pallet available, like iron oxides or even earth colurs he could find in the soil. If the wax contained some honey, it would have a yellowish colour and he could paint directly with it. Although Ângelo enjoyed the results obtained with encaustic, this was an extremely laborious technique and he had to move forward into something else. In 1961 Ângelo and António Quadros[114], started working with PVAc.

Ângelo had seen, in an English magazine called *The Studio,* a painting by Sidney Nolan, an Australian artist, catalogued as PVAc. One day Ângelo bought some white wood glue, which was described as PVAc, he thought it might have been what Nolan was using and tried it for a while himself. As Ângelo recalled the glue dried to a whitish film, but mixed with gouache, watercolours or pigments it worked fine. In 1961 a *Robbialac* worker gave him a poly(vinyl acetate) sample as well as some pigments. By that time he was introduced to engineer Ernestina Lima, who worked at *Soberana*[115] and she would provide him and António Quadros with a more transparent PVAc medium. ‘It was great’, Ângelo exclaims, ‘I would

---

[110] ‘*Isso é uma questão de sorte*.’ (Interview with Ângelo de Sousa, 2005; Appendix VI.1)

[111] Ângelo was a student (1955-1963) and a professor at the Fine Arts School in Porto (*Faculdade de Belas Artes da Universidade do Porto*, former *Escola Superior de Belas Artes do Porto*). As a student, Ângelo had a grant attributed by *Caixa Económica Postal*.

[112] In the period between 1960 and 1961 Ângelo worked again on a series of oil paintings.

[113] ‘A European brand name for a household enamel paint. Ripolin paints were used by Picasso (Mayer 1969).’ [176]

[114] António Quadros (1933-1994) was another painter who graduated from the Fine Arts School in Porto [177].

[115] An industrial paints’ manufactory in Porto area.

exchange ideas with Quadros and I don't even know which one of us used it first'[116]. Ernestina Lima also sold them high quality pigments. Ângelo prepared his own vinyl paints by mixing the emulsion with gouache, pigments and other things like gypsum or small paper pieces to create textures. He used PVAc for about ten years.

Ângelo believes his high school background in science influenced his work. He knew how to make use of tri or tetrachromy and decided to simplify his technique; he talked to someone who supplied offset ink colours and got 1 Kg cans of cyan, magenta, yellow, black and white as well as a can of medium[117]. Ângelo says 'it had the advantage of mixing with gasoline, which was cheap then, (…) and it would dry in twenty minutes'[118]. He would prepare some paperboards with matte household *Robbialac* paint and then painted with the offset colours. Ângelo painted directly on the paperboard and then had someone[119] glue them on to hardboard or plywood, using only the best ones and throwing the others away. During the 1960s Ângelo used PVAc and offset inks on and off. In the late 1970s, early eighties, Ângelo worked on a series of paintings for which he used other printing primary colours and black (*Van Son*'s serigraphic inks).

Since the 1970s Ângelo has used acrylic paints. Ângelo received support from a chemical engineer, Joaquim Simões[120] who for many years provided Ângelo with good quality paints[121], which he produced in the colours Ângelo needed. Throughout the years, he worked with his friends' paints and also with *Talens*'. On the *monochromatic* series he used yellow, red and blue acrylics only[122]. Besides the preparation with white paint, Ângelo has used *Talens*' acrylic gesso and *Talens*' varnish as a protective layer. For the last 10 years he has decided to use any colour in his paintings. He now has more than sixty different acrylic colours of different brands; he rarely uses primary colours. 'Now I use anything I think of!'[123].

Ângelo has always been concerned about protecting his paintings. When working with encaustic it was obvious to him that the wax layer was prone to trap the dust. There were no good quality commercial varnishes available in Porto and Ângelo found several varnish

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[116] '(…) *ficou bestial, entretanto ia trocando ideias com o Quadros e nem sei quem fez primeiro ou depois*, (…)'. (Interview with Ângelo de Sousa, 2005; Appendix VI.1)

[117] 'I hardly ever used the black, probably still have it somewhere, and never used the white'.

[118] '*Comecei a pintar com aquilo porque tinha a vantagem de misturar com gasolina que era mais barato; a terebentina era cara e tinha um cheiro horrível, a gasolina também, mas eu tinha um quarto ventilado; pintava com aquilo e vinte minutos depois estava seco, embora a espessura fosse maior que no caso do offset*.' (Interview with Ângelo de Sousa, 2005; Appendix VI.1)

[119] Mr Manuel Campos, who worked at the Fine Arts School in Porto.

[120] Introduced by a mutual friend, Nuno Barreto, who was also a painter and professor at the Fine Arts School in Porto.

[121] Although Ângelo initially referred to the paints as being acrylic, infrared analysis have shown they are vinyl emulsions. When asked to clarify this, Ângelo sated he does not recall if he was told by Joaquim Simões they were acrylic or vinyl based.

[122] As he recalls there was no magenta available and the similar colours were not lightfast; Ângelo tried to find acrylics as close to primary colours as possible.

[123] '*Agora uso tudo o que me dá na bolha*!' (Interview with Ângelo de Sousa, 2005; Appendix VI.1)

recipes in the Dörner's book. He bought dammar at a chemical drugstore and prepared a varnish to apply to the wax paintings. Most of the PVAc paintings were on paper, which made them unsuitable to apply a dammar protective layer; instead, Ângelo used wax dissolved in turpentine for a while[124]. Normally he would apply a PVAc layer over the painting and only then applied the wax for final protection. This became Ângelo's regular procedure, even when working with acrylics: a biding medium layer between the painting and the varnish. The dust lies on the varnish, being safer to remove than if directly on the paint.

> *It is now generally accepted that an overall awareness of the ways in which artists apply their materials is crucial to an appreciation of twentieth-century art. However the role played by the choice of those materials has frequently been overlooked.*
>
> Crook and Learner, 2000

Ângelo once mentioned that his work in part derives from the materials he uses [121]. As stated above, oils frustrated Ângelo. At the Louvre he saw some encaustic paintings from the end of the first millennium BC and the first millennium AD and found them interesting. In contrast to oil, wax would become hard immediately and Ângelo decided to try to work with this material. He was optimistic about it and thought he had considered all the problems about encaustic. Although it hardened very quickly, it was a laborious process. The available colour palette was reduced and Ângelo experimented with wax's relative transparency, translucency or opacity, depending on how it was applied and on what pigment was used. This was one of the wax's main plastic attractions and Ângelo got used to testing it. He enjoys spontaneity in the course of the work, which seems contradictory. How could one reconcile that experience with such a time-consuming technical process? In general Ângelo didn't have a precise plan and things would just happen. In some cases the surface of his paintings would be so rough after hardening that he had to sculpt them and some fissures would show the colour beneath the wax. The result of each step in the work would often lead to another.

Ângelo spent three months in Mozambique in the autumn of 1960. So far, colour had been a complex problem for him; initially, he was avoiding it with wax painting. In Mozambique Ângelo bought some oil colours and paper and felt at ease to work. He explains: 'if I had 20 sheets of paper and wasted 15, maybe I would have 5 good ones'[125]. He confesses he produced some unimportant works, which allowed him to understand how it all fitted together. He was no longer afraid.

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[124] Years later Ângelo concluded it was not a good protection.

[125] '*Com o papel cavalinho estava à vontade, se tivesse vinte folhas e estragasse quinze, talvez aproveitasse cinco*'. (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

In an interview conducted by Bernardo Pinto de Almeida [121], Ângelo said ‘I have the means to do other things, I will not paint with wax anymore’[126]. Nevertheless, there was something about the wax that still fascinated him; when he started painting with vinyls, Ângelo would mix small pieces of paper with the paint to create some wax like texture. He even tried to reproduce the translucency / opacity effect using different white pigments and to create relieves. It is interesting to notice how a particular composition appears on and on in his works, initially with the beeswax and oil paint and later with PVAc and offset ink. In a way, the later works are a remake of the initial series.

For Ângelo it was important to have a material which was inexpensive and would allow him to work fast. He explains ‘if I have a lot(...), it works’[127]. The idea was to feel comfortable and not worry about wasting paint, in the same way he felt about the paper. This was first accomplished with the vinyls and later with the offset inks. When he saw the reproduction of a PVAc painting by Nolan in *The Studio* magazine, Ângelo was excited to find out that artists were using something other than oil. The poly(vinyl acetate) had several advantages. Ângelo explained that one can make anything he wants with polyvinyl, whereas with oil one remains captive. ‘With polyvinyl it was a total impunity. (...) there were no bad results.’[128] He really appreciated the advantages of fast drying, low cost and availability. Ângelo was, and still is, interested in this kind of independence and autonomy.

When asked about how his mental project was formed considering the material he was using on a particular series, Ângelo explains the main differences between working with PVAc and with offset inks. The ink dries to a texture close to watercolour’s. In these works, Ângelo reduces the formal elements and simplifies the composition. Usually he did not have a preliminary design; these inks were so thin and incredibly fast drying that either he got it right within an hour or would put it away. His aesthetic concern was to make use of all four colours of ink that he had. With the PVAc Ângelo thickens the paint layer. He could follow a plan. This medium would allow him to go back, experiment and paint several layers somehow like an oil painting. His work has always been extremely experimental; it is about the materials and about painting itself.

Prior to his stay in England, in 1967, and after creating his first sculptures, Ângelo produced a series of abstract paintings (Figure 4.28). Here, Ângelo assumed the poly(vinyl acetate) materiality, he was not trying to recreate other techniques. It was PVAc mixed with watercolours or gouache. This was like enamel; he was no longer creating textures. In his

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[126] ‘*Portanto, se noutro momento, como agora, por exemplo, tenho meios para fazer outras coisas, já não vou voltar a pintar com cera,* (..)’. (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

[127] ‘(…) *se tiver muitos papéis funciona*’. (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

[128] ‘*Com o polivinilo era a impunidade total. Ninguém me castigava, não havia maus resultados’*. (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

own words, ‘it was almost industrial painting’[129]. Although these works were very rational and geometric, they had no preliminary design. They would just happen. Nevertheless, Ângelo created some rules that he would adapt throughout the process, to make it faster and more efficient. They were done by collage of painted pieces of paper on a white support, by painting random areas with a certain geometric figure or using adhesive tape to create areas that would be further painted. Ângelo exclaimed ‘There is a great arbitrariness in the process. The idea is to have rules of the game, rules for the game, but without being inflexible, that I do not do.’[130]

Figure 4.28. (Cat. 71.) *Geométrico Grande*, 1967. Poly(vinyl acetate) on hardboard, 170 x 138 cm. *Caixa Geral de Depósitos* collection, Lisbon; Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

There is a clear relationship between Ângelo’s sculpture and painting. Like the abstract paintings, his sculpture has a geometric and organic nature at the same time. Again, depending on the materials used, the work could be somehow random or could be done according to a project. The acrylic sheets were heated and then folded, this process was difficult to control and it was not possible to obtain a previously planned shape. On the contrary, with steel and aluminium Ângelo could make a sketch and figure out the final

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[129] ‘*Era quase pintura industrial*.’ (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

[130] ‘*Há uma parte muito grande de acaso nisto tudo. A ideia é ter regras do jogo, regras para o jogo, mas não uma rigidez de não sair dali, isso não faço*.’ (Interview with Ângelo de Sousa, 2008; Appendix VI.2)

format. He explained ‘it was a game for which I already knew the result’. These works are not sculpture in its traditional sense; Ângelo finds the three dimensions from a pre-existing volume or even creates that volume. He researches the ways in which a flat form can be transformed into a three dimensional object and what are the possibilities for that to happen and to give mobility to the sculpture. Ângelo is curious and enjoys experimenting. He is able to benefit from all possibilities of materials both in formal and aesthetic aspects.

4.3.1.1 Summary

Following what was described above and with further clarification on some topics, it is possible to summarize the main events concerning the painting materials used by Ângelo de Sousa (Table 4.7). For the first experiments with vinyl medium, Ângelo used commercial white glue. After that, he started to work with a PVAc binding medium supplied by *Soberana*, a Portuguese paint manufactory. The support used in these works was mainly paper or paperboard. The works that Ângelo considered worthwhile were glued onto hardboard or plywood. In some cases, he could also paint directly on hardboard or on jute canvas. The paintings on hardboard were made on the screen pattern side, as Ângelo considered it would allow a better adhesion of the paint to the support, except in cases where the board was reused and the paint was applied on the smooth side. The canvas was, and still is, bought in rolls and stretched by Ângelo. This last operation is now performed by a carpenter who was taught by Ângelo. For the preparation layer, PVAc mixed with a white pigment (although it was bought as *alvaiade*, Ângelo could not confirm if it was lead- or zinc-based) or industrial white vinyl paints[131] was used; depending on the support several layers were applied until a fine surface was obtained. The colour paints were prepared by the artist by mixing the binding medium with gouache, watercolours, or pigments (usually kept for special tasks as, during those times, good quality pigments were difficult to find). For texture effects, Ângelo sometimes mixed small pieces of sketch or toilet paper, or even sawdust. The paint layer was further protected with beeswax or wax over a layer of PVAc medium (for extra protection and easier removal of the wax layer if needed) and later with acrylic varnish by *Talens*[132].

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[131] According to Ângelo the white paint was probably by *Soberana* or *Barbot* (Porto).

[132] As Ângelo concluded wax was not a good protection, in the 1980s he removed the wax layer from some vinyl paintings, with white erasers, and protected them with acrylic varnish *à tableaux* (*Talens*).

Table 4.7. Summary of the painting materials and techniques used by Ângelo de Sousa

Oils Mozambique, 1953-55; 1960 Porto, 56-61	***Support***: paperboard; cotton fabric; hardboard; paperboard glued on hardboard ***Preparation***: alkyd (*Ripolin*); casein + *alvaiade*[a] ***Paints***: tube paints; the white was prepared with linseed oil + *alvaiade* ***Protective varnish***: -
Casein Porto, 1956-58; 1960s	***Support***: jute ***Preparation***: casein + *alvaiade* ***Paints***: casein (dairy store SUIL)[b] + pigments; tube casein temperas (*Talens*)[c] ***Protective varnish***: -
Wax Porto, 1958/59 - 61/62	***Support***: hardboard ***Preparation***: - ***Paints***: warm beeswax + pigments (*alvaiade*, iron oxides, 'earth pigments' prepared by himself and cigarette/cigar ashes); yellow wax (coloured due to the presence of honey) ***Protective varnish***: Dammar
Poli(vinyl acetate) Porto, 1961-62; 67; 1971-73	***Support***: paperboard; jute; hardboard; paperboard glued on hardboard ***Preparation***: industrial white vinyl paints ***Paints***: PVAc emulsion[d] + gouache or watercolours, pigments[e]; for texture: sketch paper, toilet paper or sawdust ***Protective varnish***: wax; PVAc layer + wax; acrylic varnish *à tableaux* (Talens)[f]
Offset Inks Porto, 1964-66	***Support***: paperboard; paperboard glued on hardboard ***Preparation***: industrial white vinyl paints ***Paints***: offset inks diluted with petrol ***Protective varnish***: -
Acrylics Porto, 1972-	***Support***: commercial canvas, hardboard ***Preparation***: industrial white vinyl paint + acrylic gesso (*Talens*) ***Paints***: acrylic tube paints (*Talens*; others more recently) ***Protective varnish***: acrylic medium layer + acrylic varnish *à tableaux* (Talens)

[a] Strictly the Portuguese word "alvaiade" translates as ceruse (basic lead carbonate) [178]; according to the artist the salesman did not know if it was a lead or zinc based white pigment.

[b] For academic works Ângelo would paint with casein, a fast drying medium, and finish with a layer of linseed oil to mimic oil painting.

[c] Only a few paintings in the early 1960s.

[d] The first vinyl emulsion that Ângelo used was a white wood glue, followed by a PVAc medium by *Soberana*.

[e] Pure colours; durable pigments.

[f] Applied in the 1980s.

As for Joaquim Rodrigo, colour is of particular importance for Ângelo de Sousa. Nevertheless, these artists have very different approaches to exploring and constructing colour. Unlike Rodrigo, Ângelo prefers the intensity of pure colours, and for a long period in his career, he used mainly bright yellows, reds, blues, and greens, *i.e.*, primary colours or as close to them as possible. Except in some cases in which he mixed the colours to obtain a precise hue, the final colour was achieved by superimposition of different paint layers (Figure 4.29).

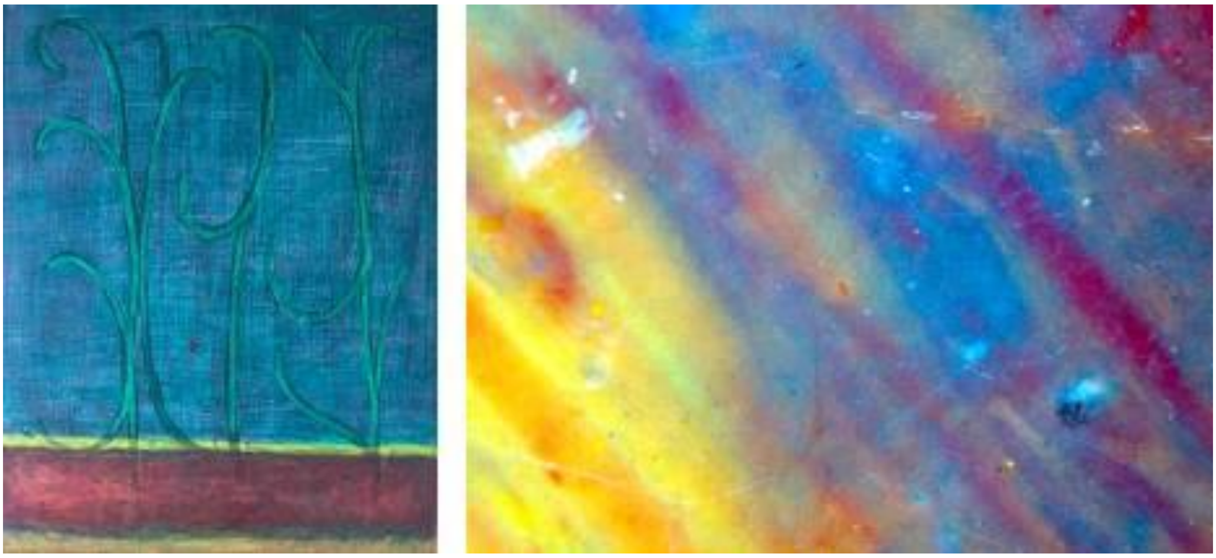

Figure 4.29. Left - *Plantas*, Ângelo de Sousa (1962); Right - detail from *Plantas* (30x).

> *Ângelo, throughout his whole life, did no more than conceive sets of movement of colour: he is a colourographer. A painter intoxicated with and addicted to colour: a chromo-addict.*[133]
>
> José Gil, 1993

4.3.2 Characterization – materials and conservation condition

The five paintings analyzed in this study (Appendix VI.3) were selected, with the artist, as examples of Ângelo's first vinyl works, and the samples were collected in his studio.

4.3.2.1 Painting materials and techniques: molecular approach

A description of the paint samples collected from Ângelo's studio as well as the results on the colourants and fillers is presented in Table 4.8 (infrared and Raman peaks assignment is depicted in Tables 4.9 and 4.10 for the pigments identified). From the infrared spectrum it was possible to conclude that, with the exception of *Sem título* (study) painted in 1964,

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[133] '*Ângelo, em toda a sua vida, não fez mais do que conceber conjuntos de movimentos de côr: é um côreógrafo. Um pintor bêbado, toxicodependente da côr: um cromómano*.' [119]

Ângelo used a PVAc homopolymer (this will be further discussed). In the painting *Natureza Morta* (1965), only the white preparation/background layer was prepared with PVAc and it was the only colour analysed in this work (according to Ângelo, offset inks were used for the colours). A phthalate plasticizer was possibly still present (Figure 4.30), as indicated by its absorption at 1073 cm^{-1}, in the samples with a clear window for this region. The painting *Árvore,* from 1962, presents a homogeneous protection layer identified as wax (with infrared absorption peaks at 2920 and 2850 cm^{-1} [171]), in agreement with Ângelo's description of his usual procedure. It is also important to stress here that, for these works, Ângelo would prepare the colour paints by mixing the vinyl binder mainly with gouache colours; the presence of gouache, depending on its nature and concentration, may imprint some changes in the PVAc spectrum. Spectra for all paintings are presented in Appendix VI.4.

Table 4.8. Colourants and fillers found in Ângelo de Sousa's paintings

			µ–FTIR	**µ–EDXRF**	**µ–Raman**	**Observations**
 *Sem título,*1961/2	Whitish	○	$BaSO_4$ clay mineral [a]	**Zn**, **Pb**, **Ba**, Fe, Ca, Si, Al, K, Mg	Ultramarine	Sample with several layers
	Red	🔴	Organic based colourant	**Zn**, **Ba**, **Fe**, Pb, Ca, K, Ni, Si	Organic based colourant	Over a metallic platelets layer
	Green	🟢	**-**	**Ba**, **Zn**, Fe, K, Ca, Se, Cu, S, Cd	Hostasol green [b]	Green transparent layer with red spots
 *Plantas,* 1962	Red	🔴	-	**Zn**, **Ba**, Cu, Ca, S	Organic based colourant	-
	Green	🟢	-	**Ti/Ba**, **Zn**, Fe, Ca, K	Hostasol green [b]	-
 *Sem título* (study), 1964	White	○	$BaSO_4$	**Zn**, **Ba/Ti**, Ca, Fe, S, Si	TiO_2, $BaSO_4$	Over a green layer
	Green	🟢	$BaSO_4$ Prussian Blue	**Zn**, **Ba**, S, Ca, Fe, Co	Hostasol green [b]	Over a thick white layer
	Light blue	🔵	$BaSO_4$	**Zn**, **Ba**, S, Ca, Fe, Co	Phthalocyanine	Over a thick white layer
	Dark blue	●	-	[c]	[c]	-
 *Natureza Morta*, 1965	White	○	$BaSO_4$	**Zn**, **Ba**, S, Ca	$BaSO_4$	-

[a] Fingerprint similar to talc [$Mg_3Si_4O_{10}(OH)_2$]. [b] Possibly a xanthene yellow dye with a blue pigment (see text for more details).
[c] It was not possible to recuperate the µ-sample after IR and therefore µ-EDXRF and µ-Raman analysis were not performed for this sample.

Table 4.9. Infrared assignment for the pigments in the paint samples from Ângelo de Sousa

Compound identified	**Band (wavenumber/cm^{-1})**	**Reference**
Barium sulfate ($BaSO_4$)	~1180(sld), 1120(sld), 1079(vs), 984(w)	[160]
Prussian blue ($Fe_4[Fe(CN)_6]_3$)	~2100 (w)	[171]
Talc [$Mg_3Si_4O_{10}(OH)_2$]	3678(vw), 1018(vs), 670(m)	[160]

m – medium; sld – shoulder; vs – very strong; vw – very week; w – week.

Table 4.10. Raman assignment for the pigments in the paint samples from Ângelo de Sousa

Compound identified	**Band (wavenumber/cm^{-1})**	**Reference**
Barium sulfate ($BaSO_4$)	453(m), 461(w), 616(w), 647(w), 988(vs)	[173]
Titanium dioxide (TiO_2)[a]	141(w), 233(m), 445(vs), 610(vs)	[174]
Ultramarine blue ($\sim Na_7Al_6Si_6O_{24}S_3$)	257(m), 290(sld), 548(vs), 584(sld), 807(m), 1096(s)	[172]

[a] Rutile crystalline form.

m – medium; sld – shoulder; vs – very strong; w – week.

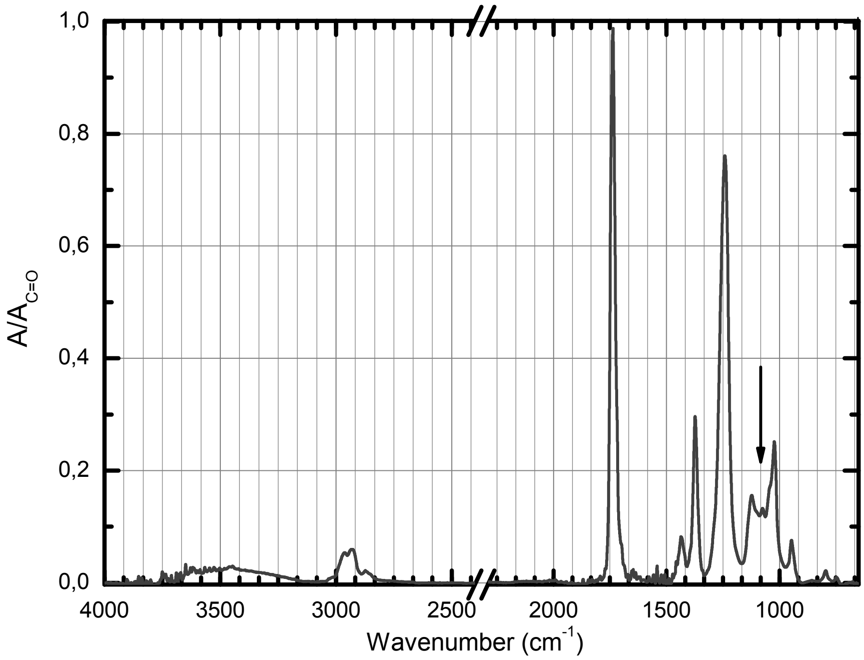

Figure 4.30. Infrared spectra of green sample from *Sem título* by Ângelo de Sousa (1961-62), with absorptions normalized for the C=O stretching. The arrow indicates a characteristic absorption of the plasticizer (phthalate).

Organic pigments and dyestuffs

Organic pigments or dyestuffs were the main colourants used in the paintings studied, namely for greens, blues, and reds. Concerning the red samples, it was not possible to identify the colourant present, but both by infrared small peaks at approximately 1448, 1474, 1501, 1563 and 1619 cm^{-1} (Figure 4.31 A) and Raman fingerprint (Figure 4.31 B), they could be assigned to an organic pigment or dyestuff. Three green samples are tentatively described as hostasol green, based on the best match for the Raman spectra (Figure 4.32 A); this green dye is possibly a mixture of a xanthene yellow dye (also referred to as hostasol yellow) with a blue pigment. Although in the green paint samples from *Sem título* (1961-62) and *Plantas* (1962) μ-EDXRF revealed the presence of copper (Figure 4.32 B), it was not possible to relate it to any pigment by Raman or infrared probably due to its low concentration. On the other hand, it was possible to find Prussian blue in the infrared spectrum (2094 cm^{-1}, Figure 4.32 C) of the green sample from *Sem título* (study) (1964). The light blue from the same painting was identified by μ-Raman as phthalocyanine (Figure 4.33 A); the element found was cobalt (Figure 4.33 B), and therefore it is most likely a cobalt phthalocyanine.

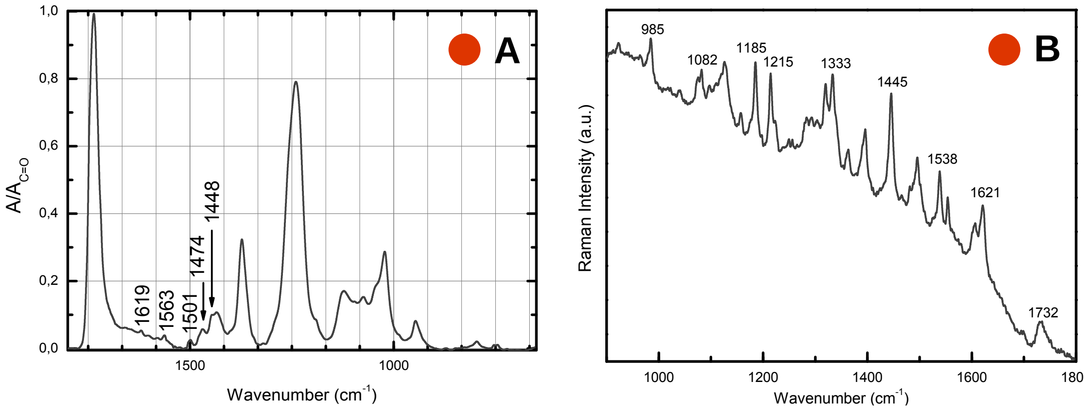

Figure 4.31. Representative spectra of colourants found in a red sample from *Sem título,* 1961-62*:* A – infrared spectrum (organic red); B – Raman spectrum (organic red).

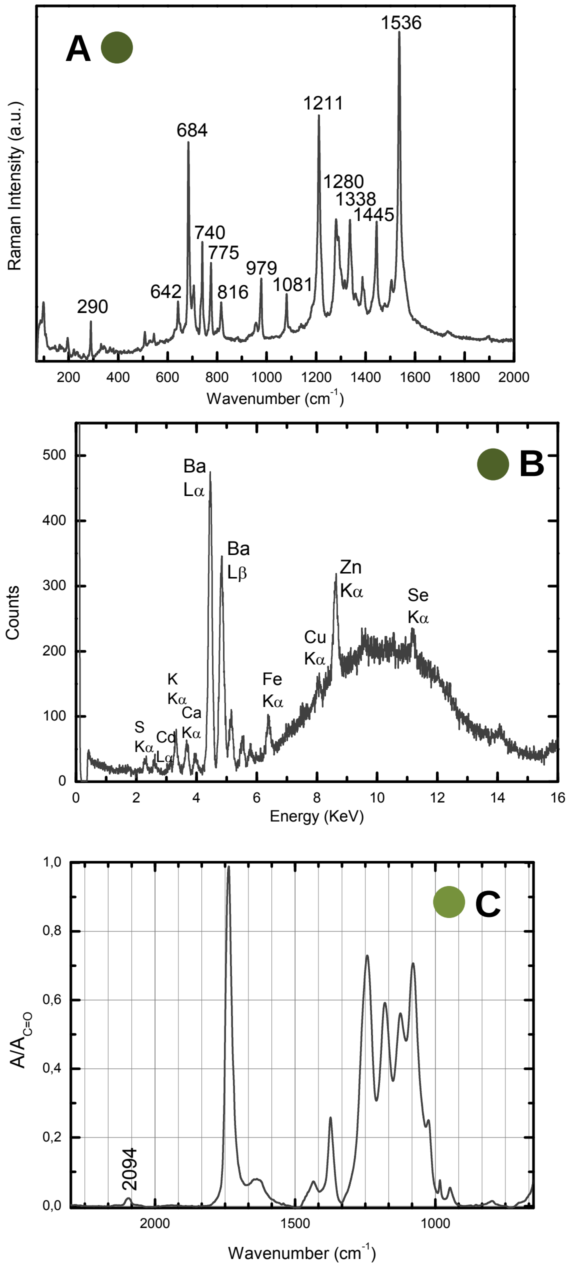

Figure 4.32. Representative spectra of colourants found in green samples from the works by Ângelo de Sousa: A and B – Raman (hostasol green) and EDXRF specta (Cu) - *Sem título*, 1961/2; C – infrared spectrum (Prussian blue) - *Sem título* (study), 1964.

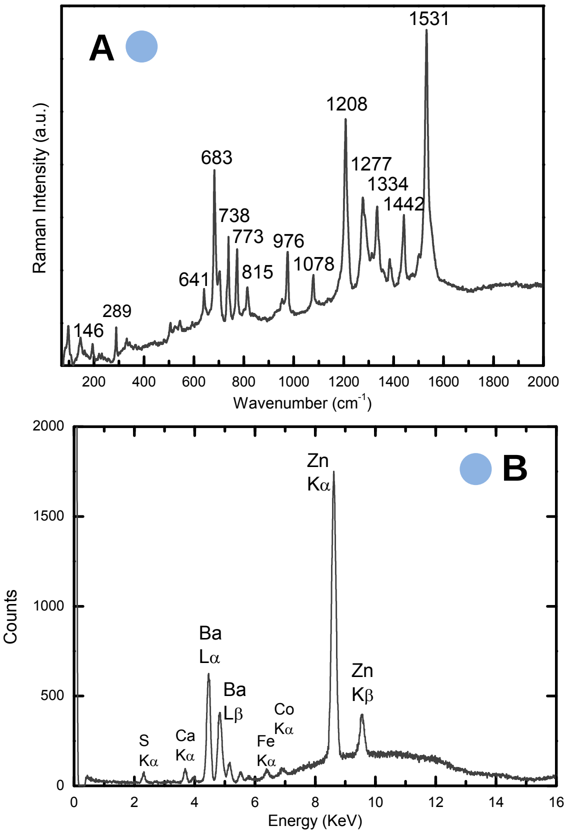

Figure 4.33. Representative spectra of colourants found in a light blue sample from *Sem título* (study), 1964: A – Raman spectrum (phthalocyanine); B – EDXRF spectrum (Co).

Inorganic pigments and/or extenders

In the 10 paint samples analysed, the main inorganic compounds found were white pigments or extenders. Titanium white, mainly the in rutile form, was identified by μ-Raman (Figure 4.34 A) in the white sample from *Sem título* (study) (1964) and in two other samples where titanium was the major element identified. In all studied samples, zinc and barium were found (Figure 4.34 B). In five of the ten analysed samples, barium sulfate could be identified both by infrared (Figure 4.34 C) or/and by Raman (Figure 4.34 A). This suggests that lithopone or a mixture of barium sulfate plus zinc oxide may be present in all paintings as fillers and/or in the preparation (Table 4.8). A talc type clay mineral was also identified in the whitish paint sample from *Sem título* (1961-62) by its infrared fingerprint with peaks at 670, 1016 and 3677 cm^{-1} (Figure 4.35 A). Besides the whites, ultramarine blue and aluminium based metallic platelets were the only inorganic pigments identified, and both were from the same painting (*Sem título*, 1961-62). The ultramarine was identified in the whitish paint sample by its characteristic Raman peaks at 258, 546, 579, 812, 1091 cm^{-1} (Figure 4.35 B); although it has a characteristic fingerprint, this pigment was not found in the infrared spectrum, which may be explained by its presence as a very thin layer. According to Ângelo, in some paintings he used good quality aluminium platelets or copper-based pigments. The copper-based pigments soon became green. Identification of the aluminium-based platelets was possible by the presence of that metal (μ-EDXRF, Figure 4.35 C) in the sample and confirmed by its pristine appearance.

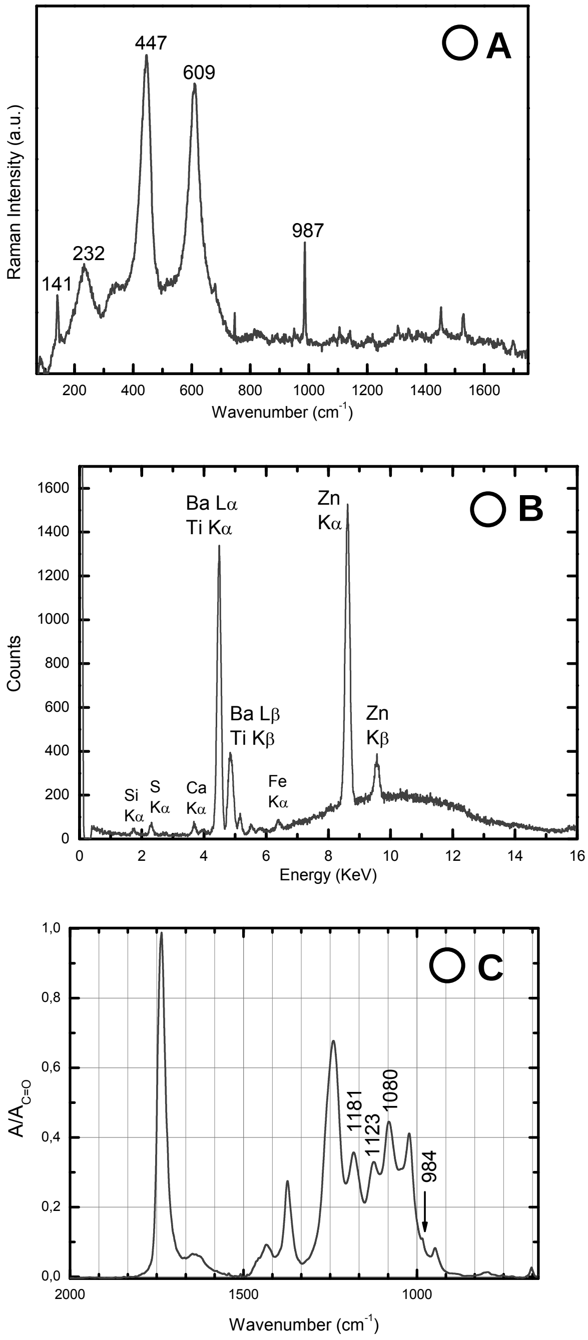

Figure 4.34. Representative spectra of colourants found in of a white sample from *Sem título* (study), 1964: A – Raman spectrum (titanium dioxide - rutile - and barium sulfate); B – EDXRF spectrum (Ti, Ba, Zn, S); C – infrared spectrum (barium sulfate).

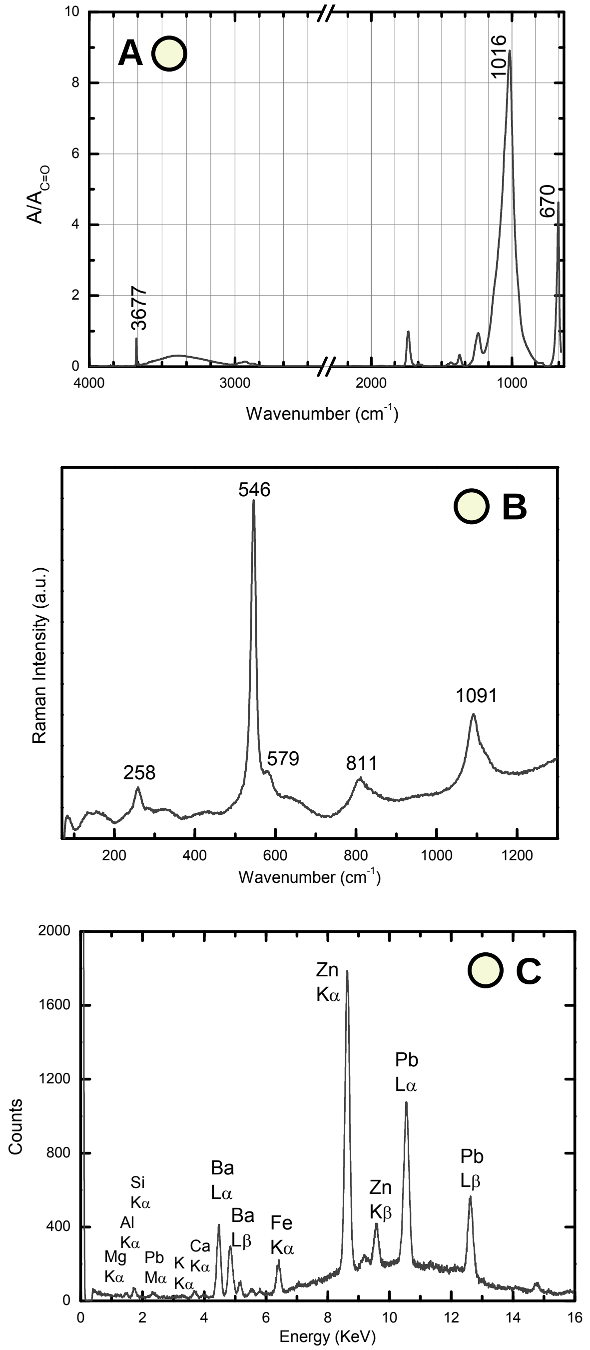

Figure 4.35. Representative spectra of colourants found in of a whitish sample from *Sem título* – 1961-62: A – infrared spectrum (talc); B – Raman spectrum (ultramarine); C – EDXRF spectrum (Al).

Colour construction

As previously mentioned, in the works by Ângelo de Sousa the colour is constructed by superimposition of several paint layers rather than by pigment mixture (Figure 4.29). The whitish paint sample from *Sem título* (1961-62) is presented as a representative example in which it was possible to characterize the different layers, Figure 4.36. In the top, a whitish layer of a barium based white is present with small orange grains. The second layer is an organic red painted over aluminium-based metallic platelets. The pigment from the thin bottom layer found in the sample (not the preparation layer) was identified as ultramarine blue, possibly with talc as extender.

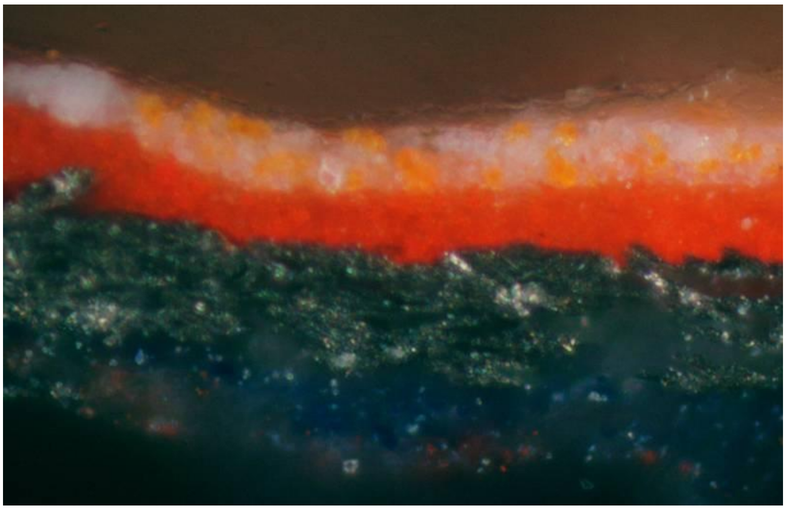

Figure 4.36. Cross-section (amplification, 40x) from *Sem título*, 1961-62, whitish area, in which it is possible to distinguish four different layers.

Binding medium

The binding media used by Ângelo the Sousa, in the majority of the studied paints, was a PVAc homopolymer. The painting *Sem título* (study) (1964) was an exception, and the dark blue paint sample is the one that differs the most from a PVAc homopolymer, Table 4.11. The infrared analysis suggests the presence of a vinyl-acrylic copolymer (or a mixture of both). In this sample, the C=O absorption is shifted towards lower wavelengths (1735 cm^{-1} versus 1739 cm^{-1}) and presents a broadening of *ca* 36% when compared to a PVAc homopolymer (Table 4.11). Also, the $\delta CH_3/\nu C{=}O$ and $\nu C\text{-}O/\nu C{=}O$ ratios are lower than those ascribed to a PVAc homopolymer (Table 4.11), with a shift on the main C-O peak and broadening of the C-H_2 bending. Furthermore, a peak at 1165 cm^{-1} is ascribed to a C-C stretch not present in the fingerprint region of PVAc. The red sample collected from *Sem título* (1961-62) also presents some different features; although the main peak ratios (Table 4.11) are in agreement with what characterizes a PVAc homopolymer, the carbonyl peak is found at 1735 cm^{-1} and presents a small broadening (peak width at half maximum is 22.83) when compared with the unaged homopolymer (Table 4.11).

Concerning the assessment of the conservation condition of the binder, for the cases in which it was possible to have a clear window for the main diagnostic peaks, the δCH_3/ $\nu C{=}O$ and $\nu C\text{-}O/\nu C{=}O$ ratios are in agreement with those displayed by a PVAc unaged emulsion, Table 4.11. The broadening for the carbonyl band was also below 8%, again in agreement with an unaged PVAc. Furthermore, as observed for Joaquim Rodrigo paintings, the paint films are in a very good conservation condition, presenting no signs of cohesion or adhesion losses.

Table 4.11. Paint samples from the paintings by Ângelo de Sousa: infrared absorptions at 1373 cm^{-1} ($\delta_{C\text{-}H_3}$) and 1242 cm^{-1} ($\nu_{C(=O)\text{-}O\text{-}C}$), normalized for ($\nu_{C=O}$), at 1738 cm^{-1}; and fitting parameters for the C=O absorption, peak centre (μ), full width at half maximum (σ) and correlation coefficient (ρ) (Gaussian function)

Sample		$\delta_{C\text{-}H_3}$	$\nu_{C(=O)\text{-}O\text{-}C}$	$\nu_{C=O}$		
				μ	σ	ρ
Sem título 1961/2	White/Red	0.34	-	1738.1	19.65	*0.994*
	Red	0.33	0.79	*1735.4*	*22.83*	*0.973*
	Green	0.30	0.76	1737.2	21.32	*0.990*
Plantas 1962	Binder	0.29	0.74	1738.0	20.04	*0.990*
	Red	0.30	0.75	1737.6	20.20	*0.991*
	Green	0.29	0.74	1737.5	20.25	*0.987*
Sem título (study) 1964	White/Green	0.28	[a]	*1735.9*	*23.07*	*0.978*
	Green	0.26	[a]	*1736.7*	*22.61*	*0.975*
	Light blue	0.28	[a]	1737.9	20.75	*0.988*
	Dark blue	0.24	0.56	*1735.2*	*26.79*	*0.980*
Natureza Morta 1965	White	0.31	[a]	1738.5	19.84	*0.996*
PVAc standard		0.31	0.77	*1738.5*	*19.72*	*0.933*
Vulcano V7		0.28	0.72	*1737.6*	*20.68*	*0.988*

[a] Although the C-O absorption is masked by the presence of barium sulfate; the C=O/C-O ratio is still lower than that presented by the standard samples.

The same was observed for the vinyl emulsions which had been acquired from one of Ângelo's suppliers, engineer Joaquim Simões, and stored in glass bottles (Figure 4.37), Table 4.12. Besides the peaks ascribed to the polymer, the spectra from these emulsions present some peaks due to an additive present in the emulsion formulation, namely in the C-H stretching region (*ca* 2960, 2930, 2874 and 2961 cm^{-1}) and at 1174 cm^{-1}.

Figure 4.37. Examples of the vinyl emulsions supplied by Joaquim Simões stored in glass containers and vinyl emulsions supplied by *Soberana* kept in plastic bottles; in the smaller plastic bottle the emulsion had been diluted with extra water, the emulsion in the larger bottle has become a yellowish gel.

Table 4.12. Varnish and vinyl paint medium from Ângelo’s studio : δC-H$_3$ and ν**C(=O)-O**-C, infrared absorptions normalized for νC=O; and fitting parameters for the C=O absorption, peak centre (μ), full width at half maximum (σ) and correlation coefficient (ρ), with a Gaussian function

		$\delta_{C\text{-}H_3}$		$\nu_{C(=O)\text{-}O\text{-}C}$			$\nu_{C=O}$	
		(norm)	*$(cm^{-})^{1}$*	(norm)	*$(cm^{-})^{1}$*	μ	σ	ρ
Varnish JS[a]	Gloss	0.30	*1373*	0.74	*1242*	1738.2	20.35	*0.990*
	Mate	0.33	*1373*	0.78	*1242*	1738.0	21.03	*0.992*
	Gel	0.28	*1373*	0.72	*1242*	1738.7	19.41	*0.995*
Emulsion *Soberana*[b]	v1[c]	0.36	*1373*	0.80	*1245*	1732.4	27.69	*0.959*
	v2[d]	0.33	*1373*	0.75	*1242*	1735.9	21.92	*0.972*
	v1 aged	0.38	*1373*	0.82	*1249*	1728.3	33.04	*0.962*
	v2 aged	0.49	*1375*	0.91	*1255*	1723.6	34.69	*0.961*
PVAc standard		0.31	*1373*	0.77	*1242*	1738.5	19.72	*0.993*
PVAc + PVAL (90:10)		0.31	*1373*	0.77	*1242*	1738.0	21.41	*0.994*
PVAc + PVAL (80:20)		0.34	*1373*	0.76	*1242*	1737.3	23.63	*0.982*
PVAL (≈ 90% hydrolysed)		0.75	*1375*	1.10	*1252*	1727.5	35.80	*0.933*

[a] JS – Joaquim Simões was Ângelo’s paint supplier; [b] Portuguese paints manufactory in Porto; [c] yellowish gel; [d] sample diluted in extra water.

On the other hand, the analysis of the emulsion samples from *Soberana*, kept in plastic bottles at the artist’s studio for over thirty years (diluted and undiluted with water, which became a yellowish gel), Figure 4.37, gave different results. These samples have been kept in the laboratory, during 4 years, both on glass slides and in small plastic containers (a 1.5 mL Eppendorf). In 2005, the first spectra acquired (Figure 4.38 A) showed the presence of PVAL, up to 10 - 20% and may indicate that the emulsion had undergone hydrolysis (Table 4.12). The same films have been analyzed after four years and have not changed. In contrast, the sample kept in the *Eppendorf* (Figure 4.38 B) reveals that the hydrolysis reaction has not stopped, especially in the case where the emulsion is mixed with extra water, in which a conversion of PVAc into PVAL of approximately 50% (in volume) is observed (according to the O-H/C=O ratios obtained from computer simulations and confirmed by reconstructions of PVAL on a PVAc matrix, Appendix IV.1.6). These results point to the fact that a PVAc film may be stable whereas the same polymer in an aqueous emulsion may undergo extensive acidic hydrolysis with consequent loss of the ester function, which is transformed into an alcohol. The reaction is likely to be auto-catalyzed in the presence of water by the release of acetic acid which, when enclosed in a small container, becomes highly concentrated.

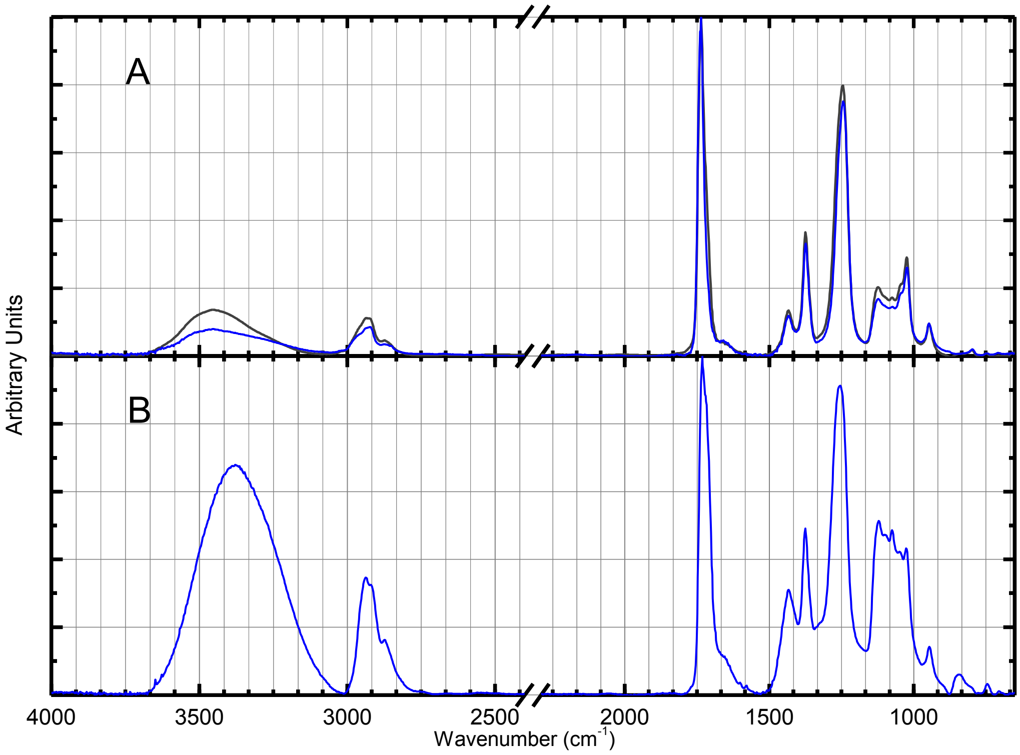

Figure 4.38. Infrared spectra for two samples, v1 (yellowish gel) and v2 (diluted in extra water), of a PVAc emulsion from the Portuguese company *Soberana*: A - v1 (black line) and v2 (blue line); B - v2 naturally aged as a wet emulsion. Please see text for more details.

The acidity of the *Soberana* sample naturally aged as a wet emulsion (v2) was confirmed by its pH = 2.4. Furthermore, the pH of three *Vulcano V7* emulsions (kept in plastic containers) was also measured. Two emulsions that have been kept in closed containers, *i.e.*, not frequently opened to use, for approximately five and ten years were acidic, with pH values of 3.7 and 2.8, respectively. The third emulsion, which has been continuously used for five years, presents a neutral pH (6.7). These data suggest that the acidity of the PVAc in emulsions is possibly related with free acetic acid present in the formulation, from the polymer synthesis, which could catalyse its hydrolysis. With a continuous use of the emulsion, for which the container is open, the acid is released and the emulsion becomes neutral. On the other hand, the apparent decrease of pH with time in closed containers is probably related with the acidic hydrolysis of the PVAc, leading to the formation of PVAL and acetic acid (with an increase in its concentration).

4.4 *Sabu* paints catalogue

New, Plastic, Modern-Opaque tempera colours
Sabu advertisement, 1950s/60s

4.4.1 The *Sabu* hand-painted catalogue

Until the 1970s, *A Favrel Lisbonense* produced hand-painted catalogues for its colours, Figure 2.11. For the research on the vinyl based artist's paints available for Portuguese artists one of those catalogues made with the original paints from the *Sabu* line, which used a PVAc emulsion as binding medium (see Chapter 2.2) was studied. The catalogue is a 16.3 x 20.1 cm piece of cellulose cardboard, with 21 colours applied on 2.7 cm equilateral cardboard triangles. As described in Chapter 2.2, the *Sabu* paints were produced with *Vinamul* emulsions. Although, we were only able to find indication on the specific *Vinamul* references used since 1985. It is also known that on the production of the *Sabu* line the pigments were first mixed with an extender and a cellulose ether in a three-roller mill. Afterwards the paste obtained was mixed with the *Vinamul* vinyl emulsion and sieved to a smooth and clean paint.[134]

4.4.2 Characterization – materials and conservation condition

The vinyl binder used on the twenty one vinyl artists' colours as well as the colorants and fillers are characterized by μ-FTIR, μ-Raman (infrared and Raman peaks assignment may be found in Table 4.13 and 4.14) and μ-EDXRF. For all colours, μ-sampling mapping and spectra are represented in appendix II.3 and II.4. The effect of metallic ions, present as pigments and fillers, on the conservation condition of the binder is evaluated by μ-FTIR and Size Exclusion Chromatography (SEC). It is worth to mention that being paints in a catalogue only seldom they have been exposed to light. Possible degradation mechanisms and pathways, such as crosslinking and chain scission, are analyzed.

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[134] According to Ricardo Caiado, Favrel's manager from 2002 to January 2006, this was the procedure followed during the last years of production. There is also a reference to a cellulose ether, and also to a second unidentified medium (possibly the same used in the *Vulcano V7* formulation) as part of the paint formulation on a notebook from 1978.

Table 4.13. Infrared assignment for the pigments in the paint samples from *Sabu* catalogue

Compound identified	**Band** (wavenumber/cm^{-1})	**Reference**
Barium sulfate ($BaSO_4$)	~1180(sld), 1120(sld), 1079(vs), 984(w)	[160]
Calcium carbonate ($CaCO_3$)	~1430(vs) , 877(m)	[160]
Chrome yellow ($PbCr_4$)	905(sld), 858(s), 833(sld)	[160]
Copper phthalocyanine ($C_{32}H_{16}N_8Cu$)	1611(m), 1587(w), 1507(s), 1466(m), 1422(m), 1334(s), 1288(s), 1167(m), 1120(vs), 1093(vs), 1068(w), 901(m), 863(m), 802(w), 772(m), 753(m), 723(vs)	[162]
Goethite (FeOOH)	798(m), 904(m), 3138(m)	[160]
Manganese blue [xBa(MnO_4)$_2$.$y$$BaSO_4$]	1435(sld), 1404(m), 1366(m), 1104(vs), 984(w), 873(w)	[160]
Ultramarine blue (~$Na_7Al_6Si_6O_{24}S_3$)	1015(vs), 700(m), 660(m)	[160]
Prussian blue ($Fe_4[Fe(CN)_6]_3$)	~2100 (w)	[171]
Zink yellow ($K_2O.4ZnCrO_4.3H_2O$)	3460(m), 955(s), 880(vs), 815(s), 718(vw)	[160]

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very week; w – week.

Table 4.14. Raman assignment for the pigments in the paint samples from *Sabu* catalogue

Compound identified	**Band** (wavenumber/cm^{-1})	**Reference**
Calcite ($CaCO_3$)	157(vw), 282(vw), 1088(vs)	[173]
Carbon (C)	1328(vs), 1580(vs)	[173]
Chrome yellow ($PbCrO_4$)	135(m), 324(vw), 336(w), 357(s), 375(m), 399(w), 838(vs)	[173]
Chrome orange (Pb_2CrO_5)	145(m), 322(w), 341(m), 354(vw), 380(m), 824(vs), 836(s), 846(vs)	[172,179]
Goethie (FeOOH)	247(m), 300(m), 387(vs), 485(w), 552(m)	[174]
Hematite (Fe_2O_3)	224(s), 245(w), 291(vs), 411(m), 611(m), 1330(m)	[174]
Manganese Blue [xBa(MnO_4)$_2$.$y$$BaSO_4$]	316(w), 354(s), 378(m), 771(vs), 982(s), 1059(vw)	Standard sample
Titanium dioxide (TiO_2)[a]	141(w), 233(m), 445(vs), 610(vs)	[174]
Ultramarine blue (~$Na_7Al_6Si_6O_{24}S_3$)	257(m), 290(sld), 548(vs), 584(sld), 807(m), 1096(s)	[172]

[a] Rutile crystalline form.

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very week; w – week.

4.4.2.1 *Sabu* catalogue: molecular approach

The colours from the *Sabu* catalogue

As can be observed from Table 4.15, a restricted number of pigments was used to obtain all 21 colours present in the hand-painted catalogue. With the exception of some iron oxide based colours and ultramarine, paint names do not reflect the pigment composition. For example, S13-Cobalt blue paint is made of ultramarine and S16-Prussian blue with a phthalocyanine.

Table 4.15. Main pigments and extenders identified on the *Sabu* catalogue. The analytical techniques used for the pigment identification are marked with Δ

Sample	Pigments and extenders	μ-FTIR	μ-Raman	μ-EDXRF
S 10 Grey	Red iron oxide		Δ	Δ
	Carbon-based black		Δ	
	Titanium white		Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate[a,b]	Δ	Δ	Δ
S 11Raw Umber	Umber[c,d]	Δ	Δ	Δ
S 14 Ochre	Yellow iron oxide[c]	Δ	Δ	Δ
S 15 Raw Sienna	Sienna[c,d]	Δ	Δ	Δ
S 29 Sepia	Umber[c,d]	Δ	Δ	Δ
S30 Burnt Sienna	Red iron oxide		Δ	Δ
	Calcium carbonate	Δ		Δ
S 12 Ultramarine	Ultramarine blue	Δ	Δ	Δ
	Calcium carbonate	Δ		Δ
S 13 Cobalt blue	Ultramarine blue	Δ	Δ	Δ
	Titanium white		Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate	Δ		Δ
S 16 Prussian blue	Phthalocyanine blue[e]	Δ	Δ	Δ
	Calcium carbonate	Δ		Δ
S 17 Turquoise blue	Manganese blue	Δ	Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate[f]	Δ		Δ
S 18 Emerald green	Chrome green[g]	Δ		Δ
	Dyestuff		Δ	
	Lithopone	Δ		Δ
	Calcium carbonate	Δ		Δ

Sample	Pigments and extenders	μ-FTIR	μ-Raman	μ-EDXRF
S 27 Véronèse green	Zinc yellow	Δ		Δ
	Dyestuff		Δ	
	Lithopone	Δ		Δ
S 28 Cyanine green	Lead chromate based	Δ	Δ	Δ
	Dyestuff		Δ	
	Calcium carbonate	Δ		Δ
S 19 Chinese vermillion	Lead chromate based[h]		Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate	Δ		Δ
S 20 Madder carmine	Dyestuff[h]			
	Calcium carbonate	Δ		Δ
S 21 Manganese violet	Dyestuff[h]			
	Ultramarine blue		Δ	Δ
	Lithopone[b]	Δ		Δ
S 22 Cyanine magenta	Dyestuff[h]			
	Ultramarine blue	Δ	Δ	Δ
	Lithopone[b]	Δ		Δ
S 23 Monolite pink	Dyestuff[h]			
	Lithopone[b]	Δ		Δ
S 24 Lemon cadmium	Zinc yellow	Δ	Δ	Δ
	Calcium carbonate	Δ		Δ
S 25 Chromate yellow	Chrome orange[i]	Δ	Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate	Δ		Δ
S 26 Monolite orange	Chrome orange	Δ	Δ	Δ
	Titanium white		Δ	Δ
	Lithopone	Δ		Δ
	Calcium carbonate	Δ		Δ

[a] Probably barium carbonate present; [b] mica present; [c] hematite and carbon-based black present in low concentration; [d] FeOOH + MnO_2 (the MnO_2 content is higher in Umbers than in Siennas); [e] probably some iron oxide present in low concentration; [f] probably magnesium carbonate present; [g] $PbCrO_4$ + $Fe_4[Fe(CN)_6]_3.nH_2O$; [h] probably some read lead present; [i] probably chrome yellow present.

Summarizing, for the whites lithopone was used as the main pigment, identified in 11 of the 21 colours by the presence of barium sulphate and zinc; in three cases titanium white was identified by Raman as a mixture of anatase and rutile. Lithopone is a very homogeneous mixture of barium sulphate and zinc sulphide, as both compounds are obtained by equimolar co-precipitation of BaS and $ZnSO_4$ [95]. Calcium carbonate was used extensively as an extender, being present in 13 of the 21 colours. Lead chromate pigments were used to obtain red, orange, yellow and green colours, with PbO also present in some of these pigments, Table 4.15. For the blues, ultramarine, manganese blue and phthalocyanine blue were used. Manganese blue is a barium manganate (VI) sulphate compound, and it was a popular pigment during the 20th century; its patent was registered in 1935 and the production ceased in the 1990s as a result of its toxic production process [175]. Prussian blue is only present in the green paint S18-emerald green.

Binding medium

The infrared spectra were used to get insight into the polymer degradation mechanism and the role of the metal ions, present in the pigments and extenders. In all samples PVAc was identified as the paint binding medium, Figure 4.39.

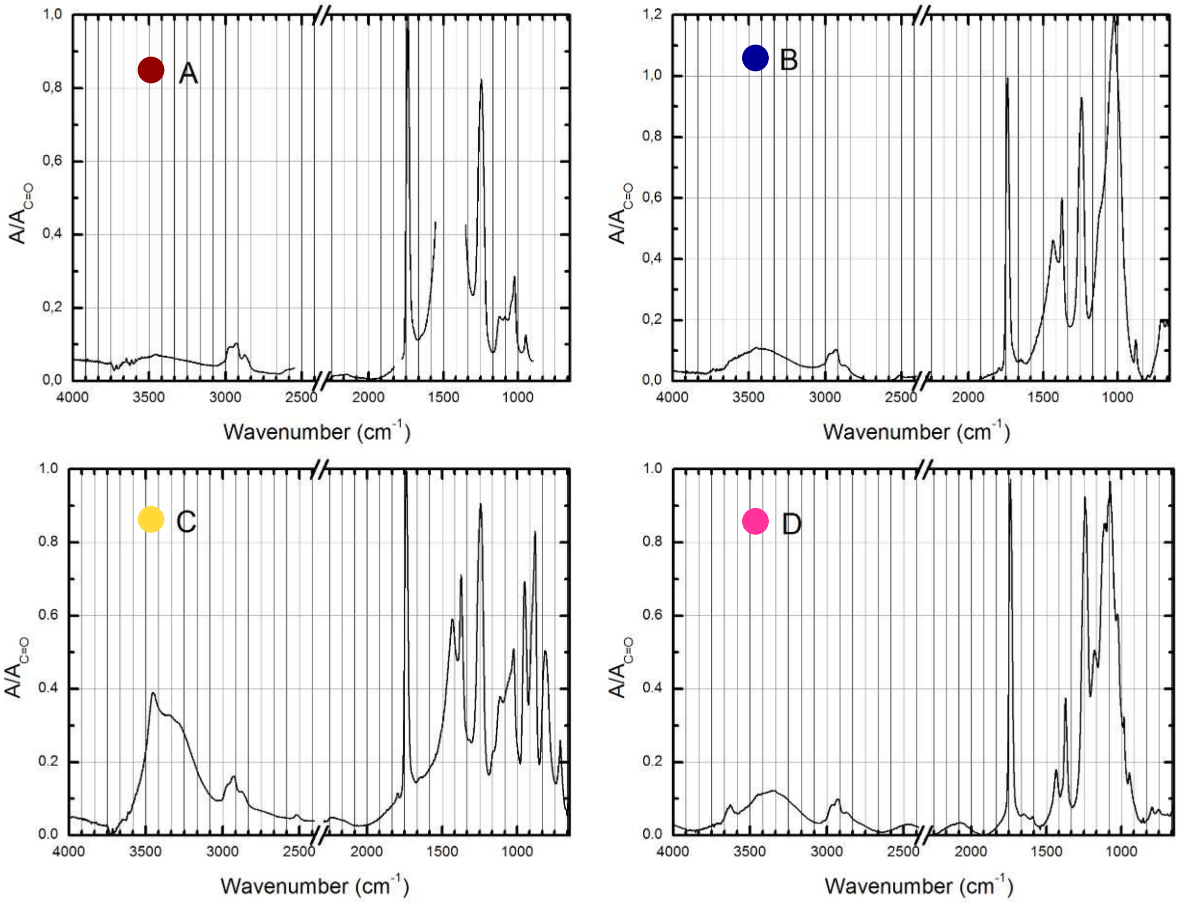

Figure. 4.39. Infrared spectra of four representative *Sabu* paint samples, where PVAc is the the binding medium: A – Sabu 30 Burnt sienna (the peaks due to the $CaCO_3$ filler were blanked); B – *Sabu 12 French ultramarine*, C – *Sabu 24 Lemon cadmium*, D – *Sabu 23 Monolite pink*. The absorptions are normalized for the C=O peak.

As previously discussed, the appearance of an O-H stretching from the alcohol group present in PVAL, together with the ratios $\nu CH_3/C=O$, $\nu CH_2/C=O$, $\delta CH_3/C=O$ and $\nu C\text{-}O/C=O$, Table 4.16, provide relevant information on the extent and type of the ester fragmentation. In the present case study the C-H bending vibrations have a limited use as they are masked by the calcium carbonate extender, which is present in many of the paints. Therefore, for monitoring the evolution of the methyl and methylene groups present in PVAc, the C-H asymmetric stretching absorptions, at approximately 2979 cm^{-1} for the tertiary C-H and at 2926 cm^{-1} for the methylene hydrogen's are the most useful [160,162]. As these peaks present low intensity, the base line was subtracted in order to allow the measurement of the exact peak height. Also, the broadening of the carbonyl stretching absorption at approximately 1737 cm^{-1} can provide relevant information in which concerns the chemistry of the ester group.

In Table 4.16, the $\nu CH_3/C{=}O$ and $\nu CH_2/C{=}O$ ratios as well as the CH_3 bending and carbonyl absorptions for a PVAc homopolymer and for the formulation sold as *Vulcano V7*, glue and binder for artists' paints, are reported. The values for the $\nu CH_3/C{=}O$ and $\nu CH_2/C{=}O$ are 0.06 for the PVAc homopolymer and higher, 0.11 and 0.9 respectively, for *V7*, due to the presence of the phthalate plasticizer as explained in Chapter 3.2. In regard to the $\nu C\text{-}O/C{=}O$ values, they are very similar in both *V7* and PVAc, 0.77 and 0.72, respectively. As may be observed from the PVAc+PVAL mixtures, Table 4.12, if ester cleavage is present with PVAL formation, this value will increase, but the more sensitive window will correspond to the hydrogen stretching from the alcohol group, O-H. The absorption found in the region of the methyl bending also increases but as a consequence of the strong PVAL absorption bands at 1373 cm^{-1} and 1427 cm^{-1}. In which concerns the colour paints form the sixties, it is possible to conclude that all the ratios fall within the values of a PVAc homopolymer, and that no PVAL could be detected.

Table 4.16. Infrared absorptions normalized for the C=O stretching for *Sabu* catalogue paints[a], PVAc homopolymer and *Vulcano V7* vinyl glue

Sample	ν_{CH3} 2970 cm^{-1}	ν_{CH2} 2930 cm^{-1}	δ_{CH3} 1373 cm^{-1}	$\nu_{(C=O)}$ 1737 cm^{-1}	$\nu_{(C(=O)-O-C)}$ 1242 cm^{-1}
S 10 Grey	0.05	0.06	___	1.00	___
S 11Raw Umber	0.06	0.08	___	1.00	___
S 14 Ochre	0.05[b]	0.05	0.30	1.00	0.75
S 15 Raw Sienna	0.06	0.07	0.35	1.00	0.78
S 30 Burnt Sienna	0.05	0.06	___	1.00	___
S 12 Ultramarine	0.06	0.07	___	1.00	___
S 16 Prussian blue	0.06	0.08	___	1.00	___
S 17 Turquoise blue	0.06	0.07	___	1.00	___
S 27 Véronèse green	0.05[c]	0.06	___	1.00	___
S 28 Cyanine green	0.06	0.07	___	1.00	___
S 20 Madder carmine	0.06	0.08	___	1.00	___
S 21 Manganese violet	0.05	0.07	___	1.00	___
S 22 Cyanine magenta	0.07 [c]	0.07	0.32	1.00	0.78
S 23 Monolite pink	0.05	0.07	0.38	1.00	___
S 25 Chromate yellow	0.06	0.07	___	1.00	___
PVAc standard	0.06	0.06	0.31	1.00	0.77
Vulcano V7	0.11[c]	0.09[d]	0.28	1.00	0.72

[a] The ratios were determined only for selected samples which showed a clear window for these peaks.
[b] @ 2976 cm^{-1}; [c] @ 2966 cm^{-1}; [d] @ 2938 cm^{-1}.

Regarding the carbonyl band position and width, it may be observed from Table 4.17 that no relevant shifts were detected in the carbonyl peak position and, when broadening is observed it falls below 10%. Also, for the paints were dyestuffs may be present it is necessary to take into account that an ester function could be present, even in low concentrations. The trends relating the presence of metal ions and the binder degradation will be next discussed. If we consider for example the paint S30-burnt sienna, composed by the pigment hematite and the filler calcium carbonate, and the S12-ultramarine, with the same extender and ultramarine, we observe that both peak position and width are very similar and compare very well with non degraded PVAc homopolymer. On the other hand, the iron, zinc and lead based pigments, such as the iron oxides, lithopone and lead chromates, could be photochemically active as sensitizers. From the results presented in Table 4.17 no trend relating the presence of these metal ions with band broadening could be consistently observed. Nevertheless it is possible to observe that, the pigments where the highest broadening is found, close to ca 10%, were S19-chinese vermilion and S26-monolite orange. Both pigments contain chrome-lead based pigment and calcium carbonate as filler; in the second paint titanium white is also present. It is worth to mention that, as it may be observed in Table 3.6 when comparing the values obtained for the paints with the binder before irradiation, some differences in the carbonyl peak width are found and could be related to differences in the sample thickness.

Overall, from the values in Tables 4.16 and 4.17, it is possible to conclude that the photochemical reactions involving the carbonyl group, if present, are still not relevant as detected by IR. Nevertheless, correlating the metal ions to the polymer condition, degradation trends may be assessed. For the pigments based on iron, zinc or lead ions no significant carbonyl peak broadening was observed when compared to the values for the PVAc homopolymer. However, the chrome red and chrome orange (where besides lead chromate PbO is also present) displayed almost a 10% broadening. In the S26-Monolite orange besides the lead based pigments, TiO_2 is also present, but being the only paint where it was detected it is not possible to conclude if its presence is relevant to the polymer photostability.

Table 4.17. Fitting parameters for the C=O absorption: peak centre (μ), peak width at half maximum (σ) and correlation coefficient (ρ) for the carbonyl stretching absorption (Gaussian function) for *Sabu* paints, PVAc homopolymer and *Vulcano V7*

Sample	**μ**	**σ**	**ρ**
S 10 Grey	*1738.2*	20.10	0.991
S 11Raw Umber	*1738.5*	21.91	0.995
S 14 Ochre	*1739.1*	19.23	0.994
S 15 Raw Sienna	*1738.6*	20.10	0.994
S 29 Sepia	*1738.5*	20.91	0.989
S 30 Burnt Sienna	*1737.9*	20.07	0.991
S 12 Ultramarine	*1738.1*	20.76	0.993
S 13 Cobalt blue	*1737.1*	21.60	0.978
S 16 Prussian blue	*1737.5*	21.39	0.993
S 17 Turquoise blue	*1738.7*	20.62	0.996
S 18 Emerald green	*1737.6*	20.26	0.991
S 27 Véronèse green	*1737.8*	21.09	0.993
S 28 Cyanine green	*1737.9*	20.20	0.995
S 19 Chinese vermillion	*1738.4*	21.42	0.995
S 20 Madder carmine	*1738.0*	19.95	0.992
S 21 Manganese violet	*1738.5*	20.73	0.996
S 22 Cyanine magenta	*1738.1*	21.64	0.996
S 23 Monolite pink	*1738.4*	21.95	0.994
S 24 Lemon cadmium	*1738.6*	20.73	0.996
S 25 Chromate yellow	*1737.7*	20.43	0.992
S 26 Monolite orange	*1737.8*	21.99	0.993
PVA standard	***1738.5***	**19.72**	**0.993**
Vulcano V7	*1737.6*	20.68	0.988

As discussed in Chapter 3.2, pigments as hematite are known to be effective photoiniators of photo-oxidative polymer degradation [63]. This led us to select S30-burnt Sienna and S12-ultramarine as representative cases[135] where the pigment may and may not act as sensitizer, respectively. The pigment used in S30 is hematite, Fe_2O_3, and in S12 ultramarine blue is an aluminosilicate; in both paints, $CaCO_3$ was used as extender.

The molecular weight distributions, weight average molecular weight, *Mw*, and respective polydispersity, PD, for the soluble fraction of both paints were calculated from chromatograms shown in Figure 4.40 and can be found in Table 4.18, as well as the values for unaged PVAc and *Vulcano V7*.

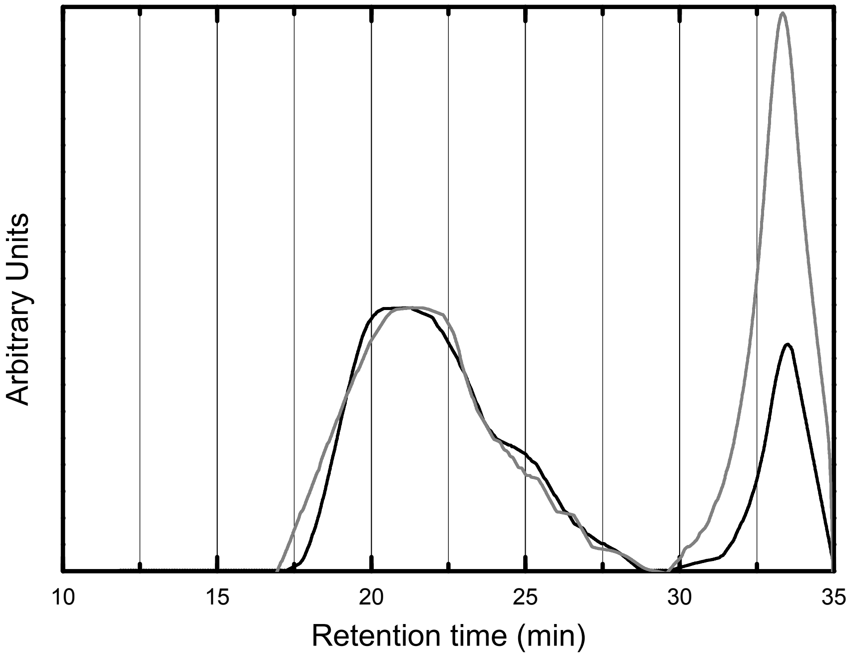

Figure 4.40. SEC chromatogram of two *Sabu* colours: black thick line – N12 French Ultramarine; grey thick line – N30 Burnt Sienna. Peaks appearing at t_R>30 min are attributed to an additive.

In Table 4.18 the values for two contemporary commercial *Sabu* paints as well as for the binder used in the formulation, a vinyl acetate-*co*-vinyl chloride-*co*-ethylene terpolymer, *Vinamul 3469* (Figure 4.41), are also reported.

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[135] The studied catalogue is considered an historical document; therefore a selection criterion on sampling had to be followed in order to collect a minimum sample amount.

Table 4.18. Weight average molecular weight (*Mw*) and polydispersity (PD) for *Sabu* paints, PVAc homopolymer, *Vulcano V7* glue, 21st century *Sabu* paints, *Vinamul* 3469 emulsion and unaged paint reconstructions

Sample	***Mw*** ($x10^5$)	**PD**
Sabu 12-Ultramarine (1960s)	33	*5.5*
Sabu 30-Burnt Sienna (1960s)	33	*5.7*
PVAc Aldrich	8.5	*2.0*
Vulcano V7	15	*2.0*
Sabu ultramarine (2000s)	11	*6.3*
Sabu ochre (2000s)	10	*7.2*
Vinamul 3469[a]	5	*4.5*
V7 + Fe_2O_3 + $CaCO_3$	4	*2.1*
V7 + Ultramarine blue + $CaCO_3$	4	*2.3*

[a] Vinyl acetate-vinyl chloride-ethylene terpolymer.

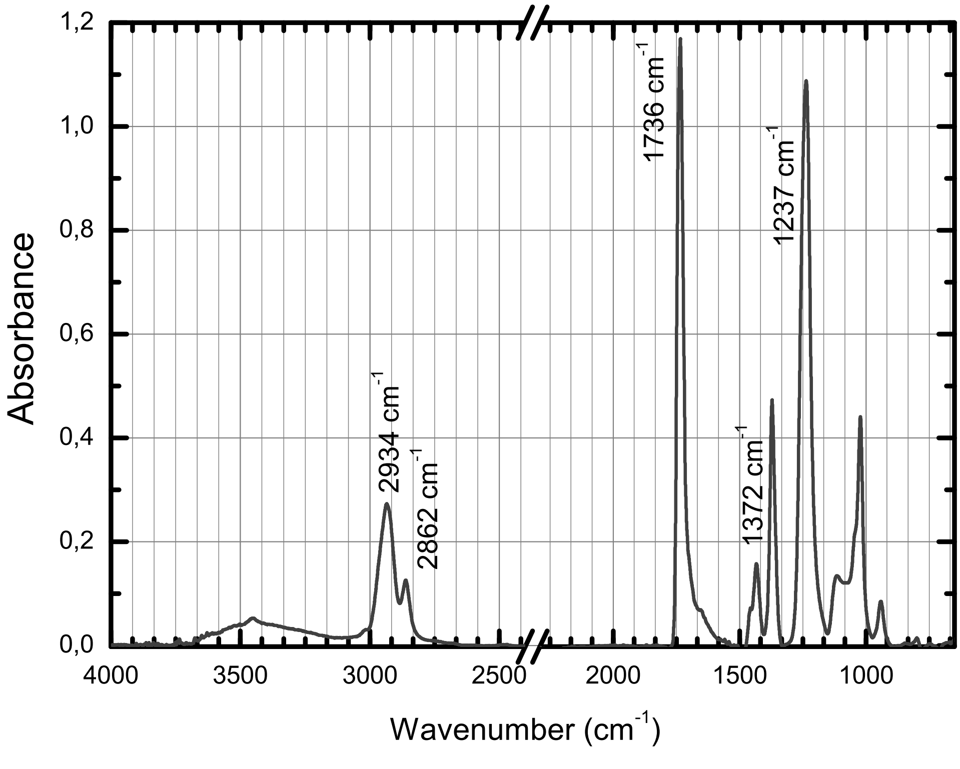

Figure. 4.41. Infrared spectra of *Vinamul* 3469 (vinyl acetate-*co*-vinyl chloride-*co*-ethylene terpolymer).

When comparing the values obtained for the *Sabu* paints from the sixties with PVAc or *V7*, one could be induced to conclude that based on the observed increase on *Mw* and PD the polymers had undergone degradation and that the higher molecular weights observed point out to the occurrence of branching, by chain transfer reactions to polymer, as an initial pathway to crosslinking as the main degradation mechanism. On the other hand, the results reflecting the 21st century *Sabu* paints and the unaged terpolymer binder used, call for a more careful interpretation. Indeed, an increase of *Mw* and PD is also observed when comparing the unaged *Sabu* binder to the 21st century *Sabu* colour paints. In this case, for both the terpolymer emulsion and the *Sabu* paints, the PD value is higher than the correspondent to the *V7* homopolymer emulsion. The increase of *Mw* observed in the unaged paints suggests that formation of aggregates can be occurring, promoted by interactions between the terpolymer chains and the additives of the paint formulation (please see Chapter 3.2). Following this line of reasoning, in which concerns the *Sabu* paints from the sixities, it is necessary to take into account that the observed increase in molecular weight could be resulting from the interaction of the polymer with other compounds present in the paint and not from degradation. Pigment-polymer or other polymer-additive interactions could provide again a possible explanation. This might be confirmed with the data discussed in Chapter 3.2, where *V7* was mixed with the pigments and $CaCO_3$ in ratios similar to the ones found in *Sabu* 12 and *Sabu* 30. When compared with the binder formulation used the *Mw* of the *V7* mixed with the pigments displays twice its value, but the PD value remains approximately 2. So, these unaged mixtures, of *V7* with hematite or ultramarine blue in the presence of $CaCO_3$, could explain the increase in *Mw* but not in PD. The higher polydispersity value presented by the paints compared to the binder, both in the *Sabu* paints from the catalogue and in the newest formulation, could be explained by the mixture of a second binder in the *Sabu* formulation (Chapter 2.2.2 and Appendix II.1).

4.5 Lourdes Castro

> *Searching for a material without texture and more in agreement with the result I wanted, I made, in 64, my first essay in plexiglas. At last, an immaterial material like the shadows*[136].
>
> Lourdes Castro, 1966

4.5.1 The artist and the PMMA shades

This Portuguese artist who lived in Paris from 1958 until 1983, has worked the shadow concept in multiple ways, including theatre, cyanotypes, embroidery, murals, easel painting, drawing, books sculpted in cellulose acetate and a number of works in acrylic sheet, *i.e.* poly(methyl methacrylate) – PMMA. Lourdes used the acrylic sheet in colour compositions as a painter uses paint colours, and she describes her PMMA sample collection as her *palette*. The artist made use of the optical properties characteristic of this material to play with transparency/opacity effects, re-projecting on the wall the shadows that she had either sculpted or painted (Figures 1.29 and 1.30). From 1964 and until 1968, Lourdes Castro worked with *Plexiglas* and *Altuglas*, a French acrylic glass trademark, using sheets that could either be transparent or opaque and were described as *transparent*, *translucide*, *fluorescent*, *mireitant*, *métalique* and *goute d'eau*.

According to Lourdes Castro, the acrylic sheets were protected with sticker paper, in which the shadows outlines would first be drawn. The artist used a *Stanley* electric saw to cut the acrylic sheets and pyrographic tools for her signature. Due to the heat produced by the saw, the sheets would be glued back together and were then separated again with a manual metal saw. To surpass this laborious procedure, Lourdes was told to apply some oil droplets over the drawing outlines and found that it worked, this minimized the heat avoiding the second cut. After this step, the holes eventually necessary to attach more than one sheet together or to hang the work on the wall were made. For finishing of the cutting edges, Lourdes used iron files and then the polishing kit from *Altuglas* – first *Altupol 1* followed by *Altupol 2* (currently *Altuglas Polish 1* and *2*), which were applied with a cotton pad or cotton cloth. Light surface scratches were also removed with these polishing products. As a final treatment, and also as a maintenance procedure, the artist washed the acrylic shadows with water and soap, and after drying applied *Altunet* (currently *Altuglas Cleaner*) as an antistatic agent with a special smooth cloth.

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[136] '*Procurando um material sem textura e mais de acordo com o resultado que pretendia obter, fiz em 1964 o meu primeiro ensaio em plexiglas. Por fim, um material imaterial como as sombras*.' [132]

4.5.2 Characterization – materials and conservation condition

Five samples from the PMMA sample collection belonging to the artist (Figure 4.42), as well as one sample collected from the work *La place en marche*, 1965 (National Museum of Contemporary Art – *Museu do Chiado*), Figure 1.29, were characterized.

Figure 4.42. The *Altuglass* PMMA palette; sample collection belonging to Lourdes Castro.

4.5.2.1 PMMA 'palette': molecular approach

All samples analysed were identified by infrared spectroscopy as poly(methyl methacrylate) homopolymer [160] (Figure 4.43) by the carbonyl stretching absorption peak at 1731 cm^{-1} and the characteristic profiles and relative intensities of the other diagnostic peaks, namely the C-O stretching at 1270, 1242, 1194 and 1150 cm^{-1} and C-H stretching at 2994 and 2950 cm^{-1}. No bands assigned to pigments, dyestuffs nor other formulation additives were detected, which might be explained by their low relative concentration compared to the polymer. The infrared spectra concerning the PMMA sheets from the PMMA sample collection are presented in Appendix VII.4.

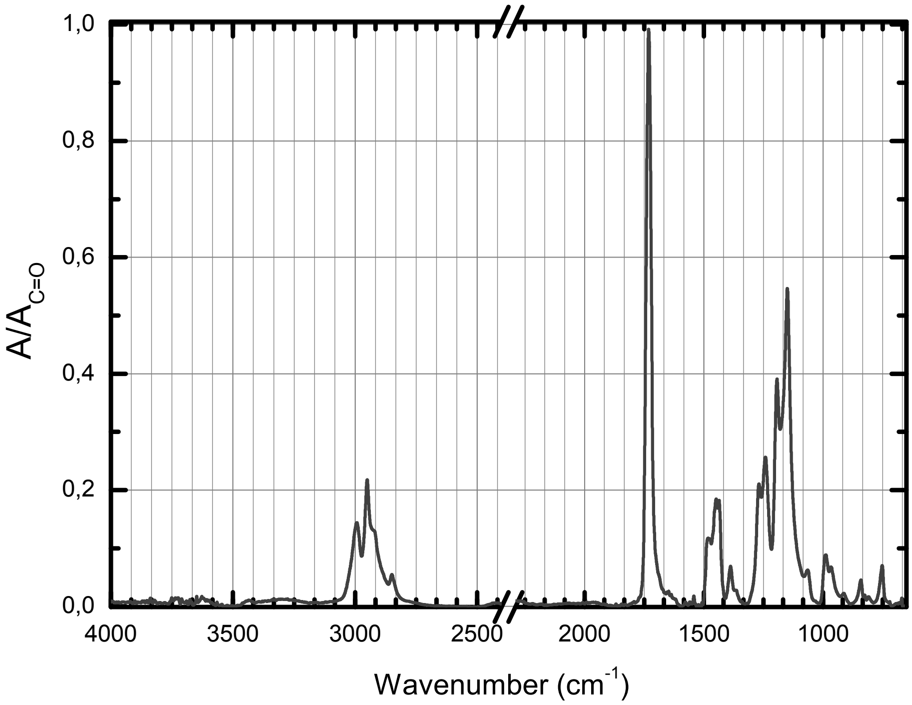

Figure 4.43. Infrared spectra of a μ-sample collected from the work *La Place en Marche*, 1965. Absorptions are normalized for the C=O stretching.

Colourants

In which concerns the colourants, it was possible to characterize the chromophores responsible for the colour in fluorescent PMMA sheets from the sample collection, by their characteristic emission spectra (Figure 4.44), belonging to a fluorescent dye family such as eosin derivatives [180].

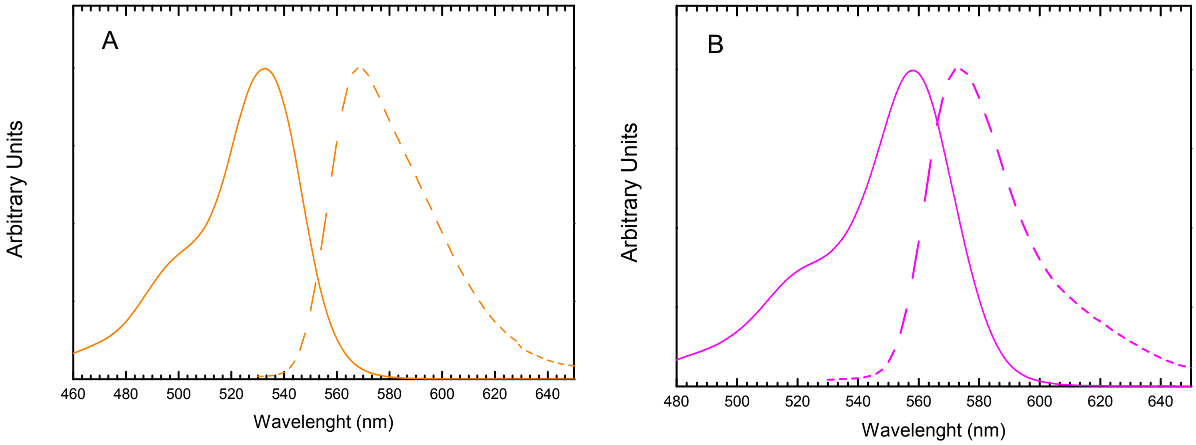

Figure 4.44. Emission and excitation spectra for: A – fluorescent orange (LC Alt T.750), $\lambda_{\text{exc max}} = 532$ nm and $\lambda_{\text{em max}} = 568$ nm; B – fluorescent pink (LC Alt T.770A), $\lambda_{\text{exc max}} = 558$ nm and $\lambda_{\text{em max}} = 572$ nm.

Also, μ-EDXRF analysis were preformed to investigate the possible presence of inorganic additives that could be present as colourants. As a first approach, *in situ* spectra were obtained and Ti was the only element detected on an standard opaque white PMMA sample,

(Figure 4.45 A) indicating that possibly titanium dioxide was used as the white pigment. Ultramarine blue, widely used as a pigment in plastics [9], was identified as the pigment responsible for the colour in the opaque blue sheet (from the sample collection), by the identification of Al, Si, S, K, Ca and Fe (with low intensity) on the ashes obtained after polymer pyrolysis (Figure 4.45 B). In this case the need for separation of the inorganic and organic components by pyrolysis is explained by the low fluorescence yields of the main elements in the composition of the ultramarine pigment and detected by X-ray fluorescence (Al, Si and S), resulting in low intensity peaks masked by the high background count rates in the Compton peak region due to the low atomic number of the organic polymer matrix [181]. For the other analyzed samples, transparent and fluorescent sheets, no elements indicating the presence of inorganic compounds were found.

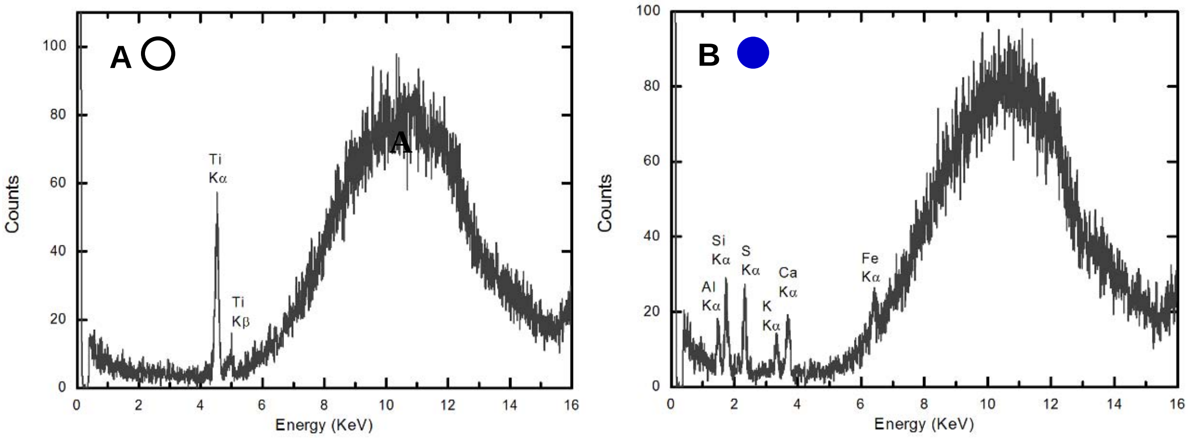

Figure 4.45. μ-EDXRF spectra: A – Standard Opaque white sample (acquired *in situ*); B – LC Opaque blue sample (acquired with He purge after polymer pyrolysis).

Polymer matrix

In order to investigate the production process of the PMMA samples, the molecular weight of two different commercial sheets known to have been produced by casting and by extrusion was determined (chromatograms in Appendix VII.3). As it might have been expected [49,50], cast PMMA was of high molecular weight (*Mw* of approximately 10×10^5) while the extruded sheet presented a molecular weight of one order of magnitude lower. The analysed PMMA samples belonging to Lourdes Castro (Figure 4.46) present high molecular weights, *Mw* ~ 12×10^5 (PD, 1.6) and 14×10^5 (PD, 1.9) for the fluorescent pink and blue samples respectively, typical for unaged cast PMMA sheets.

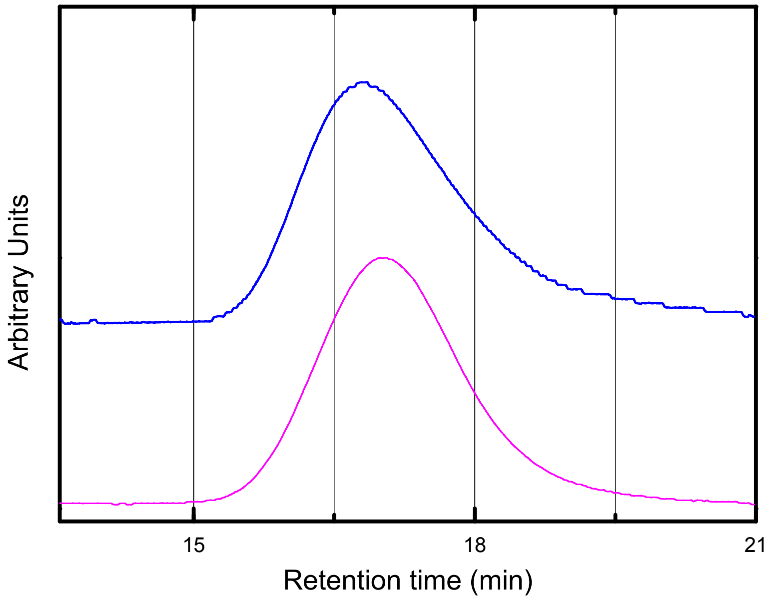

Figure 4.46. SEC chromatograms of PMMA sheets from Lourdes Castro's sample collection: top – LC Opaque blue (*Mw* ~12 x 10^5; PD, 1.6); bottom – LC Fluorescent pink (*Mw* ~14 x 10^5; PD, 1.9).

In their present conservation condition, the acrylics used by the artist show no signs of degradation. The samples analysed from the acrylic glass sample collection as well as from the work *La place en marche* from 1965, which belongs to the National Museum of Contemporary Art – *Museu do Chiado* (Figure 4.43), present the infrared spectra of PMMA hompolymer with no detectable degradation products. In the same line of reasoning of what was described for the photodegradation studies, possible variations in the νC-O/C=O absorption ratios (Table 4.19) and broadening of the carbonyl stretching peak (Table 4.20), when compared to recent PMMA sheets, were investigated and no significant changes were found.

Table 4.19. Main infrared peak absorptions normalized for the C=O stretching for standard samples from Lourdes Castro's sample collection, samples from the work *La place en marche* (1965) and standard PMMA samples. Spectra acquired from μ-samples compressed in a diamond-anvil cell (transmittance μ-FTIR)

Sample	ν_{CH_3} 2994 cm^{-1}	ν_{CH_2} 2950 cm^{-1}	$\nu_{C=O}$ 1731 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1270 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1242 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1194 cm^{-1}	$\nu_{C\text{-}O\text{-}C}$ 1150 cm^{-1}
LC Transparent Alt S310	0.14	0.20	1	0.20	0.25	0.37	0.53
LC Fluorescent pink Alt T770A	0.12	0.20	1	0.21	0.26	0.39	0.55
LC Opaque blue	0.14	0.20	1	0.20	0.24	0.36	0.50
LC Fluorescent pink	0.14	0.22	1	0.21	0.26	0.39	0.55
LC *La place en marche* (1965)	0.14	0.19	1	0.21	0.26	0.39	0.55
Standard PMMA Transparent	0.16	0.22	1	0.20	0.25	0.37	0.50
Standard PMMA film (Mw 960 000)	0.13	0.20	1	0.21	0.28	0.29	0.57

Table 4.20. Fitting parameters for the C=O absorption: peak centre (μ), peak width at half maximum (σ), peak area (A) and correlation coefficient (ρ) for the carbonyl stretching absorption (Gaussian function) for samples from Lourdes Castro's sample collection, samples from the work *La place en marche* (1965) and standard PMMA samples. Spectra acquired from μ-samples compressed in a diamond-anvil cell (transmittance μ-FTIR)

Sample	$\nu_{C=O}$ μ	σ	**A**	ρ
LC Transparent – Alt S.310	1729.6	21.32	25.81	*0,993*
LC Fluorescent pink – Alt T.770A	1729.5	21.25	25.75	*0.992*
LC Opaque blue	1730.1	20.25	24.24	*0.994*
LC Fluorescent pink	1730.8	20.65	25.37	*0.994*
LC *La place en marche* (1965)	1730.8	20.42	24.92	*0.994*
Standard Transparent PMMA	1731.5	21.69	26.89	*0,998*
Standard PMMA film (Mw 960 000)	1730.0	21.18	25.94	*0.986*

4.6 Conclusion

The paints from works by Joaquim Rodrigo and Ângelo de Sousa are in a good conservation condition, with no signs of physical changes or molecular degradation. These works were created with very different techniques, using different PVAc emulsion brands and colourants. Rodrigo's colours were based on inorganic pigments, where iron oxides are omnipresent, and were applied as mixtures. Also, the paintings were left unvarnished. On the other hand, Ângelo's colour system is closer to a medieval illumination: primary colours are chosen, bright and pure chroma are selected, visual effects are created not by mixture but by superposition of coloured layers, and maximum effect is sought with a minimum of means. Organic dyes were used for bright reds, greens, and yellows, and protective coatings were applied in all paintings. The works studied cover a period of years, in the case of Ângelo (1961-1965), to several decades for Rodrigo (1961-1990). As such, they broaden the relevance of the conclusions concerning vinyl paints' stability. A comparison is possible to be made with the results obtained for the twenty one paint samples analysed from the *Sabu* catalogue, which have aged mainly protected from light for over forty years. In all cases the samples characterized show a fingerprint similar to that of the unaged homopolymer. The results obtained are in agreement with the studies on the photodegradation mechanisms of PVAc, which proved that the homopolymer applied as a solution, emulsion, or coloured paint is very stable to light. Furthermore, the present study allowed a correlation to be made between paint samples aged naturally and those aged under artificial conditions, where both sets display the fingerprint of an unaged PVAc homopolymer.

On the other hand, it was possible to observe that the same formulation may be stable as a film but not when kept in a closed container. This was indeed the case for the *Soberana* aqueous emulsion that was kept for four years in a small *Eppendorf* and underwent extensive hydrolysis, the acetate being converted into alcohol by 50%. To draw general conclusions, it would be necessary to fully characterize the additives present in these emulsions, namely the presence of acetic acid and buffers.

Concerning the conservation of poly(vinyl acetate) in works of art, our studies have proven their molecular stability; nevertheless, further testing is needed on their physical performance and on the influence of T_g in dirt pick up. As previously described, Ângelo de Sousa is concerned about the conservation of his works and usually applies a protection layer. On the contrary, Joaquim Rodrigo intended to keep the colour and texture of the pigments as close to their natural characteristics as possible, and his paintings present the vulnerability of unvarnished surfaces.

As a final remark, it is worth mentioning that both artists show a particular interest and knowledge of painting materials and techniques, which has an impact on the final result of their works and possibly on their preservation for future generations.

Also the PMMA used by Lourdes Castro on her shadows from the 1960s are in a good conservation condition. The samples analyzed from the sample collection, and also from the work *La place en marche* (1965), present both the infrared spectra and molecular weight of unaged PMMA cast sheets.

Chapter 5 – General Conclusion

Vinyl emulsions have been used in Portugal for the production of both household and artists quality paints since the 1950s, by *Robbialac* and *A Favrel Lisbonense*. About the same time the Portuguese chemical industry launched the polymer production, first with *Indústrias Químicas Synres Portuguesa* followed by *Resiquímica – Resinas Químicas*, using the technology of leading international companies. Furthermore, it has been shown that Portuguese artists used a poly(vinyl acetate) binding medium since the early 1960s.

PVAc as pure homopolymer or as an emulsion paint proved to be very stable to light when irradiated in interior conditions ($\lambda \geq 300$ nm) and that the mechanism(s) operating are different from those studied with different irradiations. Based on these results, it is possible to suggest that, for the irradiated films, no side-group scission is taking place and that main chain scission is the foremost photodegradation mechanism. The results obtained for the PVAc homopolymer present a more straightforward interpretation than those observed for the *Vulcano V7* formulation which was actually used by Portuguese artists. However, the general trend and main conclusions may be applied to both systems, PVAc and *V7* glue. Also, the metal ions present in the pigments do not affect the photochemical stability of the polymer. Even well-known photocatalysts as TiO_2 (present in the rutile form) and Fe_2O_3 proved to be harmless. Concerning the colouring performance of the vinyl emulsions, no relevant yellowing was observed for the white paints.

The paints from works by Joaquim Rodrigo and Ângelo de Sousa are in a good conservation condition, with no signs of physical changes or molecular degradation. These works were created with very different techniques, using different PVAc emulsion brands and colourants. It is worth mentioning that both artists show a particular interest and knowledge of painting materials and techniques, which has an impact on the final result of their works and possibly on their preservation for future generations. The works studied cover a period of years, in the case of Ângelo (1961-1965), to several decades for Rodrigo (1961-1990). As such, they broaden the relevance of the conclusions concerning vinyl paints’ stability. The results obtained for the samples from paintings by these artists are in agreement with the study on the photodegradation mechanisms of PVAc, which proved that the homopolymer applied as a solution, emulsion, or coloured paint is very stable to light. Also, these results are in agreement with those obtained for the samples collected from the *Sabu* paints present in the studied catalogue, which have probably been protected from light.

The present work allowed a correlation to be made between paint samples aged naturally and those aged under artificial conditions, where both sets display the fingerprint of an unaged PVAc homopolymer. These conclusions are also in agreement with Thomson’s and Feller's pioneer studies [3,13-16] initiated in the 1950s on the solubility of vinyls during photodegradation. Nevertheless, further testing is needed on the paints physical performance and on the influence of T_g on the paints tendency for dirt pick up.

Furthermore, it is concluded that the same formulation may be stable as a film but not as a wet emulsion kept in a closed container. This was observed for an aqueous emulsion kept in a small container and which underwent extensive hydrolysis. A full characterization of the additives present in these emulsions, namely to assess the presence of acetic acid and buffers, will be necessary to draw general conclusions. Considering the contradictory results published in the conservation literature concerning the stability of vinyl formulations, and based on the present results, it is possible to conclude that both polymer and formulation will be relevant in photostability. We have shown that PVAc homopolymers are very stable to light, but we do not know if the new vinyl generations of terpolymers will perform as well. Systematic and consistent research in this field is necessary in order to reach general and relevant conclusions. A deeper knowledge of these materials will enable not only better preservation and access to contemporary art but also the ability to develop made-to-measure products that may be used in works of art as well as conservation products. The results showing the very good stability of PVAc to light are in accordance with the suggestion that it will be possible to develop a stable emulsion that could be used as artists' quality paints and in conservation and restoration [79].

In which concerns the photostability of PMMA, both as thin films or thick sheets, this polymer proved to be stable when irradiated under the conditions used in this study. The main degradation pathway found is main-chain scission with a low reaction quantum yield, comparable to what was obtained for PVAc. Although it was not possible to identify the molecule responsible for colour in the transparent blue sheet, it was found that this colourant is highly fugitive, becoming almost colourless after the accelerated ageing experiment. The commercial cleaning product applied on the acrylic glass for surface treatment does not seem to alter its degradation mechanisms. However, it is considered that further studies are needed to assess the safety of the cleaning procedure.

The molecular characterization of the PMMA sheets used by Lourdes Castro confirms the stability of this polymer, which after over forty years of natural ageing presents the finger of unaged samples.

Finally, based on the results obtained, it is possible to conclude that PVAc and PMMA homopolymers display high photostability, constituting good choices as materials for artists.

References

[1] Morgan J. *A joint project on the conservation of plastics by the conservation unit and the Plastics Historical Society*. In: Grattan DW, editor. Saving the Twentieth-Century: The Conservation of Modern Materials. Conference Symposium ‘91 – Saving the Twentieth-Century; 1991 September 15-20; Ottawa. Otawa: Canadian Conservation Institute; 1993 p. 43-50.

[2] Mossman S. *Plastics in the Science Museum, London: a curator’s view*. In: Grattan DW, editor. Saving the Twentieth-Century: The Conservation of Modern Materials. Conference Symposium ‘91 – Saving the Twentieth-Century; 1991 September 15-20; Ottawa. Otawa: Canadian Conservation Institute; 1993 p. 25-35.

[3] Feller RL, Jones EH, Stolow N. *On picture varnishes and their solvents*. Oberlin: Intermuseum Conservation Association; 1959.

[4] Duquesne S, Lefebvre J, Delobel R, Camino G, LeBras M, Seeley G. *Vinyl acetate/butyl acrylate copolymers—part 1: mechanism of degradation*. Polymer Degradation and Stability 2004;83:19-28.

[5] Crook J, Learner T. *The impact of modern paints*. London: Tate Gallery Publishing Ltd; 2000.

[6] Aftalion F. *A history of the international chemical industry. From the ‘Early Day’ to 2000*. 2nd ed. Philadelphia: Chemical Heritage Press; 2001.

[7] Kennedy C. *ICI the company that changed our lives*. 2nd ed. London: Paul Chapman Publishing; 1993.

[8] Waenting F. *Plastics: Consumer Goods or Precious Objects? The Development of Plastics and their Use in German Society*. In: Oosten TB, Shashoua Y, Waenting F, editors. Plastics in Art. History, Technology, Preservation. Interim Meeting of the ICOM-CC Modern Materials Working group; 2001; Cologne. Munich: Anton Siegel; 2002 p.18-27.

[9] Shashoua Y. *Conservation of Plastics – materials science, degradation and preservation*. Oxford: Elsevier; 2008.

[10] Morgan L, Heuman J, Derek P, Robson S. *Exploring photogrametry and laser scanning of plastic sculptures*. In: Keneghan B, Egan L, editors. Proceedings of the Conference Plastics: Looking at the Future and Learning from the Past; 2007 May 23-25; Victoria and Albert Museum, London. London: Archetype Publications; 2008 p. 70-77.

[11] Stout GL, Gettens RJ. *Transport des fresques orientals sour de noveaux supports*. Museion. 1932 ;17-18:107-112. French.

[12] Horie CV. *Materials for conservation: organic consolidants, adhesives and coatings*. Oxford: Butterworth-Heinemann; 1987.

[13] Feller RL. *Studies on the photochemical stability of thermoplastic resins*. In: Preprints of the ICOM Committee for Conservation Fourth Triennial Meeting; 1975 October 13-18; Venice. Paris: The International Council of Museums. 75/22/4.

[14] Feller RL. *Stages in the deterioration of organic materials*. In, Williams JC, editor. Preservation of Paper and Textiles of Historic and Artistic Value. Washington: American Chemical Society; 1977 p. 314-335.

[15] Thomson G. *Test for cross-linking of linear polymers*. Nature 1956;178:807-807.

[16] Thomson G. *Picture varnishes*. Studies in Conservation 1957;3:64-79.

[17] Lemaire J, Gardette J, Lacoste J, Delprat P, Vaillant D. *Mechanisms of photo-oxidation of polyolefins: Prediction of lifetime in weathering conditions*. In: Clough RL, Billingham NC, Gillen KT, editors. Polymer durability: degradation, stabilization and lifetime predictions. Boston: American Chemical Society; 1996 p. 577-598.

[18] Chiantore O, Trossarelli L, Lazzari M. *Photooxidative degradation of acrylic and methacrylic polymers*. Polymer 2000;41:1657-1668.

[19] Melo MJ, Bracci S, Camaiti M, Chiantore O, Piacenti F. *Photodegradation of acrylic resins used in the conservation of stone*. Polymer Degradation and Stability 1999;66:23-30.

[20] Bracci S, Melo MJ. *Correlating natural ageing and Xenon irradiation of Paraloid1 B72 applied on stone*. Polymer Degradation and Stability 2003;80:533-41.

[21] Learner T, Chiantore O, Scalarone D. *Ageing studies of acrylic emulsion paints*. In: Vontobel R, editor. Preprints of the 13th Triennial Meeting of the ICOM Committee for Conservation; 2002 September 22-27; Rio de Janeiro. London: James & James; 2002 p. 911-19.

[22] Lapa P, Ávila MJ, coord. *Joaquim Rodrigo, catálogo raisonné*. Lisbon: Museu do Chiado – Instituto Português de Museus; 1999. Portuguese.

[23] Pérez MvH, Ramos M, coord. *Ângelo: 1993 uma antológica*. Porto: Fundação de Serralves; 1993. Portuguese.

[24] Castro L, Zimbro M, coord. *Lourdes Castro ‘além da sombra’*. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992. Portuguese.

[25] Learner TJS. *Modern paints: uncovering the choices*. In, Learner TJS, Smithen P, Krueger JW, Schilling MR, editors. Proceedings from the Symposium Modern Paints Uncovered; 2006 May 16-19; Tate Modern, London. Los Angeles: Getty Publications; 2007 p. 3-16.

[26] Stoye D, Freitag W, editors. *Paints, coatings and solvents*. Weinheim: Wiley-VCH; 1998.

[27] *Manual de Mowilith*. Spanish ed. Frankfurt: Faberwerk Hoechst AG. [date unknown]. Spanish.

[28] Croll S. *Overview of developments in the paint industry since 1930*. In: Learner TJS, Smithen P, Krueger JW, Schilling MR, editors. Proceedings from the Symposium Modern Paints Uncovered; 2006 May 16-19; Tate Modern, London. Los Angeles: Getty Publications; 2007 p. 17-29.

[29] Han Y-F, Kumar D, Sivadinarayana C, Goodman DW. *Kinetics of ethylene combustion in the synthesis of vinyl acetate over a Pd/SiO2 catalyst*. Journal of Catalysis 2004;224:60–68.

[30] Renneke R, McIntosh S, Arunajatesan V, et al. *Development of high performance catalysts for the production of vinyl acetate monomer*. Topics in Catalysis 2006;38:279-287.

[31] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”) [Internet]. Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.E02065. [cited 2009 Aug 15].

[32] Wicks ZW, Jones FN, Pappas SP, Wicks DA. *Organic coatings: science and technology*. 3rd ed. New Jersey: Wiley-Interscience; 2007.

[33] Bentley J, Turner GPA. *Introduction of paint chemistry and principles of paint technology*. 4th ed. London: Chapman & Hall; 1998.

[34] Painter PC, Coleman MM. *Fundamentals of polymer science: an introductory text*. 2nd ed. Boca Raton: CRC Press; 1997.

[35] Billmeyer FW. Textbook of polymer science. 3rd ed. New York: John Wiley & Sons; 1984.

[36] Learner TJS. *The characterization of acrylic painting materials and implication of their use, conservation and stability* [dissertation]. London: University of London; 1996.

[37] Jablonski E, Learner T, Hayes J, Golden M. *Conservation concerns for acrylic emulsion paints*. Reviews in Conservation 2003;4:3-12.

[38] Basset DR. *Hydrophilic coatings from emulsion polymers*. Journal of Coatings Technology 2001;912:43-55.

[39] Marques MIE. *Tintas – características dos constituintes e da película seca*. Lisbon: Laboratório Nacional de Engenharia Civil; 1985. Portuguese.

[40] Bieleman J, editor. *Additives for coatings*. Weinheim: Wiley-VCH; 2000.

[41] Sonoda N, Rioux JP. *Identification des matériaux synthétiques dans les peintures modernes. I. Vernis et liants polyméres*. Studies in Conservation 1990;35:189-204. French.

[42] Stringiari C. *The identification and characterization of acrylic emulsion paint media*. In: Grattan DW, editor. Saving the Twentieth-Century: The Conservation of Modern Materials. Conference Symposium ‘91 – Saving the Twentieth-Century; 1991 September 15-20; Ottawa. Otawa: Canadian Conservation Institute; 1993 p. 411-440.

[43] Chiantore O. *Le materie plastiche dell' arte contemporanea e la loro transformazione e decadimento*. In: Arte contemporanea – conservazione e restauro. Contibutions to the Colloquio sul restauro dell' Arte moderna e contemporanea; 1994 November 4-5; Prato. Fiesole: Nardini Editore; 1994 p. 131-155. Italian.

[44] Ferreira JL, Melo MJ, Ramos AM, Ávila, MJ. *'Eternity Is in Love with the Productions of Time': Joaquim Rodrigo's Classical Palette in a Vinyl Synthetic Medium.* In: Learner TJS, Smithen P, Krueger JW, Schilling MR, editors. Proceedings from the Symposium Modern Paints Uncovered; 2006 May 16-19; Tate Modern, London. Los Angeles: Getty Publications; 2007 p. 43-52.

[45] Gettens RJ. *Polymerized vinyl acetate and related compounds in the restoration of objects of art*. Technical Studies in the Field of Fine Arts 1935;4:15-27.

[46] Stout GL, Cross HF. *Properties of surface films*. Technical studies in the Field of Fine Arts 1937;5:242-249.

[47] Plenderleith HJ, Werner AEA. *The conservation of antiquities and works of art*. 2nd ed. London: Oxford University Press; 1971.

[48] Seymour RB, Carraher CE. *Polymer chemistry – an introduction*. New York: Marcel Dekker; 1981.

[49] Tsai W, Chen CC, Sauer JA. *Environmental effects of silicone oil on mechanical properties of low and high molecular weight PMMA*. Journal of Material Science 1984;19:3967-3975.

[50] Siampiringue N, Leca JP, Lemaire J. *Mecanisms de photo-oxidation du poly(methacrylate de methyle)*. European Polymer Journal 1991; 27:633-641. French.

[51] Altuglas International: Europe/Americas/Asia: Europe Homepage. La Garenne-Colombes: Altuglas International – Arkema Group. *Altuglas Acrylic Sheet, Altuglas Sheet Technical Brochure*; [cited 2007 Mar 15]; [about 17 pages]; Available from: http://www.altuglas. com/literature/pdf/124.pdf.

[52] Price BA, Malenka S, Sutherland K, Lins A, Carlson JH. *Naum Gabo's Construction in Space: Two Cones: history and materials*. In: Keneghan B, Egan L, editors. Proceedings of the Conference Plastics: Looking at the Future and Learning from the Past; 2007 May 23-25; Victoria and Albert Museum, London. London: Archetype Publications; 2008 p. 81-88.

[53] Beerkens L. *Plastic in modern art*. In: Oosten TB, Shashoua Y, Waenting F, editors. Plastics in art. History, technology, preservation. Interim Meeting of the ICOM-CC Modern Materials Working group; 2001; Cologne. Munich: Anton Siegel; 2002 p. 7-17.

[54] Kockott D. *Natural and artificial weathering of polymers*. Polymer Degradation and Stability 1989;25:181-208.

[55] Pospíšil J, Pilař J, Billingham NC, Marek A, Horák Z, Nešpůrek S. *Factors affecting accelerated testing of polymer stability*. Polymer Degradation and Stability 2006;91:417-422.

[56] Allen NS, Edge M. *Fundamentals of polymer degradation and stabilization*. London: Elsevier; 1992.

[57] Feller RL. *Accelerated aging: photochemical and thermal aspects*. Los Angeles: The Getty Conservation Institute; 1994.

[58] Wells CHJ. *Introduction to molecular photochemistry*. London: Chapman and Hall; 1972.

[59] Turro N. *Modern molecular photochemistry*. Mill Valley: University Science Books; 1991.

[60] Davis A, Sims D. *Weathering of polymers*. London: Elsevier Applied Science Publishers; 1983.

[61] Benavides R, González-Hernandez R, González-Cantú MC, Eyes-Vielma B, Billingham NC. *Accelerated degradation of highly loaded polypropylene*. Journal of Vinyl & Additive Technology 2003;9:41-49.

[62] Fox RF. *Photodegradation of high polymers*. In: Jenkins AD, editor. Progress in Polymer Science. Vol. 1. London: Pergamon; 1967 p. 45-89.

[63] Rabek J. *Polymer photodegradation: mechanisms and experimental methods*. London: Chapman & Hall; 1995.

[64] Rivaton A, Gardette JL, Mailhot B, Morlat-Therlas S. *Basic aspects of polymer degradation*. Macromolecular Symposia 2005;225:129-146.

[65] Mailhot B, Gardette JL. *Polystyrene photooxidation. 1. Identification of the IR-absorbing photoproducts formed at short and long wavelengths*. Macromlecules 1992;25:4119-4126.

[66] David C, Borsu M, Geuskens G. *Photolysis and radiolysis of polyvinyl acetate*. European Polymer Journal 1970;6:959-963.

[67] Geuskens G, Borsu M, David C. *Photolysis and radiolysis of polyvinyl acetate – II: volatile products and absorption spectra*. European Polymer Journal 1972;8:883-892.

[68] Geuskens G, Borsu M, David C. *Photolysis and radiolysis of polyvinyl acetate – III effect of temperature on the photolysis*. European Polymer Journal 1972;8:1347-1353.

[69] Buchanan KJ, McGill WJ. *Photodegradation of poly(vinyl esters) – I: formation and quantitative measurement of volatile products*. European Polymer Journal 1980;16:309-312.

[70] Buchanan KJ, McGill WJ. *Photodegradation of poly(vinyl esters) – II: volatile product formation and changes in the absorption spectra and molecular mass distributions*. European Polymer Journal 1980;16:313-318.

[71] Buchanan KJ, McGill WJ. *Photodegradation of poly(vinyl esters) – III: photolysis mechanism for both polymeric and low molecular esters*. European Polymer Journal 1980;16:319-324.

[72] Vaidergorin EYL, Marcondes MER, Toscano VG. *Photodegradation of poly(vinyl acetate)*. Polymer Degradation and Stability 1987;18:329-339.

[73] Montalti M, Credi A, Prodi L, Gandolfi MT. *Handbook of Photochemistry*. 3rd ed. Boca Raton: Taylor & Francis; 2006.

[74] Kaczmarek H. *Photodegradation of polystyrene and poly(vinyl acetate) blends.1. Irradiation of PS/PVAc blends by polychromatic light*. European Polymer Journal 1995;31:1037-1042.

[75] Kaczmarek H. *Photodegradation of polystyrene and poly(vinyl acetate) blends.2. Irradiation of PS/PVAc blends by fluorescent lamp*. European Polymer Journal 1995;31:1175-1184.

[76] Kaczmarek H. *Changes of polymer morphology caused by u.v. irradiation*: *2. Surface destruction of polymer blends*. Polymer 1996;37:547-553.

[77] Phelan WH, Baer NS, Indictor N. *An evaluation of adhesives for use in paper conservation*. Studies in Conservation 1971;11:58-75.

[78] Down J, MacDonald M, Tétreault J, Williams R. *Adhesive testing at the Canadian Conservation Institute – an evaluation of selected poly(vinyl acetate) and acrylic adhesives*. Studies in Conservation 1996;41:19-44.

[79] Howells R, Burnstock A, Hedley G, Hackney S. *Polymer dispersions artificially aged*. In: Brommelle NS, Pye EM, Smith P, Thomson G, editors. Adhesives and consolidants. Preprints of the Contributions to the Paris Congress; 1984 September 2-8; Paris. London: International Institute for Conservation of Historic and Artistic works; 1984 p. 36-43.

[80] Allen NS, Parker MJ, Regan CJ, McIntyre RB, Dunk WAE. *The durability of water-born acrylic coatings*. Polymer Degradation and Stability 1995;47:117-127.

[81] Allen NS, Regan CJ, McIntyre R, Johnson B, Dunk WAE. *The photostabilisation of water-borne acrylic coating systems*. Polymer Degradation and Stability 1996;52:67-72.

[82] Allen NS, Edge M, Ortega A, Liauw CM, Stratton J, McIntyre R. *Behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based acrylic and isocyanate based acrylic coatings*. Polymer Degradation and Stability 2002;78:467-478.

[83] Chiantore O, Scalarone D, Learner T. *Characterization of artists' acrylic emulsion paints*. International Journal of Polymer Analysis and Characterization 2003;8:67-82.

[84] Maxim LD, Kuist CH. *The light stability of vinyl polymers and the effect of pigmentation*. Official Digest, Federation of Societies for Paint Technology 1964;36:723-744.

[85] Allen NS, Katami H. *Comparison of various thermal and photoageing conditions on the oxidation of titanium dioxide pigmented linear low density polyethylene films*. Polymer Degradation and Stability 1996;52:311-320.

[86] Gupta MC, Viswanath SG. *Effect of metal oxides on the thermal degradation of high impact polystyrene*. Journal of Thermal Analysis and Calorimetry 1998;53:931-936.

[87] Li B. *Influence of polymer additives on thermal decomposition and smoke emission of poly(vinyl chloride)*. Polymer Degradation and Stability 2003;82:467-476.

[88] Sivalingam G, Karthik R, Madras G. *Effect of metal oxides on thermal degradation of poly(vinyl acetate) and poly(vinyl chloride) and their blends*. Industrial & Engineering Chemistry Research 2003;42:3647-3653.

[89] Vijayalakshmi SP, Madras G. *Thermal degradation of water soluble polymers and their binary blends*. Journal of Applied Polymer Science 2006;101:233–240.

[90] Zhao H, Li RKY. *A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites*. Polymer 2006;47:3207-3217.

[91] Galindo C, Jacques P, Kalt A. *Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74)*. Journal of Photochemistry and Photobiology A-Chemistry. 2001;141:47-56.

[92] Mattsson A, Leideborg M, Larsson K, Westin G, Österlund. *Adsorption and solar light decomposition of acetone on anatase TiO_2 and niobium doped TiO_2 thin films*. Journal of Physical Chemistry B 2006;110:1210-1220.

[93] Silva CG, Wang W, Faria JL. *Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation*. Journal of Photochemistry and Photobiology A-Chemistry 2006;181:314-324.

[94] Wu T, Li Y, Chu M. *Photoinduced metal deposition on semiconductor particles*. In: Nalwa HS, editor. Handbook of photochemistry and photobiology, Vol. 1: Inorganic photochemistry. Los Angeles: American Scientific Publishers; 2003. p. 249-282.

[95] Buxbaum G, editor. *Industrial inorganic pigments*. Weinheim: Wiley-VCH: 1998.

[96] Charlesby A, Thomas DK. *A comparison of the effects of ultra-violet and gamma radiation in polymethylmethacrylate*. Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences 1962;269:104-124.

[97] Fox RB, Isaacs LG, Stokes S. *Photolytic degradation of poly(methyl methacrylate)*. Journal of Polymer Science Part-A-1-Polymer Chemistry 1963;1:1079-1086.

[98] Grassi N. *Photodegradation of methacrylate/acrylate polymers*. Pure and Applied Chemistry 1973;34:247-257.

[99] Kaczmarek H, Kamińska A, van Herk A. *Photooxidative degradation of poly(alkyl methacrylate)s*. European Polymer Journal 2000;36:767-777.

[100] Gupta A, Liang R, Tsay FD, Moacanin J. *Characterization of a dissociative excited state in the solid state: photochemistry of poly(methyl methacrylate). Photochemical processes in polymeric systems*. Macromolecules 1980;13:1696-1700.

[101] Torikai A, Fueki K. *Photodegradation of poly(methyl methacrylate) studied by electron-spin-resonance and viscosity measurements*. Polymer Photochemistry 1982;2:297-308.

[102] Torikai A, Ohno M, Fueki K. *Photodegradation of poly(methyl methacrylate) by monochromatic light - quantum yield, effect of wavelengths, and light-intensity*. Journal of Applied Polymer Science 1990; 41:1023-1032.

[103] Mitsuoka T, Torikai A, Fueki K. *Wavelength sensitivity of the photodegradation of poly(methyl methacrylate)*. Journal of Applied Polymer Science 1993; 47:1027-1032.

[104] Alisson JP. *Photodegradation of poly(methyl methacrylate)*. Journal of Polymer Science Part-A-1-Polymer Chemistry 1966;4:1209-1221.

[105] Rodrigo J. *O complementarismo em pintura. Contribuição para a ciência da arte*. Lisbon: Livros do Horizonte; 1982. Portuguese.

[106] Lapa P. *Tempo e inscrição*. In: Lapa P, Ávila MJ, coord. Joaquim Rodrigo, catálogo raisonné. Lisbon: Museu do Chiado – Instituto Português de Museus; 1999 p. 14-85. Portuguese.

[107] França JA. *Joaquim Rodrigo ou o 'pintar certo'*. Colóquio Artes 1984;60:12-22. Portuguese.

[108] França JA. *Joaquim Rodrigo ou 'o pintar certo'*. Porto: Edições Galeria Nazoni; 1988. Portuguese.

[109] Ávila MJ. Catálogo raisonné – comentários. In: Lapa P, Ávila MJ, coord. *Joaquim Rodrigo, catálogo raisonné*. Lisbon: Museu do Chiado – Instituto Português de Museus; 1999 p. 118-293. Portuguese.

[110] Ávila MJ. *1960-1980 Anos de normalização artística nas colecções do Museu do Chiado*. Castelo Branco: Museu de Francisco Tavares Proença Júnior – Instituto Português de Museus; 2003. Portuguese.

[111] Redinha, J. *Paredes pintadas da Lunda*. Lisbon: Companhia dos diamantes de Angola; 1953. Portuguese.

[112] Rodrigo J. *Pintar certo*. Lisbon: Salamandra; 1995. Portuguese.

[113] França JA. *Verificação do cinzento na pintura de Joaquim Rodrigo (1994)*. In: Lapa P, Ávila MJ, coord. Joaquim Rodrigo, catálogo raisonné. Lisbon: Museu do Chiado – Instituto Português de Museus; 1999 p. 86-88. Portuguese.

[114] Almeida BP. *Ângelo de Sousa*. Lisbon: Imprensa Nacional Casa da Moeda; 1985. Portuguese.

[115] Todolí V. *Apresentação*. In: Ramos M, coord. Ângelo de Sousa, sem prata. Porto: Fundação de Serralves; 2001. Portuguese.

[116] Pernes F. *Ângelo (entrevista conduzida por Fernando Pernes)*. Lisbon: Galeria Valentim de Carvalho; 1985. Portuguese.

[117] Pernes F. *Ângelo, entre a alegria e a melancolia*. In: Pérez MvH, Ramos M, coord. Ângelo: 1993 uma antológica. Porto: Fundação de Serralves; 1993. p. 8-10. Portuguese.

[118] Rodrigues A. *Questões práticas acerca da obra de Ângelo de Sousa*. Artes & Leilões 1994;23:18-24. Portuguese.

[119] Gil J. *O experimentador do acaso*. In: Pérez MvH, Ramos M, coord. Ângelo: 1993 uma antológica. Porto: Fundação de Serralves; 1993 p. 13-17. Portuguese.

[120] Pinharanda JL. *O declínio das vanguardas: dos anos 50 ao fim do milénio*. In: Pereira P, dir. História da arte Portuguesa, Vol. 3. Lisbon: Círculo de Leitores; 1997. Portuguese.

[121] Almeida BP. *B e A (em continuação)*. In: Pérez MvH, Ramos M, coord. Ângelo: 1993 uma antológica. Porto: Fundação de Serralves; 1993 p. 18-34. Portuguese.

[122] França JA. *Os quatro vintes*. In: Andrade E, França JA, Pernes F. 'Os quatro vintes': Ângelo de Sousa, Armando Alves, Jorge Pinheiro, José Rodrigues. Porto: O Oiro do Dia & Simão Guimarães e Filhos; 1985 p.19-34. Portuguese.

[123] Ribeiro JS. *Introduction*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 13. Portuguese.

[124] Burmester M, coord. *Lourdes Castro, Manuel Zimbro. À luz da sombra*. Porto: Fundação de Serralves; 2010. Portuguese.

[125] Lapa P. *Lourdes Castro*. In: Carvalho E, coord. Pintura Portuguesa: séc. XX. Coimbra: Câmara Municipal de Coimbra; 2001 p. 103-106. Portuguese.

[126] Castro L. *Serigrafia*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 50. Portuguese.

[127] Freitas MH. *O duplo do mundo*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 45-47. Portuguese.

[128] Macedo R. *Desafios da arte contemporânea à conservação e restauro: documentar a arte portuguesa dos anos 60/70* [dissertation]. Lisbon: Univesidade Nova de Lisboa; 2008. Portuguese.

[129] Zimbro M. *A sombra da flecha*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 14-20. Portuguese.

[130] Castro L. *Sombras projectadas e contornos (1963)*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 51. Portuguese.

[131] Restany P. *Lourdes Castro: prefácio, a presença da ausência (1965)*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 36-38. Portuguese.

[132] Castro L. *Sombras em plexiglas (Paris, 1966)*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 53. Portuguese.

[133] Cabane P. *La montreuse d'ombres (Le Matin, 1978)*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 104. French.

[134] Castro L. *Teatro de sombras*. In: Castro L, Zimbro M, coord. Lourdes Castro 'além da sombra'. Lisbon: Centro de Arte Moderna – Fundação Calouste Gulbenkian; 1992 p. 56-57. Portuguese.

[135] Ribeiro JS, Ruivo MB, coord. *Lourdes Castro – à sombra*. Lisbon: Fundação Arpad Szenes - Vieira da Silva; 2005. Portuguese.

[136] Costa RM. *Synres – Indústrias Químicas Synres Portuguesa, Lda*. Boletim Informativo da Sociedade Nacional de Sabões, Lda e Empresas Associadas 1980;2:8-9. Portuguese.

[137] Veiga CB. *A S.N.S. e as empresas associas*. Boletim Informativo da Sociedade Nacional de Sabões, Lda e Empresas Associadas 1980;1:6-7. Portuguese.

[138] DSM – Composite Resins [internet]. Schaffhausen: DSM Composite Resins AG*. Our company, History, History DSM Composite Resins*; [cited 2009 Jun 27]; [about 1 screen]. Available from: http://www.dsm.com/en_US/html/drs/history_2007.htm.

[139] Branco V. *Synres muda de denominação*. Boletim Informativo da Sociedade Nacional de Sabões, Lda e Empresas Associadas 1984;13:2-3. Portuguese.

[140] DSM – Composite Resins [internet]. Schaffhausen: DSM Composite Resins AG*. About DSM home, History, DSM - Over a century of evolution*; [cited 2009 Jun 27]; [about 1 screen]. Available from: http://www.dsm.com/en_US/html/about/dsm_history.htm.

[141] Silva JPSF. *Optimização das condições de produção de resinas de poliéster insaturado. Caracterização da situação actual, optimização à escala industrial das condições existentes* [master's thesis]. Lisbon: Universidade Técnica de Lisboa; 2008. Portuguese.

[142] Resiquímica [internet]. Mem Martins: Resiquímica – Resinas Químicas S.A. *Quem somos, História*; [cited 2005 Feb 3]; [about 1 page]. Ailable from: http://resiquimica2.multinet.com/historia.php.

[143] Resiquímica [internet]. Mem Martins: Resiquímica – Resinas Químicas S.A.; c2008. *Quem somos, História*; [cited 2009 Jun 27]; [about 1 screen]. Available from: http://www.resiquimica.pt/site/PT/hist.html.

[144] APT – Associação Portuguesa de Tintas [internet]. Lisbon: Associação Portuguesa de Tintas. *Indústria, Dados indicativos do sector, Enquadramento do sector na indústria nacional*; [cited 2008 Apr 4]; [about 1 screen]. Available from: http://www.apftv.pt/dados Sector.aspx.

[145] CIN coatings [internet]. Maia: CIN – Corporação Industrial do Norte S.A. *Sobre nós, Perfil de um líder Ibérico*; [cited 2009 Jun 30]; [about 1 screen]. Available from: http://www. cin.pt/portal/portal/user/anon/page/contactos.psml?categoryOID=17818080808280GC&contentid=9C81808080CO&nl=pt&findcategory=1.

[146] Pereira ATS. *Optimização do sistema produtivo-logístico da Robbialac para minimizar as rupturas de stocks* [master's thesis]. Lisbon: Universidade Técnica de Lisboa; 2007. Portuguese.

[147] Tintas Sotinco [internet]. Maia: CIN – Corporação Industrial do Norte S.A. – Divisão Sotinco. *Empresa*; [cited 2009 Jun 30]; [about 1 screen]; Available from: http://www.sotinco. pt/cgibin/eloja21.exe?myid=sotinco&lang=pt&mn=empresa&titles=23&id=1&cli=sn&tpl=textos&main=mainconts.

[148] CIN coatings [internet]. Maia: CIN – Corporação Industrial do Norte S.A. *Grupo CIN, História da CIN – Corporação Industrial do Norte, 1917 – O início*; [cited 2009 Jun 29]; [about 1 screen]; Available from: http://www.cincoatings.com/portal/portal/user/anon/page/scchistoria.psml?categoryOID=59818080808180GC&contentid=C981808780CO&nl=pt.

[149] CIN coatings [internet]. Maia: CIN – Corporação Industrial do Norte S.A. *Grupo CIN, História da CIN – Corporação Industrial do Norte, 1950 – Uma nova visão*; [cited 2009 Jun 29]; [about 1 screen]; Available from: http://www.cincoatings.com/portal/portal/user/anon/ page/scchistoria.psml?categoryOID=59818080808180GC&contentid=C981808780CO&nl=pt.

[150] [Robbialac [internet]. Lisbon: Tintas Robbialac S.A.; c2004. *Company, History*; [cited 2005 Feb 3]; [about 1 page]; Available from: https://www.robbialac.pt/english/company/ history/.

[151] Tintas Robiallac [internet]. Lisbon: Tintas Robbialac S.A.; c2008. *Empresa, Quem somos* [cited2009 Jun 29]; [about 1 screen]; Available from: http://www.robbialac.pt/.

[152] Engenharia para o futuro – Futureng [internet]. São João da Talha: Futureng, Lda.; c2003-2009. *Futureng, Parceria, Fornecedores, Tintas Robbialac S.A.*; [cited 2009 Jun 29]; [about 1 screen]; Available from: http://futureng.wikidot.com/robbialac.

[153] Robbialac Portuguesa. *Manual de pintura*. Vol. 1. *Os Materiais de Pintura*. Lisbon: Serviços Técnicos da Robbialac Portuguesa; 1958. Portuguese.

[154] Doménech-Carbó MT, Bitossi G, Osete-Cortina L, Cruz-Cañizares J, Yusá-Marco DJ. *Characterization of polyvinyl resins used as binding media in paintings by pyrolysis-silylation–gas chromatography–mass spectrometry*. Analytical and Bioanalytical Chemistry 2008;391:1371-1379.

[155] Learner TJS. *Analysis of modern paints. Los Angeles*: The Getty Conservation Institute; 2004.

[156] Callapez, M. *Os plásticos em Portugal – a origem da indústria transformadora*. Lisbon: Editorial Estampa; 2000. Portuguese.

[157] Langley A, Burnstock A. *The analysis of layered paint samples from modern paintings using FTIR microscopy*. In: Bridgland J, editor. Preprints of the 12th Triennial Meeting ICOM Committee for Conservation; 1999 August 29 – September 3; Lyon. London: James & James; 1999 p. 234-41.

[158] Peek M, Brokerhof A. *Seminar 14 - documentation and registration of artists' materials and techniques*. In: Hummelen I, Sillé D, editors. Modern Art: Who Cares? An Interdisciplinary Research Project and an International Symposium on the Conservation of Modern and Contemporary Art; 1997 September 8-10; Amsterdam. Amsterdam: The Foundation for the Conservation of Modern Art and the Netherlands Institute for Cultural Heritage; 1999 p. 388-390.

[159] Ferreira JL, MJ Melo, AM Ramos. *A mural painting by Estrela Faria: a FTIR study of a vinyl synthetic medium*. Poster session presented at IRUG 7. Abstracts and Executive Summaries of Contributions Volume of the Seventh Biennial Gathering of the Infrared and Raman User's Group; 2006 March 38-31; New York MoMA; p. 75-76.

[160] Infrared Spectroscopy Committee of the Chicago Society for Paint Technology, editor. *Infrared spectroscopy, its use in the coatings industry*. Philadelphia: Federation of Societies for Paint Technology; 1969.

[161] Schrader B, editor. *Infrared and Raman spectroscopy – methods and applications*. Weinheim: VCH; 1995.

[162] Hummel DO. *Atlas of plastics additives, analysis by spectrometric methods*. Berlin: Springer; 2002.

[163] de Sá MH, Eaton P, Ferreira JL, Melo MJ, Ramos AM. *Ageing of vinyl emulsion paints – an atomic force microscopy study*. Surface and Interface Analysis. (DOI 10.1002/sia.3664).

[164] Pina F, Moggi L, Manfrin MF, Balzani V, Hosseini M, Lehn JM. *Photochemistry of supramolecular systems – size and charge effects in the photoaquation of adducts of the hexacynocobaltat (iii) anion with polyammonium macrocyclic receptors*. Gazzetta Chimica Italiana 1989;119:65-67.

[164a] Chalmers JM, Griffith PR. *Handbook of vibrational spectroscopy*. Vol. 3. New York: John Willey & Sons; 2002 p. 1806.

[165] de Sá MH, Ferreira JL, Melo MJ, Ramos AM. *An AFM contribution to the understanding of surface effects caused by ageing and cleaning on acrylic glass. The Shadows by Lourdes Castro, a case study*. Surface and Interface Analysis. (DOI 10.1002/sia.3663).

[166] Ferreira JL, Melo MJ, Ramos AM. *PVAc paints in works of art: a photochemical approach - Part 1*. Polymer Degradation and Stability 2010;95:453-461.

[167] Le Gac A. *As dificuldades inerentes à conservação da obra de Joaquim Rodrigo*. In: Lapa P, Ávila MJ, coord. Joaquim Rodrigo, catálogo raisonné. Lisbon: Museu do Chiado – Instituto Português de Museus; 1999 p. 89-117. Portuguese.

[168] MFA Boston: CAMEO Home. Boston: Museum of Fine Arts. *Material name: hardboard*; [cited 2009 Dec 11]; [about 1 screen]; Available from: http://cameo.mfa.org/materials/record.asp?key=2170&subkey=4456&Search=Search&MaterialName=hardboard&submit.x=0&submit.y=0.

[169] Pedroso J. *Estudo da degradação de óleos secativos, aplicado a tintas usadas por Amadeo de Souza-Cardoso, Silva Porto e Gustave Courbet* [master's thesis]. Lisbon: Univesidade Nova de Lisboa; 2009. Portuguese.

[170] Stuart B. *Analytical Techniques in Materials Conservation*. West Sussex: John Wiley & Sons; 2007.

[171] Derrick MR, Stulik D, Landry JM. *Infrared spectroscopy in conservation science*. Los Angeles: The Getty Conservation Institute; 1999.

[172] Correia AM, Clark RJH, Ribeiro MI, Duarte MLTS. *Pigment study by Raman microscopy of 23 paintings by the Portuguese artist Henrique Pousão (1859–1884)*. Journal of Raman Spectroscopy 2007;38:1390-1405.

[173] Bell IM, Clark RJH, Gibbs PJ. *Raman spectroscopic library of natural and synthetic pigments (pre- ~1850 AD)*. Spectrochimica Acta Part A 1997;53:2159-2179.

[174] Edwards HGM, Chalmers JM, editors. *Raman spectroscopy in archeology and art history*. Cambridge: Royal Society of Chemistry; 2005.

[175] Eastaugh N, Walsh V, Chaplin T, Siddall R. *The pigment compendium: a dictionary of historical pigments*. Amesterdam: Elsevier Butterwoth-Heinemann; 2004.

[176] MFA Boston: CAMEO Home. Boston: Museum of Fine Arts. *Material name: Ripolin*; [cited 2009 Jan 29]; [about 1 screen]; Available from: http://cameo.mfa.org/materials/record.asp?key=2170&subkey=7989&Search=Search&MaterialName=ripolin&submit.x=0&submit.y=0.

[177] Secca AF, dir. *António Quadros, o sinaleiro das pombas*. Porto: Árvore – Cooperativa de Actividades Artísticas; 2001. Portuguese.

[178] Claro A, Lemos A, Melo MJ, Miguel C, Miranda A. *À descoberta da cor na iluminura medieval com o Apocalipse do Lorvão e o Livro das Aves* [internet]. Lisbon: Publication in the framework of the project *A cor na iluminura medieval portuguesa: uma abordagem interdisciplinar* (POCTI/EAT/33782/2000); 2007 [cited 2009 Dec 10]; Available from: http://www.dcr.fct.unl.pt/index.php?lang=pt&section=4&subsection=18&mode=0.

[179] Gautier G, Bezur A, Muir K, Casadio F, Fiedler I. *Chemical fingerprinting of ready-mixed house paints of relevance to artistic production in the first half of the twentieth century. part I: inorganic and organic pigments*. Journal of Applied Spectroscopy 2009;63:597-603.

[180] Berlman IB. *Handbook of fluorescence spectra of aromatic molecules*. 2nd ed. London: Academic Press; 1971.

[181] Metz U, Hoffmann P, Weinbruch S, Ortner H. *A comparison of x-ray-fluorescence spectrometric (XRF) techniques for the determination of metal traces, especially in plastics*. Mikrochimica Acta 1994;117:95-108.

[182] Altuglas International: Europe/Americas/Asia: Europe Homepage. La Garenne-Colombes: Altuglas International – Arkema Group. *Altuglas Acrylic Sheet, Altuglas Acrylic Sheet - Auxiliary Products, Altuglas Acrylic Sheet Cleaner Brochure*; [cited 2007 Mar 15]; [about 2 pages]; Available from: www.altuglas.com/literature/pdf/156.pdf.

[183] Berns RS. Billmeyer and Saltzman priciples of colour technology. 3rd ed. New York: John Willey & Sons; 2000.

[184] Kurata M, Tsunashima Y. *Viscosity – molecular weight relationships and unperturbed dimensions of linear chain molecules*. In: Brandrup J, Immergut E, editors. Polymer handbook. New York: John Wileys & Sons; 1989. p. VII.

[185] Hummelen I. *The conservation of modern art: new methods and strategies?* In: Corzo MA, editor. Mortality Immortality? The Legacy Of 20th Century Art. Based on the Conference held at the Getty Center; 1998 March 25-27; Los Angeles. Los Angeles: Getty Conservation Institute; 1999 p. 171-174.

[186] Hummelen, IJ. *Conservation strategies for modern and contemporary art*. Conservering en Restauratie [Internet]. 2005 Oct [cited 2009 Jul 6];3:22-26. Available from: http://www.inside-installations.org/OCMT/mydocs/HUMMELEN%20Conservation%20Strategies%20for%20Modern%20and%20Contemporary%20Art_1.pdf.

[187] Hummelen I, Sillé D, editors. Modern art: Who Cares? An Interdisciplinary Research Project And An International Symposium On The Conservation Of Modern And Contemporary Art; 1997 September 8-10; Amsterdam. Amsterdam: The Foundation for the Conservation of Modern Art and the Netherlands Institute for Cultural Heritage; 1999.

[188] Weyer C, Heydenreich G. *Seminar 14 - documentation and registration of artists' materials and techniques. From questionnaires to a checklist for dialogues*. In: Hummelen I, Sillé D, editors. Modern Art: Who Cares? An Interdisciplinary Research Project and an International Symposium on the Conservation of Modern and Contemporary Art; 1997 September 8-10; Amsterdam. Amsterdam: The Foundation for the Conservation of Modern Art and the Netherlands Institute for Cultural Heritage; 1999 p. 385-388.

[189] Gantzert-Castrillo E. *The archive of techniques and working materials used by contemporary artists*. In: Corzo MA, editor. Mortality Immortality? The Legacy Of 20th Century

Art. Based on the Conference held at the Getty Center; 1998 March 25-27; Los Angeles. Los Angeles: Getty Conservation Institute; 1999 p. 127-130.

[190] Mancusi-Ungaro C. *Seminar 14 - documentation and registration of artists' materials and techniques. Original intent: the artist's voice*. In: Hummelen I, Sillé D, editors. Modern Art: Who Cares? An Interdisciplinary Research Project and an International Symposium on the Conservation of Modern and Contemporary Art; 1997 September 8-10; Amsterdam. Amsterdam: The Foundation for the Conservation of Modern Art and the Netherlands Institute for Cultural Heritage; 1999 p. 392-393.

[191] Ávila MJ. *A Conservação da Arte Contemporânea: um novo desafio para os museus*. Boletim Interactivo da Associação Portuguesa de Historiadores de Arte [Internet]. 2007 Dec [cited 2009 Jul 13];5:9pp. Available from: http://www.apha.pt/boletim/boletim5/pdf/3-MariaJesusAvilaConservacao.pdf. Portuguese.

Appendix I

Experimental

I.1 Questionnaires

A written questionnaire with general questions about the materials used was prepared and sent (2005) to forty seven Portuguese artists who started their careers between the 1940s and 1970s.

I.2 Interviews

January 13th 2005 – Interview with Ricardo Caiado, manager of *A Favrel Lisbonense* from 2002 until January 2006. Interview held at the facilities of *A Favrel Lisbonense* in Lisbon and conducted by Joana Lia Ferreira and Maria João Melo.

February 7th 2005 – Interview with Mário Varela Gomes, manager of *A Favrel Lisbonense* from 1970 until 1985. Interview held at the facilities of *A Favrel Lisbonense* in Lisbon and conducted by Joana Lia Ferreira and Maria João Melo.

April 30th 2005 – Informal interview with Sofia Agrela. Interview held at Sofia Agrela´s home in Dafundo and conducted by Joana Lia Ferreira and Maria João Melo.

March 21st 2005 – Informal interview with Dr. José Alberto Alves, CIN Technical Director – Decorative Products (PhD) and Engineer José Luís Nogueira, CIN R&D and Quality Director. Interview held at CIN facilities in Maia (Porto).

May 6th 2005 – Informal interview with Engineer Raúl Morgado Costa, former head of *Indústrias Químicas Synres Portuguesa*, Lda. Interview held at DCR and conducted by Joana Lia Ferreira and Ana Maria Ramos.

October 28th 2005 – First interview with Ângelo de Sousa. Interview held at the artist’s home in Porto and conducted by Joana Lia Ferreira and Maria João Melo.

June 5th 2008 – Second interview with Ângelo de Sousa. Interview held at the storage facilities of *Culturgest* – Fundação Caixa Geral de Depóstios in Lisbon and conducted by Joana Lia Ferreira and María Jesús Ávila.

I.3 Workshops

Four workshops were held at the DCR with Sofia Agrela on the painting techniques of Joaquim Rodrigo: May 2005, November 2005, October 2006 and May 2008.

I.4 Samples from case studies

Nine paintings by Joaquim Rodrigo were selected as case studies: *S.M.*, 1961; *M.L.*, 1961; *Kultur – 1962*, 1962; *Mondo Cane I*, 1963; *Liberté*, 1963; *Lisboa – Oropeza*, 1969; *Alassio – Nice*, 1971; *Port-Ligat – Granada*, 1980; *Os quintais*, 1989. The painting *Os quintais,* representative of the final 'correct paintings' by Rodrigo, was studied at DCR in November 2009. With the exception of *Os quintais* (private collection), all paintings were either owned by or deposited at the National Museum of Contemporary Art (MNAC – Museu do Chiado). Samples from five paintings (selected with the help of the artist) made by Ângelo de Sousa in the 1960s and belonging to the artist's collection, were studied: *Untitled*, 1961/2; *Árvore*, 1962; *Plantas*, 1962; *Untitled* (mock-up), 1964; *Natureza Morta*, 1965.

A total of thirty-seven paint μ-samples from dated works were analyzed

A hand painted paint catalogue from the *Sabu* vinyl paints by *A Favrel Lisbonense* was studied; the catalogue is a 16.3 x 20.1 cm cardboard, in which the paints (twenty one colours) are applied on 2.7 x 2.7 x 2.7 cm cellulose cardboard triangles.

For this study some of the PMMA sheets belonging to Lourdes Castro's sample collection were characterized. One transparent (LC transparent Alt S.310 – 3 mm thick) and two fluorescent sheets (LC fluorescent orange Alt T.750 – 2 mm thick; LC fluorescent pink Alt T.770A – 2 mm thick) from the *Altuglas* palette and two PMMA sheets offered by the artist for our studies (LC fluorescent pink and LC opaque blue). Also, samples from the work *La place en marche* (1965), which belongs to the National Museum of Contemporary Art – *Museu do Chiado*, were analysed.

I. 5 Other samples

Furthermore, some materials kept by the artists in their studios were collected and characterized. A sample of white paint left by the artist in his studio (probably the last one he produced in 1990) was analysed, as well as a pigment collection used as reference. Two samples of a vinyl medium from *Soberana* used by Ângelo de Sousa to prepare his paints in the sixties, which were stored in two different plastic bottles (in one bottle the medium was kept as pure emulsion and had become a yellowish gel, in the second bottle it was mixed with water); three samples of vinyl based emulsions from a later supplier (Engineer Joaquim Simões), stored in glass bottles and labelled as gel, mate, and gloss varnishes.

Also, two hand painted catalogues by *Robbialac* were analyzed: REP – series 24-100 and REP *cores fortes* – series 24-400.

I.6 Materials

Poly(vinyl acetate) beeds, powder poly(vinyl alcohol) (90% hydrolyzed) and powder PMMA (medium and high molecular weight) were purchased from *Aldrich*, each with average molecular weight (*Mw*) ≈83000, 30-70000, ≈120000, ≈960000 (as given by the supplier) respectively. *Vulcano V7* (described as water soluble acryl-vinyl polymer resin) was purchased from *Casa Varela*. Titanium white (TiO_2, predominantly in the rutile crystalline form) and ultramarine blue (Ult) were purchased from *Casa Varela; Rouge de pouzzoles* - PC13 (Fe_2O_3), *Ocre rouge* 2202 and O*cre jaune* 2202 by *Lefranc & Bourgeois* were obtained from the pigment collection left by Joaquim Rodrigo in his studio; *Nero di mars* was purchased from *Zecchi*; calcium carbonate - ML 7 ($CaCO_3$, calcite crystalline form) was obtained from *A Favrel Lisbonense*; a sample of manganese blue was obtained from the *Instituut Collectie Nederland* collection. Contemporary *Sabu* paints (Ultramarine and Ochre) from *A Favrel Lisbonense*, purchased from *Casa Varela*, *Vinamul* 3469 (emulsion based on a vinyl acetate-vinyl chloride-ethylene terpolymer) from *Sarcol* and di-iso-buthyl phthalate from *Aldrich* were included for comparison. Cast (transparent colourless, transparent blue and opaque white) and extruded (transparent) 3 mm PMMA sheets were obtained from *Paraglass* (Portugal). A commercial cleaning product (*Altuglas Cleaner* – described by the manufacturer as an emulsion of silicone oil and cationic detergent in water, whose anti-static properties require less frequent cleaning since it leaves a protective film on the surface of the material [182] was purchased from *Altumax* (Spain). For the preparation of a chemical filter, potassium chromate (K_2CrO_4) and NaOH pallets were used. Potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$) was used as actinometer. Reagents and solvents were of reagent (polymers, acetone and alcohol) or analytical (chloroform) grade; the water used was Millipore grade.

I.7 Instruments and methods

I.7.1 Sample preparation

Two sets of samples were prepared for the photodegradation experiments under polychromatic light. Paint reconstructions were prepared with *Vulcano V7* as the binding medium (set 1). For comparison, reference paint samples were prepared using a solution of pure PVAc (set 2). *Vulcano V7* was diluted with water in 1.5/1 ratio (v/v). A solution of PVAc 20% (w/v) was prepared in acetone. Samples were prepared by mixing the binding media with selected pigments (TiO_2, Fe_2O_3, Ultramarine blue and $CaCO_3$, a common extender used in paints) in weight by weight ratios, which represent the paints analysed from particular case studies. As presented in Table I.1, the following mixtures were prepared, for TiO_2, Fe_2O_3, Ultramarine and $CaCO_3$: 50/50 (binder/pigment); for TiO_2 + $CaCO_3$: 50/18/32; for TiO_2 + Fe_2O_3: 50/20/30; for Fe_2O_3 + $CaCO_3$: 50/10/40; for Ultramarine + $CaCO_3$: 50/30/20.

Table I.1. Paint reconstructions and reference paint samples

Samples	**Contents (% by weight)**
Binder [a]	(100)
Binder + TiO_2	(50/50)
Binder + Fe_2O_3	(50/50)
Binder + Ult	(50/50)
Binder + $CaCO_3$	(50/50)
Binder + TiO_2 + $CaCO_3$	(50/18/32)
Binder + TiO_2 + Fe_2O_3	(50/20/30)
Binder + Fe_2O_3 + $CaCO_3$	(50/10/40)
Binder + Ult + $CaCO_3$	(50/30/20)

[a] The binding media used were *Vucano V7* emulsion (set 1) for paint reconstructions and PVAc homopolymer (set 2) for reference samples.

For each set nine series of six samples were prepared: the binder (6), the binder mixed with each of the four selected pigments (24) and with pigment mixtures (24). A series of PMMA films (cast from a 20% w/v solution in acetone) was also included as a reference. A four sided *Zehntner GmbH* film applicator (ZAF 2010), prepared to apply a 200 μm wet film, was used for film application on glass slides. A total of 113 films (for accelerated ageing studies, Figure I.1) were obtained by placing the wet samples on 2.5 x 1.9 cm glass slides; set 1 – paint films with an average mass of approximately 42 mg after solvent evaporation – and set 2 – paint films with an average mass of approximately 35 mg after solvent evaporation. The samples were kept in horizontal position at room temperature for two weeks (for solvent release), after that they were kept under controlled humidity in a desiccator until a constant mass was reached. For FTIR transmittance analysis, the pure PVAc solution and *Vulcano V7* emulsion, as well as their mixtures with each of the four pigments studied, were further diluted and placed on Si disks. With the exception of SEC and dynamic light scattering, all analyses were carried out on dry film samples.

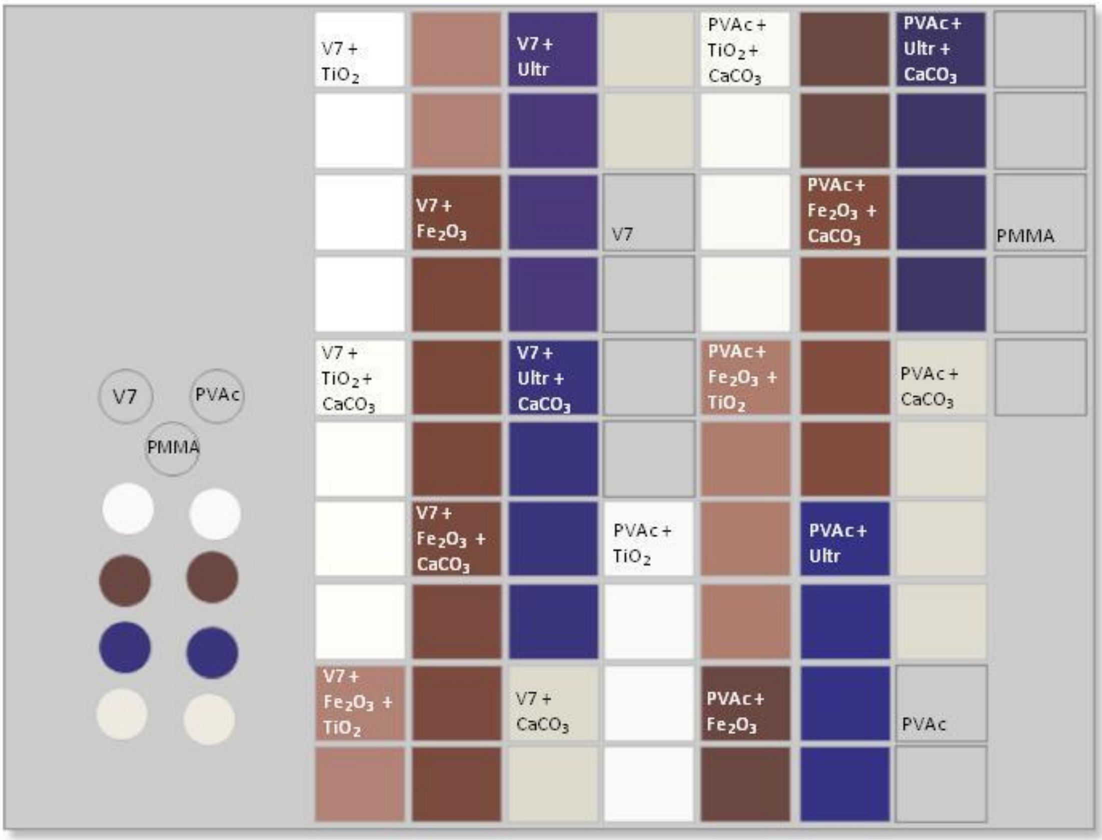

Figure I.1. Paint reconstructions experimental set for photodegradation studies under a Xenon-arc lamp, λ >300 nm.

The PMMA sheets studied were cut with a diamond ring saw into 35 mm x 25 mm pieces and the external plastic protection was then removed. To ensure the same initial surface state for all sheets, the samples were cleaned with *Altuglas Cleaner* prior to the ageing experiment. Also, at regular intervals (500h, 1750h, 3000h and 4250h irradiation) the samples were cleaned using *Altuglas Cleaner*, the same product used by the artist as final treatment and maintenance of her PMMA shadows. The *Cleaner* was applied with lens tissue in gentle circular movements (4 to 6 circles); this procedure was completed by wiping the surface with a clean dry tissue. After cleaning, the samples were kept at room temperature for two weeks, after that they were kept under controlled humidity in a dessicator until a constant mass was reached.

For reaction quantum yield (Φ_r) determinations, four PVAc and four PMMA films were prepared by placing the wet samples on 3 cm^2 glass slides, corresponding to *ca* 20 mg per slide after solvent evaporation.

Also, solutions of PVAc and PVAL, 5% (w/v), were prepared in acetone and ethanol respectively; mixtures of PVAc and PVAL solutions were prepared, in 90:10 and 80:20 (v:v) ratios, simulating the increase of PVAL on a PVAc matrix. Films were obtained by placing the samples on glass slides for dry film formation.

I.7.2 Micro-sampling

The artworks selected as case studies, paint catalogues and the PMMA palette belonging to Lourdes Castro, as well as some reference materials (previously placed on glass slides for dry film formation), were μ-sampled. Micro-sampling was performed with a *Ted Pella* micro-tool under a *Leica* MZ16 stereomicroscope with a 7.1x to 115x zoom range, equipped with an integrated *Leica* ICD digital camera and a *Leica* KL 1500 LCD external cold light source with two flexible optic fibre cables. The samples were stored between two glass slides used as sample holders.

I.7.3 Accelerated ageing

The irradiation tests were carried out in a CO.FO.ME.GRA accelerated ageing apparatus (*SolarBox 3000e*) equipped with a Xenon-arc light source ($\lambda \geq 300$ nm) with constant irradiation of 800 W/m^2 and black standard temperature of 50 ^{o}C (inside the chamber temperature was maintained at approximately 24 ^{o}C and RH at 40%). The films cast on glass slides and Si disks, as well as the PMMA sheets, were placed in the SolarBox. With the exception of PVAc and *Vulcano V7* films on Si disks that were irradiated for a period of approximately 5000h (total irradiance=13762 MJ/m^2), all other films were irradiated for a maximum period of 3500h (total irradiance=10130 MJ/m^2). Before irradiation and after 500h, 1500h, 2500h and 3500h the following determinations were made on glass slide samples: 1) mass loss; 2) colourimetry; 3) surface changes (only for PVAc, *V7* and *V7* + TiO_2 at 0h and 3500h); 4) solubility; 5) molecular weight; 6) particle size (only for PVAc). The PMMA sheets were irradiated for a maximum period of 4250h (total irradiance=12455 MJ/m^2). Before irradiation and after 500h, 1750h, 3000h and 4250h the following determinations were made on PMMA sheets: 1) mass loss; 2) colourimetry; 3) surface changes (only for 0h and 4250h); 4) molecular weight. Molecular changes were inspected by infrared spectroscopy at all intervals (transmittance mode for the thin films deposited on Si disks and reflectance mode for the PMMA sheets). The same determinations were performed on control samples which were kept in the dark during the experiment.

I.7.4 Mass loss

Sample weight determinations were obtained with a *Sartorius* CP225 D micro analytical scale. Weight measurements were performed on the glass slide samples and PMMA sheets, mass loss was determined by comparison of irradiated samples with t=0h. After irradiation in the SolarBox, the samples were kept in a desiccator for four days until a constant mass was reached, three independent measurements were performed.

I.7.5 Colourimetry

Colour determinations were made using a *Datacolour International* colourimeter (*Microflash*). The optical system of the measuring head uses diffuse illumination from a pulsed Xenon-arc lamp over a 8 mm-diameter measuring area, with 10º viewing angle geometry; the reference source was D65. Before colour determinations, calibration was performed with bright white and black standard plates. The equipment measuring head was positioned with the aid of a positioning mask allowing future measurements on the same area; in the case of the samples used in the ageing experiment, samples were placed on filter paper with a 1.5 cm support and the measurements were performed on control samples (non-irradiated) and on irradiated samples; for each determination of *Lab** values the mean value and standard deviation of three independent measurements were calculated. Total colour variation (ΔE^*) was further calculated according to the expression $\Delta E^* = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2}$ [183].

I.7.6 Solublity

The solubility of the films cast from PVAc solution after different irradiation periods was determined gravimetrically after immersion of the films in chloroform and filtration with pre-weighted membrane filters (0.45 µm). Before and after filtration, filters were kept in a desiccator until a constant mass was reached; the possible polymer insoluble fraction (gel formation) was determined by weight gain. The gravimetric experiment was conducted on polymer solutions (from PVAc and PMMA films before and after irradiation; control samples kept in the dark for six months) and also on pure solvent ($CHCl_3$). The relative standard deviation, s_r (%), was calculated as a measure of the filters relative weight-gain after filtration.

I.7.7 Extraction

After mass loss determination and colourimetry, the soluble polymer in the samples matrix was extracted in chloroform. For extraction, 3 mg (pure polymer), 6 mg (V7 emulsion) and 8.5 mg (paint) were collected from the films with the cutting edge of a spatula and immersed in chloroform. Preliminary tests were performed to determine the extraction time for paints prepared with *Vulcano V7* emulsion: 1h, 3h, 5h, 24h and 48h. By means of gravimetry and SEC analysis, it was concluded that 5h were enough to extract the soluble polymer present in the film. As those were the most difficult to extract, 5h was also the average time applied to extract all the other films. The same procedure was performed for the PMMA sheets.

I.7.8 Size Exclusion Chromatography

Molecular weight distributions were determined with a Size Exclusion Chromatography (SEC) apparatus (*Waters*), including a solvent delivery system composed by a model 510 pump, a Rheodyne injector and a refractive index detector model 2410. A series of three *Waters* Ultrastyragel columns, 10^3 Å, 10^4 Å and 10^5 Å porosity, was used for separation. The operating temperature was 30° C, using chloroform as eluent with a flow rate of 1 ml/min. Universal and relative calibrations were performed with monodisperse poly(methyl methacrylate) (PMMA) standards from *Polymer Laboratories* (in the range of 1.14×10^3 to 1.25×10^6). Butyl-hydroxytoluene (BHT) was used as a reference substance. The values of Mark-Houwink-Sakurada constants used for the pairs PVAc/chloroform and PMMA/chloroform, were respectively K=0.0203 ml/g; a=0.72 and K=0.00493 ml/g; a=0.8 [184]. Average molecular weights (M_w and M_n) and polydispersity (PD=M_w/M_n) were determined with the *Waters* software *Millenium 32*. Solutions (ranging from 0.3% for the pure polymer to 0.85% for the paints (w/v) in chloroform) were prepared and filtered with 0.45μm pore filters; 200 μl of sample solution were injected.

I.7.9 Dynamic Light Scattering

The particle size was determined by dynamic light scattering (DLS) with a *Zetasizer Nano-ZS* Series ZEN3600 equipped with a 633 nm He–Ne laser (*Malvern*). Extra cleaned glass material was used and solutions 0.35% (w/v) were prepared with filtered acetone and with filtered chloroform; no further filtration was done after solution preparation as the analyses were performed in order to investigate possible crosslinking with an increase in the particle size.

I.7.10 μ-FTIR

Infrared (IR) spectra were acquired with a *Nicolet Nexus* spectrophotometer equipped with a *Continuum* microscope and a MCT-A detector cooled by liquid nitrogen. The analyses were performed in films applied on Si disks for irradiated film samples; in μ-samples previously compressed with a *Thermo* diamond anvil cell; or directly on the sample surface. Spectra were obtained in transmittance mode, with a resolution of 8 cm^{-1} and 64 scans (for films on Si disks), of 4 cm^{-1} and 128 scans (for μ-samples) and in reflectance mode using an attenuated total reflectance (ATR) accessory with Si crystal, with a resolution of 8 cm^{-1} and 128 scans (for surface analysis). Spectra are shown as acquired, without corrections or any further manipulation, except for the removal of the CO_2 absorption at approximately 2300-2400 cm^{-1} and eventual base line correction. Furthermore, values of peak centre (μ), area (A), and full width at half maximum (σ), for the C=O stretching absorption peak were obtained by fitting with a Gaussian function; the fitting was performed with *Origin* software (*OriginLab* Corporation).

I.7.11 UV-VIS spectroscopy

Ultraviolet-visible absorption spectra of PVAc and PMMA films were recorded using a *Varian-Cary* 100 *Bio* spectrophotometer, using air as reference. Estimated errors (relative standard deviation) for the absorbance of the PVAc and PMMA films at 313 nm are 15% and are the result of five independent measurements. Absorption spectra of PMMA sheets were recorded in a *Shimadzu* UV-2501PC spectrophotometer, using air as reference. Reflectance spectra of powder pigments were recorded in a *Shimadzu* UV-2501PC spectrophotometer equipped with an integrating sphere, using $BaSO_4$ as reference.

I.7.12 μ-Spectrofluorimetry

The measurements for the fluorescent PMMA samples (*Altuglas*) from the sample collection belonging to Lourdes Castro were obtained with a *microSPEX* instrument, with the *Spex Fluorog* apparatus 3-2.2 connected to an *Olympus* BX51 M confocal microscope. Spatial resolution was controlled with a pinhole (8) corresponding to a 32 μm analysis spot with a 50 X lens. Emission spectra were acquired using a 500 nm dichroic filter, exciting at 503 nm for the fluorescent orange (LC Alt T.750) and pink (LC Alt T.770A) PMMA samples. Excitation spectra where obtained with a 570 nm dichroic filter.

I.7.13 μ-Raman

Raman spectra were obtained from μ-samples (except for the *Sabu* catalogue, which was analysed *in situ*) using a *Jobin Yvon dispersive* Raman Spectrometer *Lab Ram 300* model (Stigmatic 300mm focal length spectrograph) equipped with a BX 40 confocal microscope; He-Ne 17mW laser light-source (632.8nm) and solid state laser (532nm); a Peltier cooled CCD detector. The laser beam was focused with a 100 X *Olympus* objective lens, with a spot size of 2 μm. Collection time was 2 to 15 seconds and 5 to 15 scans were performed on each colour analyzed; depending on the sample the laser power was varied with neutral density filters (optical densities: 0.6, 1.0 and 2.0)

I.7.14 μ-EDXRF

Energy dispersive X-ray fluorescence spectra were recorded from μ-samples or *in situ* with an *Intax GmbH ArtTax* spectrometer, equipped with a mobile arm, molybdenum anode, Xflash detector, offering a spatial resolution of 70 μm. Spectra were obtained at 40 kV, 300 μA and with measuring times of 150s.

I.7.15 Measurement of I_0 and Φ_R

Solid state chain scission quantum yields were determined for pure PVAc and PMMA for irradiation at 313 nm; the films (cast on 3.3 and 3.06 cm^2 glass slides, corresponding to 19.81 and 15.90 mg per slide after solvent evaporation) were irradiated for a maximum period of 1850h (total irradiance=5260 MJ/m^2). In order to isolate the 313 nm wavelength from the Xe-arc lamp emission spectrum, a potassium chromate (K_2CrO_4) chemical filter was prepared according to the literature [73]: 175 mg of K_2CrO_4 were dissolved in 0.5 L of NaOH (0.05 M). Three quartz cells of 75 x 25 x 10 mm were assembled and used as filter containers. The samples were placed under the filters in the ageing chamber (Figure I.2) and analyzed by SEC after three different irradiation times: 350h, 1200h and 1850h.

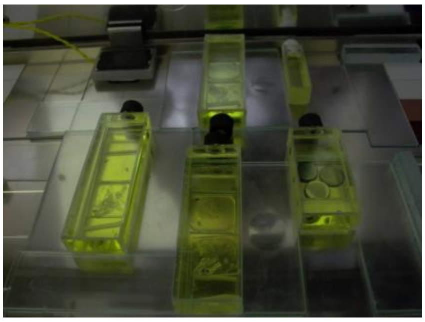

Figure I.2. Setup for monochromatic irradiation under a Xenon-arc lamp at λ = 313 nm.

The intensity of the incident light (I_0) at 313 nm was calculated using 3 ml solution of potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$) actinometer 10^{-2} M in water, pH=2, with an optical path lenght of 1 cm. A UV-vis spectrum of the solution was aqired every 30 minutes and the formation of pentacyanocobaltat(II) ($[Co(CN)_5(H_2O)]^{2-}$), eq. I.1, was followed at 380 nm, with a quantum yield of 0.31 [164].

$$Co(CN)_6^{3-} + H_3O^+ \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + HCN \qquad (I.1)$$

The I_0 was calculated, with correction for the absorbed light according to equation 1 (Chapter 3.2). The quantum yields of reaction in homogeneous media were calculated with equations 4 (Chapter 3.2) and 7(Chapter 3.3). Estimated errors for the Φ_R are 20% and are the result of one measurement.

Appendix II

A Favrel Lisbonense [1]

II.1 Interview with Ricardo Caiado, manager from 2002 until January 2006

Ricardo Caiado, Joana Lia Ferreira and Maria João Melo
Lisbon, January 13th 2005

Ligações Perigosas: Quando, e por quem, foi fundada *A Favrel Lisbonense*?

Ricardo Caiado: Não temos bem a certeza. Pensamos que foi pelo avô de José Netto Varella, no Porto; era a *Favrel Portuense*. Crê-se que em 1781[2] já existia uma oficina na Rua dos Caldeireiros na cidade do Porto. Encontramos uma referência à *Favrel*[3] datada de 1856, num catálogo antigo, do princípio do século, onde se escreve que José Netto Varella era gerente técnico da *Favrel Portuense*. Terá vindo para Lisboa mais tarde, e sobre a abertura desta loja também temos dados. 'A *Favrel Portuense* abriu uma sucursal em Lisboa em 1873'. Na mesma data, é cedido o alvará para A *Favrel Lisbonense*; houve uma altura em que trabalharam as duas em conjunto, mas depois fechou a *Favrel* do Porto e ficou só a de Lisboa, aqui neste sítio. Em '1891 terminou a actividade industrial da *Favrel Portuense*, passando a sede e a sua produção para *A Favrel Lisbonense*'.

L.P.: Foi então esta a profissão de José Netto Varella durante toda a vida?

R.C.: Exactamente. Ouvi histórias de que foi a França aprender a trabalhar o ouro, já no tempo dele a *Favrel Portuense* era uma fábrica de folha de ouro; vendia artigos para artistas, para pintura, para talha, mas também fabricava a folha de ouro. Depois começou a produzir a folha de ouro também em Lisboa.

L.P.: Será possível sabermos qual a motivação inicial da *Favrel*?

R.C.: Os meus tios saberão melhor do que eu; já ouvi histórias de ter sido, na sua origem, uma pequena fábrica de tintas para pintar barcos mas essa é uma referência vaga. Nestes catálogos antigos que aqui tenho são referidos muitos artigos; mas não remontam às origens da fábrica, os primeiros catálogos que temos são de finais do século XIX. O meu avô, António Varela, é que desenvolveu a produção das tintas; durante a guerra havia

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[1] The full interviews are presented here in Portuguese, the language in which they were conducted; the main information is discussed in the core of the thesis.

[2] No fim da entrevista lemos num catálogo que José Netto Varella era neto do fundador da *Favrel Portuense*, fundada em 1752.

[3] Embora o nome da empresa seja *A Favrel Lisbonense*, em alguns momentos da entrevista foi referida como *Favrel* (abreviatura pela qual é habitual esta empresa ser referida).

dificuldades e os artigos estrangeiros aumentavam de preço, o ideal seria produzir internamente, o que não significa que não se produzisse algum material para pintura antes, há um verniz que já no princípio de século fazíamos, o *Verniz Ideal*, para dourar. Mas vendíamos muitos produtos importados, de marcas conhecidas como a *Lefranc* ou a *Reeves*.

L.P.: A *Favrel* não fabricava apenas, era também uma loja?

R.C.: Sim, era uma loja que importava e fornecia essencialmente artigos para artistas, apesar de ter também outras coisas; mas isso no fim do século passado era normal. Por exemplo, nos catálogos aparecem olhos de vidro (para modelos, bonecos e até olhos de vidro mesmo para pessoas), não sei se vendiam foguetes. Há uma loja no Porto, de materiais para Belas Artes, que ainda hoje vende pirotecnia.

L.P.: Qual a relação entre a *Favrel* e a *Casa Varela*?

R.C.: A *Casa Varela* não é mais do que a *Favrel Lisbonense*, é a porta de entrada; como o dono era o Varela, ficou o nome. No seu início, a firma era *Favrel Lisbonense*, depois é que mudaram o nome da loja para o nome da família, *Varela Gomes – Artes Plásticas*, mas nunca ficou registada como *Casa Varela*.

L.P.: A *Favrel* não fabrica exclusivamente para a *Casa Varela*, ou sim?

R.C.: Antigamente fábrica e loja eram a mesma coisa, só há 20 anos é que se separaram. E antigamente a fábrica fornecia a loja e, através da loja, as ex-colónias e o país inteiro. Quando as colónias acabaram, ficou a fornecer o país, mas sempre através da loja, tinham revenda de artigos nossos e artigos estrangeiros. E tínhamos a venda ao público, ao balcão. Sempre produzimos essencialmente para a loja, que depois distribuía. Como agora a loja e a fábrica estão separadas, os clientes que antigamente iam à loja vêm à fábrica, mas também compram na loja alguns artigos de marcas estrangeiras; principalmente clientes do interior que vêm cá muito e ainda compram coisas ali. Isto para não terem que comprar ao fornecedor, para já porque têm que ir à procura, utilizar o computador; para além disso, como não vendem tanto também não se justifica. Temos clientes muito antigos, já do tempo do meu avô, espalhados pelo país todo, continente e ilhas.

L.P.: Da venda ao público, interessa comparar a comercialização dos produtos de fabrico próprio com os importados.

R.C.: Antigamente, no tempo do meu avô, havia mais dificuldades financeiras e os nossos artigos saíam mais do que agora; actualmente há um maior poder de compra. Mas é mais barato e há pessoas que não se importam. A qualidade é aceitável, apesar de não termos produção que se compare com as grandes marcas. Isto é uma ‘fabriqueta pequenina’, ainda artesanal, tenho máquinas do tempo do meu avô. Alguns produtos de marca estrangeira são de melhor qualidade, mas outros são iguais! As pessoas hoje, por mais algum dinheiro preferem os artigos estrangeiros. O nosso artigo hoje também já não é tão barato, por causa das importações da matéria-prima; como isto é uma coisa pequena, a quantidade de matéria-prima que eu compro não é igual à de uma fábrica grande, a quem podem fazer preços mais baixos. As diferenças de preço já não são tão grandes, já não é o abismo que era antigamente. No tempo do meu avô havia artistas que trocavam material por quadros, hoje em dia já ninguém faz isso.

L.P.: Nessa altura compravam mais os vossos produtos?

R.C.: Não sei, agora também há mais gente… Não consigo comparar a venda dos artigos estrangeiros com os nacionais.

L.P.: Têm registos em arquivo onde possamos comparar?

R.C.: Houve um grande incêndio aqui na casa em 1954 e destruiu tudo, isto ficou em cinzas, foram os registos todos, quadros antigos que havia aí, ficou tudo em pó.

L.P.: E de 54 para a frente?

R.C.: Há alguma coisa, mas muito pouco. Para já porque não havia a preocupação de guardar; tenho aí artigos do tempo do meu avô, mas pouca coisa, ‘monos’ que ficam esquecidos e de vez em quando vou ver em cima de um armário e está lá um frasco antigo, mas é raríssimo. Muita coisa foi para o lixo, na altura não deram valor; estavam para ali uns frascos, caixas de papéis, coisas sem valor! No sótão da loja ainda há alguns registos, mas nada assim tão antigo; a contabilidade, há uns anos, exigia que guardássemos as facturas durante 10 anos. Possivelmente só teríamos os últimos 10 anos, o que é pouco. Mas tivemos muitos artistas conhecidos que compraram cá, aliás quase todos, eram poucos os que não compravam, no princípio do século havia a nossa casa e outra na baixa. A *Casa Ferreira* abriu na década de 30, foi um antigo funcionário nosso que abriu a casa na Rua da Rosa, uns quarteirões abaixo da *Casa Varela*.

L.P.: E por volta dos anos 50, sabe se haveria outras casas de materiais para Belas Artes, especificamente tintas para artistas?

R.C.: Éramos os únicos, nós e a *Casa Ferreira*, pelo menos em Lisboa e refiro-me a casas especializadas, não quer dizer que uma papelaria não vendesse algumas tintas. Não sei bem quando abriu a *Corbel*, mas acho que é posterior. Hoje, claro, já não temos os clientes que tínhamos; apesar de haver mais pessoas, a concorrência também aumenta. Hoje em dia vai-se a qualquer supermercado e compra-se uma tinta para artistas, já não é um produto especializado.

L.P.: Referiu que existem por aí algumas coisas, alguns frascos. Será possível fazermos uma amostragem?

R.C.: O que temos ali é uma tinta de sub-capa que era feita cá. Como tinta acho que é só isso que tenho, posso ver se arranjo aí mais qualquer coisa, mas não tenho nada de específico, não há frascos cheios. Tenho algumas embalagens vazias, rótulos antigos.

L.P.: Para o nosso trabalho é muito importante termos alguns padrões, de modo a podermos comparar com as nossas amostras e conhecer a cronologia precisa e exaustiva; o que nos pode dizer sobre as vossas marcas?

R.C.: A nível de resinas, por exemplo para a cola *Vucano V7* e para a *Sabu*, os fornecedores foram mudando. Talvez consigamos encontrar registos antigos com as matérias-primas utilizadas.

L.P.: Acha mesmo que não conseguimos encontrar alguma coisa para análise?

R.C.: Acho. Encontra mais depressa num atelier de um artista do que aqui. Posso ver, mas apesar de as fórmulas de fabrico não terem mudado muito, às vezes mudam; deixa de haver um artigo e dão-nos um outro para substituir; o Eng.º Químico da firma que nos vende traz outra resina que diz ser igual. Como eu não percebo nada de química, confio e faço a experiência. Se der, muito bem.

L.P.: Temos vindo a encontrar sucessivamente tintas vinílicas em obras de alguns artistas. Pensa existirem vantagens na utilização das tintas vinílicas em relação a outras tintas sintéticas? Só recentemente começaram a fabricar uma tinta acrílica.

R.C.: Para essa tinta acrílica usamos o *Plextol B500*.

L.P.: Antes disso fabricavam uma tinta vinílica, a *Sabu*.

R.C.: Essa tinta já vem do tempo do meu avô. Até tenho ali o registo da marca, mas mesmo antes do registo já se fazia. Por exemplo para a cola *V7*, foi feito o pedido a 15 de Outubro de 1968 e o registo foi concedido em Fevereiro de 70. Os registos foram todos pedidos mais ou menos na mesma altura. Depois há datas na família que sabemos; no outro dia estive a falar com o meu tio e ele disse-me que em 57 já se usava a *Sabu*, houve uma feira em que o meu avô pintou o *stand* com tintas *Sabu*.

L.P.: Não lhe parece então que tenha havido uma procura preferencial das tintas vinílicas em relação às acrílicas?

R.C.: Não sei qual foi a ideia do meu avô, nem como é que surgiu a ideia de fazer a tinta *Sabu*.

L.P.: E como é que surge a ideia, agora, de fazer a tinta acrílica?

R.C.: Foi ideia do meu pai; vimos que começava a haver procura de uma tinta acrílica para as telas. Como muitos artistas pintavam com *Sabu* ou com a cola *V7* misturada com *Cenógrafa*, percebemos que havia mercado e experimentámos. O meu pai experimentou ver como é que se fazia, escolher a resina, etc., como muitos dos nossos fornecedores são Eng.ºs Químicos também foram dando algumas opiniões. E o meu pai acabou por fazer a tinta acrílica, que é mais barata, é nacional.

L.P.: Tem tido uma boa aceitação?

R.C.: Ao princípio nem por isso, por causa da embalagem. É um bocado difícil competir com um artigo estrangeiro; as pessoas olham para os artigos estrangeiros e, como ‘os olhos também comem’, olham para uma embalagem nossa e pensam que não deve prestar! Ao princípio houve alguma aceitação por causa do preço. Agora mudei as embalagens, consegui encontrar quem me vendesse tubos e, como ficou com melhor aspecto, começou a vender-se mais.

L.P.: Tem alguma ideia das razões que levaram ou que levam à escolha dos nomes?

R.C.: Em relação à tinta *Sabu*, conta-se que era o nome de um *boxer* que havia na altura, e que o meu avô quando fez a tinta deu-lhe o nome desse *boxer*. Mas já ouvi tantas histórias... E havia nomes que surgiam em conversa com artistas; antigamente alguns rótulos eram feitos por artistas, temos rótulos feitos pelo Hilário Teixeira Lopes, ou por outros artistas que eram amigos do meu avô e que passavam aí a vida.

L.P.: E em relação à cola *Vulcano* e ao acrónimo *V7*? A *Casa Ferreira* também comercializa uma cola vinílica, a cola *V2*...

R.C.: Tenho impressão que a nossa cola foi para o mercado primeiro, embora não tenha a certeza, e eles escolheram *V2*, porque a nossa era *V7*; talvez por uma questão de *marketing*, para as pessoas associarem. E ainda há uma outra empresa, também de antigos funcionários nossos, que comercializa uma *V5* (*J.A. Cabral*).

L.P.: Então não terá nada a ver com a resina que era usada?

R.C.: Não sei. *Vulcano* também é nome de esquentadores!

L.P.: E estas duas linhas, a cola *Vulcano* e a tinta *Sabu*, que são as duas vinílicas que vendem; sabe dizer-me qual era, e qual é ainda hoje, a importância em termos de vendas para a empresa?

R.C.: São os nossos artigos que mais se vendem.

L.P.: Que outros produtos comercializam / produzem ou produziram ao longo da história?

R.C.: Bem, houve alguns que acabaram e outros que ainda continuam e ainda há outros que só embalamos, como os óleos de linho e a essência de terebintina, compramos embalagens grandes e dividimos. Há alguns vernizes que também fazemos, por exemplo o *Verniz Ideal* é muito antigo, já aparece em alguns dos primeiros catálogos e ainda hoje fazemos.

L.P.: Tem alguma listagem dos produtos que aparecem nesses catálogos antigos e que ainda fazem hoje em dia?

R.C.: Não; por exemplo, os óleos hoje em dia chamam-se *Velasquez* mas já chegou a haver duas qualidades de óleo para artistas. Sei que o *Verniz Ideal* é um dos nossos produtos mais antigos e que ainda hoje fazemos; o betume judaico não sei há quanto tempo produzimos. Também temos aqui uns vernizes acrílicos, com resinas acrílicas.

L.P.: Produzidos por vocês ou re-embalados?

R.C.: Produzidos. Há de acabamento brilhante e mate.

L.P.: Qual a hierarquia e diferença de preços das tintas (da *Sabu* em relação à nova tinta acrílica)?

R.C.: Não é comparável. Embora ainda haja quem pinte em tela com tinta *Sabu*, hoje em dia tem-se a percepção de que para pintar na tela, ou se pinta a óleo ou com tinta acrílica.

L.P.: E porque é que se tem essa ideia?

R.C.: Por causa das marcas, não sei... Talvez o que ensinam nas escolas.

L.P.: Portanto, como fornecedor não vê que uma tinta acrílica tenha mais vantagens que uma vinílica?

R.C.: Não vejo a vantagem da durabilidade; compreendo que haja, mas sei que o cliente de uma maneira geral é leigo nisso, nem se interessa (desde que tenha cor!).

L.P.: Então qual pensa ser a vantagem da tinta acrílica?

R.C.: Tenho a certeza que a resina acrílica é superior à vinílica. Já trabalhei na loja, no balcão, e há artistas que sabem o que querem. Cada vez há menos, mas ainda há alguns e a primeira coisa que vão ver é o conteúdo, de que é feito, mesmo a nível de pigmentos.

L.P.: Voltando à questão dos preços, dizia-me que não são comparáveis.

R.C.: Se alguém aparece a dizer que tem uma mesa em madeira para pintar, o próprio funcionário dá-lhe tinta *Sabu*, não dá uma tinta acrílica; a *Sabu* vende-se em recipientes de maior quantidade e é mais barata proporcionalmente, enquanto que o acrílico vendemos praticamente só para quem quer uma tinta acrílica para pintar uma tela. E até porque eu acho que os nossos acrílicos não se adequam a todos os objectivos; não por causa da resina, mas da maneira como é feito; nós misturamos o corante na resina e a tinta fica um pouco transparente. Para os acrílicos compramos já o pigmento líquido, não fazemos a mistura no moinho como por exemplo nos óleos, no fundo coramos a resina; eu sei que se preparasse o pigmento líquido, com pigmentos em pó, ficava mais opaco, mas começou-se a fazer assim e é mais simples.

L.P.: Quando fala em pigmento líquido...

R.C.: É corante líquido, feito nas fábricas. Pigmento e água já misturados, não sei se terá algum estabilizador, emulsionantes, deve ter. No fundo é um corante. Mas isto só nos acrílicos, para a tinta *Sabu* usamos pigmentos em pó. A *Sabu* também já não é tão barata como tudo isso, os espanhóis têm artigos mais baratos do que os nossos e os próprios lojistas às vezes não querem comprar a nossa tinta *Sabu*, porque é mais cara. Mas depois chegam lá os clientes e preferem a tinta *Sabu*, é mais cara só que rende mais, é uma tinta consistente, nós podíamos dilui-la, mas não o fazemos; a *Sabu* é uma tinta que tem corpo e os clientes gostam disso, podem misturar mais água, fazem a diluição que querem, e há quem goste de pintar com a tinta mais espessa. Essa é a grande vantagem da *Sabu* em relação às outras tintas, especialmente as espanholas, que têm preços baixos; é também o que acontece com o betume judaico, o que os espanhóis vendem é muito diluído e toda a gente prefere o nosso apesar de ser mais caro.

L.P.: Em relação à matéria-prima: polímeros, pigmentos, cargas e outros aditivos, o que é nacional e o que é estrangeiro? De que países importam?

R.C.: Nós compramos tudo em Portugal mas através de intermediários, são firmas estrangeiras que têm escritórios ou representantes em Portugal.

L.P.: Não compram aos produtores?

R.C.: Um ou dois artigos. Isto mais uma vez por causa da nossa dimensão, é uma coisa familiar e por isso não posso comprar uma tonelada ou duas de pigmento. Antigamente, mesmo o pigmento que vendíamos na loja, era comprado no estrangeiro, mas cada vez menos porque as próprias firmas têm cá representantes. Chegámos a ser nós os representantes de muitas marcas, como por exemplo a *Tallens*, dantes era directamente com eles e agora não; nós continuamos a fazer a encomenda directamente, mas eles mandam para o intermediário e o intermediário para nós e isto vai acontecendo com todas as marcas, já não se compra directamente às fábricas.

L.P.: A escolha dos pigmentos e aditivos, nomeadamente a percentagem das cargas utilizadas, prende-se com o tipo de ligante ou com factores económicos?

R.C.: Há razões económicas e há outras razões; não exactamente razões de qualidade, porque eu, como já lhe disse, não percebo nada de química, sei o básico da escola, portanto falo com os fornecedores; normalmente os vendedores são Eng.º Químicos e ajudam-me nesses casos. Apesar de eu já ter tudo, quando vim para cá já o meu pai tinha isto montado, quando o pigmento falha o próprio fornecedor dá-me outra coisa que diz ser exactamente igual. Mas às vezes não é! Depois experimento e, se vir que é a mesma coisa, começo a comprar esse pigmento; o controlo de qualidade aqui é a experiência de quem faz as tintas e também usar a cabeça. Tenho ali um branco que fiz para um cliente que não comprava cá há muito tempo. Comprou cá, no tempo do meu avô, há mais de 30 anos, uma marca de tinta de óleo branca, e agora veio cá e pediu se conseguíamos fazer-lhe aquele óleo; por acaso consegui encontrar a fórmula e fiz. Como é um pintor conhecido é um bocado arriscado; por exemplo, se amarelasse... Mas encontrámos a fórmula, usámos exactamente o que lá estava, os artigos eram os mesmos. Para a firma que é, para o tamanho que tem, a qualidade é muito razoável.

L.P.: Na nossa área de pesquisa dividimos as tintas em 'tintas industriais' e 'tintas para artistas'; que diferenças poderemos esperar a nível da formulação?

R.C.: A qualidade dos materiais. Por exemplo, as cargas, se calhar a nível industrial usam cargas do mais ordinário que há, mais baratas, enquanto que eu uso uma carga melhor; principalmente será a estabilidade dos materiais. Mas actualmente também vendemos algumas marcas feitas com tinta industrial; temos a *Plasteco*, que é uma tinta de esmalte, que já fizemos, mas hoje em dia enchemos com uma tinta da *Robbialac* ou análogo. E eu sei que há artistas que pintam telas com aquilo! Hoje em dia há menos interesse pela qualidade dos materiais, desde os anos 70 que o que interessa é borrar, são 'os borra telas'!

L.P.: Sabemos que, a resina utilizada no fabrico da *Sabu* é *Vinamul 3469*; que a resina de base da cola *Vulcano V7* foi até 1999/2000 a *Imofan AV44/11*, altura pela qual foi substituído o fornecedor e passou a ser utilizada a resina *Albucol 25P*[4]. Que razões os levaram a mudar de fornecedor (ou de polímero)?

R.C.: O vendedor, que nos vendia a *Imofan* (ligante da cola *Vulcano V7*) e a *Vinamul* (ligante das tintas vinílicas *Sabu*), saiu dessa firma e foi para outra, a *Globalcor*. Quando mudou para a nova firma apareceu com uma amostra da resina *Albucol*, que dizia ser exactamente a mesma coisa que a *Imofan* e que passamos a utilizar; também tentou vender uma nova resina para a tinta *Sabu*, mas foram feitas algumas experiências e não resultou.

L.P.: Por que razão utilizam marcas diferentes para o fabrico da tinta e da cola?

R.C.: Não sei precisar, quando para cá vim já era assim; mas provavelmente porque o resultado não é o mesmo e, em fórmula que resulta não se mexe, é uma regra de ouro. Quando substituí a *Imofan* pela *Albucol* na formulação da cola *Vulcano V7*, verifiquei que servia como cola. Mas por outro lado, quando fiz uma experiência para substituição da *Vinamul*, verifiquei que resultava mas a tinta ficava diferente, não era *Sabu*, a *Sabu* que as pessoas estão habituadas; achei que não ia mexer, embora a resina fosse mais barata. Há

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[4] Homopolímero de poli(vinil acetato), da *Globalcor* Lda.

uns anos misturavam uma pequena parte de cola (*Imofan*) no ligante base/principal (*Vinamul*) da tinta *Sabu* para lhe dar maior plasticidade, porque a tinta estalava em condições ambientais adversas. Hoje em dia, essa questão foi resolvida; no entanto, o pigmento é misturado num outro médium, constituído por água e por um éter de celulose (*Metocel*) e só posteriormente, esta pasta é adicionada à resina *Vinamul*.

L.P.: Folheando o catálogo...

R.C.: Os óleos que agora se chamam *Velasquez*, na altura chamavam-se *Belarte*; a tinta *Vitry* era feita de outra maneira, foi uma das fórmulas que modificámos; e tínhamos muitos vernizes que deixámos de fazer; o óleo da *Lefranc* era 8 escudos e o da *Favrel* era 6; já havia o verniz *Mica*, apesar de só estar registado em 1962; o *Verniz Ideal*: 'fabricamos desde 1891', possivelmente ainda era anterior, vinha do Porto. A *Favrel* 'foi fundada em 1891 na cidade de Lisboa e o seu proprietário e fundador, José Netto Varella, já trabalhava em casa dos seus avós, *Favrel Portuense*, firma que datava de 1752'. Mas não temos nenhum registo, nenhum documento oficial em relação à data de 1752, como muita coisa ardeu com o incêndio... só investigando no Porto. Já lá estive na rua, mas não há vestígios.

II.2 Interview with Mário Varela Gomes, manager from 1970 until 1985

Mário Varela Gomes, Joana Lia Ferreira and Maria João Melo
Lisbon, February 7th 2005

Ligações Perigosas: Porque razão escolheu trabalhar com o seu pai na Favrel?

Mário Varela Gomes: Até o meu pai falecer não posso dizer que trabalhei, frequentei a fábrica; apenas por curiosidade e interesse por saber e por conhecer aquele processo, quase alquímico, de fazer as tintas e manipular as cores.

L.P.: Quando e como se efectuou a sua aprendizagem?

M.V.G.: Todos os dias vinha aqui; interessava-me por estes aspectos.

L.P.: Não se pode dizer que tenha havido uma formação, uma transmissão de conhecimentos.

M.V.G.: Não. Posso dizer que na vida, quase tudo o que aprendi, aprendi sozinho.

L.P.: Um auto-didacta?

M.V.G.: Sim. Mesmo os cursos que fiz, as universidades que frequentei, enfim, sempre se aprende algumas coisas; mas aquilo que de facto me interessou saber sempre procurei, e até falando com pessoas, mas mais numa relação de amizade com alguns mestres que tive do que propriamente numa relação académica.

L.P.: E desde que idade é que aqui vinha?

M.V.G.: Desde sempre. O meu pai deixava-me andar a ver.

L.P.: E ele estava na fábrica ou mais frequentemente na loja?

M.V.G.: Às vezes não estava nem num sítio nem no outro. O meu pai era uma pessoa que não vivia 100% para a empresa; era uma pessoa que se dispersava por interesses vários, nomeadamente relativos a arte. Mas em certas épocas tinha como que um impulso que o levava a conceber materiais novos para pintura – tintas, vernizes; ou a produzir em Portugal coisas que já se produzia nos outros países e que cá não se fazia, investigava esses materiais e conseguia depois fazê-los.

L.P.: Referiu o interesse do seu pai pela arte. Como coleccionador?

M.V.G.: Sim. O meu pai coleccionava pintura, gravuras, desenhos... Tinha um grande contacto com artistas plásticos, através da *Casa Varela* e não só. Era um homem que se interessava por literatura, poesia, história, etc.

L.P.: Qual era a formação do seu pai?

M.V.G.: Era um auto-didacta. Frequentou um antigo curso comercial, mas não tinha uma formação académica superior.

L.P.: O seu pai prosseguiu o projecto do seu bisavô, a *Favrel Lisbonense*. Quais são as inovações, que considera mais relevantes, introduzidas pelo seu pai?

M.V.G.: Há um conjunto de materiais que eram excessivamente caros, porque eram importados. As taxas alfandegárias eram altíssimas, os transportes custavam muito dinheiro; havia muita dificuldade no câmbio, as importações eram bastante restringidas. Havia uma série de dificuldades e entraves, para além dos preços altos que os materiais estrangeiros tinham. Devido aos elevados preços, os artistas plásticos tinham muita dificuldade em trabalhar; as telas vinham da Holanda, França ou Inglaterra; as tintas de óleo, os vernizes, os diluentes, tudo isso era importado. O meu pai teve uma atitude, penso eu, decisiva no desenvolvimento das artes plásticas em Portugal, nomeadamente no campo da pintura a óleo; produziu uma tinta, que ainda hoje existe, a tinta *Velasquez* a preços muito baixos; julgo que a 1/5 ou 1/6 de uma tinta estrangeira; devo dizer que, evidentemente, com uma qualidade algo inferior.

L.P.: Porque afirma que a qualidade era inferior?

M.V.G.: Porque conheço, experimentei e percebi. Não porque os pigmentos fossem diferentes, os pigmentos eram importados e eram de belíssima qualidade; mas porque os mecanismos de transformação, nomeadamente os moinhos, não eram tão bons e portanto não produziam pastas tão finas como os equipamentos que existiam em algumas fábricas no estrangeiro. Mais tarde, julgo que nos anos 60, a pequena fábrica foi equipada com os moinhos que ainda hoje temos a funcionar, o que permitiu produzir com uma qualidade idêntica à de muitas marcas estrangeiras.

L.P.: Também importavam o óleo?

M.V.G.: Penso que o óleo de linho também era importado, acho que não se fabricava cá. Com estes preços, de facto muito mais baixos, houve a possibilidade de dedicação a projectos mais ambiciosos, houve uma popularização e uma maior divulgação, nomeadamente nas camadas escolares, gente que andava nas Belas Artes; o que levou ao desenvolvimento desta marca portuguesa e da própria produtividade artística. Ainda hoje não há outra fábrica a produzir tintas de óleo. Houve mais dois produtos também inventados, ou refeitos, por ele. Um desses produtos foi uma tinta vinílica, a muito célebre *Sabu*, uma tinta que não existia em Portugal; embora existissem outras tintas de água, mas não com cores tão fixas, tão vivas, tão resistentes como as da *Sabu*. Esta tinta permitiu também um grande desenvolvimento, sendo possíveis algumas produções artísticas, dos anos 70 e 80, graças à sua existência; e, por isso, muitos dos artistas contemporâneos ainda trabalham com a *Sabu*. Posso dizer-lhe que alguns dos nossos melhores artistas, dos mais conhecidos no estrangeiro, trabalham com essa tinta. O outro produto corresponde aos lápis de cera *Grão Vasco*. Também não se produziam em Portugal lápis de cera e o meu pai foi o primeiro que o fez, permitindo oferecer um preço muito baixo e uma grande divulgação junto das escolas. Durante muitos anos, nos programas do ensino primário e pré-primário, os lápis de cera tiveram um papel muito importante, porque permitem uma série de técnicas. Hoje já pouco se utiliza o lápis de cera, mas esta fábrica produziu milhões de caixas; nos anos 80 apareceram lápis de cera espanhóis, de qualidade inferior mas muito mais baratos, e hoje materiais semelhantes japoneses e chineses a preços irrisórios.

L.P.: Mas ainda mantêm estas três linhas.

M.V.G.: Mantemos. A *Sabu* com muito êxito; a *Velasquez* com menos, porque os pintores a óleo estão quase a extinguir-se, são muito mais ao artistas que pintam com tintas vinílicas do que com óleos; e os lápis de cera *Grão Vasco* quase não têm venda, porque há muita concorrência e também porque deixaram de integrar os programas escolares.

L.P.: Recorda-se de quando o seu pai teve a ideia de fazer a tinta *Sabu*?

M.V.G.: Não me recordo. Posso dizer-lhe que em 1957 ou 58 vi pintarem com *Sabu*, não só quadros mas também decorações murais, em madeira e cerâmica; existem fotografias da ‘Feira de Artes da Estrela’ onde isso aconteceu. Aparece no *Diário de Notícias*[5] a participação da *Casa Varela* numa outra feira ‘O jardim das Belas Artes’, no Jardim do Príncipe Real em 1956, organizada por Leitão de Barros. Não tenho a certeza se já havia *Sabu* nesse ano, mas acho que sim, porque parece-me que muitos estudantes já pintavam com *Sabu* nessa altura. Depois há outros produtos que também proporcionaram o desenvolvimento de certos aspectos da pintura e da didáctica das Belas Artes, como por

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[5] ‘”Varela dá as tintas. Você dá o talento.” - Visitantes de todas as idades e estilos, em torno das estantes – com papel, tintas e pincéis à descrição – produzem em série e gozam a existência, existencialmente.’

exemplo as tintas *Cenógrafa*, que são tintas em pó; servem, não só aos cenógrafos, mas também às crianças em idade escolar.

L.P.: Essa marca também foi criada pelo seu pai?

M.V.G.: Sim, a *Cenógrafa*. E também vendemos toneladas desta tinta. É uma tinta em pó que depois se mistura com dextrina e com água. Foi muito utilizada pelos cenógrafos e também adoptada pelas escolas e pelos artistas. O Julião Sarmento ainda pinta com esses pigmentos da tinta *Cenógrafa*, que mistura com a cola *V7*.

L.P.: E esses pigmentos são os mesmos que utilizam na *Sabu*, na *Velasquez* e que os pigmentos vendidos em frascos?

M.V.G.: Não. Na *Cenógrafa* há alguns pigmentos que têm menos qualidade e é-lhes adicionada uma carga[6]. Depois na afinação da cor da *Sabu* utilizamos pigmentos aqua-dispersos. Antigamente, muitos dos pigmentos eram tóxicos, mas hoje em dia já não o são.

L.P.: Qual a sua motivação para dirigir a *Favrel* depois da morte do seu pai em 1970?

M.V.G.: Primeiro porque sempre me tinha interessado pela empresa. Eu era estudante de arquitectura e esta era uma empresa de Belas Artes, de materiais ligados à produção artística, na qual também estive envolvido; era um negócio que estava ligado a um meio que me dizia respeito. Havia também o encargo, era uma empresa que tinha cerca de 40 funcionários e que era preciso andar para a frente com ela. Depois tinha também o testemunho de uma coisa que tinha sido fundada pelos meus bisavós, em Lisboa pelo meu bisavô, documentalmente atestada, mas no Porto pelo pai dele e, antes do pai, pelo avô dele. E havia ainda o aspecto financeiro, eu era estudante, não tinha ordenado e era aqui que o vinha buscar. Foram vários factores; a empresa sempre me interessou e continua a interessar, embora já não seja gerente, mas sou um dos sócios, por herança.

L.P.: Que razões estiveram na escolha da sua formação académica base, a arquitectura?

M.V.G.: Acho que a arquitectura é, como já Vitrúvio considerava, a arte mais completa. Está envolvida com concepções, não só de carácter filosófico, mas também com o espaço, com aquilo que nós construímos, a nível físico e também a nível mental. Não descurei a possibilidade de ser pintor, mas achei que a arquitectura oferecia essa noção da

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[6] Usava *carbocal* (carbonato de cálcio), que comprava numa empresa em Leiria, na *Cenógrafa*; na *Sabu* acho que usava uma carga mais fina.

compreensão do espaço e essa abrangência, que depois permitiam pontes para outras ciências ou para outras actividades, como a arqueologia, a pintura, o cinema, etc.

L.P.: Que aspectos curiosos intervieram na escolha da sua actual profissão de arqueólogo?

M.V.G.: A arqueologia foi essa necessidade de conhecer o passado; de perceber porque é que chegámos até aqui; porque é que fazemos tintas, por exemplo. Perceber a evolução, mental, tecnológica, económica, social e sobretudo ideológica, do homem. Eu entro na arqueologia pela arte.

L.P.: E quando é que começou a trabalhar em arqueologia?

M.V.G.: A arqueologia esteve sempre presente; aos 9 anos já lia muita coisa e quase obrigava o meu pai, que nos levava com muita frequência a visitar museus de arte, a ir a museus de arqueologia. Depois comecei a participar em escavações, com 14 ou 15 anos, com o pai de um amigo meu que fazia escavações e pertencia à Sociedade Portuguesa de Espeleologia. Mais tarde, em 1972 e já estudante de arquitectura, comecei a trabalhar com amigos meus da Faculdade de Letras de Lisboa, nas gravuras rupestres do Vale do Tejo. Já arquitecto e a trabalhar, frequentei o curso de história e estudei arqueologia em Espanha, Itália e na Suécia. Ainda continuo a fazer arquitectura, embora trabalhe em arqueologia todos os dias, dou aulas mas, depois, tenho sempre 2 ou 3 projectos de arquitectura em mãos.

L.P.: Após a gerência do seu pai quais os progressos mais significativos por si introduzidos?

M.V.G.: A minha gerência não introduziu grandes progressos, digamos que houve uma modernização na apresentação dos produtos, uma maior divulgação; foi um período em que apareceram muitos produtos novos e, por isso, houve possibilidade de melhorar, reformular algumas coisas. Enfim, foi mais uma gerência de manutenção do que de inovação. Tentámos também começar a fazer uma tinta acrílica, mas isso foi implementado posteriormente. Foi um período, não direi difícil, mas com alguns problemas. Veio o 25 de Abril, com reflexos na evolução política, económica e social; com reflexos positivos e negativos. Proíbem-se totalmente as importações e se, por um lado, não há importação de tintas de marca estrangeira, também não há importação de material para fabricar as tintas *Favrel*. As vendas caíram vertiginosamente; embora não tivéssemos problemas de carácter social dentro da empresa, mas os factores conjunturais provocaram um forte abalo económico durante um período de 3 ou 4 anos. Hoje, esta pequena indústria está no fio da navalha, a competição é cada vez maior, há a globalização, a nossa mão de obra já não é especialmente barata e os produtos que vêm de fora chegam cá, mesmo com boa qualidade, a um preço que nós não conseguimos. Nós sempre fomos os fornecedores das especialidades; por exemplo, quando o Almada Negreiros quis fazer o painel da Fundação Gulbenkian e queria grafite para passar o desenho veio aqui falar com o meu pai, saber o que havia e arranjou-se o produto; para o Espiga Pinto fazíamos *Sabu* numa cor que ele usava, mas que não era uma cor de catálogo; fizemos guaches para o Walt Disney, quando ele passou por Espanha há muitos anos; fizemos verniz para isolar os parafusos da ponte sobre o Tejo! Uma vez o Joaquim Rodrigo apareceu aí com umas pedras e queria que o meu pai as moesse, queria obter pigmentos naturais!

L.P.: Possivelmente eram de Monsanto.

M.V.G.: Pois! Mas o meu pai recusou-se, estragava os moinhos! Existiam ocres de boa qualidade à venda nas cores que ele desejasse.

L.P.: O que nos pode dizer sobre a evolução da *Favrel* desde o seu início mais remoto, ou seja 1752?

M.V.G.: Dessa data não há qualquer registo. É uma data que foi transmitida pelo meu bisavô ao meu pai. Sobre a *Favrel* do Porto, andámos a pesquisar e sabemos que houve uma *Favrel Portuense*, na Rua dos Caldeireiros e que era do avô do meu bisavô, mas isso não vai até 1752. José Netto Varella, o meu bisavô, nasceu em 1858. A tradição é de que no Porto a *Favrel* fazia tintas para barcos e não para Belas Artes, isso foi começado pelo meu pai ainda antes da 2ª Guerra. O meu bisavô importava materiais para pintura e produzia para as artes decorativas. Foi ele que fez a primeira tinta com purpurinas, com pó de alumínio, técnica que aprendeu em França.

L.P.: Disse-nos que a produção de tintas foi desenvolvida no tempo do seu pai, António Varela, cuja gerência começa em 35. Terá havido alguma influência da 2ª Guerra Mundial nesse desenvolvimento?

M.V.G.: Antes da 2ª Guerra já fazia tintas para artistas, embora tenha chegado a fazer tintas para a construção civil e as tais tintas para barcos, produzindo também as tintas de óleo. Todavia, é essencialmente no pós-guerra, nos anos 50, que se desenvolve a produção.

L.P.: Como eram escolhidos os nomes das tintas?

M.V.G.: Em relação à *Sabu*; havia um artista plástico que, na juventude foi *boxer*, o Abílio Belo Marques, e que tinha a alcunha de Sabu, por aparentar um certo ar oriental. Sabu era um personagem dos contos do *Sandokan - o Tigre da Malásia* do Emilio Salgari. O meu pai achou piada à alcunha, era muito amigo dele e deu à tinta o nome *Sabu*. Trata-se de um nome com força. O meu pai tinha muita imaginação, imaginava as tintas e, também, rótulos, catálogos e nomes.

L.P.: No encontro anterior referiu a existência de postais de obras pintadas com *Sabu*, mas no verso encontra-se escrito que a técnica utilizada é acrílico.

M.V.G.: Embora esteja escrito acrílico estes quadros foram pintados com *Sabu*. Estes postais são fotografias de obras de artistas contemporâneos, pintadas em 1986 com *Sabu*.

L.P.: Lembra-se de algumas obras públicas em que a pintura mural tenha sido feita com *Sabu*?

M.V.G.: Na Ericeira havia muitos restaurantes com painéis pintados com *Sabu*. Aqui em Lisboa havia nos anos setenta os murais do MRPP. Aliás, a maioria dos murais que havia em Lisboa eram pintados com *Sabu*.

M.V.G.: Havia um alvará do rei D. Luís para a *Favrel Lisbonense* produzir ouro em folha.

II.3 Micro Sampling

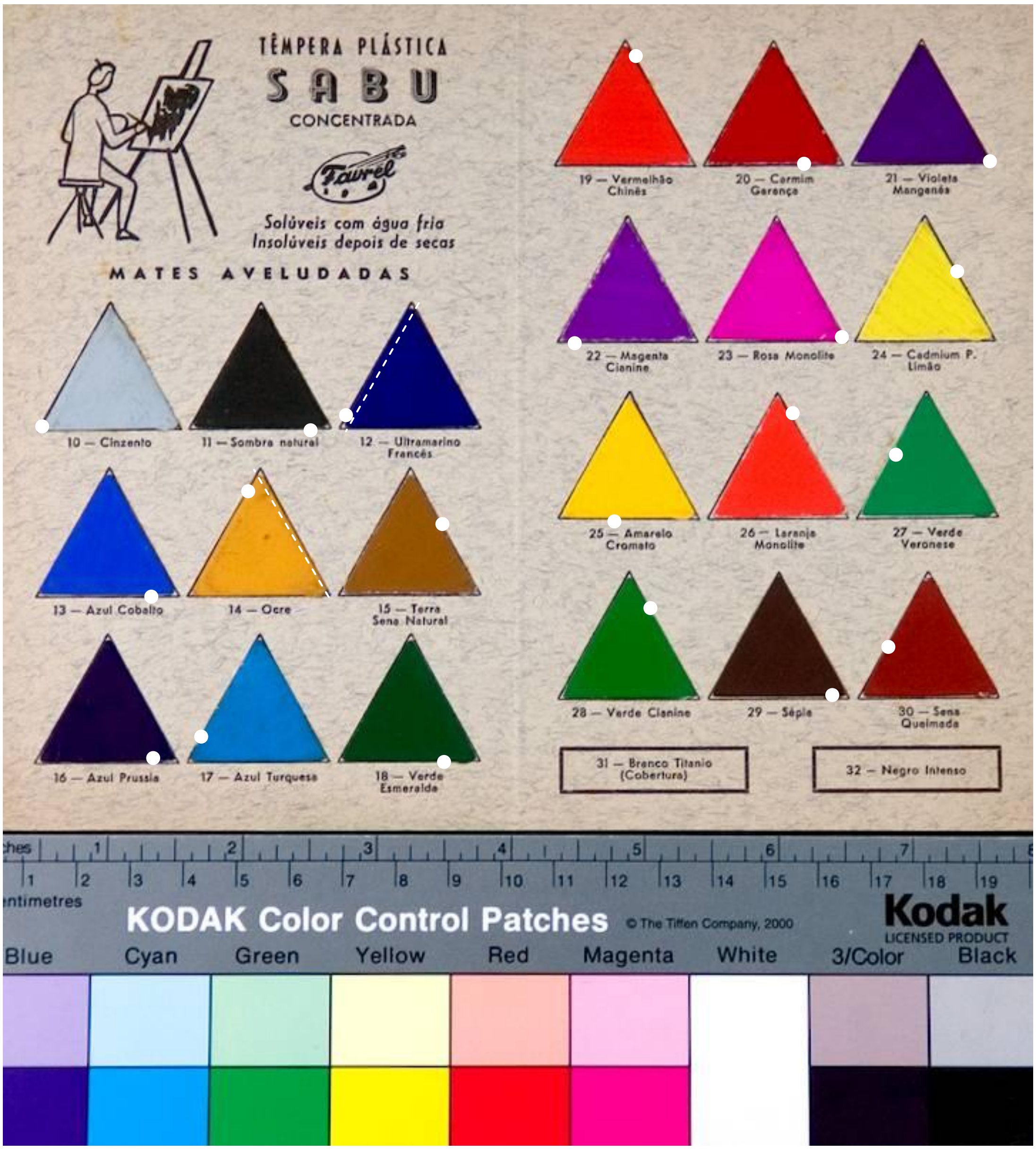


Figure II.1. *Sabu* catalogue sample collection. White circles – µsampling; white dashed line –sample collected for SEC analysis.

Figure II.2. Sample collected from *Sabu 18 Emerald green*.

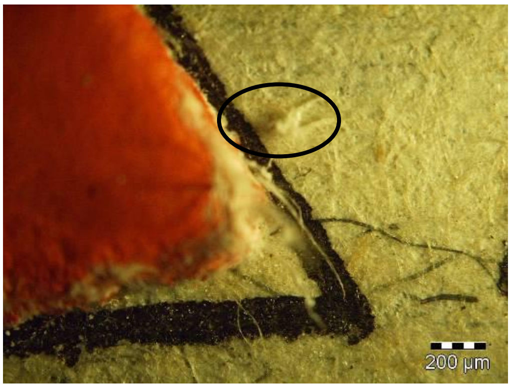


Figure II.3. Cardboard fibre collected from *Sabu 19 Chinese vermilion*.

II.4 Spectra

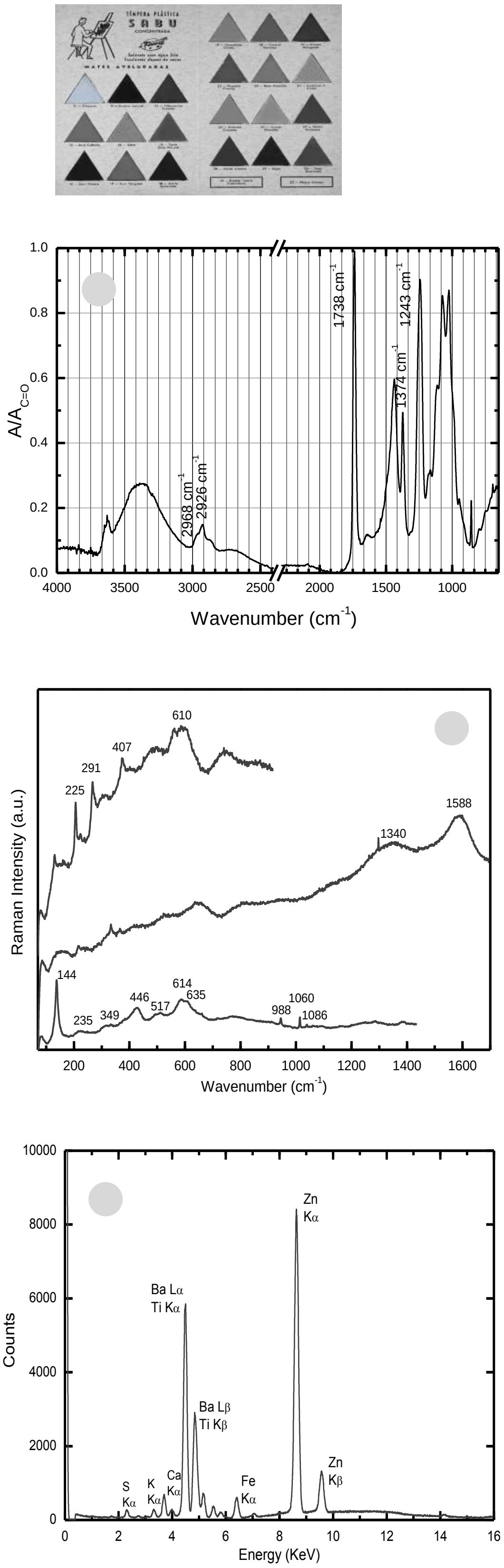


Figure II.4. Spectra from *Sabu 10 Grey*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

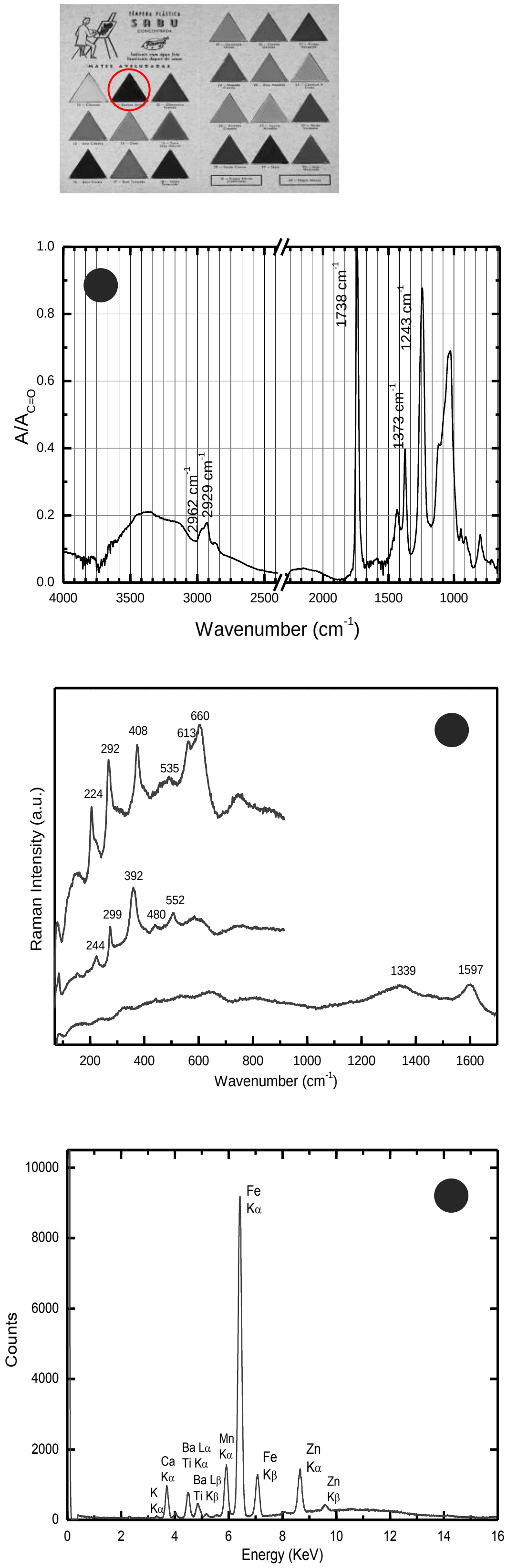


Figure II.5. Spectra from *Sabu 11 Raw umber*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

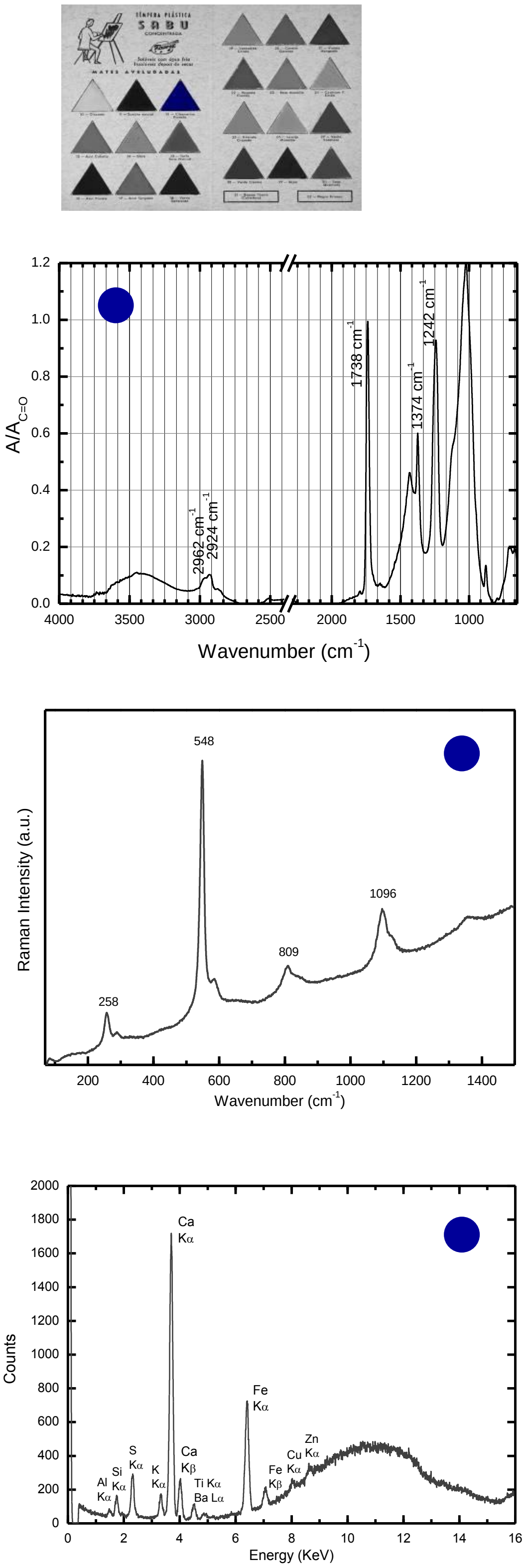


Figure II.6. Spectra from *Sabu 12 French ultramarine*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

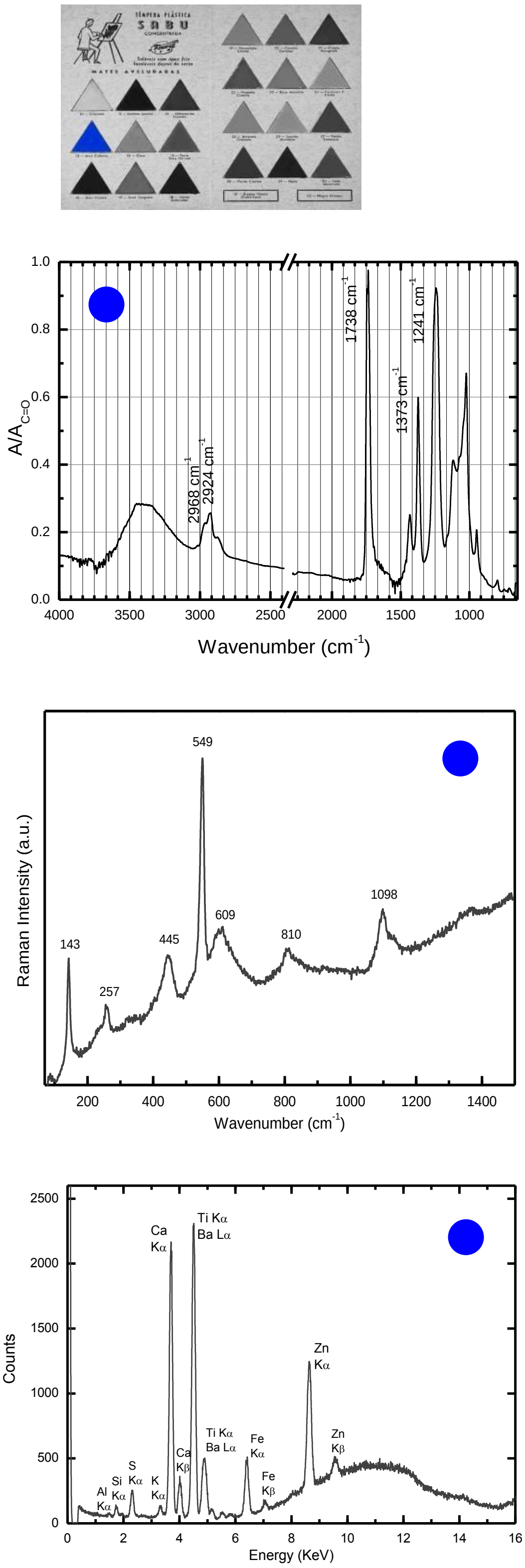


Figure II.7. Spectra from *Sabu 13 Cobalt blue*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

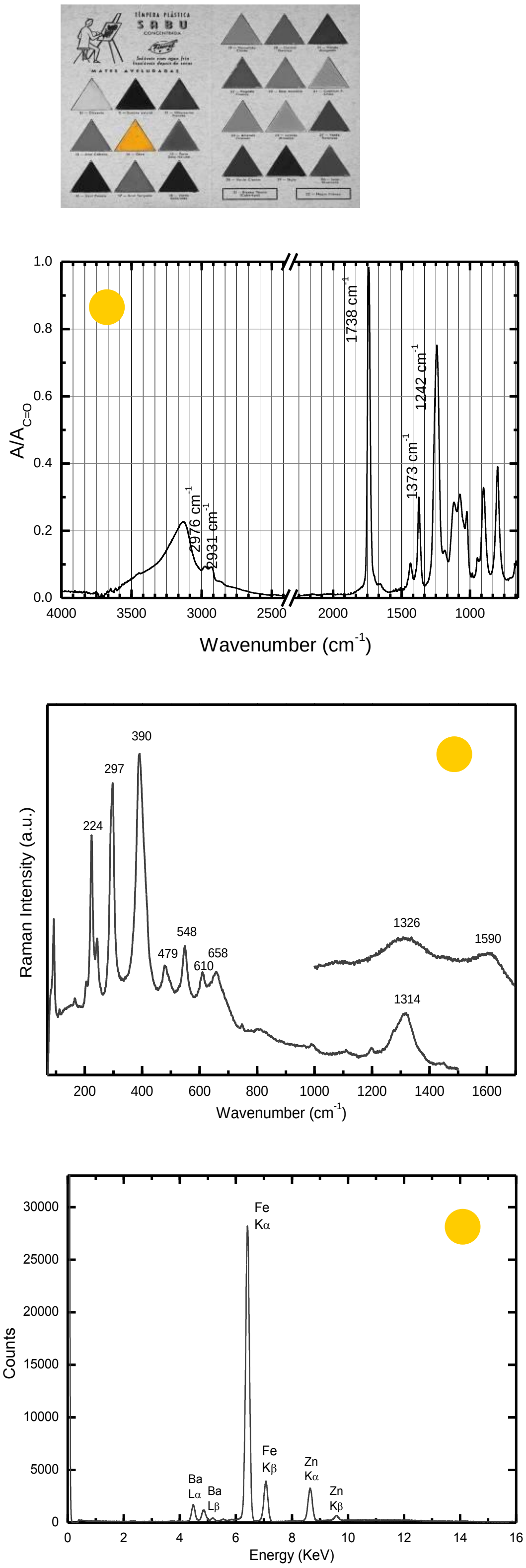


Figure II.8. Spectra from *Sabu 14 Ochre*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

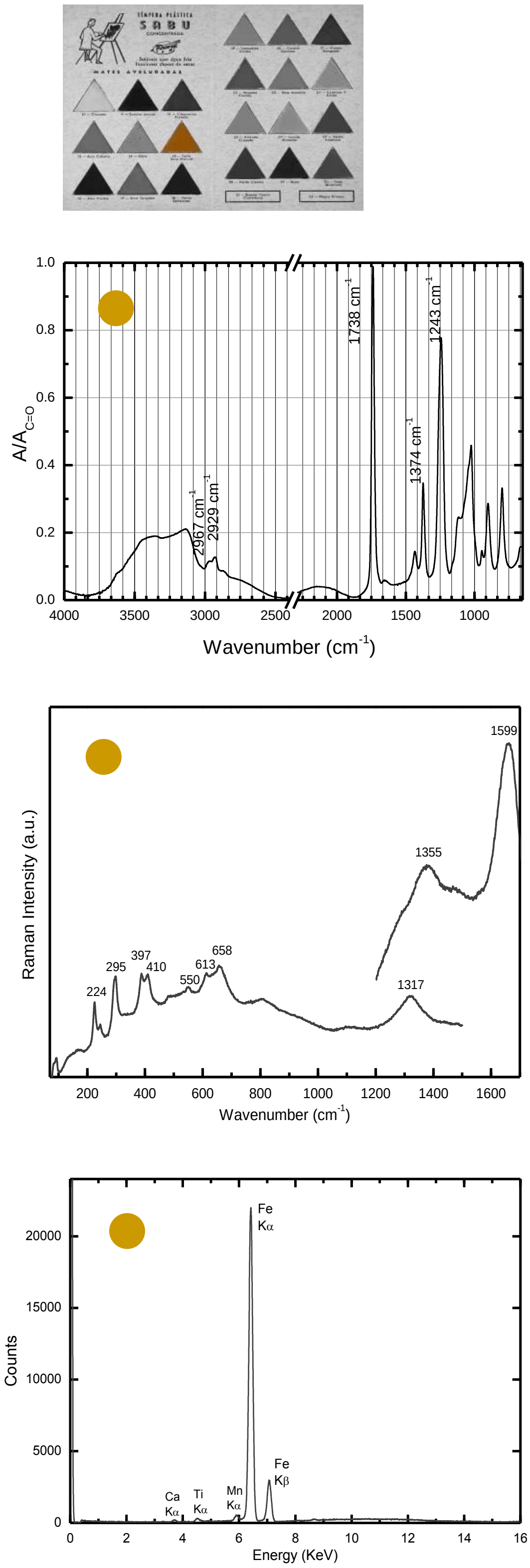


Figure II.9. Spectra from *Sabu 15 Raw sienna*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

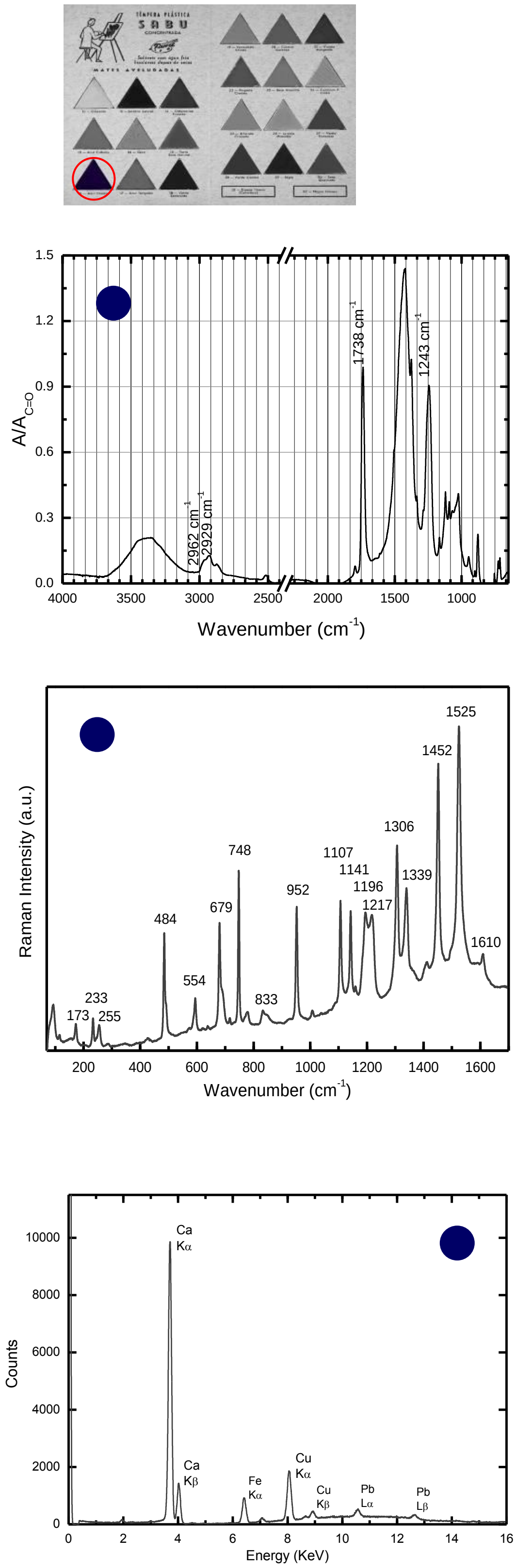


Figure II.10. Spectra from *Sabu 16 Prussian blue*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

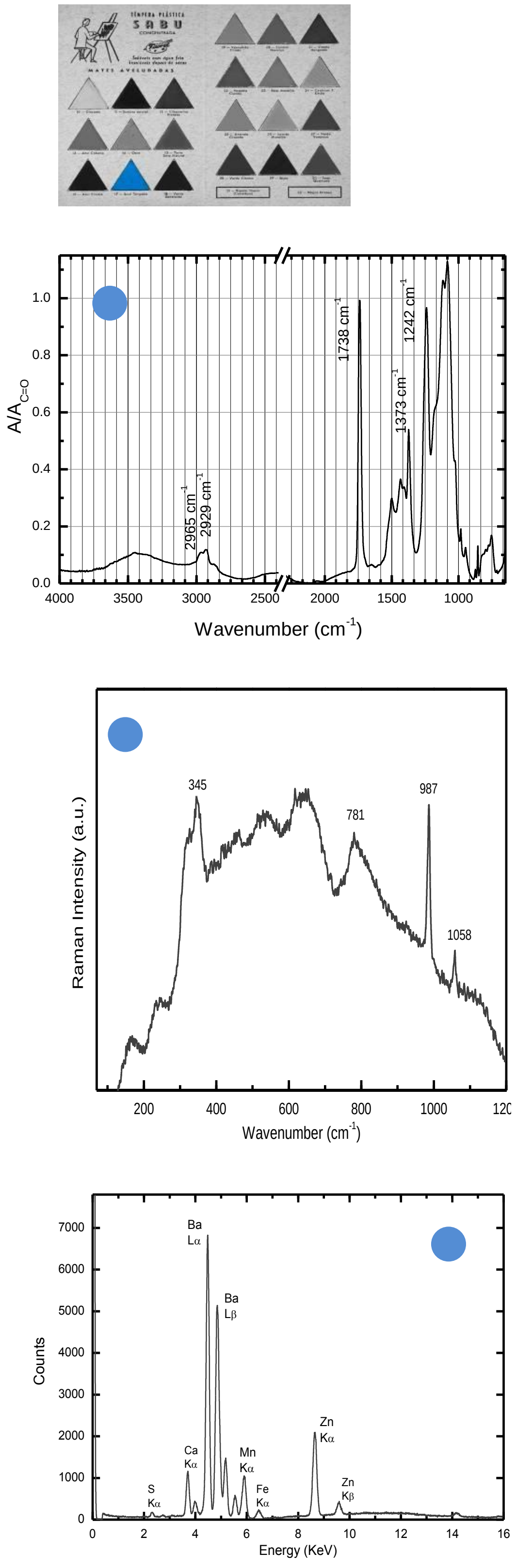


Figure II.11. Spectra from *Sabu 17 Turquoise blue*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

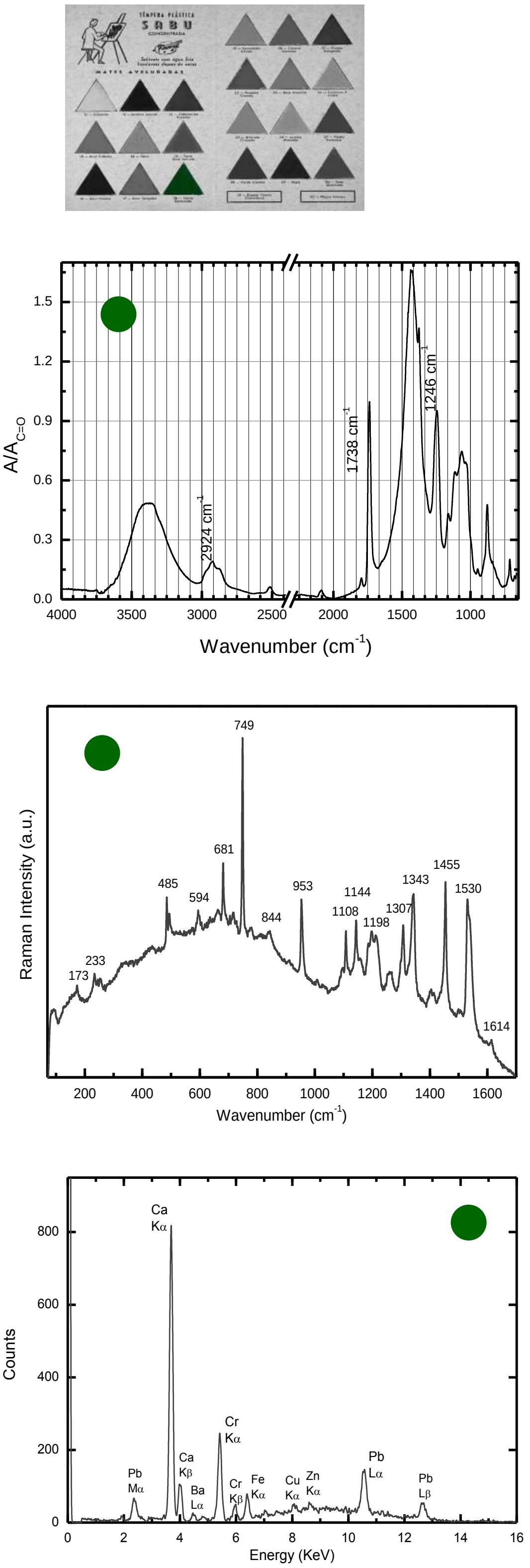


Figure II.12. Spectra from *Sabu 18 Emerald green*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

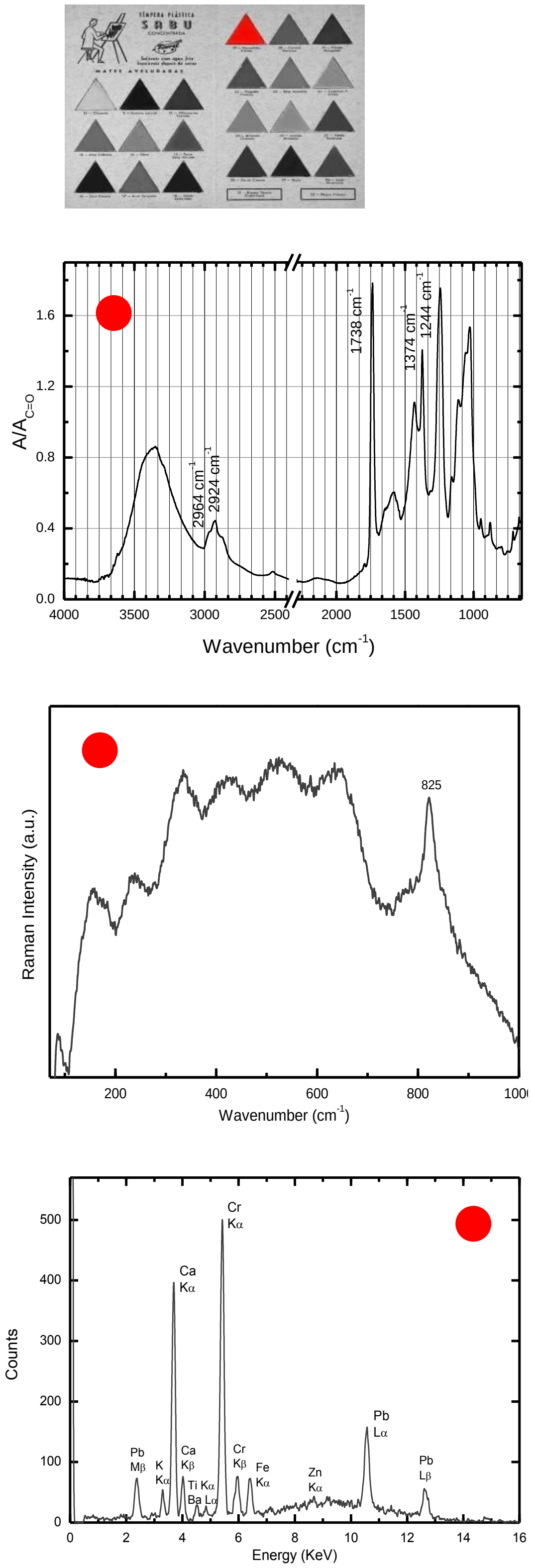


Figure II.13. Spectra from *Sabu 19 Chinese vermillion*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

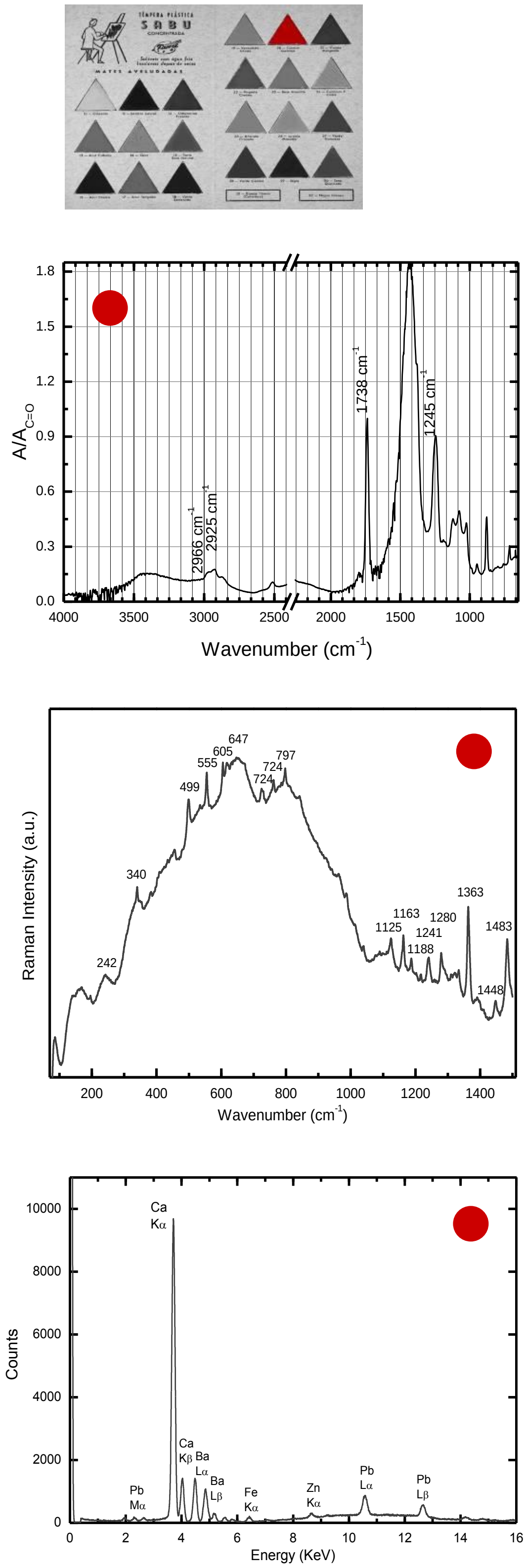


Figure II.14. Spectra from *Sabu 20 Madder carmine*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

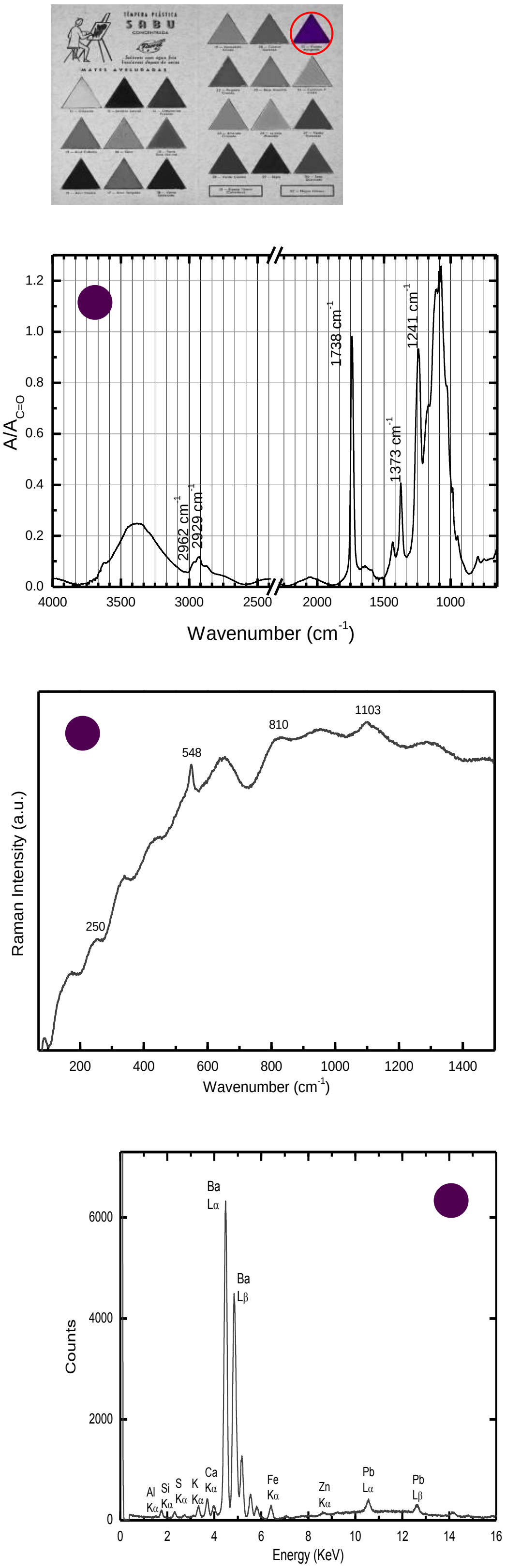


Figure II.15. Spectra from *Sabu 21 Manganese violet*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

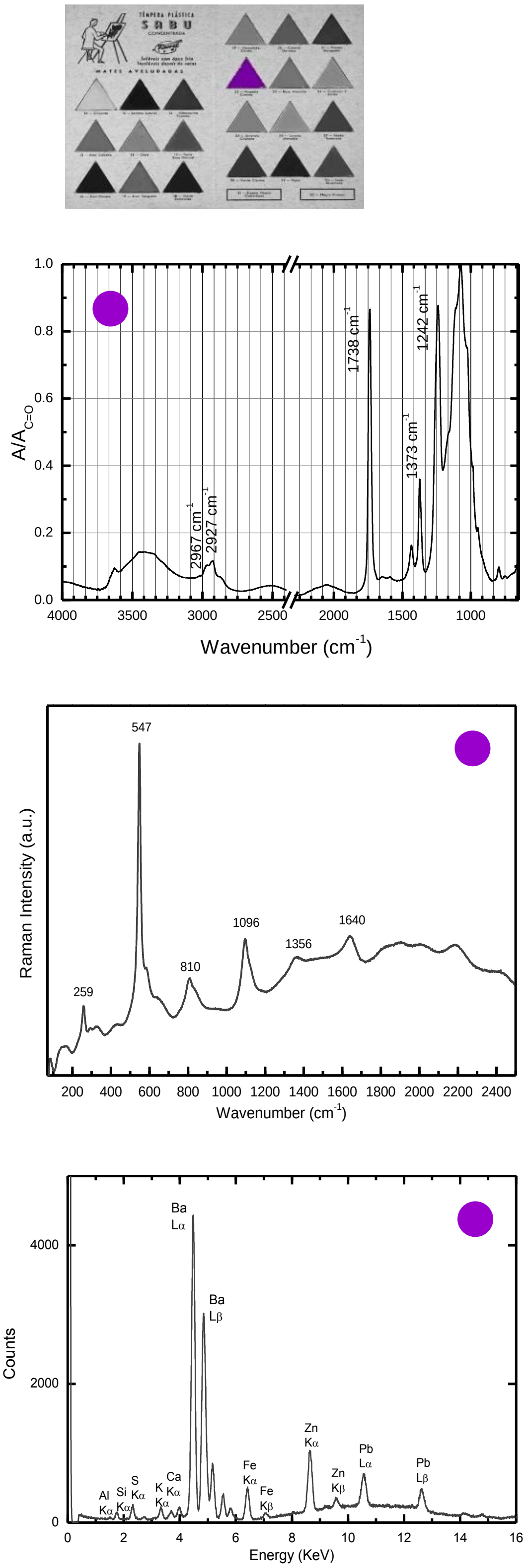


Figure II.16. Spectra from *Sabu 22 Cyanine magenta*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

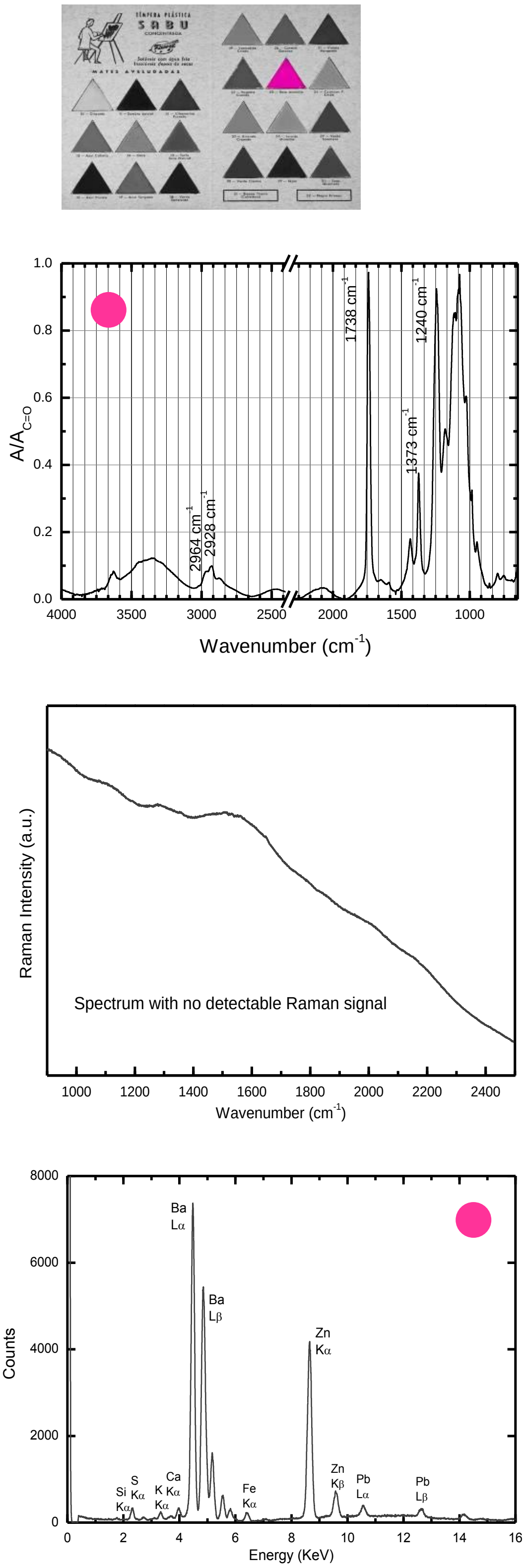


Figure II.17. Spectra from *Sabu 23 Mololite pink*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

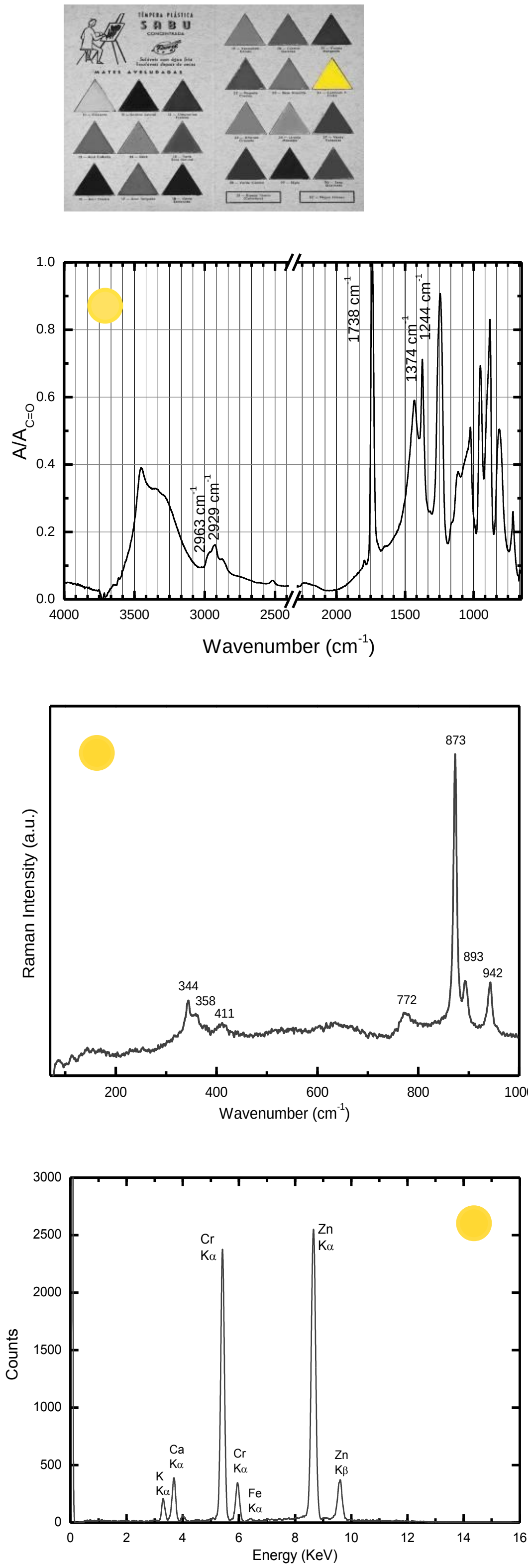


Figure II.18. Spectra from *Sabu 24 Lemon cadmium*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

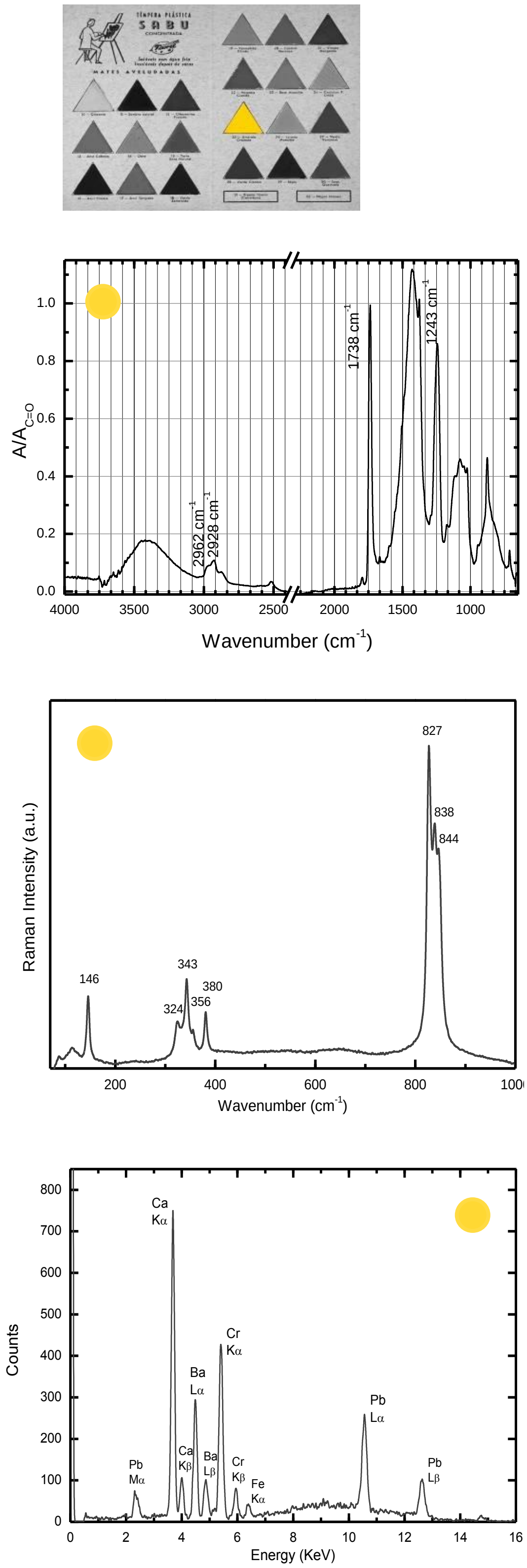


Figure II.19. Spectra from *Sabu 25 Chromate yellow*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

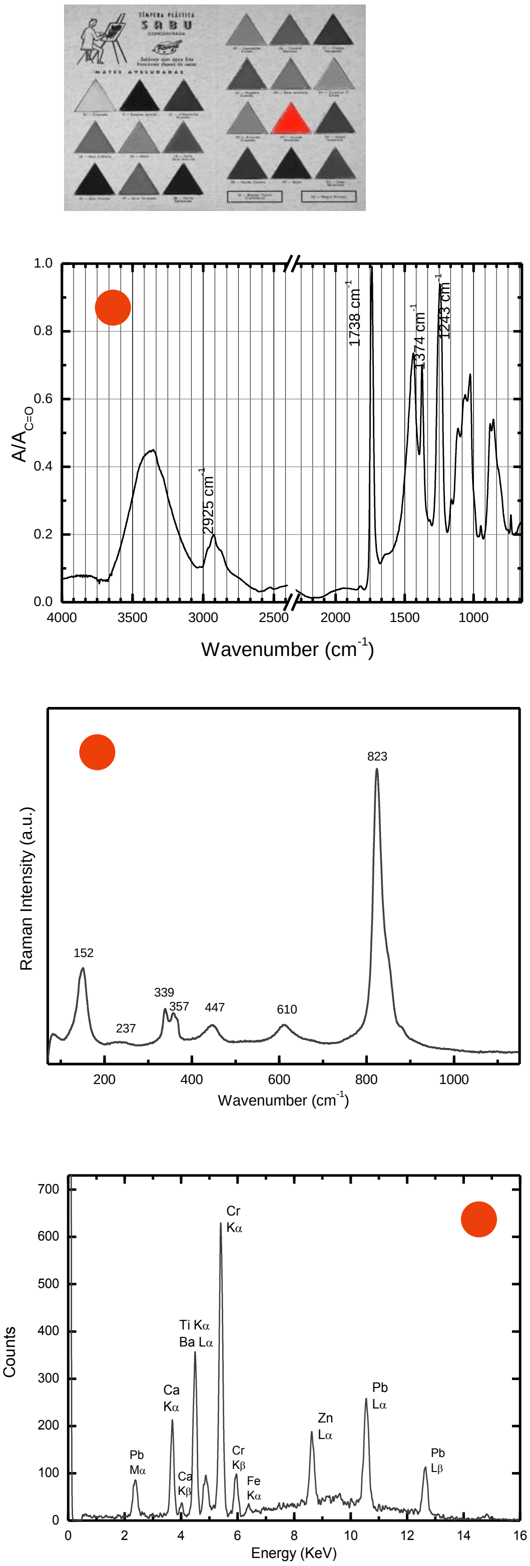


Figure II.20. Spectra from *Sabu 26 Monolite orange*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

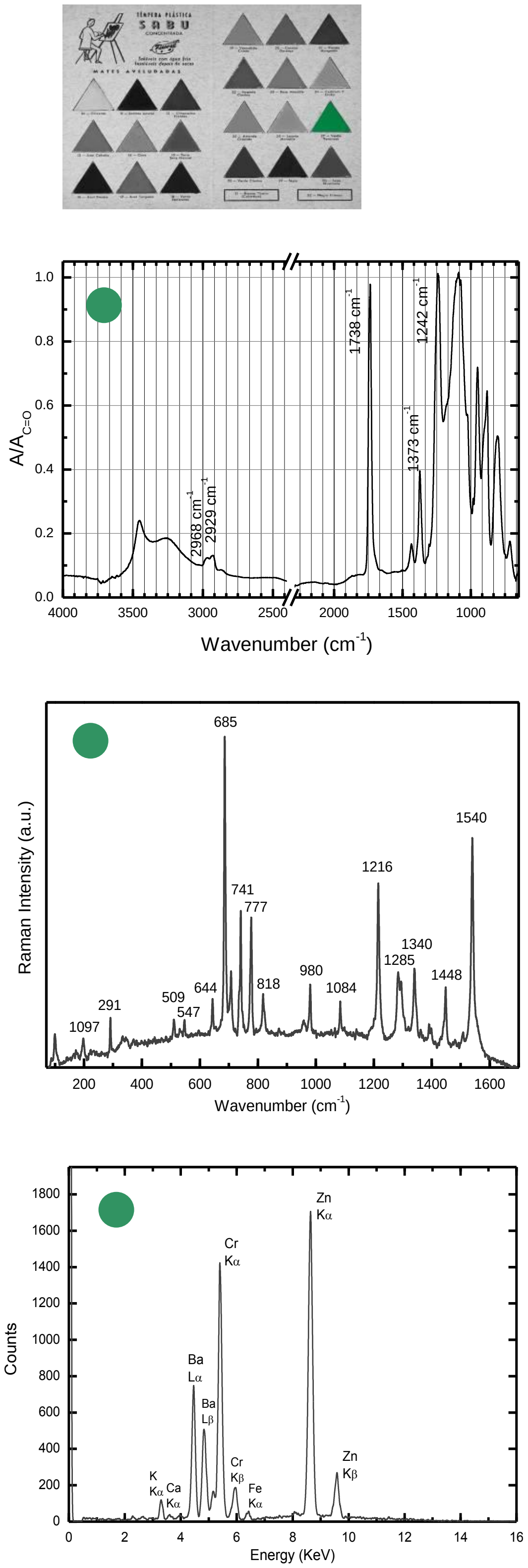


Figure II.21. Spectra from *Sabu 27 Véronèse green*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

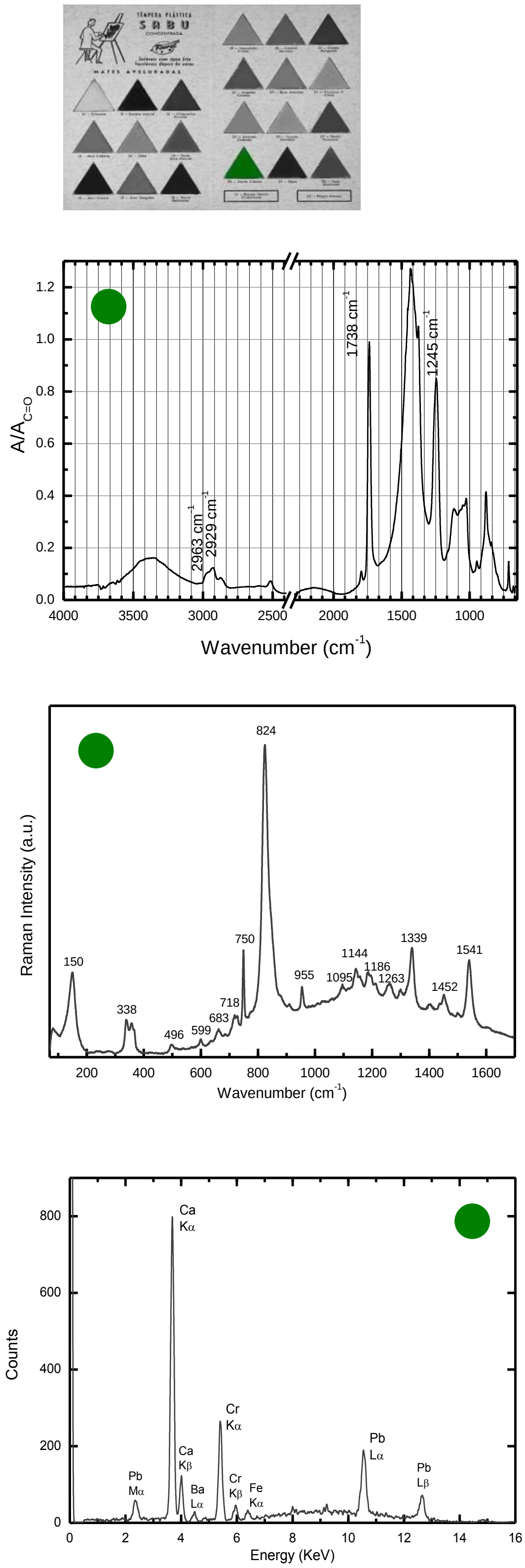


Figure II.22. Spectra from *Sabu 28 Cyanine green*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

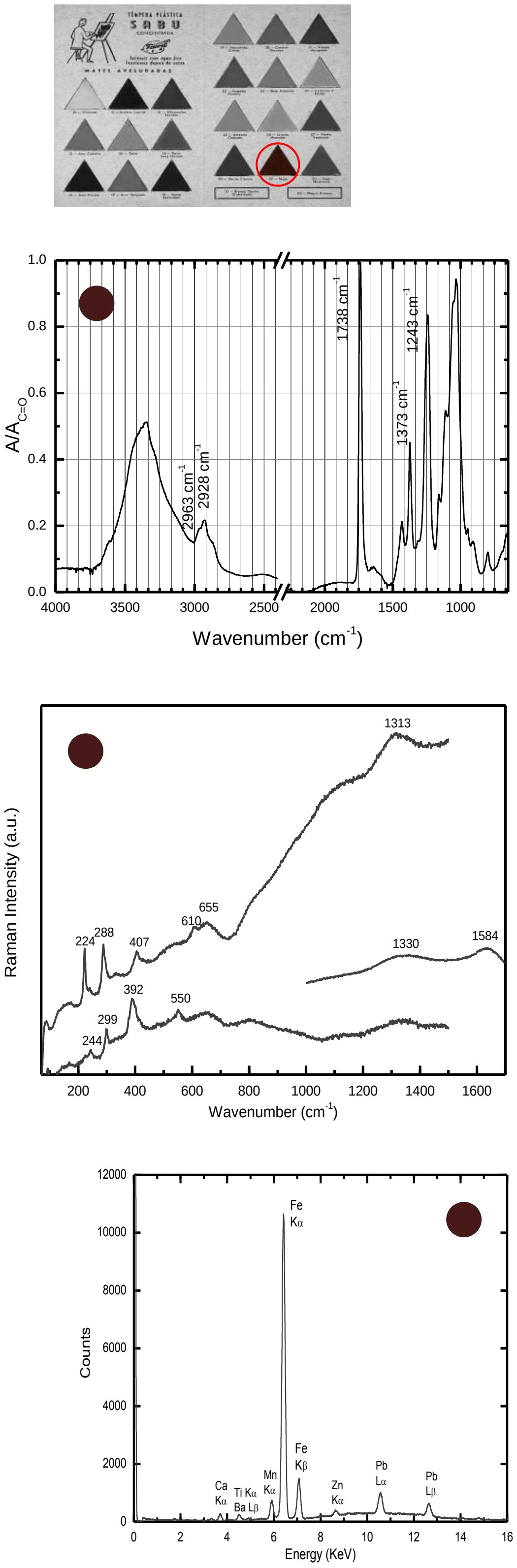
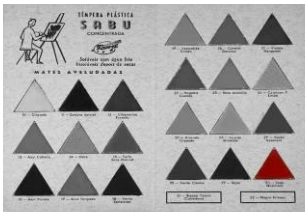


Figure II.23. Spectra from *Sabu 29 Sepia*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.



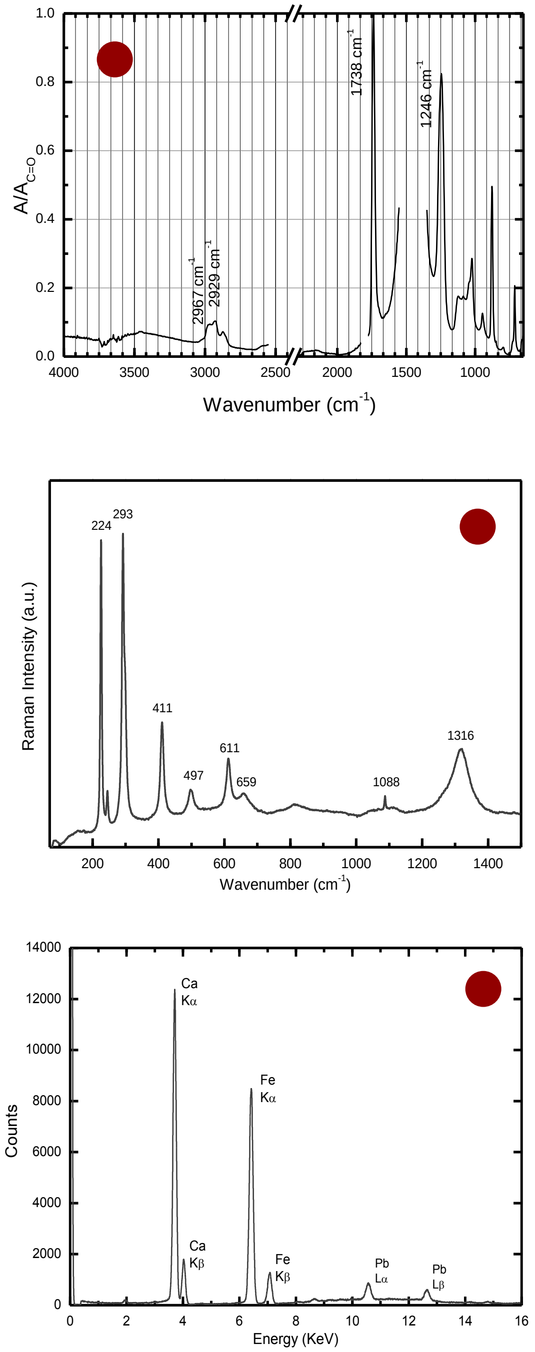


Figure 24. Spectra from *Sabu 30 Burnt sienna*: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

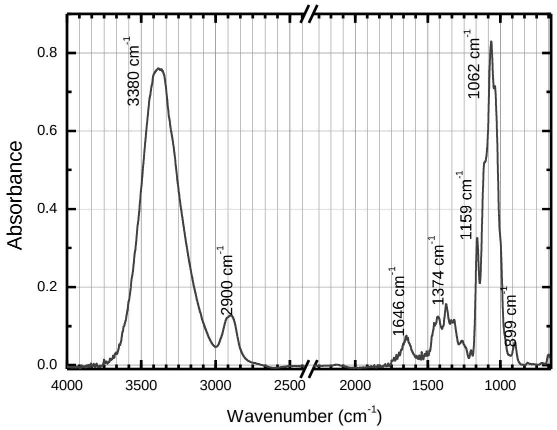


Figure II.25. IR spectrum of a cardboard fibre collected from *Sabu 19*.

Appendix III

Questionnaire sent to Portuguese Artists[1]

2005

III.1 Documentation on artists' materials

Over the years art historians, art critics and curators have theorized about twentieth century works of art, in comparison very little has been considered about the materials used to create them [5,185,186]. Interviewing the artists and manufacturers is fundamental for the collection of information about the materials [5,187]. It should be stressed here that not all artists are sensitive to conservation issues or agreeable to discuss their materials and techniques [128]. However, artists become more aware of how important it is to share information about the materiality of their works.

In the beginning of the twentieth century Büttner Pfänner Zu Thal was the first to inquiry artists in a systematic way, however out of 200 artists only three returned his questionnaire [188]. In 1939 the painter George Rueter, working for the *Supervisory and Advisory Commission on Paintings* (Amsterdam), sent a letter to the artists represented in the city collections, in an attempt to systematically collect 'knowledge considered necessary to ensure the sustainability of artworks'. Artists were inquired about the nature of the materials and techniques used and also about the co-relation with the artistic intention [186]. Years later several projects were carried out in Germany and Switzerland. Erich Gantzert-Catrillo started to work at the Museum Wiesbaden in 1968 and launched a project on materials' data collection sending questionnaires to artists from the German speaking countries. In 1979 the 140 completed questionnaires were published as the first volume of the *Archive of Techniques and Working Materials Used by Contemporary Artists* [189]. After these first steps, several projects have been launched. Another key example is the *Artists' Documentation Program* started by Carol Mancusi-Ungaro in 1990, aiming 'to record information from living artists that would assist conservators in future restoration efforts' [190].

In the Portuguese context the awareness with contemporary art conservation issues has not been established until recently. This delay may be related with the artistic development and also with a slow standardization in the cultural policy, with some hindrance in consistent cultural infrastructures that sustain the artistic practice [191].

---

[1] The questionnaires are presented here in Portuguese. The completed questionnaires are archived at DCR FCT/UNL. A list of the artists inquired is also presented.

III.2 Questionnaire – Portuguese

MATERIAIS NÃO TRADICIONAIS NAS OBRAS DE ARTE PORTUGUESAS

Alguma vez utilizou novos materiais nas suas obras?
Sim _______
Não _______

Em caso de resposta negativa,
o inquérito termina aqui.

Se sim,
dos seguintes materiais, quais utilizou e em que anos?
Tintas sintéticas _______
Vidros acrílicos (*Plexiglas*) _______
Outros vidros, quais? _______
Materiais compósitos e metais mais leves, quais? _______
Espumas _______
Outros ____
____

Poderá dar referência de obras ou bibliografia que possam ilustrar estas aplicações?
____
____
____
____

Se não utilizou tintas sintéticas,
o inquérito termina aqui.

Se utilizou tintas sintéticas,
de que tipo?
Emulsões acrílicas _____
Emulsões vinílicas _____
Alquídicas _____
Nitrocelulósicas _____
Outras ____

Tintas para artistas ou tintas industriais (p.e. tintas de parede)? ____________________________

Tipo de tinta[2]	Nacional ou estrangeira	Local de aquisição	Marca	Anos de utilização	Observações
Emulsões acrílicas					
Emulsões vinílicas					
Alquídicas					
Nitrocelulósicas					

Alguma vez preparou as suas próprias tintas?

Sim _______

Não _______

Se sim,

o que utiliza ou utilizou como aglutinante?

____

Normalmente que razões o(a) levam a optar por uma tinta acrílica ou vinílica?

____

____

Nome do Artista ____

Telefone de contacto ____

e-mail ____

NOTA: Se necessitar pode escrever no verso das folhas

---

[2] Se desconhece a que família química pertencem as tintas utilizadas, pode preencher a tipologia com a nomenclatura comum nos espaços em branco.

III.3 Questionnaire – Ângelo de Sousa

MATERIAIS NÃO TRADICIONAIS NAS OBRAS DE ARTE PORTUGUESAS

Alguma vez utilizou novos materiais nas suas obras?
Sim ___▲___
Não _______

Em caso de resposta negativa,
o inquérito termina aqui.

Se sim,
dos seguintes materiais, quais utilizou e em que anos?
Tintas sintéticas ___▲___
Vidros acrílicos (*Plexiglas*) ___▲___
Outros vidros, quais? ___ Espelhos (1993…) ____
Materiais compósitos e metais mais leves, quais? ___ Aglomerados de madeira, de fibra, alumínio __
Espumas _______
Outros ____
____

Poderá dar referência de obras ou bibliografia que possam ilustrar estas aplicações?
____ Trabalho de pintura e escultura desde início e meados dos anos setenta, respectivamente. Catálogos e livros correspondentes ____
____

Se não utilizou tintas sintéticas,
o inquérito termina aqui.

Se utilizou tintas sintéticas,
de que tipo?
Emulsões acrílicas __ Desde o início dos anos setenta __
Emulsões vinílicas __ A partir de 1961 (cola de PVA) + pigmentos ou guache ou aguarela (em tubo)
Alquídicas _____
Nitrocelulósicas _____
Outras ___ Encáustica (anos 50) durante 3 ou 4 anos ______________________________________

Tintas para artistas ou tintas industriais (p.e. tintas de parede)? ____________________________

Tipo de tinta[3]	Nacional ou estrangeira	Local de aquisição	Marca	Anos de utilização	Observações
Emulsões acrílicas	Talens (em geral)	Papelarias especializadas	Talens	Desde 1972 até ao presente	
Emulsões vinílicas	Nacional	Fábrica de tintas Soberana (Porto)		Desde 1961 até aos anos 70	
Alquídicas	Industriais	Fábrica	Barbot (Porto)	2ª metade dos anos 60	Para pintar as esculturas em ferro, aço ou alumínio
Nitrocelulósicas	Nacional Robbialac	Robbialac	Robbialac	Esporadicamente	Para pintar pequenas esculturas (à pistola)
Tintas de off-set (cores primárias)	Van Son Holanda	Distribuidor comercial	Van Son Holanda	Anos sessenta	Pintura em cartolina preparada com PVA + branco; colada

Alguma vez preparou as suas próprias tintas?

Sim __▲(quási sempre) __

Não _______

Se sim,

o que utiliza ou utilizou como aglutinante?

__ Cêra de abelha (fim dos 50); PVA; tintas de off-set; acrílicos (por ordem cronológica). ____

Normalmente que razões o(a) levam a optar por uma tinta acrílica ou vinílica?

___ Secagem rápida; ausência relativa de cheiro; económicas (nos primeiros anos); tipo de acabamento desejado na altura. ____

____

Nome do Artista ____ Ângelo de Sousa ______________________________

Telefone de contacto ___ - ____

e-mail ___ - ____

NOTA: Se necessitar pode escrever no verso das folhas

---

[3] Se desconhece a que família química pertencem as tintas utilizadas, pode preencher a tipologia com a nomenclatura comum nos espaços em branco.

III.4 Questionnaire – Lourdes Castro

MATERIAIS NÃO TRADICIONAIS NAS OBRAS DE ARTE PORTUGUESAS

Alguma vez utilizou novos materiais nas suas obras?

Sim ___▲____

Não _______

Em caso de resposta negativa,
o inquérito termina aqui.

Se sim,
dos seguintes materiais, quais utilizou e em que anos?

Tintas sintéticas ___▲____

Vidros acrílicos (*Plexiglas*) ___▲____

Outros vidros, quais? _______

Materiais compósitos e metais mais leves, quais? _______

Espumas _______

Outros ____Nos desenhos: Lápis de cera (ex. *Caran d'Ache*); lápis de cor (ex. *Faber-Castell*); lápis de aguarela; grafite; canetas de feltro____

Poderá dar referência de obras ou bibliografia que possam ilustrar estas aplicações?

____Em qualquer dos meus catálogos______________________________________

____

Se não utilizou tintas sintéticas,
o inquérito termina aqui.

Se utilizou tintas sintéticas,
de que tipo?

Emulsões acrílicas _____

Emulsões vinílicas ___▲___

Alquídicas _____

Nitrocelulósicas _____

Outras ____*Glycerophtalique*[4]; tinta de alumínio____

Tintas para artistas ou tintas industriais (p.e. tintas de parede)? ____Industriais_____________

---

[4] O mesmo que resina alquídica.

Tipo de tinta[5]	**Nacional ou estrangeira**	**Local de aquisição**	**Marca**	**Anos de utilização**	**Observações**
Emulsões acrílicas					
Emulsões vinílicas	Francesa	Paris		Essencialmente antes de 1964	
Alquídicas	Nota: ver *Glycerophtalique*				
Nitrocelulósicas					
Glycerophtalique	Francesa	Paris		10 anos pelo menos, 1964…	
Tinta de alumínio	Francesa	Paris	Eclador	1961-63	Tinta resistente a altas temperaturas, vendida para isolar tubos de aquecimento

Alguma vez preparou as suas próprias tintas?

Sim _______

Não ___▲___

Se sim,

o que utiliza ou utilizou como aglutinante?

____

Normalmente que razões o(a) levam a optar por uma tinta acrílica ou vinílica?

____maior aderência ao *plexiglas* (*glycerophtalique*)___________________

____

Nome do Artista ____Lourdes Castro________________________________

Telefone de contacto ____-____

e-mail ____-____

NOTA: Se necessitar pode escrever no verso das folhas

---

[5] Se desconhece a que família química pertencem as tintas utilizadas, pode preencher a tipologia com a nomenclatura comum nos espaços em branco.

III.5 Portuguese artists to whom the questionnaire was sent

Table III.1. List of the Portuguese artists to whom the questionnaire was sent

Artist	**Did not complete the questionnaire**	**Completed the questionnaire**	**Used ‘new materials’**	**Did not use ‘new materials’**
Alberto Carneiro		x		x
Albuquerque Mendes	x			
Alice Jorge		x	x	
Álvaro Lapa	x			
Ana Hatherly		x	x	
Ana Jotta		x	x	
Ana Vieira		x	x	
Ângelo de Sousa		x	x	
António Charrua	x			
António Palolo	x			
António Sena	x			
Armando Alves	x			
Artur Rosa	x			
Carlos Calvet		x	x	
Clara Meneres	x			
Eduardo Batarda		x	x	
Eduardo Nery		x	x	
Eurico Gonçalves	x			
Fernando Lanhas	x			
Fernando Lemos		x	x	
Gerardo Burmester	x			
Graça Morais	x			
Helena Almeida	x			
João Vieira	x			

Artist	**Did not complete the questionnaire**	**Completed the questionnaire**	**Used ‘new materials’**	**Did not use ‘new materials’**
Jorge Martins		x	x	
Jorge Pinheiro	x			
José de Guimarães		x	x	
José Rodrigues		x	x	
Julião Sarmento		x	x	
Júlio Pomar		x	x	
Júlio Resende		x		x
Leonel Moura		x	x	
Lourdes Castro		x	x	
Manuel Cargaleiro	x			
Manuel Casimiro		x	x	
Maria Keil		x		x
Nadir Afonso		x	x	
Nikias Skapinakis		x		x
Noronha da Costa	x			
Paula Rego		x	x	
Querubim Lapa		x		x
Ricardo da Cruz Filipe		x	x	
Rocha de Sousa		x	x	
Sofia Areal	x			
Vítor Pomar	x			
Vítor Pires Vieira		x	x	
Zulmiro de Carvalho		x		x

Appendix IV

Accelerated Ageing

IV.1 Poly(vinyl acetate)

IV.1.1 Weight Loss Measurements

In Tables IV.1 (PVAc) and IV.2 (*Vulcano V7*) weight measurements, for the different irradiation times and control samples are presented; the values obtained are the result of three independent measurements.

Table IV.1. Weight loss (mg) for PVAc paint reconstruction samples with ageing

Sample	**500 h**			**1500 h**			**2500 h**			**3500 h**			**Control Sample (3500 h in the dark)**		
	Initial mass (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)
PVAc	24.69	*1.07*	***4.35***	25.22	*1.11*	***4.40***	28.39	*1.34*	***4.71***	24.89	*1.21*	***4.85***	27.04	*1.34*	***4.94***
+TiO_2	33.37	*0.45*	***1.36***	41.09	*0.69*	***1.69***	26.06	*0.47*	***1.80***	30.59	*0.70*	***2.28***	19.74	*0.34*	***1.71***
+Fe_2O_3	44.94	*0.96*	***2.13***	13.84	*1.17*	***8.43***	74.17	*0.85*	***1.15***	32.79	*0.84*	***2.55***	37.03	*0.66*	***1.79***
+Ult.	43.58	*0.87*	***2.00***	27.21	*0.57*	***2.10***	38.90	*1.05*	***2.71***	28.74	*0.83*	***2.89***	49.74	*1.05*	***2.11***
+$CaCO_3$	52.56	*0.85*	***1.62***	41.13	*0.85*	***2.06***	48.20	*1.29*	***2.67***	32.07	*0.91*	***2.85***	38.88	*0.74*	***1.90***
+$CaCO_3$+TiO_2	49.28	*0.74*	***1.51***	41.42	*0.96*	***2.33***	41.34	*0.68*	***1.65***	41.96	*0.84*	***1.99***	40.49	*0.63*	***1.55***
+$CaCO_3$+Fe_2O_3	53.36	*0.98*	***1.84***	45.51	*0.91*	***1.99***	46.43	*0.98*	***2.12***	39.73	*0.83*	***2.08***	31.07	*0.45*	***1.46***
+$CaCO_3$+Ult.	36.73	*0.67*	***1.82***	34.23	*0.69*	***2.01***	44.03	*1.11*	***2.52***	35.47	*1.29*	***3.65***	21.56	*0.27*	***1.27***
+TiO_2+Fe_2O_3	39.08	*0.70*	***1.78***	20.41	*0.31*	***1.53***	20.40	*0.41*	***2.03***	33.17	*0.75*	***2.27***	40.46	*0.78*	***1.92***

Table IV.2. Weight loss (mg) for *Vulcano V7* paint reconstruction samples with ageing

Sample	**500 h**			**1500 h**			**2500 h**			**3500 h**			**Control Sample (3500 h in the dark)**		
	Initial mass (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)	**Initial mass** (mg)	***Mass loss*** (mg)	***Mass loss*** (%)
V7	31.41	*0.06*	***0.20***	30.89	*0.37*	***1.20***	28.00	*1.70*	***6.06***	19.67	*2.80*	***14.25***	a	a	a
+TiO_2	45.12	*0.87*	***4.99***	30.73	*2.09*	***6.80***	46.56	*3.09*	***6.64***	44.77	*3.07*	***6.86***	a	a	a
+Fe_2O_3	30.51	*1.89*	***6.18***	41.75	*2.81*	***6.72***	41.98	*2.74*	***6.52***	44.13	*2.92*	***6.62***	31.63	*0.93*	***2.93***
+Ult.	42.02	*1.98*	***4.70***	36.20	*1.93*	***5.34***	40.91	*2.35*	***5.74***	42.36	*2.81*	***6.63***	37.32	*0.87*	***2.32***
+$CaCO_3$	49.39	*0.10*	***0.20***	37.46	*0.33*	***0.88***	42.10	*1.05*	***2.49***	50.25	*2.77*	***5.52***	48.38	*0.10*	***0.21***
+$CaCO_3$+TiO_2	56.35	*0.43*	***0.76***	42.40	*0.95*	***2.24***	49.12	*1.20*	***2.45***	55.57	*2.68*	***4.82***	49.36	*0.48*	***0.97***
+$CaCO_3$+Fe_2O_3	54.75	*0.49*	***0.90***	50.17	*1.20*	***2.40***	40.11	*1.40*	***3.48***	40.85	*1.43*	***3.50***	50.73	*0.25*	***0.49***
+$CaCO_3$+Ult.	54.56	*0.60*	***1.11***	47.47	*1.41*	***2.96***	38.41	*1.55*	***4.03***	54.54	*2.42*	***4.44***	42.20	*0.23*	***0.54***
+TiO_2+Fe_2O_3	47.28	*2.67*	***5.65***	34.23	*2.34*	***6.83***	39.78	*2.71*	***6.81***	40.63	*2.79*	***6.86***	23.68	*0.87*	***3.69***

[a] The sample was damaged and it was not possible to perform any measurements.

IV.1.2 Solubility

In order to determine the polymer solubility after irradiation, the weight-gain on membrane filters after filtration was determined gravimetrically as described in Appendix I. From the data in Table IV.3 it is clear that no trend is verified, with relative standard deviations being the same order of magnitude for solutions (before and after irradiation) and solvent filtration; furthermore it is possible to affirm that the polymer remains soluble after irradiation. This procedure was only possibly to perform for the pure polymer as all other samples contained insoluble additives (both pigments and emulsion additives), which would mask the results.

Table IV.3. Gravimetric determination of PVAc solubility before and after 3500h irradiation

Sample	Filter before filtration (g)	Filter after filtration (g)	Average	s	s_r (%)
PVAc (control)	0.65348	0.65395	0.65372	0.00033	***0.05***
PVAc (0h)	0.65177	0.65253	0.65215	0.00053	***0.08***
PVAc (1500h)	0.64410	0.64417	0.64413	0.00005	***0.01***
PVAc (2500h)	0.64222	0.64268	0.64245	0.00033	***0.05***
PVAc (3500h)	0.64071	0.64130	0.64101	0.00042	***0.07***
Solvent	0.64653	0.64694	0.64674	0.00029	**0.04**
Solvent	0.64374	0.64395	0.64385	0.00015	**0.02**
Solvent	0.64697	0.64723	0.64710	0.00019	**0.03**

V.1.3 Size Exclusion Chromatography (SEC)

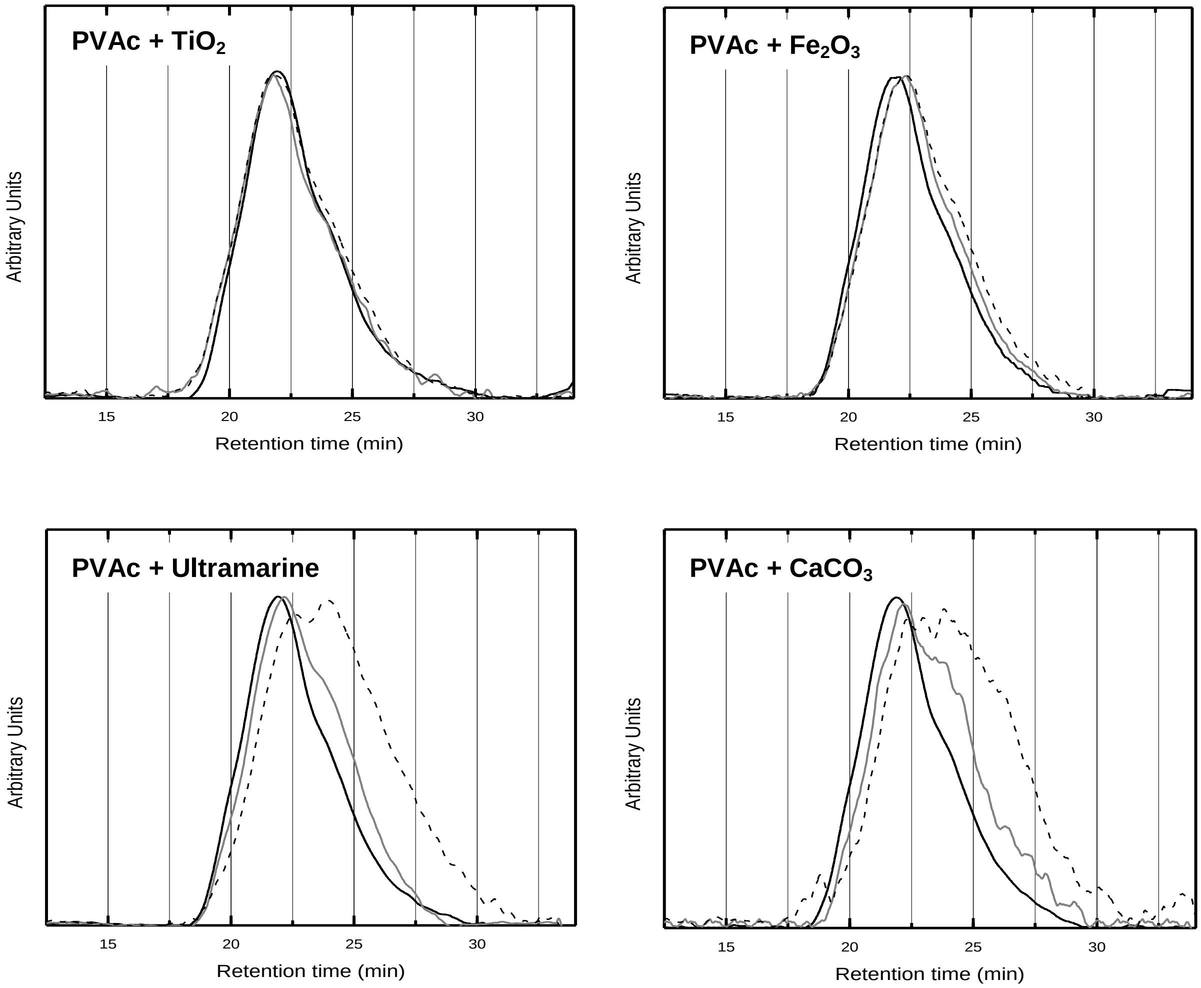


Figure IV.1. SEC chromatograms of PVAc + pigments before and after irradiation: black line – 0h; grey line – 1500h; dashed line – 3500h.

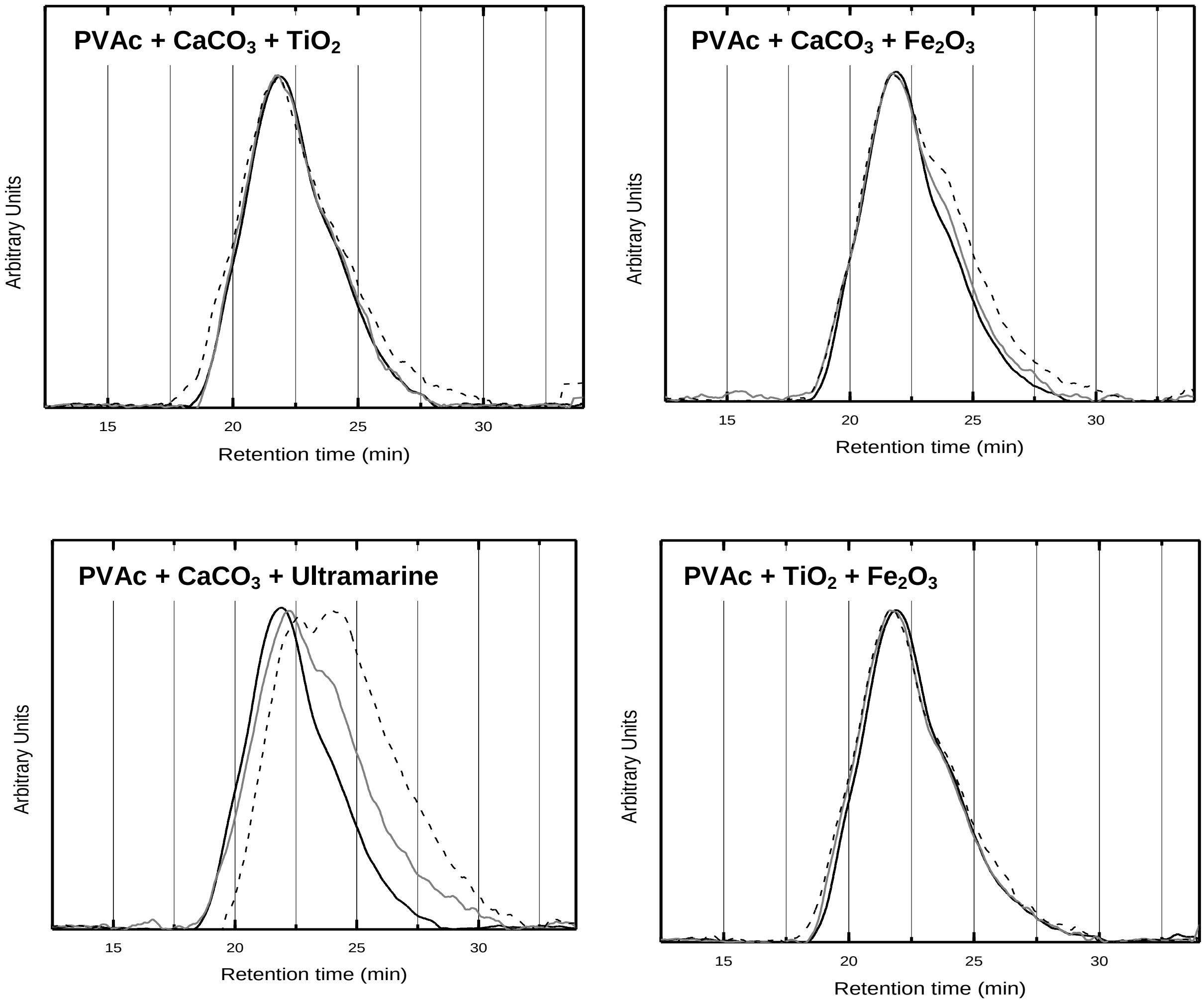


Figure IV.2. SEC chromatograms of PVAc + pigment mixtures before and after irradiation: black line – 0h; grey line – 1500h; dashed line – 3500h.

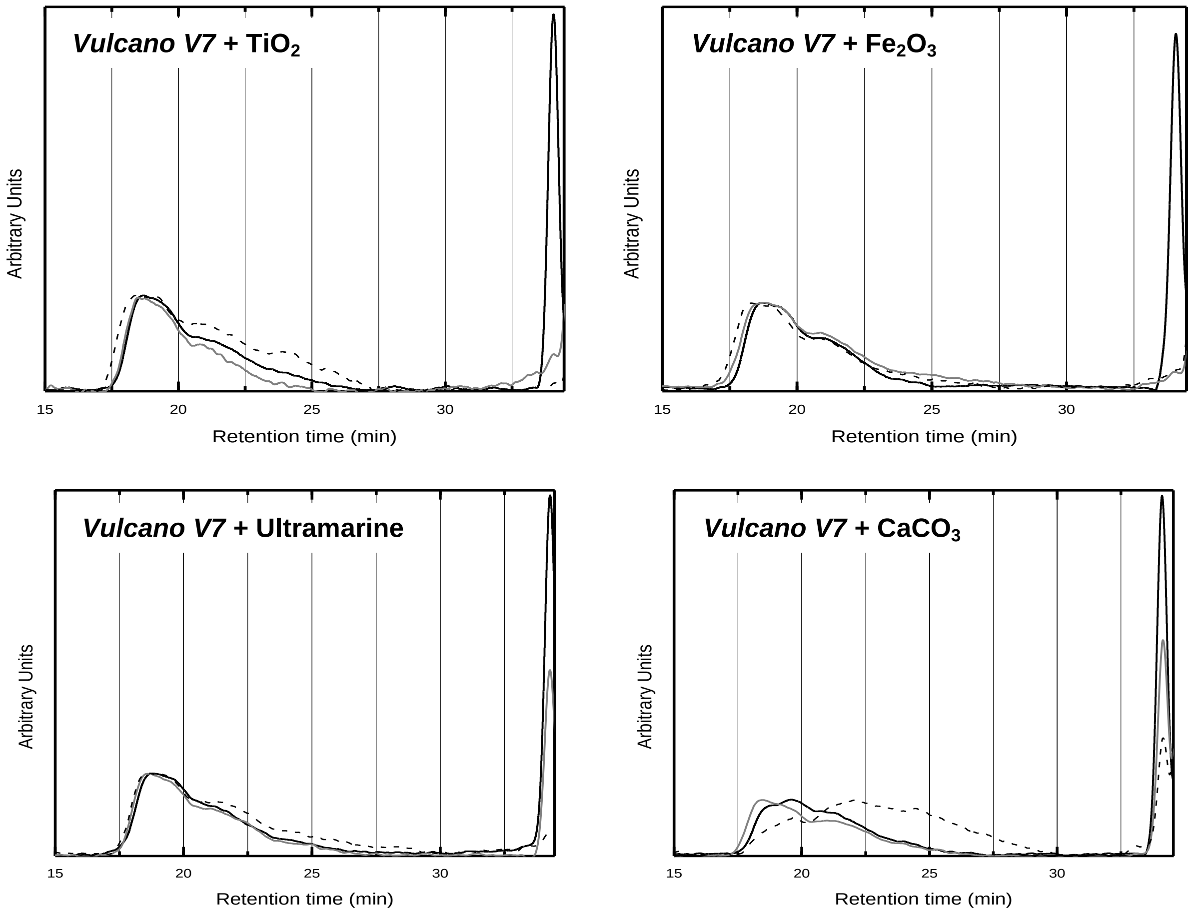


Figure IV.3. SEC chromatograms of *Vulcano V7* + pigments before and after irradiation: black line – 0h; grey line – 1500h; dashed line – 3500h.

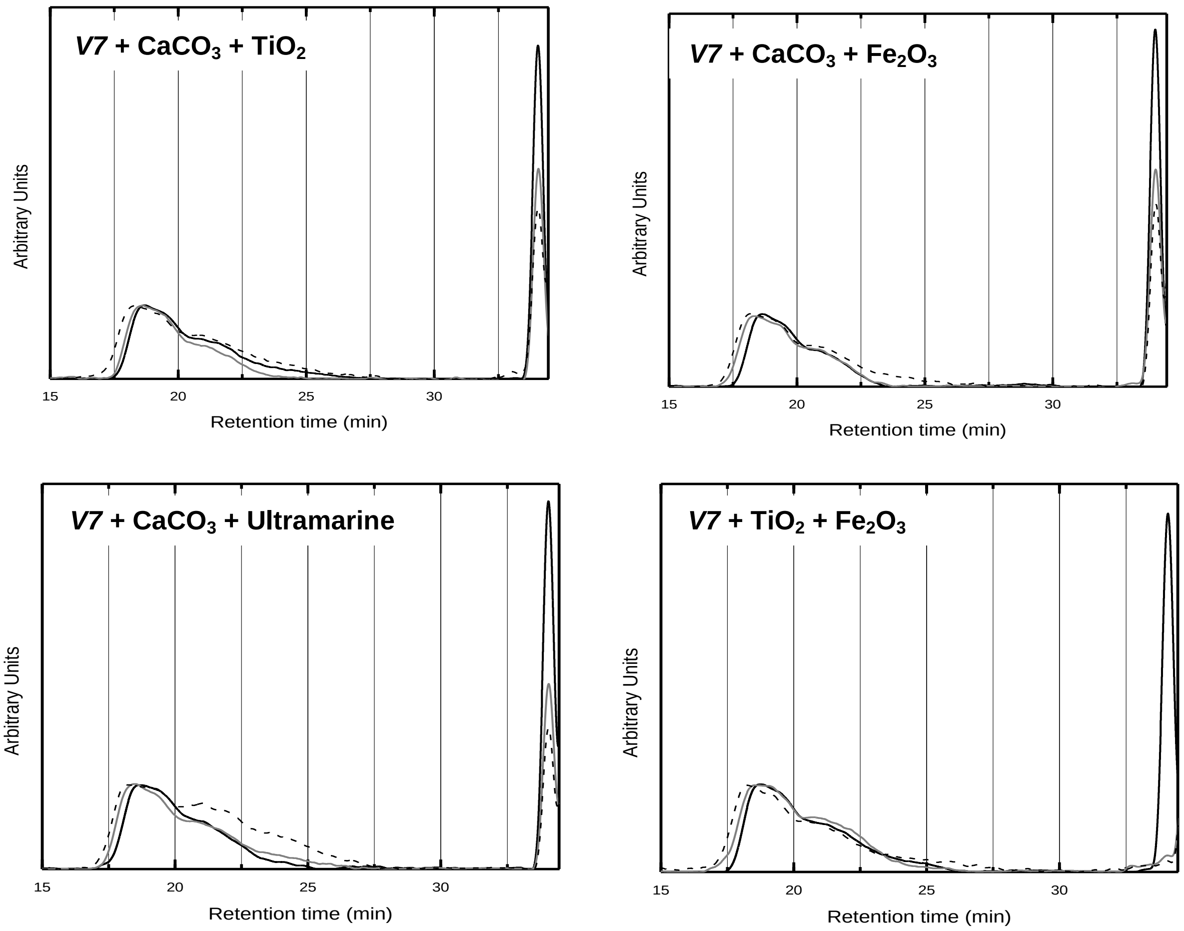
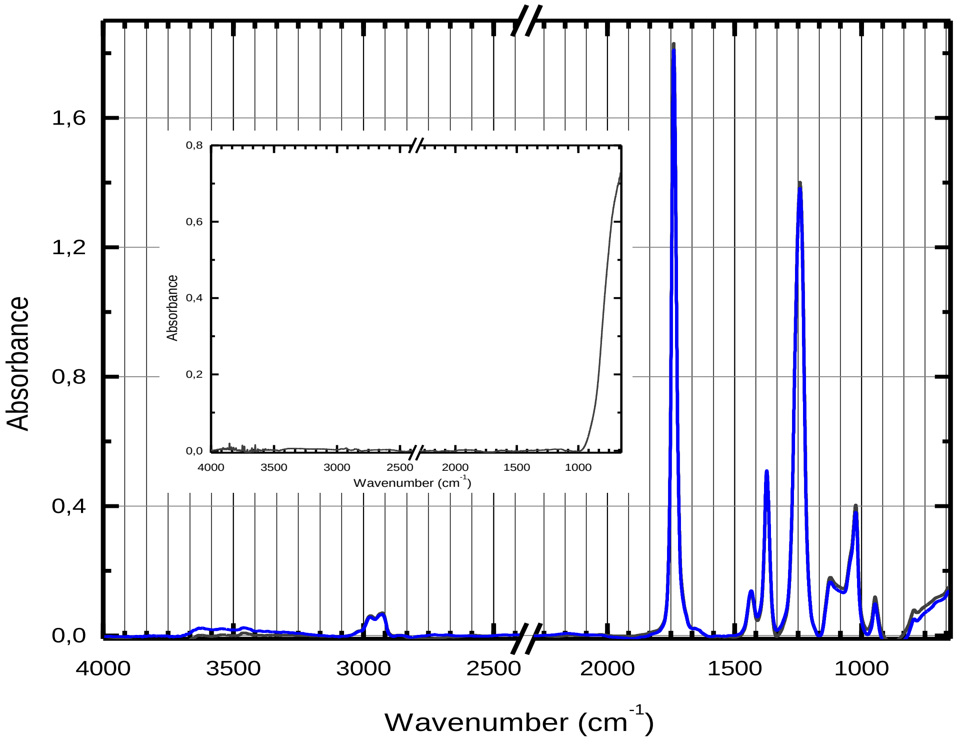
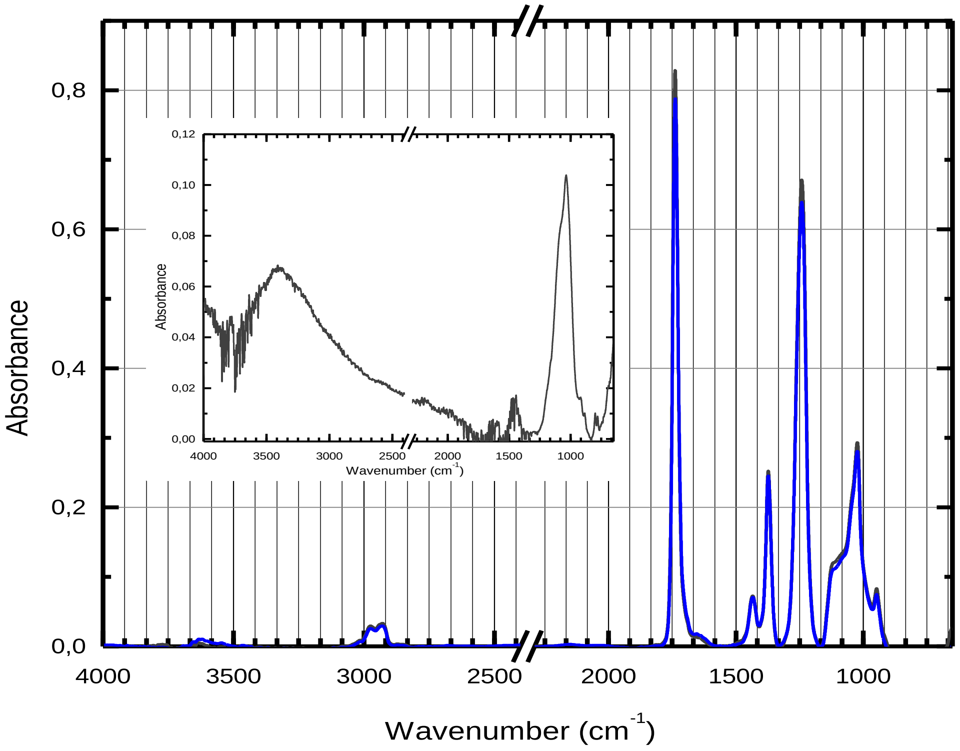


Figure IV.4. SEC chromatograms of *Vulcano V7* + pigment mixtures before and after irradiation: black line – 0h; grey line – 1500h; dashed line – 3500h.

IV.1.4 FTIR

Table IV.4. Infrared spectra of PVAc + pigments before and after irradiation: black line – 0h; blue line – 3500h. The spectra of the pigment alone is represented in the insert

Sample	Spectra
PVAc + TiO_2	
PVAc + Fe_2O_3	

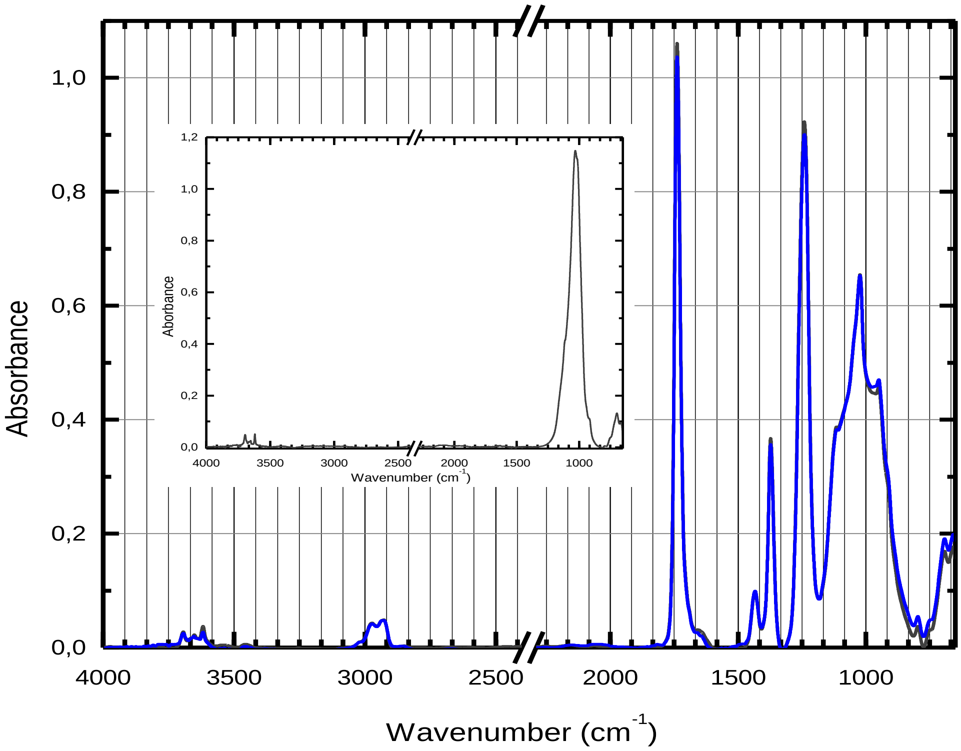
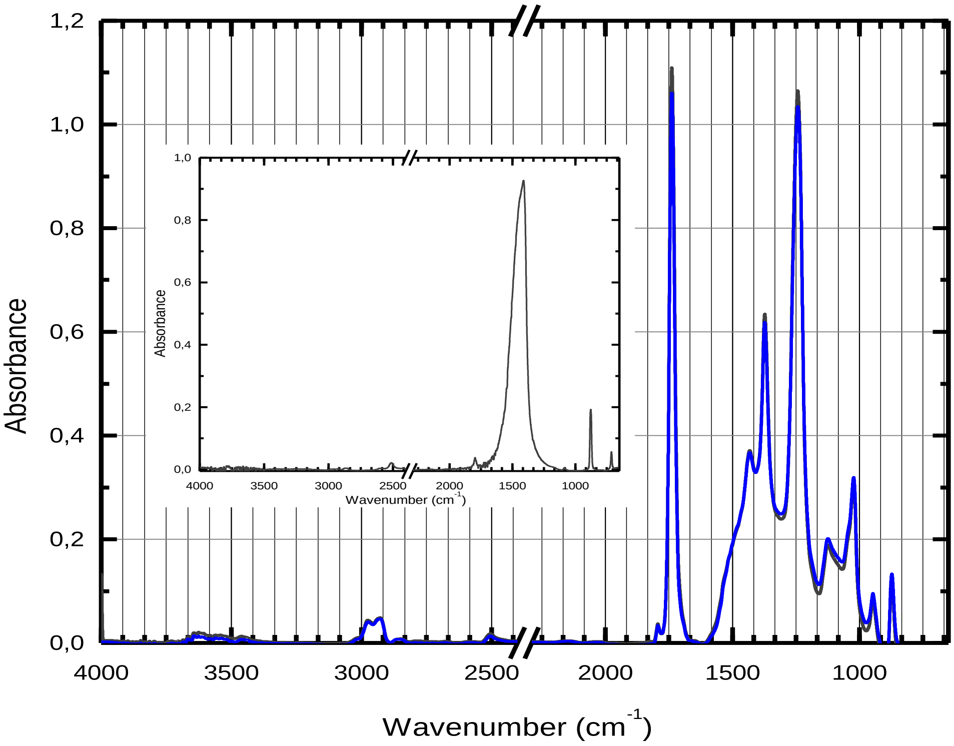
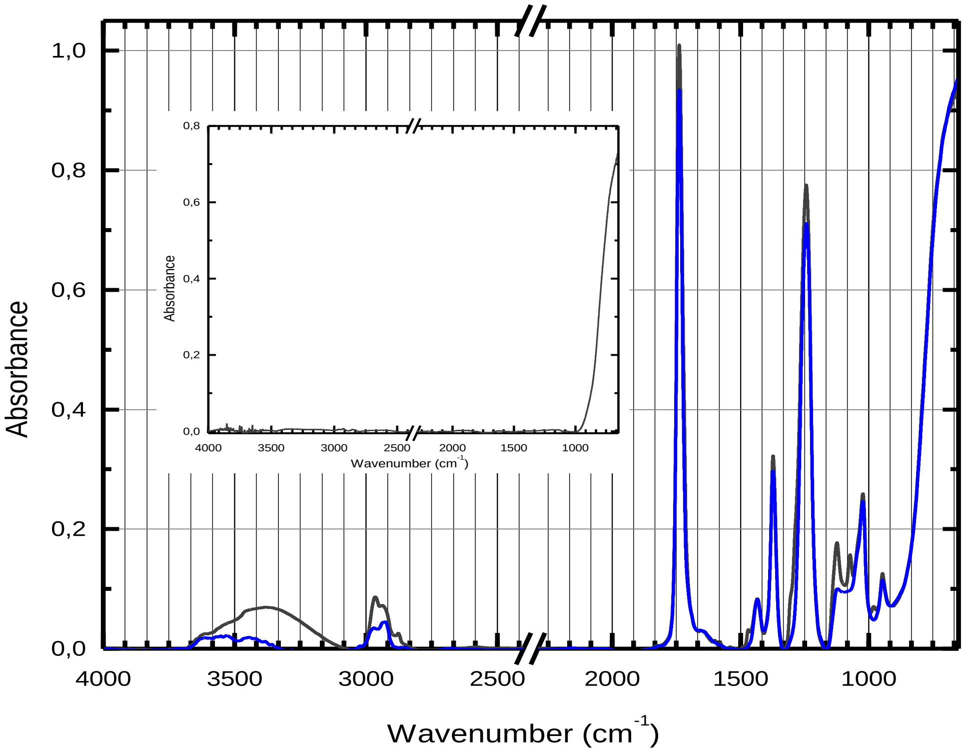
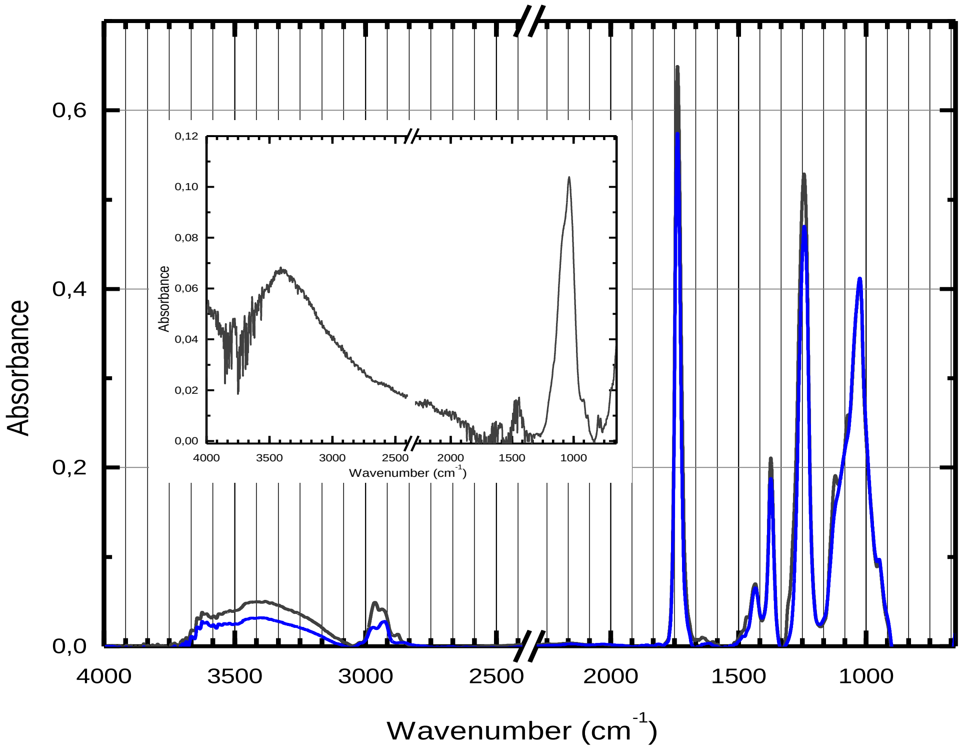
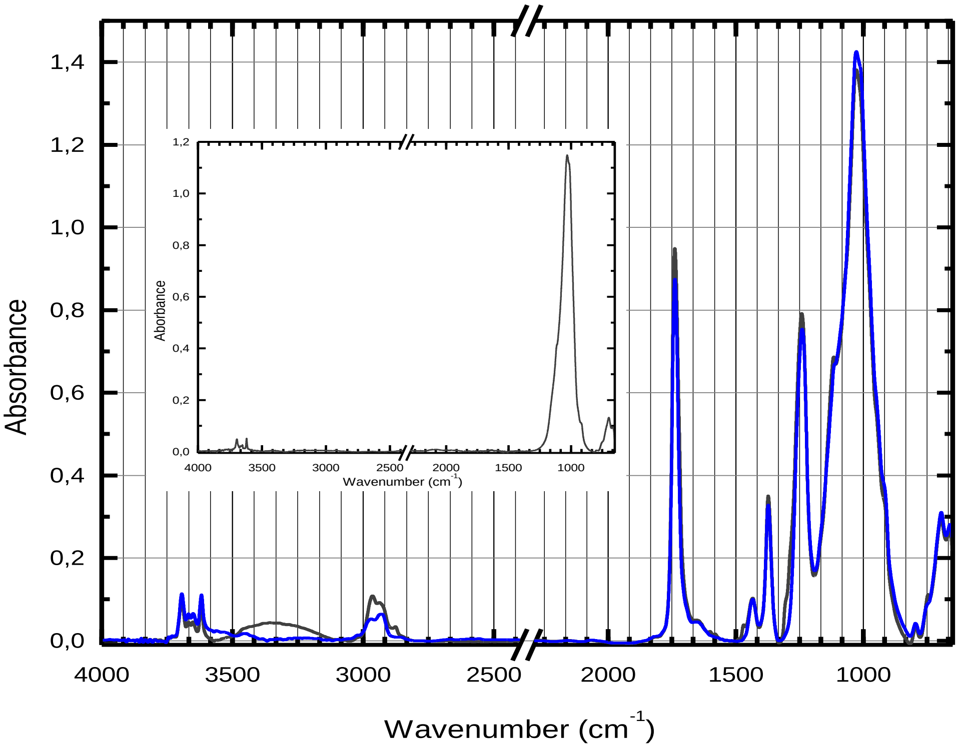
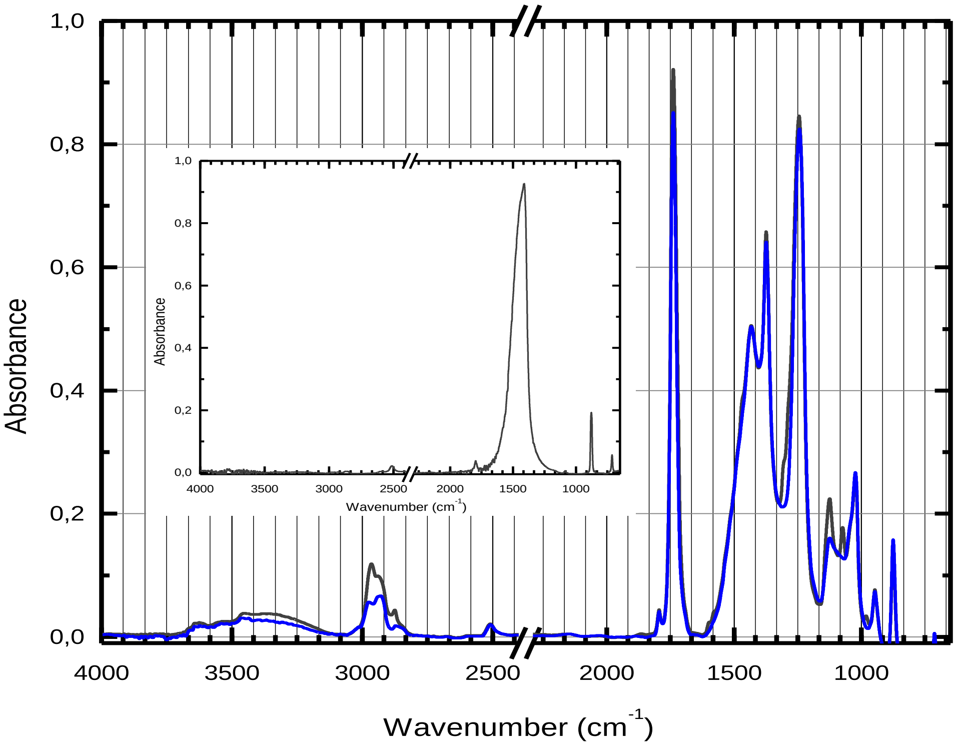
Sample	**Spectra**
PVAc + Ultramarine	
PVAc + $CaCO_3$	

Table IV.5. Infrared spectra of *Vulcano V7* + pigments before and after irradiation: black line – 0h; blue line – 3500h. The spectra of the pigment alone is represented in the inset

Sample	**Spectra**
V7 + TiO_2	
V7 + Fe_2O_3	

Sample	**Spectra**
V7 + Ultramarine	
V7 + $CaCO_3$	

IV.1.5 Simulation of PVAc hydrolysis[1]

In Figure IV.5 the infrared spectra of poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) are presented. PVAL can be present in a PVAc matrix as a copolymer, additive or as a degradation product, formed by acidic hydrolysis. A simulation of the increase of PVAL in PVAc was performed by computer spectral addition and by the analysis of standard samples obtained by mixture (Figure IV.6). This simulation was performed in order to determine the IR detection limit of the PVAL presence in a PVAc and was further confirmed by comparison of the C=O/O-H ratio (Table IV.6) with literature spectra [160]. Therefore, considering the simulation is valid, it is possible to further calculate the ratios for any given concentration of PVAL in a PVAc matrix. The value calculated for the C=O/C-H ratio in a 50:50 mixture is 1.44 (0.69 if the ratio C-H/C=O is considered instead).

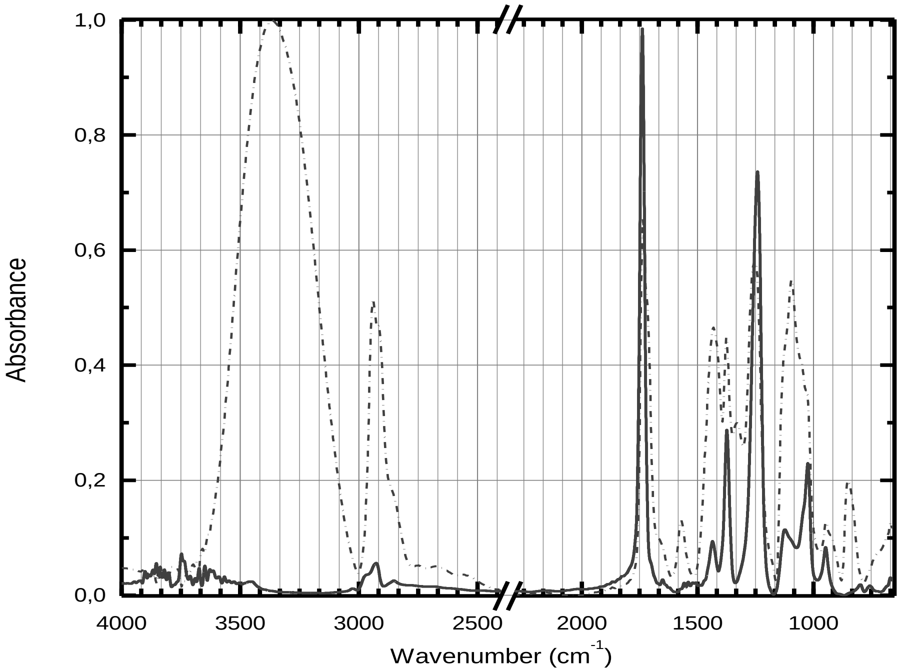


Figure IV.5. Infrared spectra of PVAc (straight line) and PVAL (dashed line).

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[1] This study was presented as a poster at The seventh biennial gathering of the Infrared and Raman Users Group held at the Museum of Modern Art in New York, March 2006 [159].

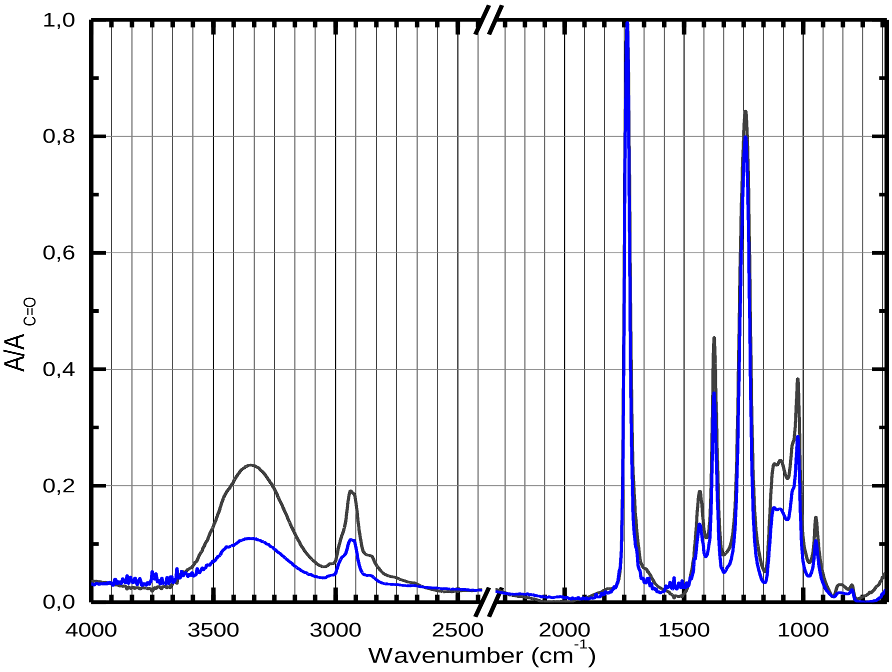


Figure IV.6. Infrared spectra of PVAc and PVAL mixtures in proportions of 80:20 (black line) and 90:10 (blue line).

Table IV.6. C=O/O-H peak ratios on PVAc spectra containing 10, 20, or 50% PVAL

	Mixture		**Computer Simulation**			**Literature Copolymers**	
PVAc:PVAL	90:10	80:20	90:10	80:20	50:50	90:10	80:20
Ratio	9.17	4.20	8.60	4.34	1.44	10.00	4.35

The analysis of the spectra show that the increase of the alcohol concentration would first be detected by the formation of an O-H band centred at approximately 3350 cm^{-1} accompanied by a drop of the PVAc νC-H$_3$ peak and an increase of the absorption centred at 2940 cm^{-1}. These changes are followed by a decrease, shift to lower wavenumbers and broadening of the C=O; shift to higher wavenumbers (1255 cm^{-1} for PVAL) and broadening of the C-O stretching; and also the formation of another C-O intense absorption peak (1094 cm^{-1} for PVAL).

Based on the results it is possible to predict that only above 10% the presence of PVAL is easily detectable. Therefore, if PVAL is used as an additive in lower amounts or if it is produced in the earlier steps of degradation it will be difficult to detect and quantify by FTIR.

IV.2 Poly(methyl methacrylate)

IV.2.1 Weight Loss Measurements

In Table IV.7 weight measurements for PMMA samples, at different irradiation times, are presented; the values obtained are the result of three independent measurements.

Table IV.7. Weight loss (g) for transparent colourless and colourless blue PMMA sheets with ageing

Sample	**Initial mass** (g)	**500 h**		**1750 h**		**3000 h**		**4250 h**	
		Mass loss (g)	***Mass loss*** (%)	***Mass loss*** (g)	***Mass loss*** (%)	***Mass loss*** (g)	***Mass loss*** (%)	***Mass loss*** (g)	***Mass loss*** (%)
Colourless	3.378	*0.012*	***0.36***	*0.011*	***0.34***	*0.012*	***0.35***	*0.004*	***0.13***
Colourless + cleaning	3.334	-	-	*0.012*	***0.34***	*0.013*	***0.40***	*0.006*	***0.19***
Blue	3.243	*0.013*	***0.40***	*0.015*	***0.47***	*0.016*	***0.49***	*0.009*	***0.29***
Blue + cleaning	3.371	-	-	*0.014*	***0.41***	*0.014*	***0.43***	*0.008*	***0.23***

IV.2.2 Solubility

As described for PVAc in V.1.2, the polymer solubility after irradiation was determined gravimetrically and data are presented in Table IV.8.

Table IV.8. Gravimetric determination of PMMA solubility before and after 3500h irradiation

Sample	Filter before filtration (g)	Filter after filtration (g)	Average	s	s_r (%)
PMMA (control)	0.63629	0.63685	0.63657	0.00039	*0.06*
PMMA (0h)	0.64646	0.64693	0.64670	0.00033	*0.05*
PMMA (1500h)	0.64540	0.64609	0.64575	0.00049	*0.08*
PMMA (2500h)	0.63931	0.63968	0.63950	0.00026	*0.04*
PMMA (3500h)	0.63777	0.63823	0.63800	0.00033	*0.05*
Solvent	0.64653	0.64694	0.64674	0.00029	**0.04**
Solvent	0.64374	0.64395	0.64385	0.00015	**0.02**
Solvent	0.64697	0.64723	0.64710	0.00019	**0.03**

IV.2.3 Size Exclusion Chromatography (SEC)

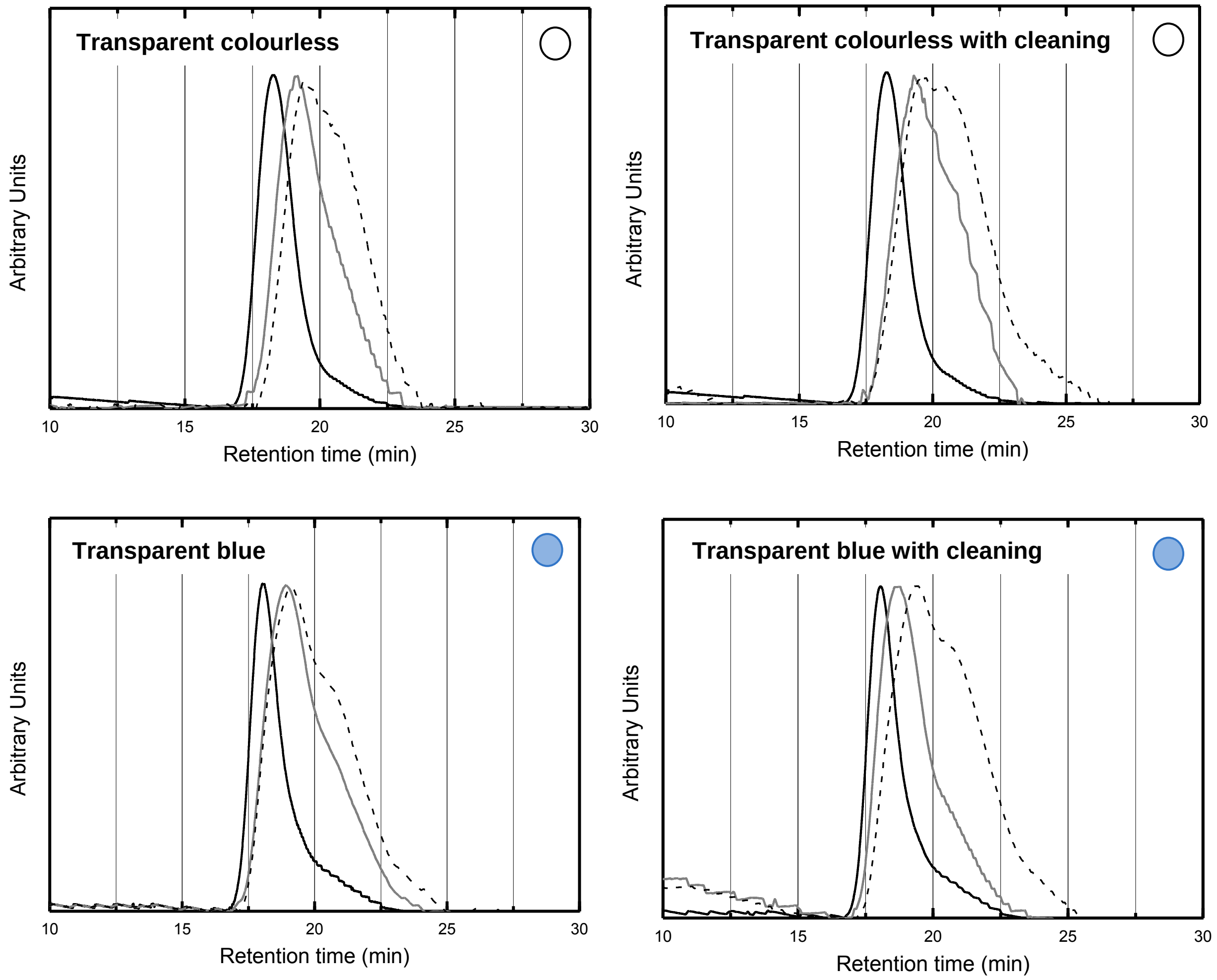


Figure IV.7. SEC chromatograms of PMMA sheets before and after irradiation: black line – 0h; grey line – 1750h; dashed line – 4250h.

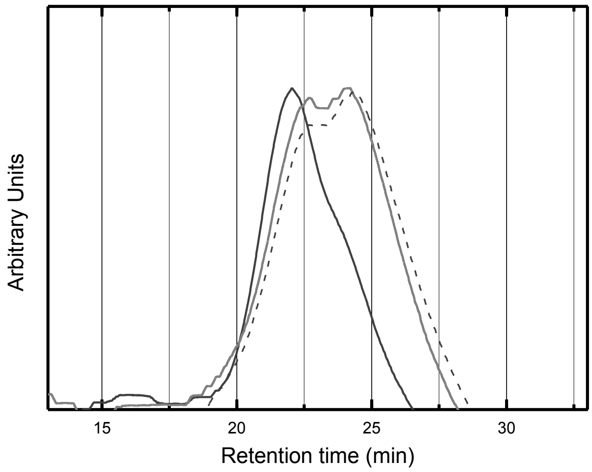


Figure IV.8. SEC chromatograms of PMMA film before and after irradiation: black line – 0h; grey line – 1750h; dashed line – 4250h.

IV.2.4 FTIR

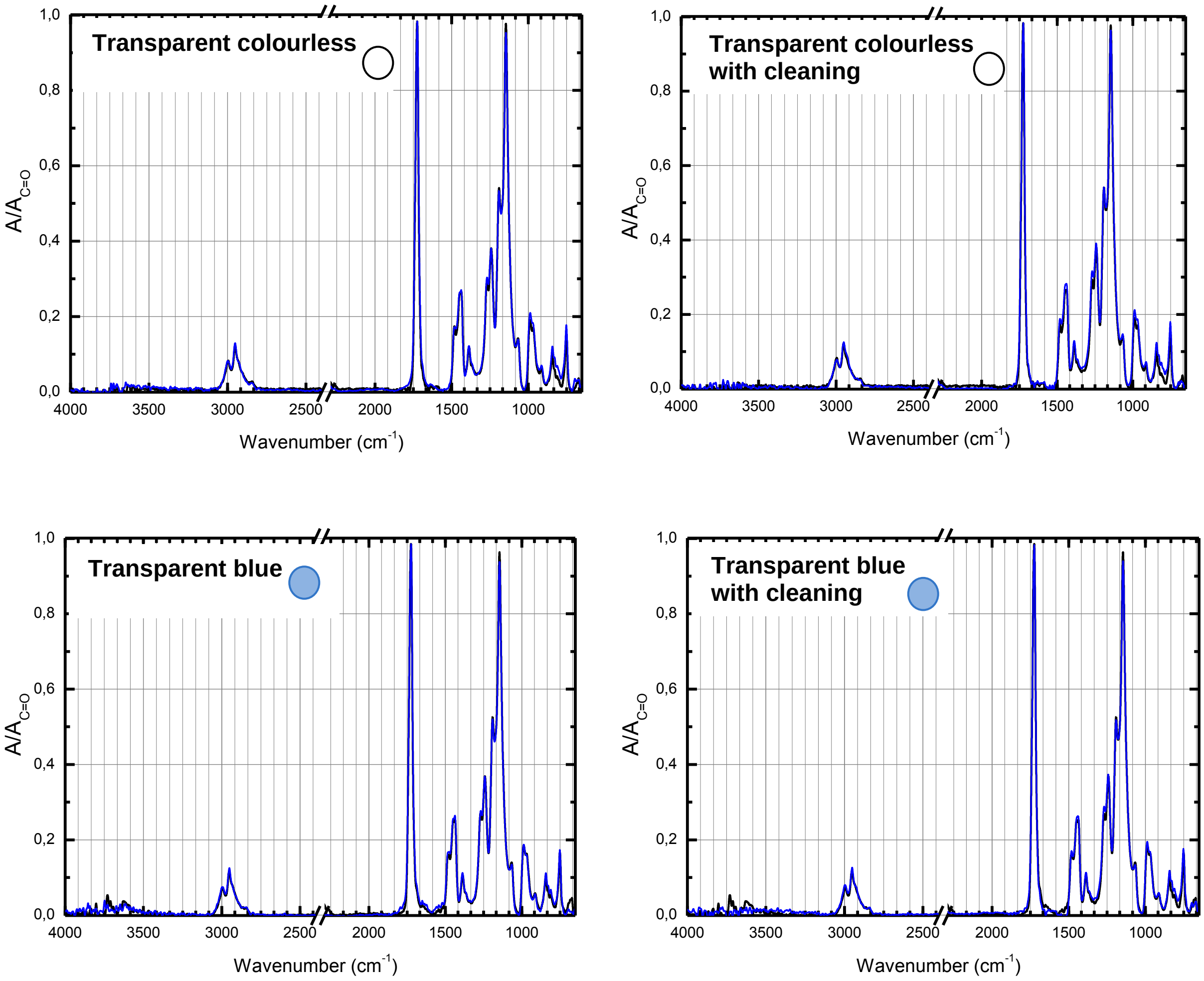


Figure IV.9. Infrared spectra of PMMA sheets before and after irradiation: black line – 0h; blue line – 4250h.

Appendix V

Joaquim Rodrigo

V.1 Information on paintings from 1961 until 1990 concerning the binder, support, dimensions and date / Catalogue *Raisonné*

Table V.1. Binder, support and dimensions of the works by Joaquim Rodrigo (from 1961 until 1990) / Catalogue *Raisonné* [22]

Title	**Year**	**Vinyl**	**Tempera**	**Oil**	**Hardboard**	**Canvas**	**Other**	**Dim. (cm)**
S. A. – Estação	1961		**x**		**x**			97x162.5
A	1961			**x**	**x**			89x130
G	1961	**x**			**x**			73x122
C	1961	**x**			**x**			89x130
S. M.	1961		**x**[a]		**x**			97.3x146
L	1961			**x**		**x**		81.5x116.5
Sem título	1961			**x**	**x**			50x50
Sem título	1961			**x**	**x**			90x130
Lisboa – Algarve	1961			**x**		**x**		90x136
Sem título	1961	**x**			**x**			90.5x130.5
G. N.	1961		**x**		**x**			125x223
"19 S" (Pesadelos)	1961	**x**			**x**			122.5x220.5
Simón Caraballo	1961		**x**		**x**			97x148
M. L.	1961	**x**					◊	73x100
Sem título	1961			**x**		**x**		65x100
Vau – Campo	1962		**x**			**x**		73x92
Mondo Cane 2	1962		**x**		**x**			122.5x185
Kultur – 1962	1962		**x**[a]			**x**		73x92
Mondo Cane I	1963		**x**[a]				▲	81x116

Title	**Year**	**Vinyl**	**Tempera**	**Oil**	**Hardboard**	**Canvas**	**Other**	**Dim. (cm)**
6 H	1963		**x**		**x**			89x130
C. de los H. P.	1963		**x**		**x**			122x185
Liberté	1963		**x**[a]		**x**			123x185
Ronda	1963			**x**		**x**		72x92
Córdoba	1963		**x**		**x**			123x221
1º M	1964	**x**			**x**			73x92
Quintais	1964	**x**				**x**		73.5x93
Cacilhas	1964			**x**		**x**		90x90x90
Londres	1964	**x**			**x**			91x122
Londres II	1964	**x**			**x**			91x122
Trás-os-Montes	1964	**x**			**x**			91x122
Painting & Sculpture of a Political Decade	1964	**x**			**x**			90.5x121.5
N. H. T. P. L.	1965	**x**					●	70x100
Lisboa – Sevilha	1968	**x**			**x**			97x146
Lisboa – Corunha – Marrocos	1968	**x**			**x**			96x147
Lisboa – Madrid	1969	**x**			**x**			97x146
Lisboa – Oropeza	1969	**x**			**x**			97x146
Sevilha – Cartaia	1969	**x**			**x**			97x146
Oropeza – Madrid	1969	**x**			**x**			97x146
Madrid – Vallauris	1969	**x**			**x**			149x200
Vallauris – Perthus	1969	**x**			**x**			150x200
Port-Ligat – Valencia	1969	**x**			**x**			114x162
Tarragona – Mojácar	1969	**x**			**x**			115x162
Lisboa – Algeciras	1969	**x**			**x**			96x145
Lisboa – La Vid	1969	**x**			**x**			97x146
Lisboa – Vitoria	1970	**x**			**x**			97.2x145.4
La Vid – Soria	1970	**x**			**x**			96.5x146.5

Title	**Year**	**Vinyl**	**Tempera**	**Oil**	**Hardboard**	**Canvas**	**Other**	**Dim. (cm)**
Lisboa – Burgos	1970	x			x			97x146
Lisboa – Caia	1970	x				x		65.5x92.5
Lisboa – Madrid	1970	x			x			97x146
Burgos – La Vid	1970	x			x			97x146
La Vid – Arenys	1970	x			x			97x146
Ventimiglia – Nice	1970	x					■	97x146
Gerona – Sueca	1970	x			x			129x189
Gerona – Sueca	1970	x			x			130x190
Lisboa – Madrid	1971	x					■	97x146
Madrid – Biarritz	1971	x					■	97x146
Soria – Nimes	1971	x			x			127x179
Lisboa – Málaga	1971	x			x			128x180
Aranda del Duero – La Vid	1971	x			x			97x146
San Esteban de Gormaz – Soria	1971	x			x			97x146
San Esteban de Gormaz – Arenys	1971	x			x			97x146
Arenys – St. Paul de Vence	1971	x			x			128x180
Arenys – St. Paul de Vence	1971	x			x			128x180
Ventimiglia – Alassio	1971	x			x			128x180
Alassio – Nice	1971	x			x			128x180
Wien	1973	x			x			97x146
Lisboa – Paris	1973	x			x			97x146
Paris – Wien	1973	x			x			97x146
Munchen- 1972 – XX Olympiade 2	1973	x			x			97x146
Triângulo	1973	x			x			73x92.5
Triângulo I	1973	x			x			73x92
Triângulo III	1973	x				x		73x92
Triângulo 2 A	1973	x			x			73x92

Title	**Year**	**Vinyl**	**Tempera**	**Oil**	**Hardboard**	**Canvas**	**Other**	**Dim. (cm)**
Triângulo 2	1973	**x**			**x**			73x92
Triângulos I	1973	**x**				**x**		81x116
Triângulos 2	1973	**x**			**x**			81x116
Triângulos 3	1973	**x**			**x**			81x116
Madrid – Avignon – Paris – Guernica	1973	**x**			**x**			130x190
Lisboa – Londres – Paris – Madrid	1973	**x**			**x**			97x146
Avignon – Paris	1974	**x**			**x**			95x120
Paris – S. Sebastian 3	1974	**x**			**x**			105x120
S. Sebastian – Villareal de Alava	1974	**x**			**x**			113x161.7
Madrid – Barcelona II	1974	**x**			**x**			73x92
Barcelona	1974	**x**			**x**			73x92
Elvas – Ateca I	1975	**x**			**x**			73x92
Elvas – Ateca 2	1975	**x**			**x**			73x92
Ateca – Barcelona	1975	**x**			**x**			97x146
Paris – Orio	1975	**x**			**x**			97x146
Elvas – Ateca 6	1975	**x**			**x**			97x146
Avignon – Paris	1975	**x**			**x**			97x146
Paris – Orio	1975	**x**			**x**			97x146
Euskalerri	1975	**x**			**x**			97x146
Badajoz – Aluenda	1975	**x**			**x**			97x146
Euskalerri II	1976	**x**			**x**			81x116
Aluenda - Tordesinlhas	1976	**x**			**x**			89x130
Évora – Madrid	1976	**x**			**x**			96x145
Madrid – Nice	1980	**x**			**x**			89x130
Madrid – Nice	1980	**x**			**x**			80.7x116
México	1980	**x**			**x**			81x116
Port-Ligat – Granada	1980	**x**			**x**			89x130

Title	**Year**	**Vinyl**	**Tempera**	**Oil**	**Hardboard**	**Canvas**	**Other**	**Dim. (cm)**
Évora – Madrid	1980	**x**			**x**			80.5x115.5
Madrid – Nice	1980	**x**			**x**			81x116.5
Aix-en-Provence – Altea	1980	**x**			**x**			89x130
Vau III	1980	**x**			**x**			114x162
Évora – Barcelona	1980	**x**			**x**			113.5x162
México	1980	**x**			**x**			80.7x116
Évora – Madrid	1980	**x**			**x**			81x116
Barcelona – Marselha – Algarve	1980	**x**			**x**			114x162
Vau IV	1980	**x**			**x**			100x150
España	1980	**x**			**x**			99.5x149.5
España II	1980	**x**			**x**			100x150
Portugal	1980	**x**			**x**			100x150
Portugal I	1980	**x**			**x**			81x115.5
Portugal II	1980	**x**			**x**			81x116.5
Portugal III	1980	**x**			**x**			105x120
Vau V	1980	**x**			**x**			97x146
Portugal IV	1980	**x**			**x**			100x150
Portugal V	1980	**x**			**x**			100x150
Nice – Ayamonte	1980	**x**			**x**			100x150
Évora – Nice	1980	**x**			**x**			100x150
Orio – Trujillo	1981	**x**			**x**			97x146
1918-1928	1981	**x**			**x**			97x146
1918-1928 2	1981	**x**			**x**			97x146
Vau VI	1981	**x**			**x**			97x146
Madrid – Aix-en-Provence	1981	**x**			**x**			97x146
Arles – Antequera	1981	**x**			**x**			97x146
Vau VII	1982	**x**			**x**			97x146.5

Title	Year	Vinyl	Tempera	Oil	Hardboard	Canvas	Other	Dim. (cm)
Évora – Nice	1982	x			x			97x146
Nice – Port-Ligat – Ayamonte	1982	x			x			97x146
Nice – Port-Ligat – Sevilha	1982	x			x			97x146
Espanha IV	1982	x			x			97x146
Portugal VI	1982	x			x			97x146
Elvas – Tours	1982	x			x			97x146
Elvas – Jarculet	1982	x			x			97x146
Urrne – Villareal de Álava	1982	x			x			97x146
Pirinéus	1982	x			x			97x146.5
Vau – Praia	1982	x				x		95x120
Vau – Campo	1983	x			x			89x130
Évora – Madrid	1983	x			x			105x120
Madrid – Vallauris	1983	x			x			115x120
Madrid – Barcelona – Andorra	1984	x			x			97x146
Évora – Madrid	1984	x			x			89x130
Andorra – Menton – Elche	1985	x			x			89x130
Elche – Sevilha	1985	x			x			89x130
Lisboa – Biarritz – Osma	1985	x			x			100x150
Osma – Alassio – Tarragona	1985	x			x			73x100
Elvas – Avignon – Paris	1985	x			x			89x130
Paris – Quintanilha de Arriba	1985	x			x			89x130
Badajoz – Aluenda	1986	x			x			89x130
Aluenda – Tordesillas II	1986	x			x			100x150
Memórias	1986	x			x			89x130
Lisboa – Oropeza	1986	x			x			89x130.5
A fazenda	1986	x			x			89x130
Sevilha – 1928	1987	x			x			89x130.5

Title	Year	Vinyl	Tempera	Oil	Hardboard	Canvas	Other	Dim. (cm)
Barcelona – Villareal de Álava	1987	**x**			**x**			89x130
Lisboa – Biarritz	1987	**x**			**x**			97x146
A Casa	1987	**x**			**x**			89x130
Memórias II	1987	**x**			**x**			89x130
Memórias III	1987	**x**			**x**			89x130
Memorias IV	1987	**x**			**x**			89x130
Sta Amália – Tordesilhas	1987	**x**			**x**			89x130
Elvas – Barcelona	1987	**x**			**x**			89x130
Memórias V	1988	**x**			**x**			89x130
A Rua	1988	**x**			**x**			89x130
A Rua II	1988	**x**			**x**			89x130
Visitação	1988	**x**			**x**			89x130
Évora – Barcelona II	1988	**x**			**x**			89x130
Barcelona – Béziers	1988	**x**			**x**			88.5x130
Béziers – Montpellier	1989	**x**			**x**			89x130
Le Perthus – Port-Ligat	1989	**x**			**x**			89x130
Port-Ligat – Andorra	1989	**x**			**x**			89x130
Os quintais	1989	**x**			**x**			89x130
A Casa II	1990	**x**			**x**			90x130
Uma viagem (e esqueci-me do chinês!...)	1990	**x**			**x**			89x130

[a] Identified as poly(vinyl acetate) in the framework of the present thesis.

Symbols: **x** – binder/support used; ◊ – chipboard; ▲ – canvas glued on to hardboard; ● – cardboard; ■ – wood.

Table V.2. Number of paintings by Joaquim Rodrigo per year (from 1961 until 1990) / *Catalogue Raisonné* [22]: left – ordered by year; right – by descending order

Year	**Nº**	**~ %**
1961	**15**	*9*
1962	**3**	*2*
1963	**6**	*3*
1964	**7**	*4*
1965	**1**	*1*
1966	**-**	-
1967	**-**	-
1968	**2**	*1*
1969	**10**	*6*
1970	**10**	*6*
1971	**11**	*6*
1972	**-**	-
1973	**14**	*8*
1974	**5**	*3*
1975	**9**	*5*
1976	**3**	*2*
1977	**-**	-
1978	**-**	-
1979	**-**	-
1980	**24**	*14*
1981	**6**	*3*
1982	**11**	*6*
1983	**3**	*2*
1984	**2**	*1*
1985	**6**	*3*
1986	**5**	*3*
1987	**9**	*5*
1988	**6**	*3*
1989	**4**	*2*
1990	**2**	*1*
Sum	**174**	

Year	**Nº**	**~ %**
1980	**24**	*14*
1961	**15**	*9*
1973	**14**	*8*
1971	**11**	*6*
1982	**11**	*6*
1969	**10**	*6*
1970	**10**	*6*
1975	**9**	*5*
1987	**9**	*5*
1964	**7**	*4*
1963	**6**	*3*
1981	**6**	*3*
1985	**6**	*3*
1988	**6**	*3*
1974	**5**	*3*
1986	**5**	*3*
1989	**4**	*2*
1962	**3**	*2*
1976	**3**	*2*
1983	**3**	*2*
1968	**2**	*1*
1984	**2**	*1*
1990	**2**	*1*
1965	**1**	*1*
1966	**-**	-
1967	**-**	-
1972	**-**	-
1977	**-**	-
1978	**-**	-
1979	**-**	-
Sum	**174**	

Table V.3. Number of paintings by Joaquim Rodrigo catalogued as *vinyl*, *tempera* and *oil* (from 1961 until 1990) / *Catalogue Raisonné* [22]

Binder	**Year**	**Nº**	**~ %**
Vinyl	1961-/1964-90 [a]	**154** [a]	*89*
Tempera	1961-63 [a]	**12** [a]	*7*
Oil	1961/63/64	**8**	*5*
Sum		**174**	*100*

[a] The paintings *S.M.* (1961), *Kultur* (1962), *Mondo Cane I* (1963) and *Liberté* (1963), catalogued as *tempera,* were identified as poly(vinyl acetate) in the framework of the present thesis.

Table V.4. Number of paintings by Joaquim Rodrigo per support type (from 1961 until 1990) / *Catalogue Raisonné* [22]

Support	**Year**	**Nº**	**~ %**
Hardboard	196-64/1966-90	**156**	*90*
Canvas	1961-64/70/73/82	**12**	*7*
Wood	1970-71	**3**	*2*
Chipboard	1961	**1**	*1*
Canvas on hardboard	1963	**1**	*1*
Cardboard	1965	**1**	*1*
Sum		**174**	

Table V.5. Number of paintings by Joaquim Rodrigo catalogued as *vinyl*, *tempera* and *oil* per support type (from 1961 until 1990) / *Catalogue Raisonné* [22]

Binder	**Support**	**Year**	**Nº**	**~ %**
Vinyl	Hardboard	1961/64/1966-90	**144**	*83*
	Canvas	1964/70/73/82	**5**	*3*
	Wood	1970-71	**3**	*2*
	Chipboard	1961	**1**	*1*
	Cardboard	1965	**1**	*1*
Tempera	Hardboard	1961-63	**9**	*5*
	Canvas	1962	**2**	*1*
	Canvas on hardboard	1963	**1**	*1*
Oil	Canvas	1961/63-64	**5**	*3*
	Hardboard	1961	**3**	*2*
Sum			**174**	

Table V.6. Number of paintings by Joaquim Rodrigo per support type (from 1961 until 1990) catalogued as *vinyl*, *tempera* and *oil* / *Catalogue Raisonné* [22]

Support	**Binder**	**Year**	**Nº**	**~ %**
Hardboard	Vinyl	except 62/63/65	**144**	*83*
	Tempera	1961-63	**9**	*5*
	Oil	1961	**3**	*2*
Canvas	Oil	1961/63-64	**5**	*3*
	Vinyl	1964/70/73/82	**5**	*3*
	Tempera	1962	**2**	*1*
Wood	Vinyl	1970-71	**3**	*2*
Chipboard	Vinyl	1961	**1**	*1*
Canvas on hardboard	Tempera	1963	**1**	*1*
Cardboard	Vinyl	1965	**1**	*1*
		Sum	**174**	*100*

Table V.7. Number of paintings by Joaquim Rodrigo per support dimensions (from 1961 until 1990) / *Catalogue Raisonné* [22] – smaller to larger formats

~Dim. (cm)	**Support**	**Binder**	**Year**	**Nº**	***~ %***
50 x 50	hardboard	oil	1961	**1**	*1*
65 x 100	canvas	oil	1961	**1**	*1*
66 x 93	canvas	vinyl	1970	**1**	*1*
70 x 100	cardboard	vinyl	1965	**1**	*1*
73 x 92	hardboard / canvas (3)	vinyl / tempera (2) / oil (1)	1962-64/73-75	**14**	*8*
73 x 100	hardboard / chipboard (1)	vinyl	1961/85	**3**	*2*
81 x 116	hardboard / canvas (2) / canvas on hardb. (1)	vinyl / oil (2) / tempera (1)	1961/63/73/76/80	**14**	*8*
89 x 130	hardboard	vinyl / oil (2) / tempera (1)	1961/63/76/80/83-90	**39**	*22*
90 x 90 x 90	canvas	oil	1964	**1**	*1*
90 x 136	canvas	oil	1961	**1**	*1*
91 x 122	hardboard	vinyl	1964	**4**	*2*
95 x 120	hardboard / canvas	vinyl	1974/82	**2**	*1*
97 x 146	hardboard / wood (3)	vinyl / tempera (2)	1961-62/68-71/73/75-76/80-82/84/87	**54**	*31*
97 x 163	hardboard	tempera	1961	**1**	*1*
100 x 150	hardboard	vinyl	1980/85/86	**10**	*6*
105 x 120	hardboard	vinyl	1974/80/83	**3**	*2*
114 x 162	hardboard	vinyl	1969/74/80	**6**	*3*
115 x 120	hardboard	vinyl	1983	**1**	*1*
123 x 185	hardboard	tempera	1962/63	**3**	*2*
128 x 180	hardboard	vinyl	1971	**6**	*3*
123 x 221	hardboard	vinyl / tempera	1961/63	**2**	*1*
125 x 223	hardboard	tempera	1961	**1**	*1*
130 x 190	hardboard	vinyl	1970/73	**3**	*2*
150 x 200	hardboard	vinyl	1969	**2**	*1*
			Sum	**174**	*100*

Table V.8. Number of paintings by Joaquim Rodrigo per support dimensions (from 1961 until 1990) / *Catalogue Raisonné* [22] – most to least used formats

~ Dim. (cm)	**Support**	**Binder**	**Year**	**Nº**	***~ %***
97 x 146	hardboard / wood (3)	vinyl / tempera (2)	1961-62/68-71/73/75-76/80-82/84/87	**54**	*31*
89 x 130	hardboard	vinyl / oil (2) / tempera (1)	1961/63/76/80/83-90	**39**	*22*
73 x 92	hardboard / canvas (3)	vinyl / tempera (2) / oil (1)	1962-64/73-75	**14**	*8*
81 x 116	hardboard / canvas (2) / canvas on hardb. (1)	vinyl / oil (2) / tempera (1)	1961/63/73/76/80	**14**	*8*
100 x 150	hardboard	vinyl	1980/85/86	**10**	*6*
114 x 162	hardboard	vinyl	1969/74/80	**6**	*3*
128 x 180	hardboard	vinyl	1971	**6**	*3*
91 x 122	hardboard	vinyl	1964	**4**	*2*
105 x 120	hardboard	vinyl	1974/80/83	**3**	*2*
130 x 190	hardboard	vinyl	1970/73	**3**	*2*
123 x 185	hardboard	tempera	1962/63	**3**	*2*
73 x 100	hardboard / chipboard (1)	vinyl	1961/85	**3**	*2*
150 x 200	hardboard	vinyl	1969	**2**	*1*
123 x 221	hardboard	vinyl / tempera	1961/63	**2**	*1*
95 x 120	hardboard / canvas	vinyl	1974/82	**2**	*1*
115 x 120	hardboard	vinyl	1983	**1**	*1*
125 x 223	hardboard	tempera	1961	**1**	*1*
97 x 163	hardboard	tempera	1961	**1**	*1*
50 x 50	hardboard	oil	1961	**1**	*1*
65 x 100	canvas	oil	1961	**1**	*1*
90 x 136	canvas	oil	1961	**1**	*1*
90 x 90 x 90	canvas	oil	1964	**1**	*1*
66 x 93	canvas	vinyl	1970	**1**	*1*
70 x 100	cardboard	vinyl	1965	**1**	*1*
			Sum	**174**	*100*

V.2 Pigment palette - spectra

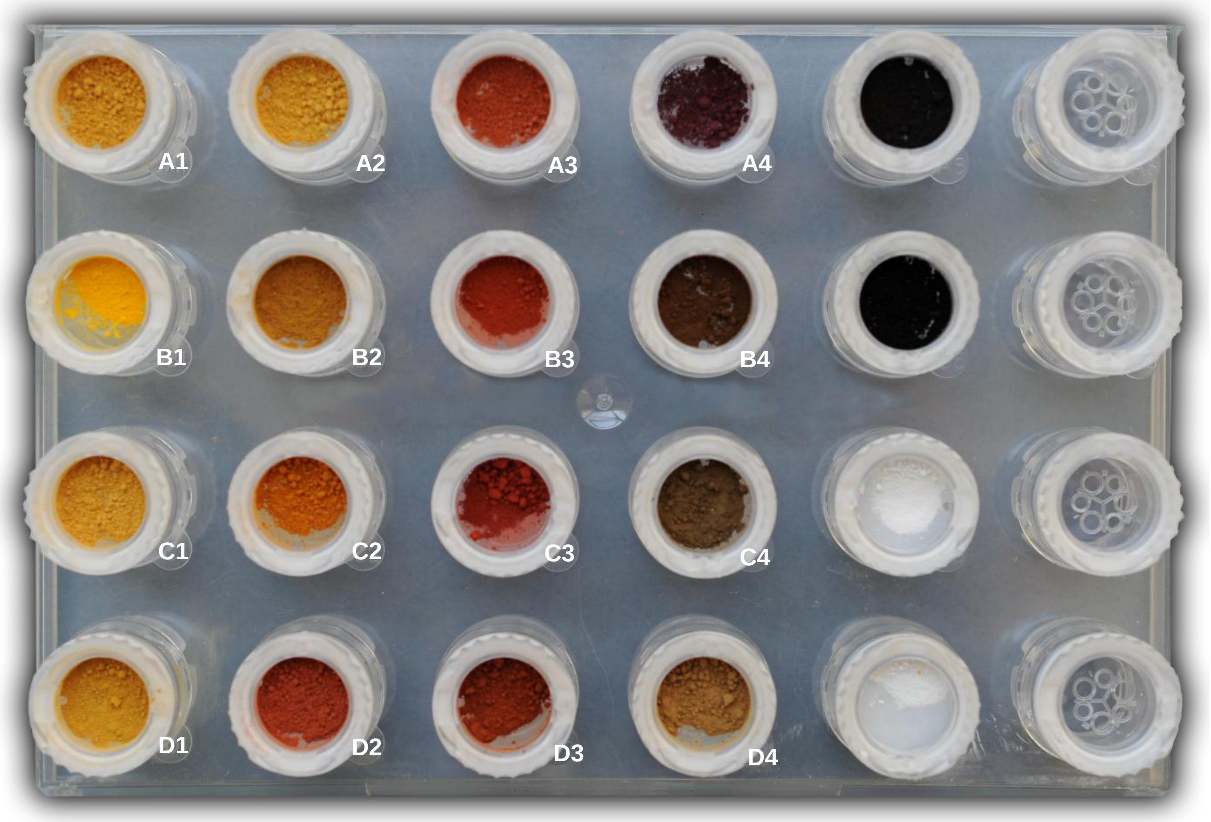
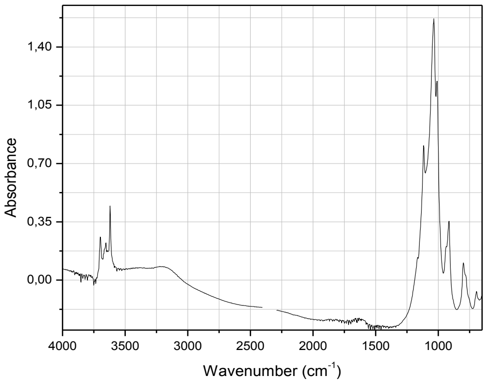
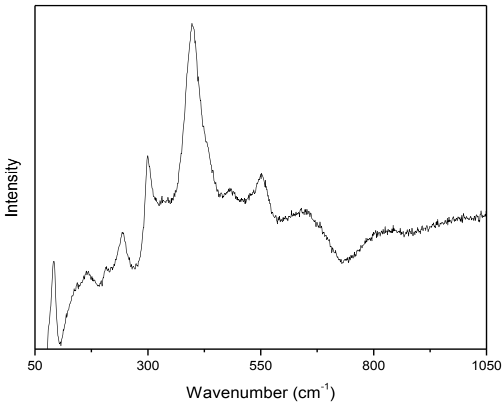
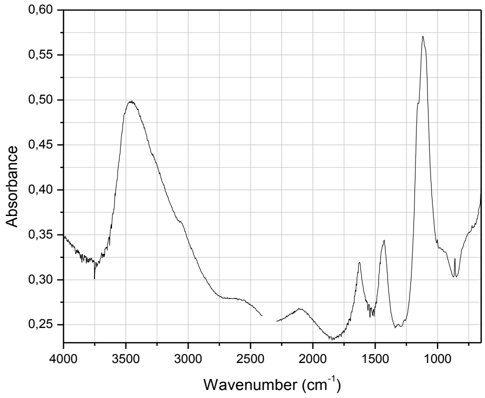
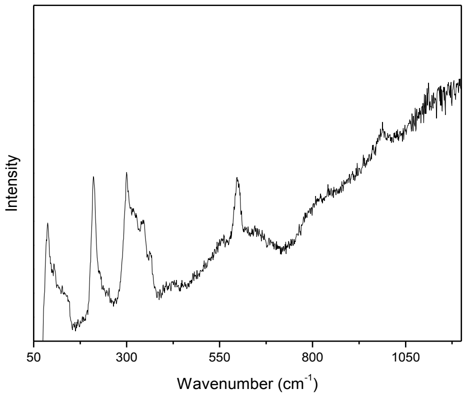
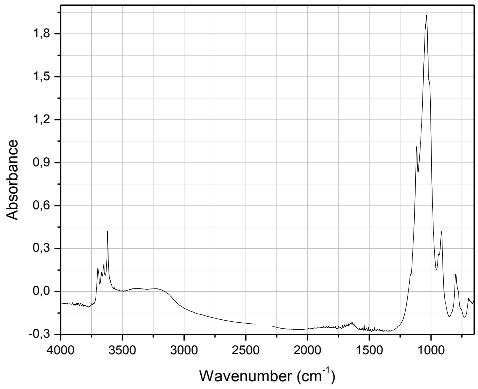
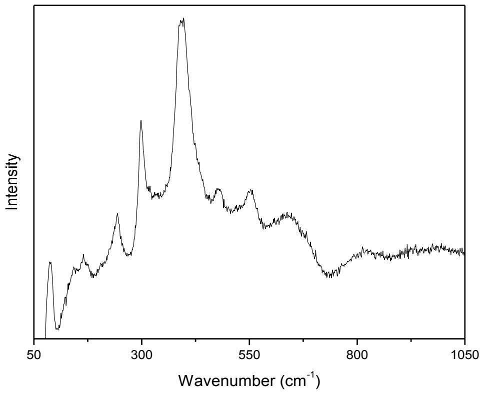
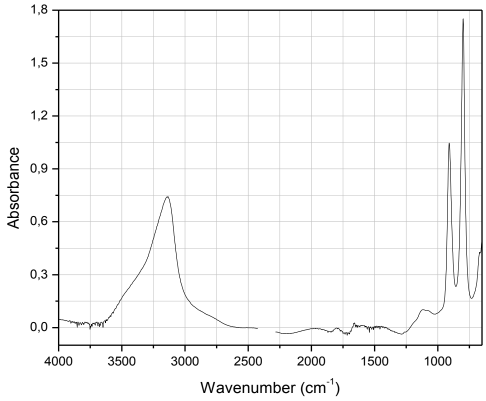
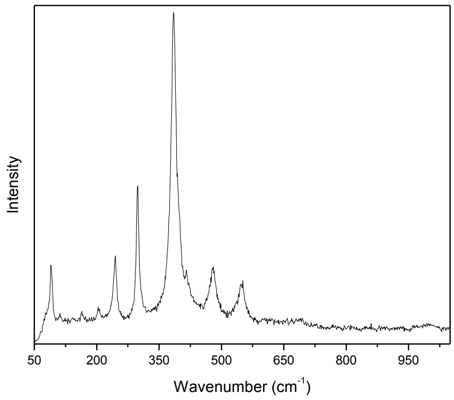
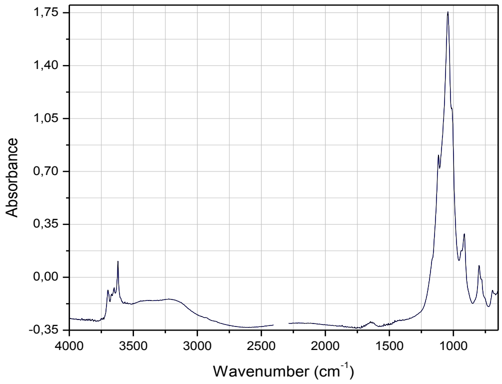
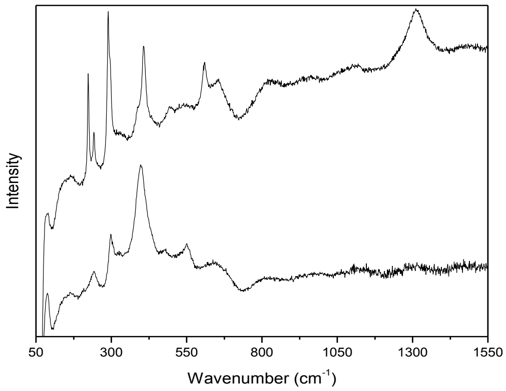
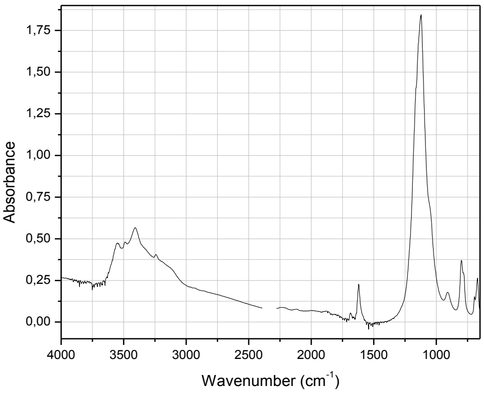
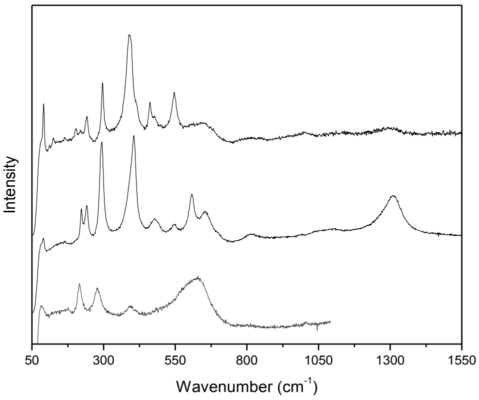
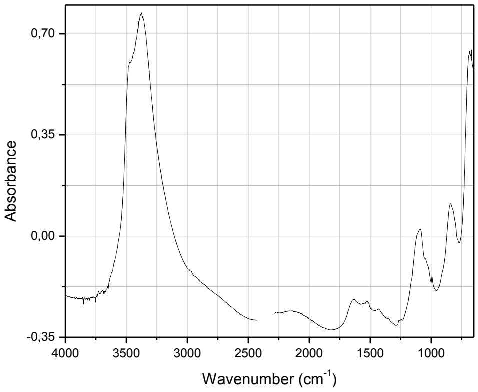
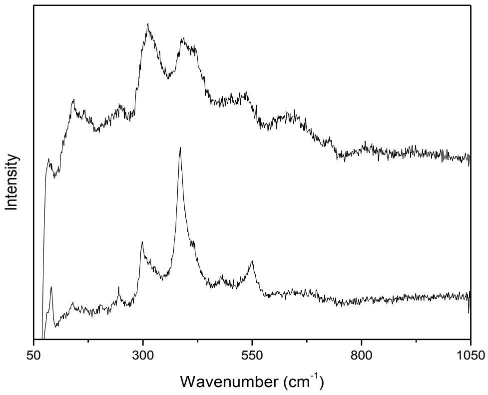
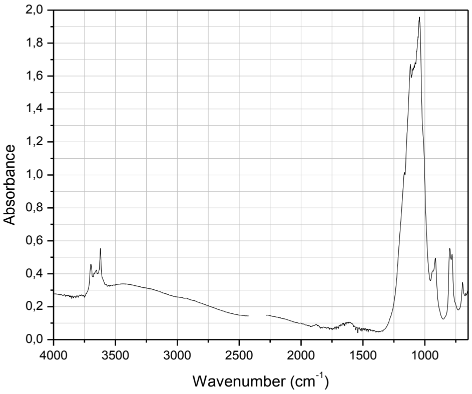
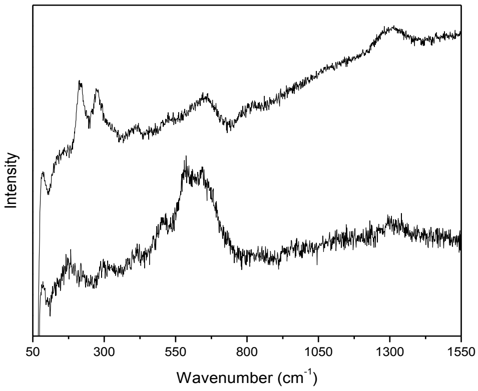
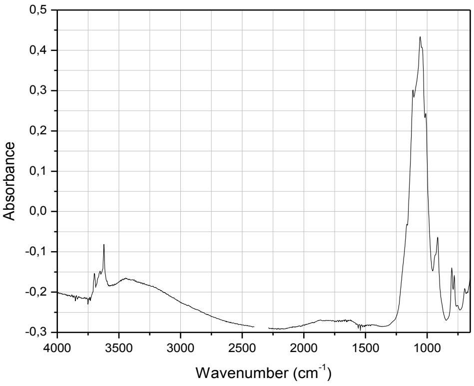


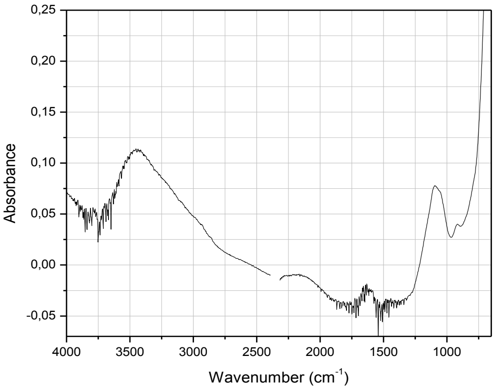
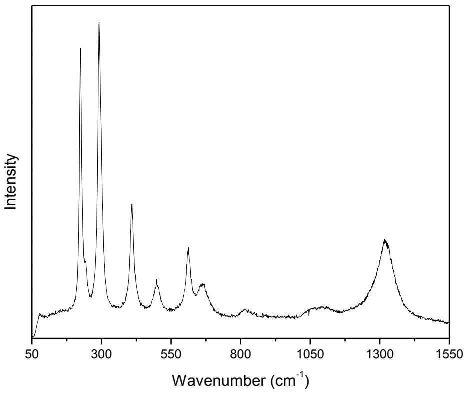
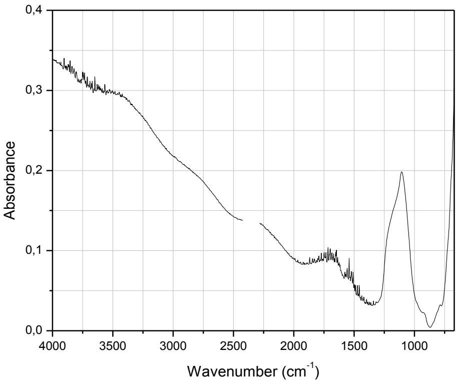
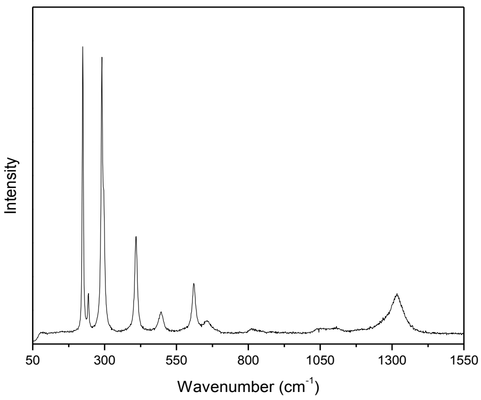
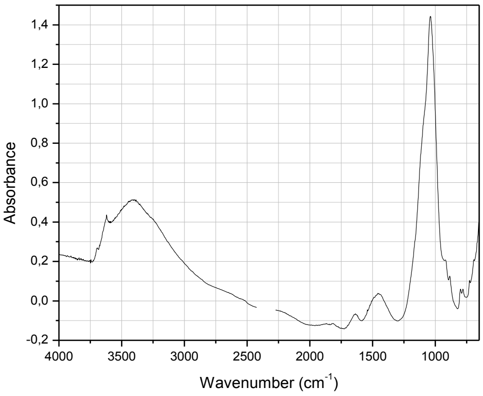
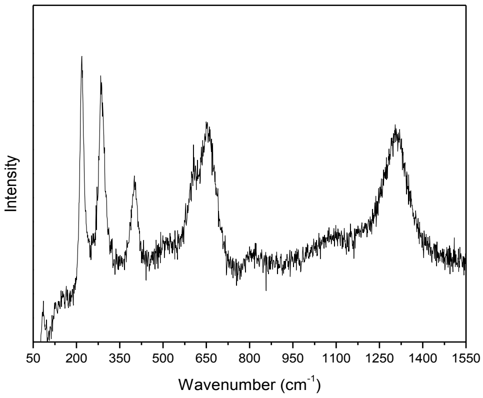
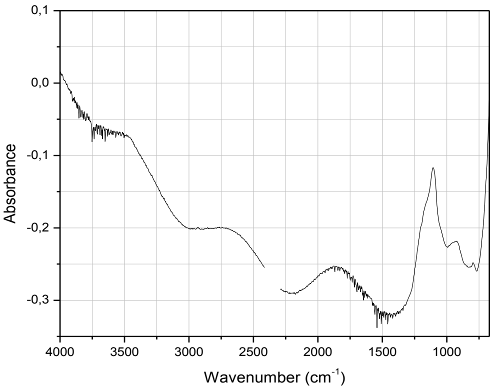
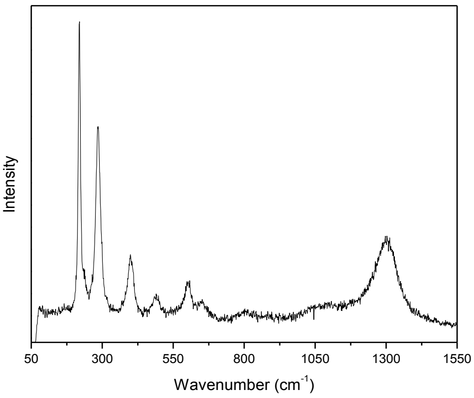
Figure V.1. Identification of the analyzed iron oxide pigments from the colour palette used by Joaquim Rodrigo.

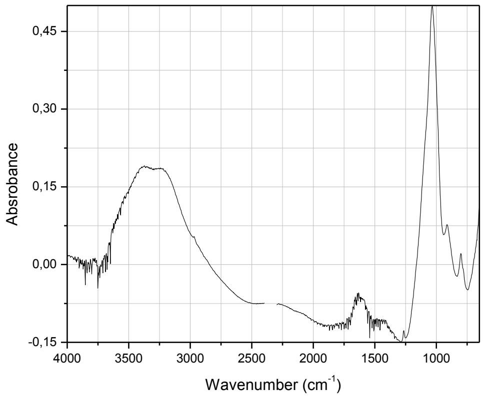
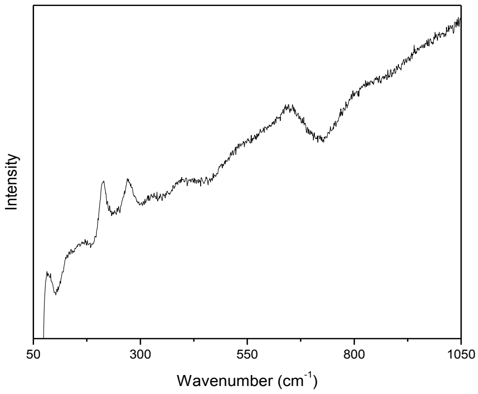
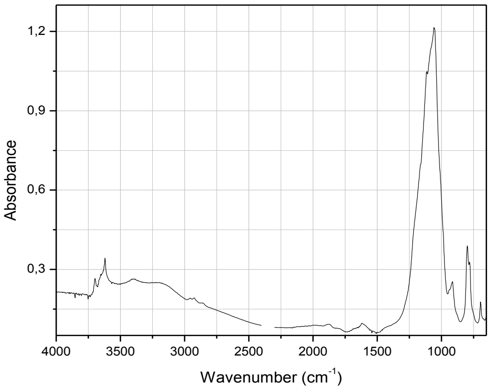
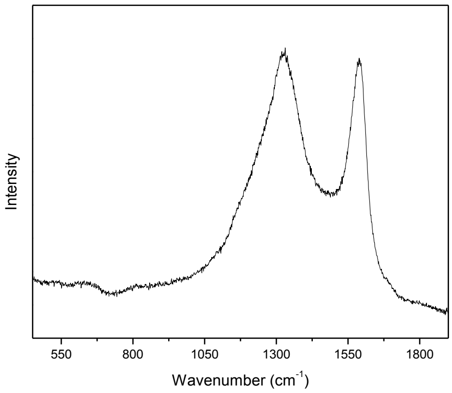
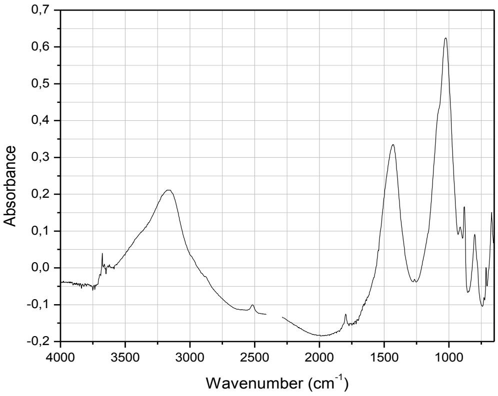
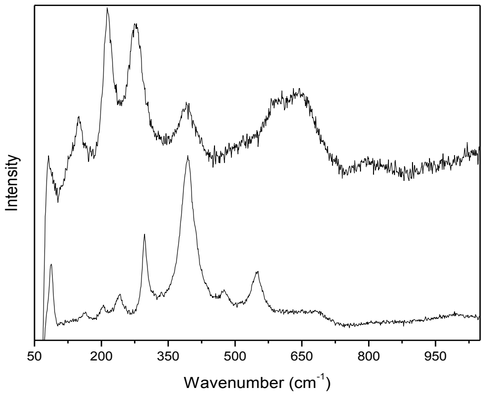
Table V.9. Infrared and Raman spectra of the iron oxide pigments from Joaquim Rodrigo's pigment palette [a]

Sample	Infrared	Raman
A1 Amarelo ocre claro ● *L&B* (?)		

Sample	**Infrared**	**Raman**
B1 Óxido de ferro ● (?)		
C1 Óxido de ferro amarelo ● Drogaria (Alto de Santo Amaro)		
D1 Ocre ouro ● *Casa Varela* (?)		
A2 C-25 ● (?)		

Sample	Infrared	Raman
B2 Ocre (fresco) ● *L&B*		
C2 (fresco) ● *L&B*		
D2 Ocre rouge (PC8) ● *L&B*		
A3 Ocre rouge (2202) ● *L&B*		No detectable Raman signal

Sample	**Infrared**	**Raman**
B3 Terre de Sienna brulee (PC21) ● *L&B*		
C3 Brun rouge (PC10) ● *L&B*		
D3 Rouge de pouzzoles (PC13) ● *L&B*		
A4 Rouge Indien (PC11) ● *L&B*		

Sample	**Infrared**	**Raman**
B4 Terre ombre naturelle (PC18) ● *L&B*		
C4 Terra Colónia ● (?)		
D4 ● (?)		

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[a] Spectra collected by Joana Pedroso in the framework of the her master's thesis (DCR - FCT/UNL, 2009) [169].

Table V.10. Compounds identified by infrared and Raman spectroscopies in iron oxide pigments from Joaquim Rodrigo's pigment palette [a]

Sample identification		**Infrared**	**Raman**
A1 - Amarelo ocre claro; *L&B* (?)	●	Kaolinite, quartz	Gohetite
B1 - Óxido de ferro; (?)	●	Calcium carbonate	[b]
C1 - Óxido de ferro amarelo; Drugstore (Alto de Santo Amaro)	●	Kaolinite, quartz	Goethite
D1 - Ocre ouro; *Casa Varela* (?)	●	Goethite, calcium carbonate	Goethite
A2 - C-25; (?)	●	Kaolinite, quartz	Goethite, hematite, magnetite
B2 - Ocre (*fresco*); *L&B*	●	Goethite, gypsum, quartz	Goethite, hematite, magnetite
C2 - (*fresco*); *L&B*	●	[b]	Goethite
D2 - Ocre rouge (PC8); *L&B*	●	Kaolinite, quartz	Hematite, magnetite [c]
A3 - Ocre rouge (2202); *L&B*	●	Kaolinite, quartz	[d]
B3 - Terre de Sienna brulee (PC21); *L&B*	●	Iron oxide III	Hematite, magnetite
C3 - Brun rouge (PC10); *L&B*	●	Iron oxide III	Hematite
D3 - Rouge de pouzzoles (PC13); *L&B*	●	Kaolinite, quartz, calcium carbonate	Hematite, magnetite [c]
A4 - Rouge Indien (PC11); *L&B*	●	Iron III oxide	Hematite
B4 - Terre ombre naturelle (PC18); *L&B*	●	Goethite, quartz	[c]
C4 - Terra Colónia; (?)	●	Kaolinite, quartz	Carbon black
D4 - (?)	●	Goethite, talc, calcium carbonate, quartz	Goethite, hematite, magnetite [c]

[a] Analyzed by Joana Pedroso in the framework of her master's thesis (DCR - FCT/UNL, 2009), [169].

[b] Non identified; [c] possibly heated magnetite; [d] no detectable Raman signal.

V.3 Micro Sampling

Figure V.2. *M. L.*, 1961. Vinyl on hardboard; 73 x 100 cm. Private collection, deposited at the National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
μSampling: A – black sample; B – white sample; C – brown sample; D – red/background sample.

Figure V.3. *S. M.*, 1961. Vinyl on hardboard; 97.3 x 146 cm. Ministry of Culture collection, deposited at the National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
μSampling: A - red sample; B - yellow sample.

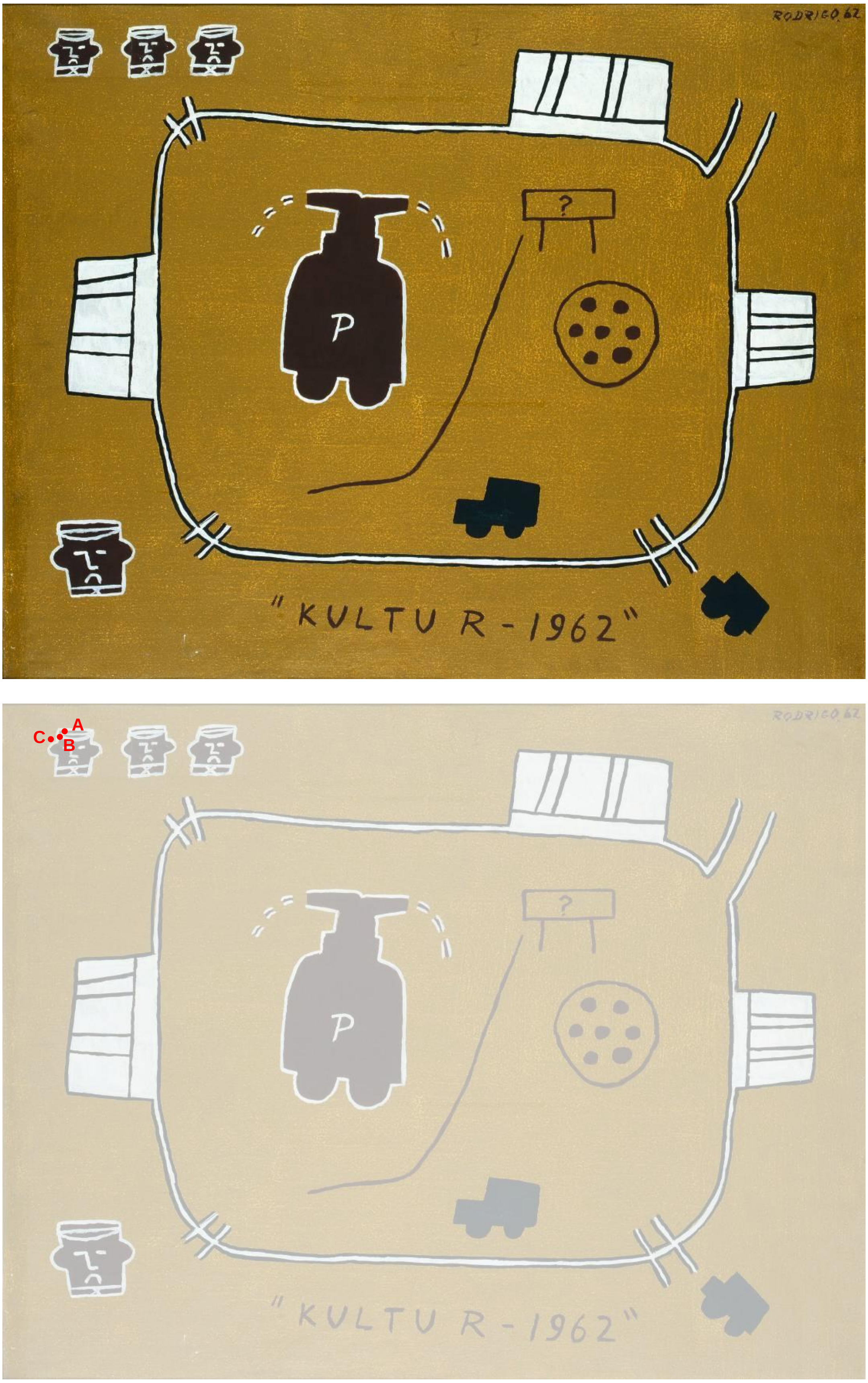


Figure V.4. *Kultur - 1962*, 1962. Vinyl on hardboard; 73 x 92 cm. National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
µSampling: A - dark red sample; B - white sample; C - yellow/background sample.

Figure V.5. *Mondo Cane I*, 1963. Vinyl on canvas glued on to hardboard; 81 x 116 cm. National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
µSampling: A - white sample; B - yellow sample.

Figure V.6. *Liberté*, 1963. Vinyl on hardboard; 123 x 185 cm. National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
µSampling: A - white sample; B - light brown sample.

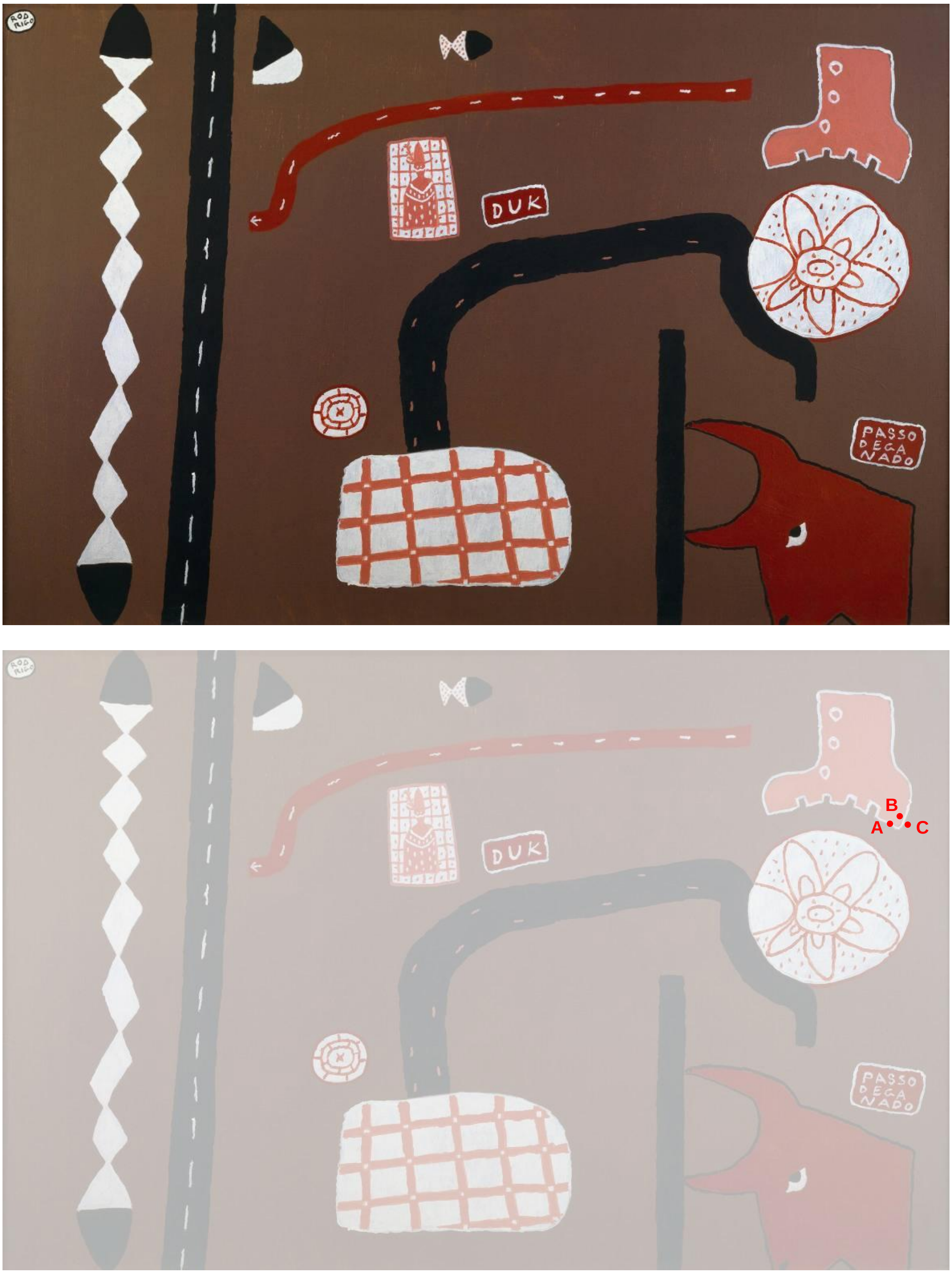


Figure V.7. *Lisboa – Oropeza*, 1969. Vinyl on hardboard; 97 x 146 cm. Private collection, deposited at the National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
µSampling: A - white sample; B - pink sample; C - brown/background sample.

Figure V.8. *Alassio – Nice*, 1971. Vinyl on hardboard; 128 x 180 cm. National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
μSampling: A - white sample; B - red sample; C - black sample.

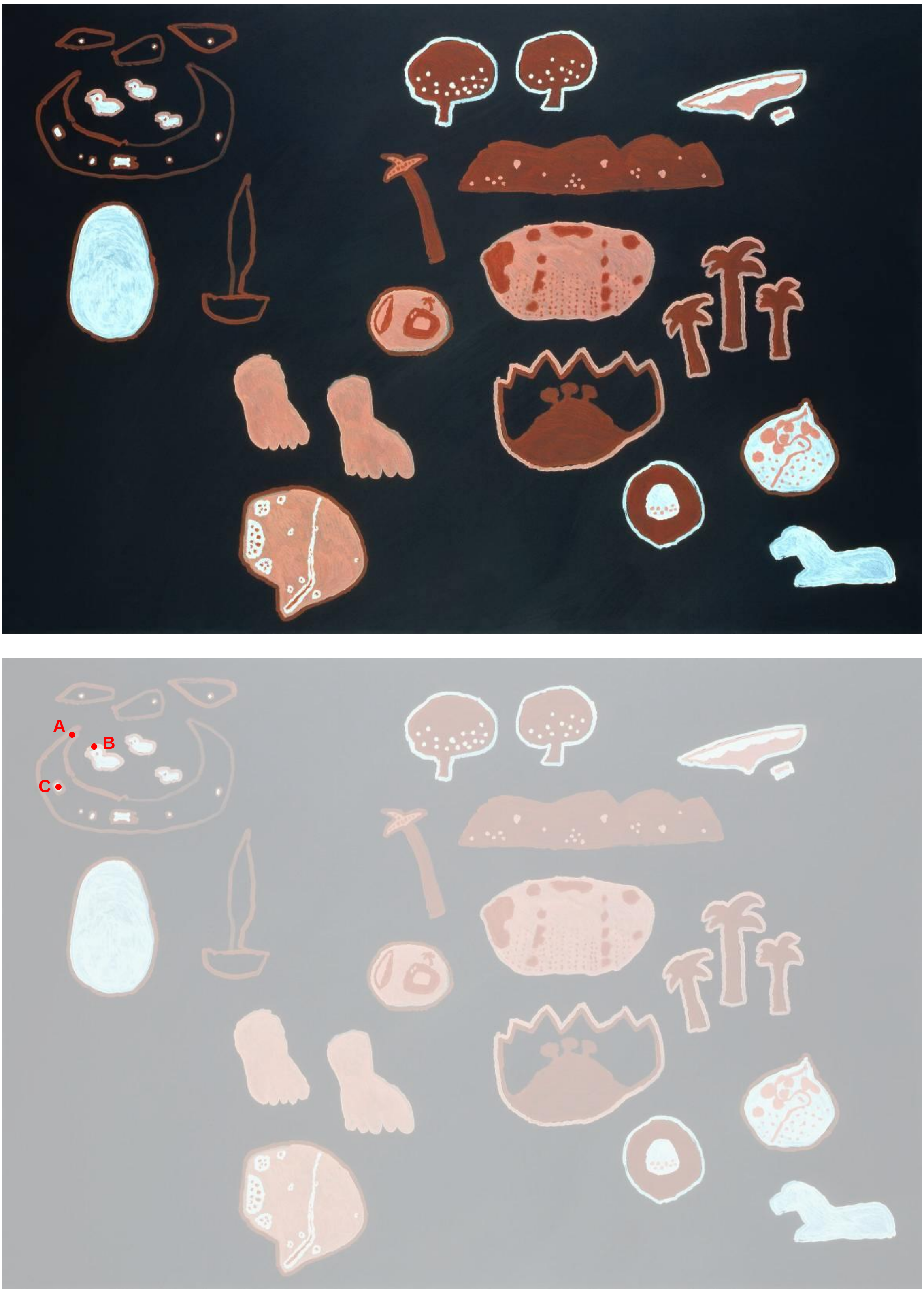


Figure V.9. *Port-Ligat – Granada*, 1980. Vinyl on hardboard; 89 x 130 cm. Private collection, deposited at the National Museum of Contemporary Art (MNAC - *Museu do Chiado*). Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*.
µsampling: A – dark brown/background sample; B – pink sample; C – white sample.

Figure V.10. *Os quintais*, 1989. Vinyl on hardboard; 89 x 130 cm. Private collection. Photo: José Pessoa, *Divisão de Documentação Fotográfica – Instituto Português de Museus*. μsampling: A, B, C – yellow/background samples; D, E, F – black samples; G, H, I – red samples; J, L, M – white samples; N, O, S – grey samples.

V.3 Spectra

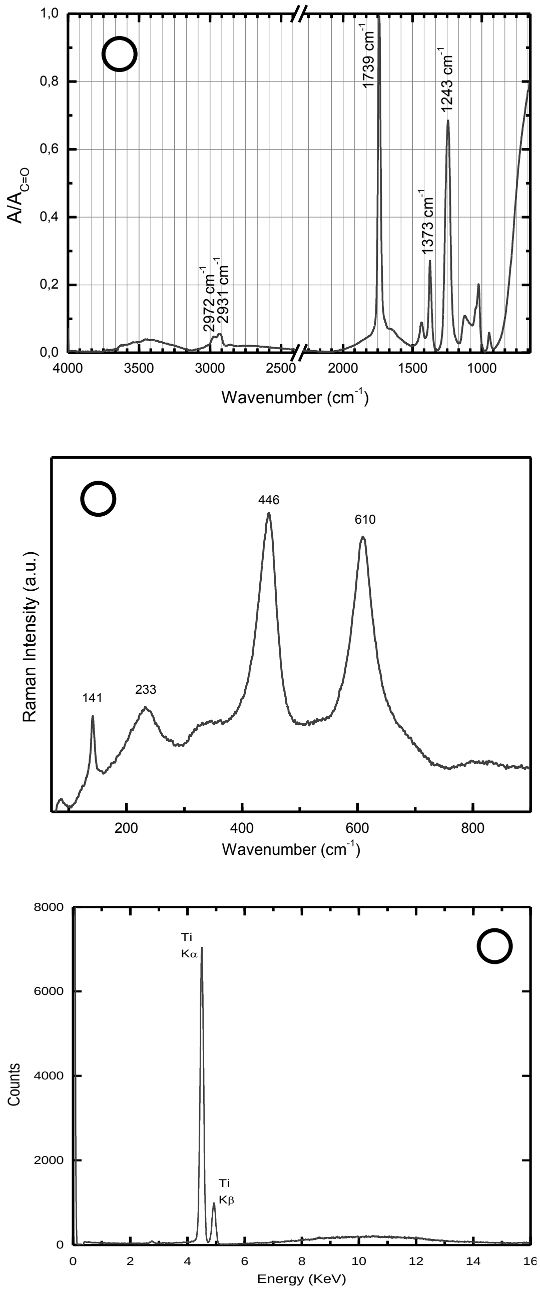


Figure V.11. Spectra of a white sample from *M.L.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

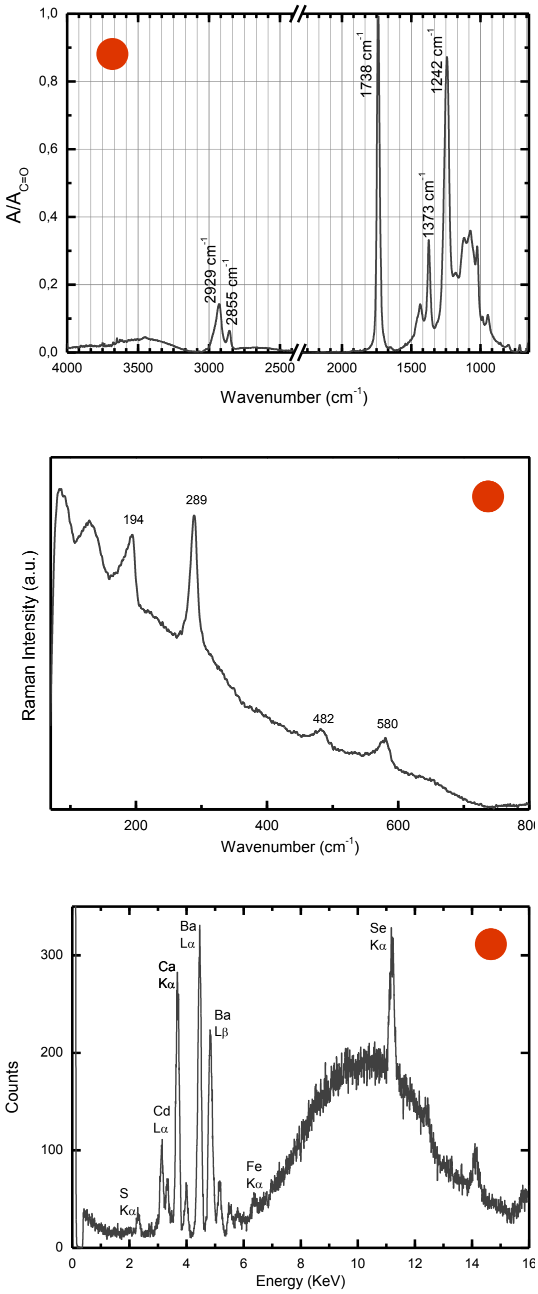


Figure V.12. Spectra of a red sample from *M.L.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

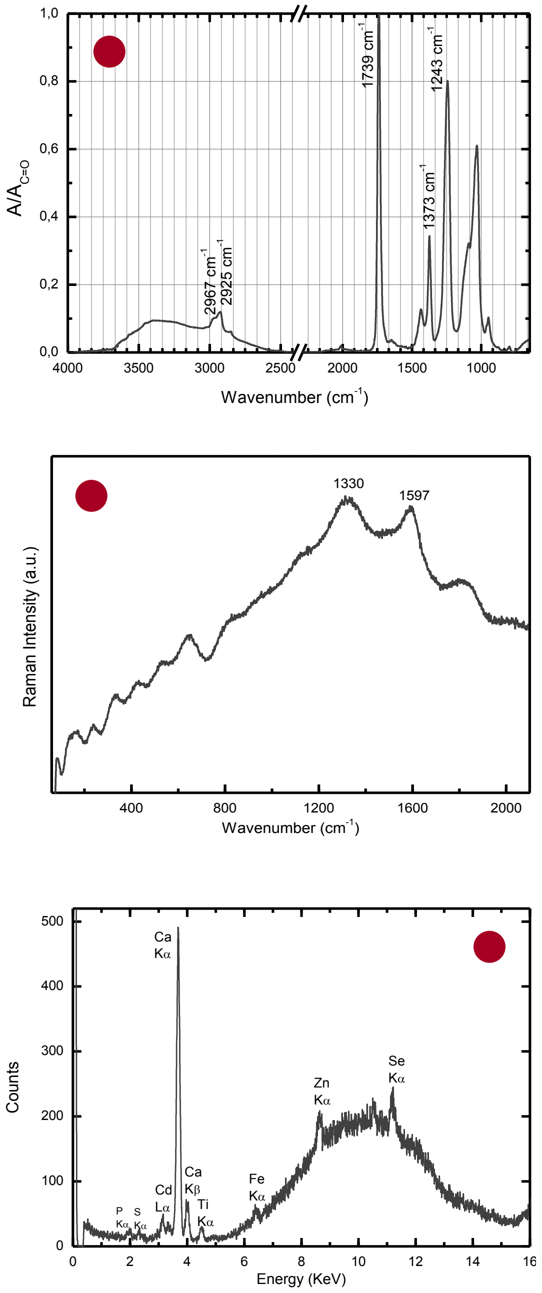


Figure V.13. Spectra of a brown sample from *M.L.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

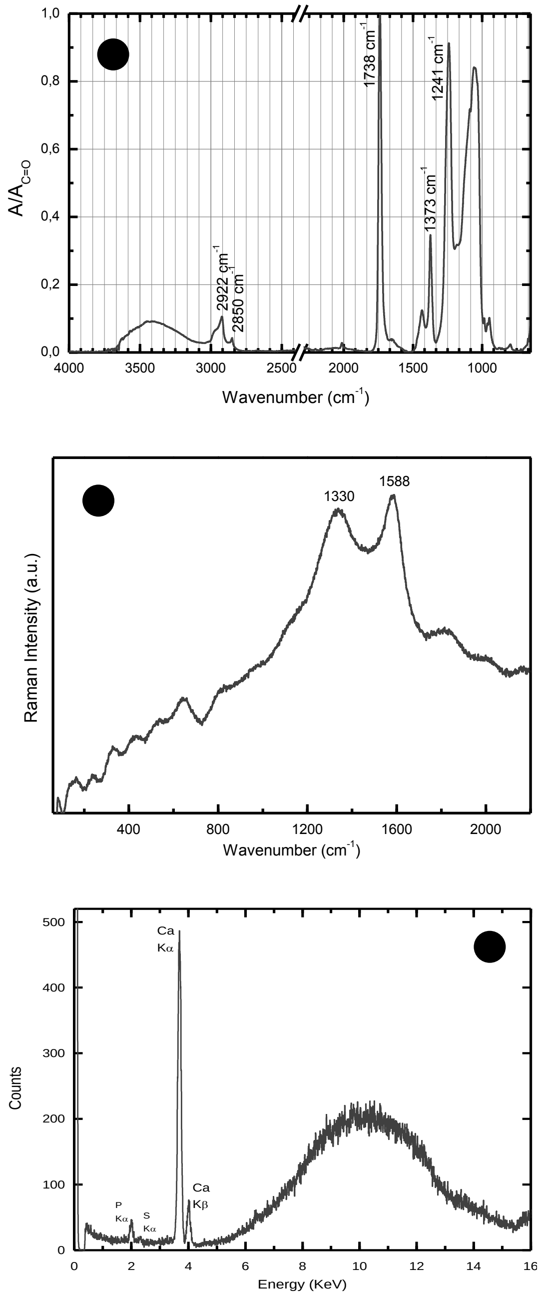


Figure V.14. Spectra of a black sample from *M.L.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

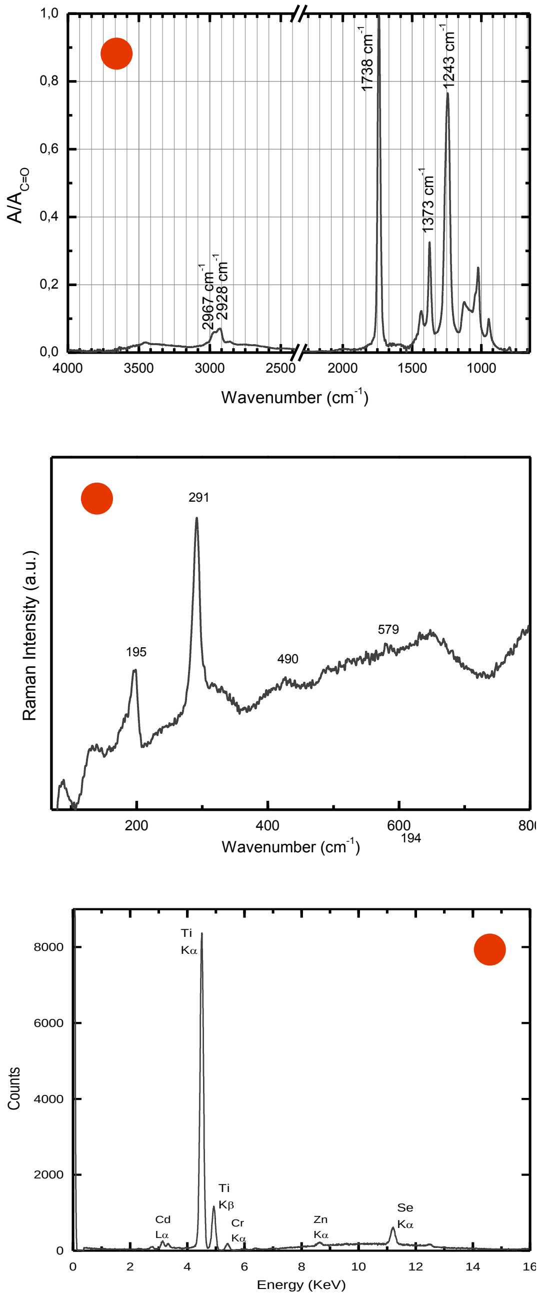


Figure V.15. Spectra of a red sample from *S.M.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

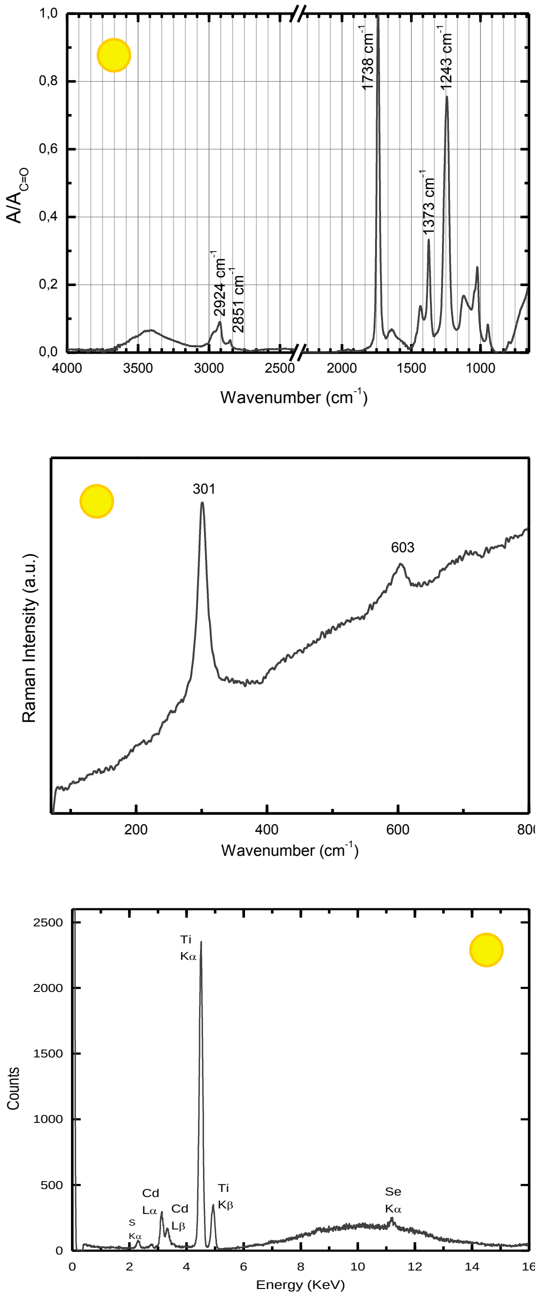


Figure V.16. Spectra of a yellow sample from *S.M.*, 1961: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

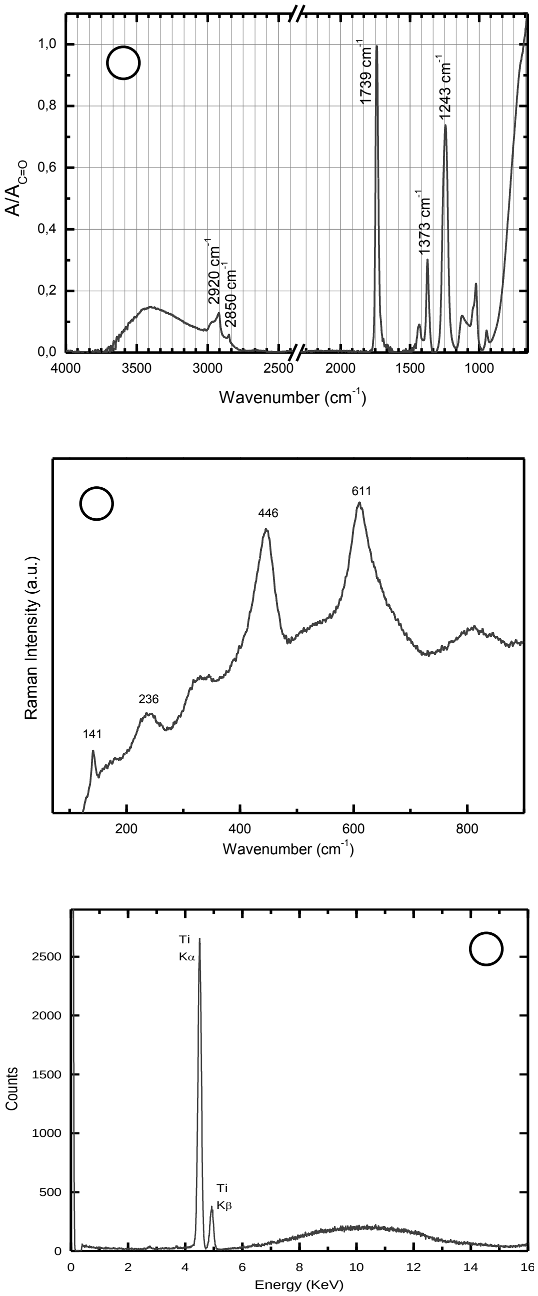


Figure V.17. Spectra of a white sample from *Kultur – 1962*, 1962: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

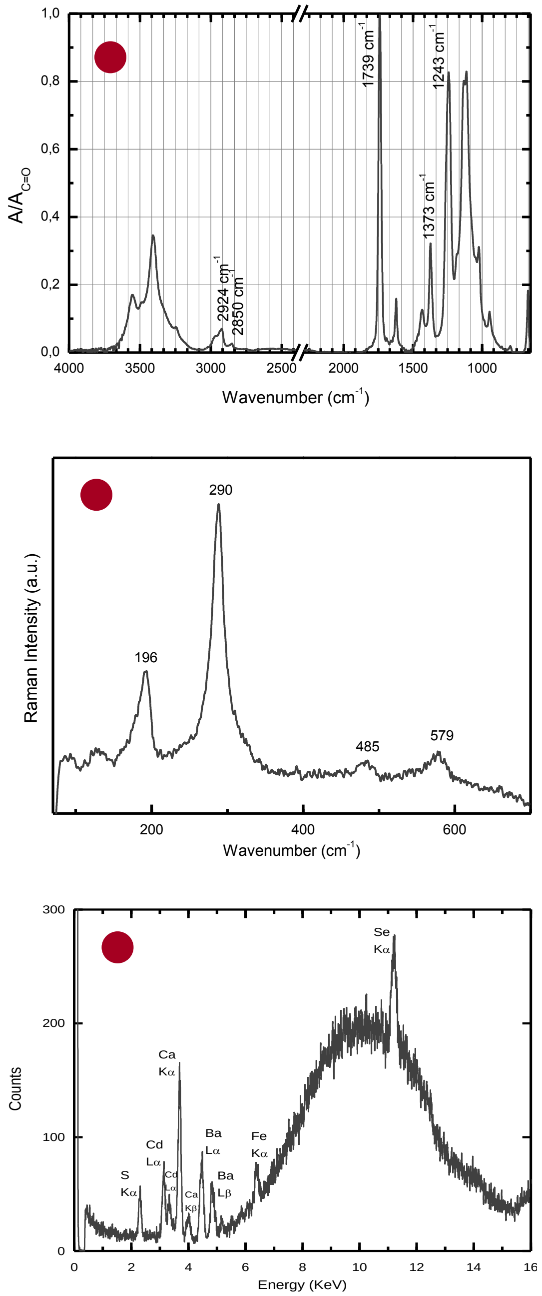


Figure V.18. Spectra of a red sample from *Kultur – 1962*, 1962: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

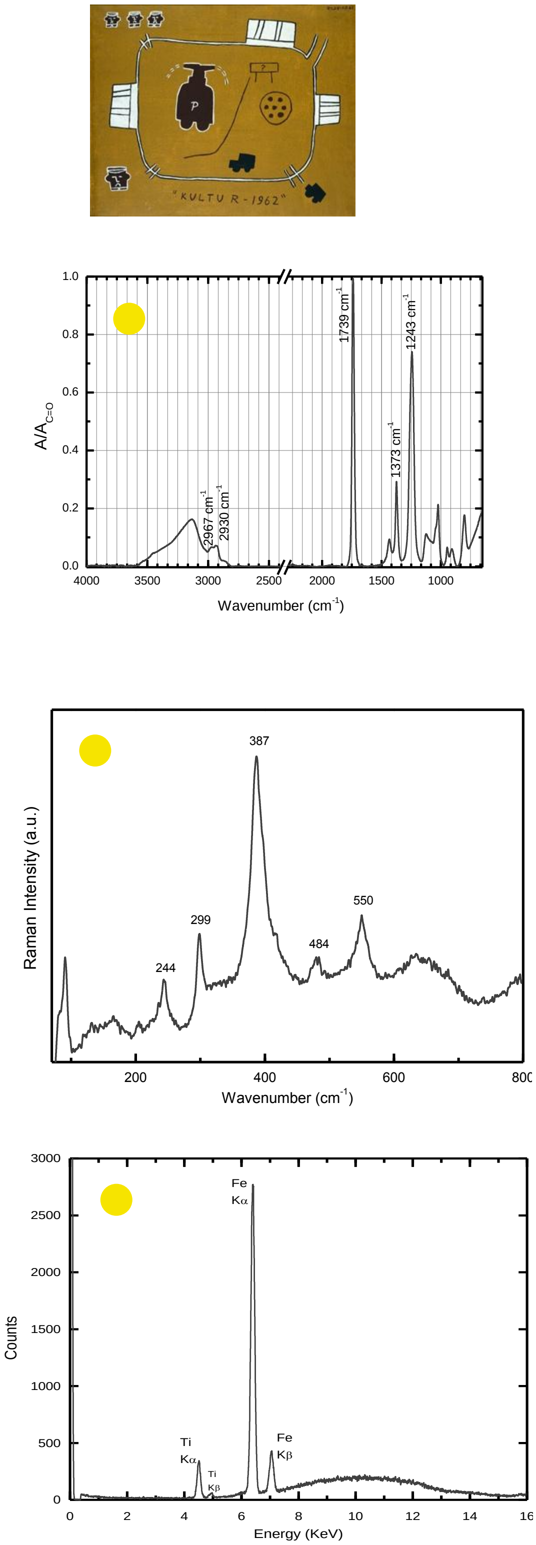


Figure V.19. Spectra of a yellow/background sample from *Kultur – 1962*, 1962: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

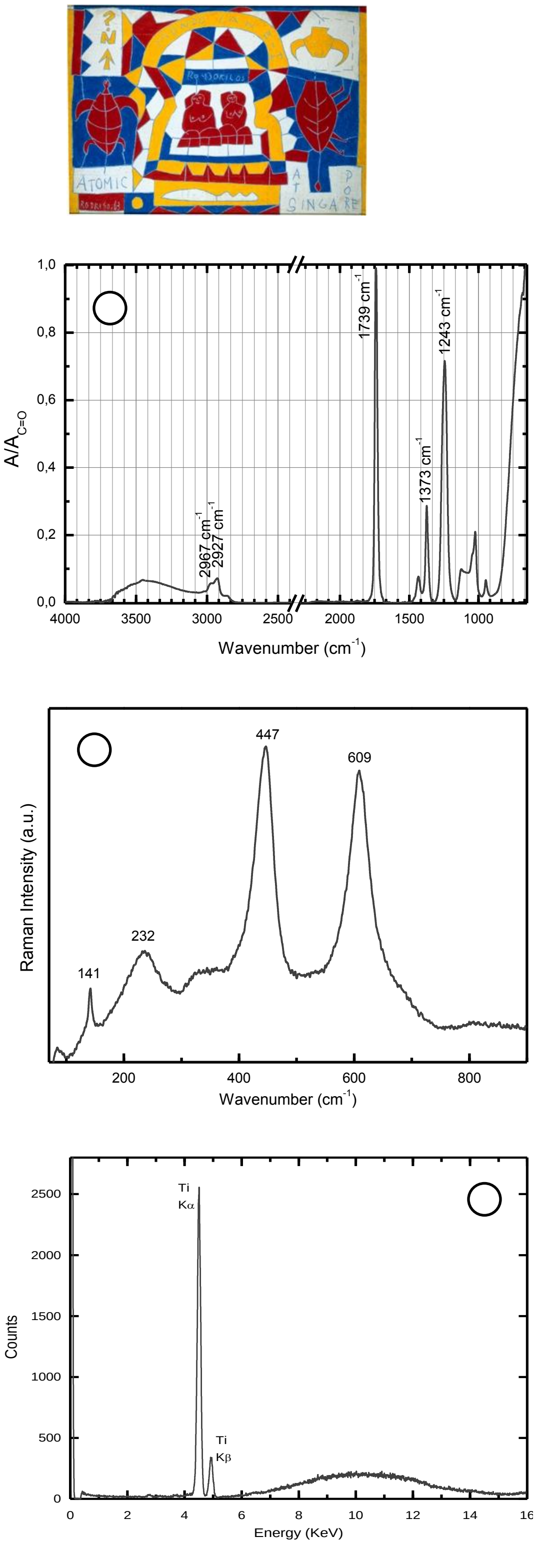


Figure V.20. Spectra of a white sample from *Mondo Cane I*, 1963: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

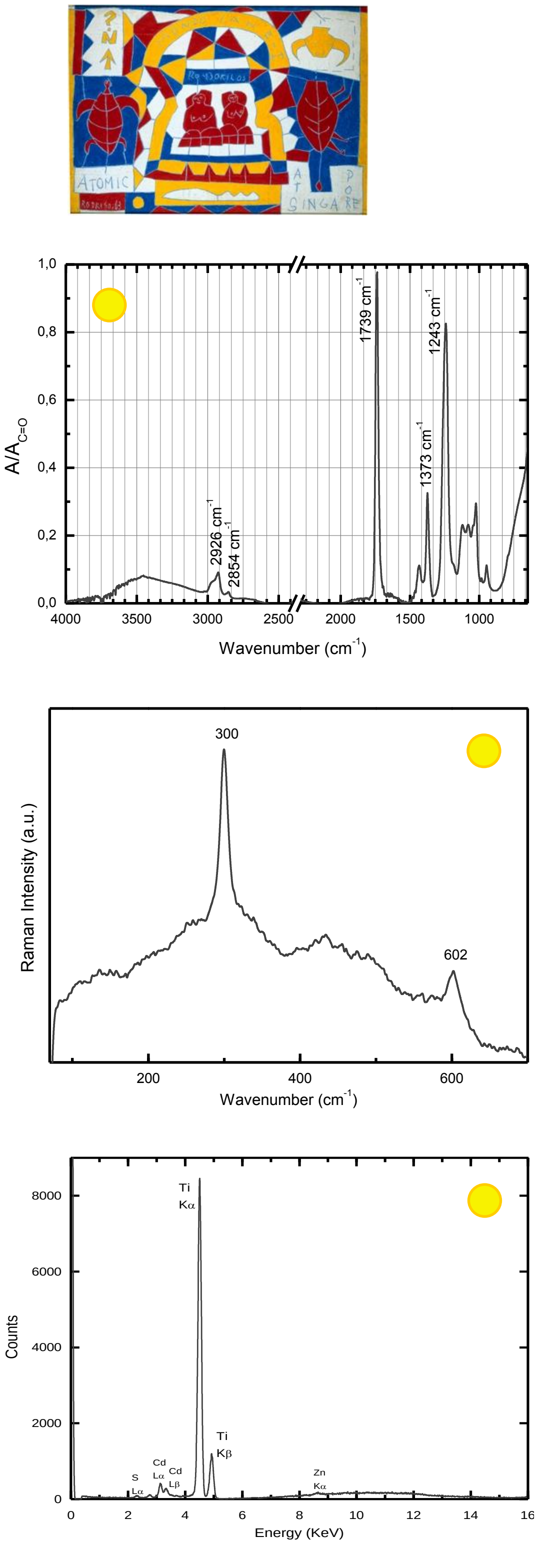


Figure V.21. Spectra of a yellow sample from *Mondo Cane I*, 1963: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

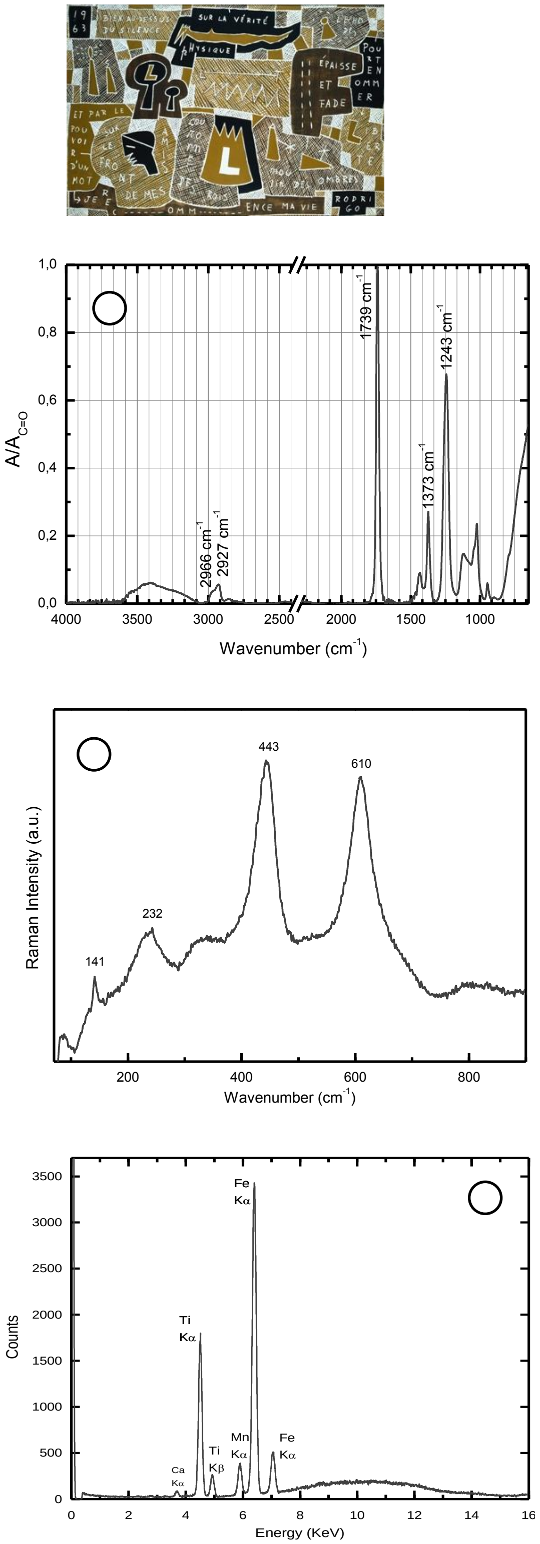


Figure V.22. Spectra of a white sample from *Liberté*, 1963: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

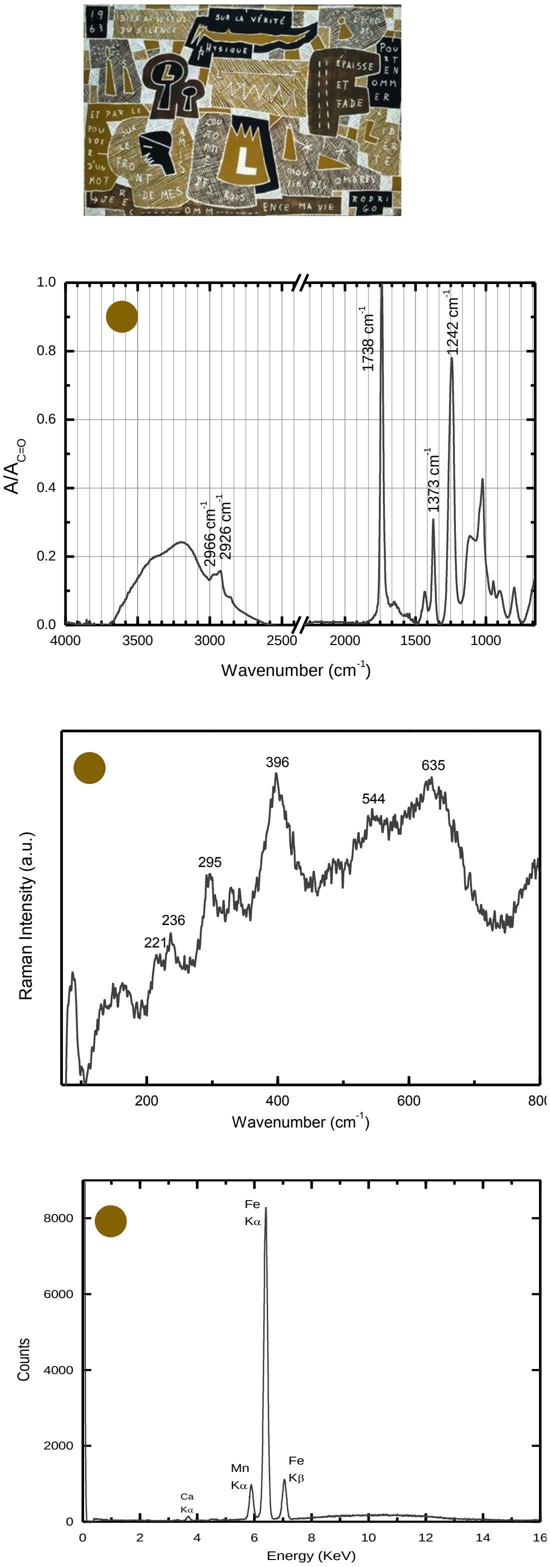


Figure V.23. Spectra of a light brown sample from *Liberté*, 1963: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

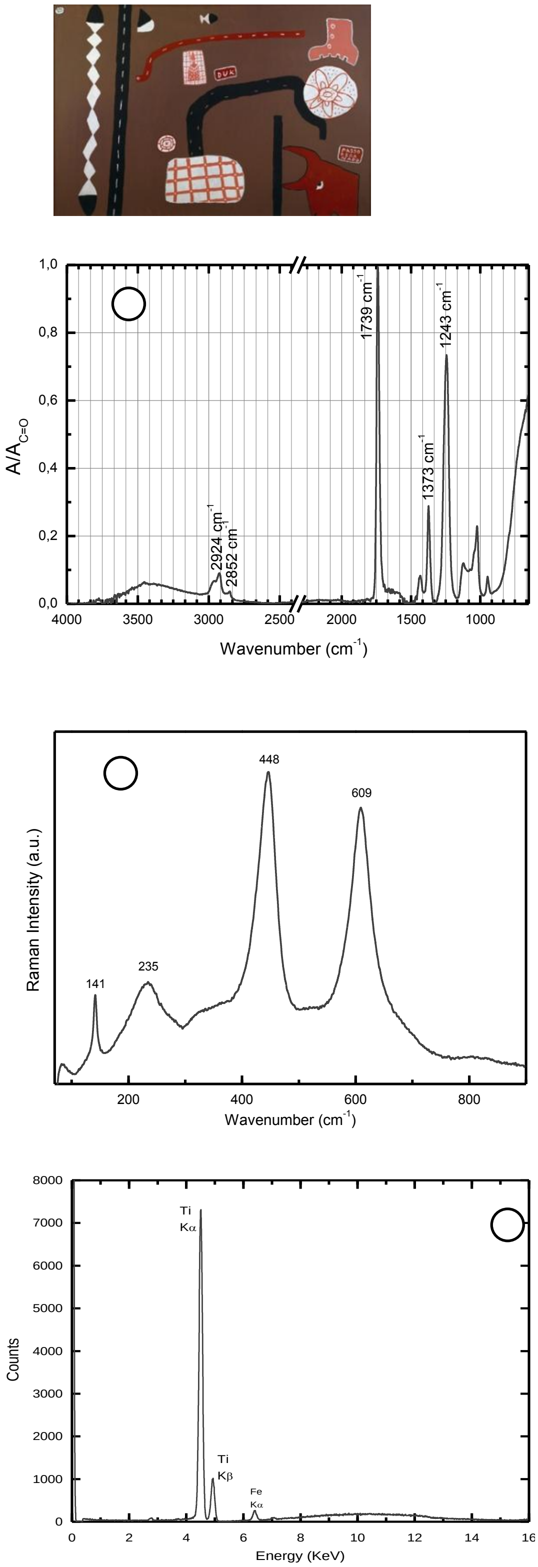


Figure V.24. Spectra of a white sample from *Lisboa - Oropeza*, 1969: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

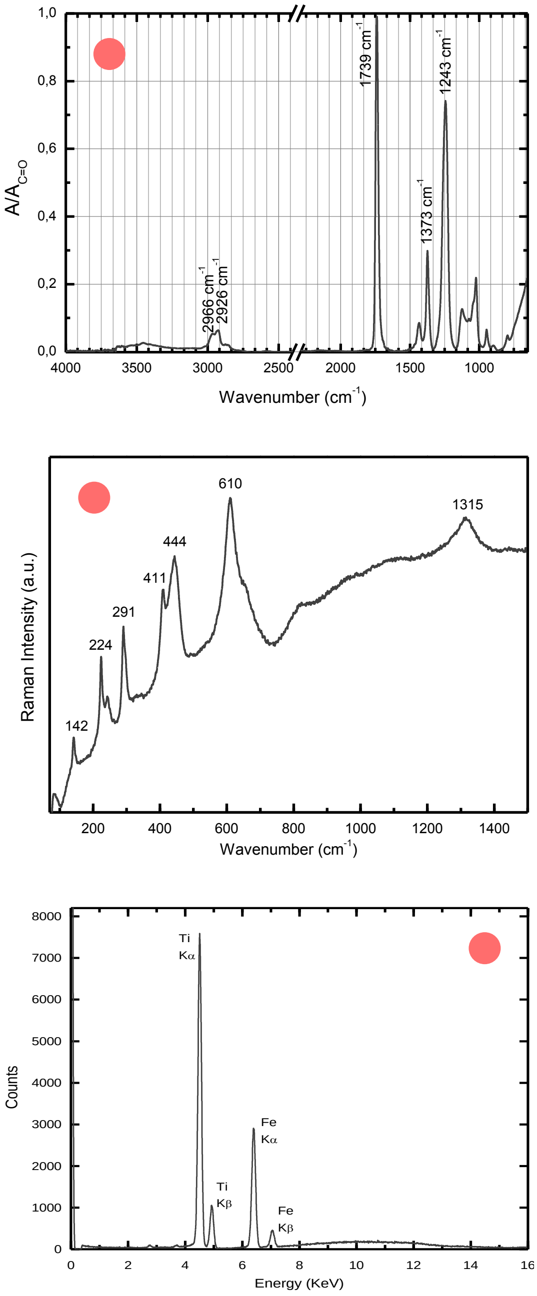


Figure V.25. Spectra of a pink sample from *Lisboa – Oropeza*, 1969: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

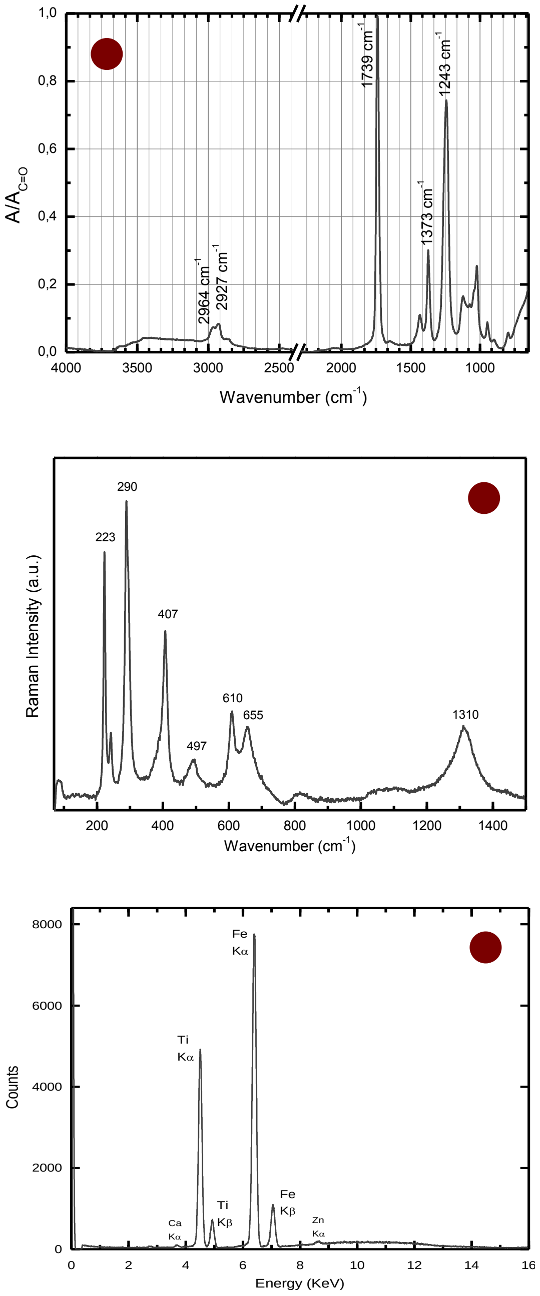


Figure V.26. Spectra of a brown sample from *Lisboa – Oropeza*, 1969: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

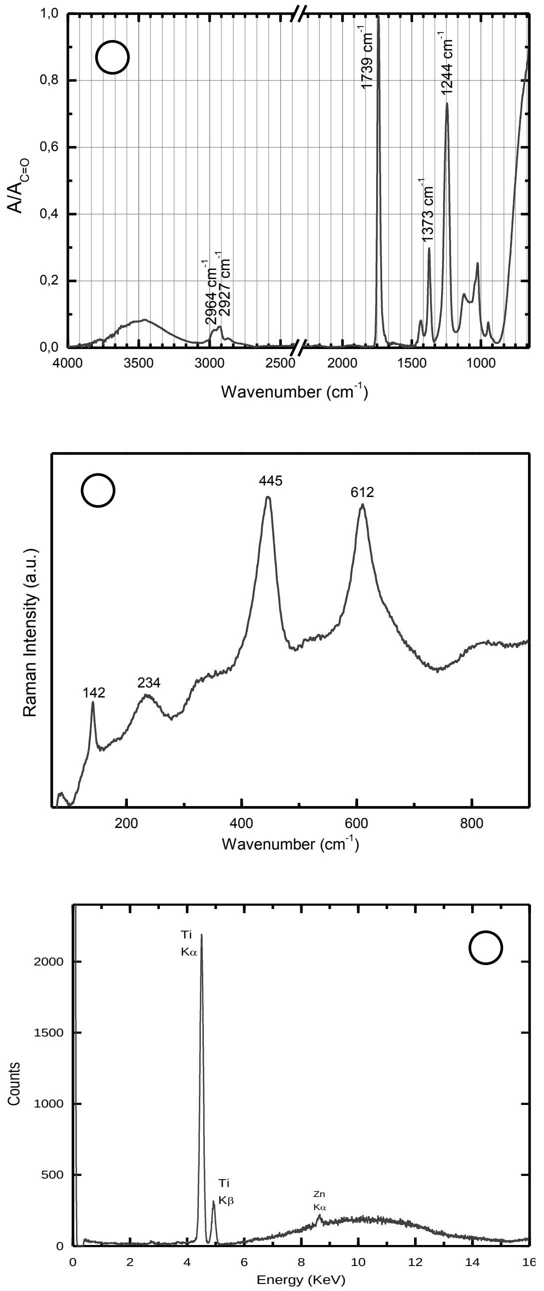


Figure V.27. Spectra of a white sample from *Alassio – Nice*, 1971: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

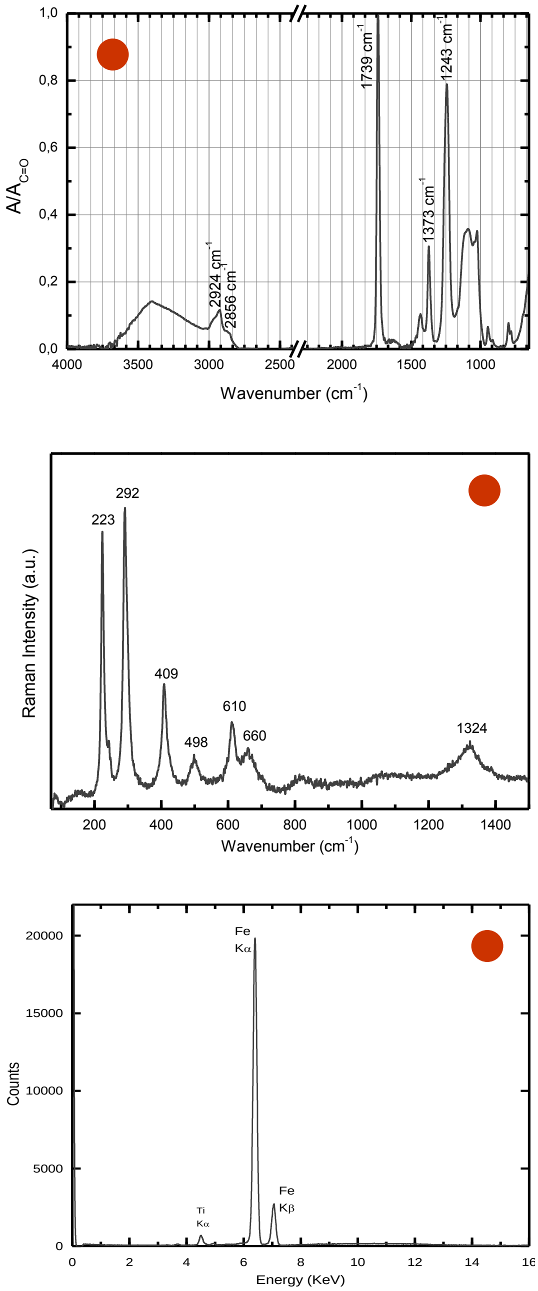


Figure V.28. Spectra of a red sample from *Alassio – Nice*, 1971: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

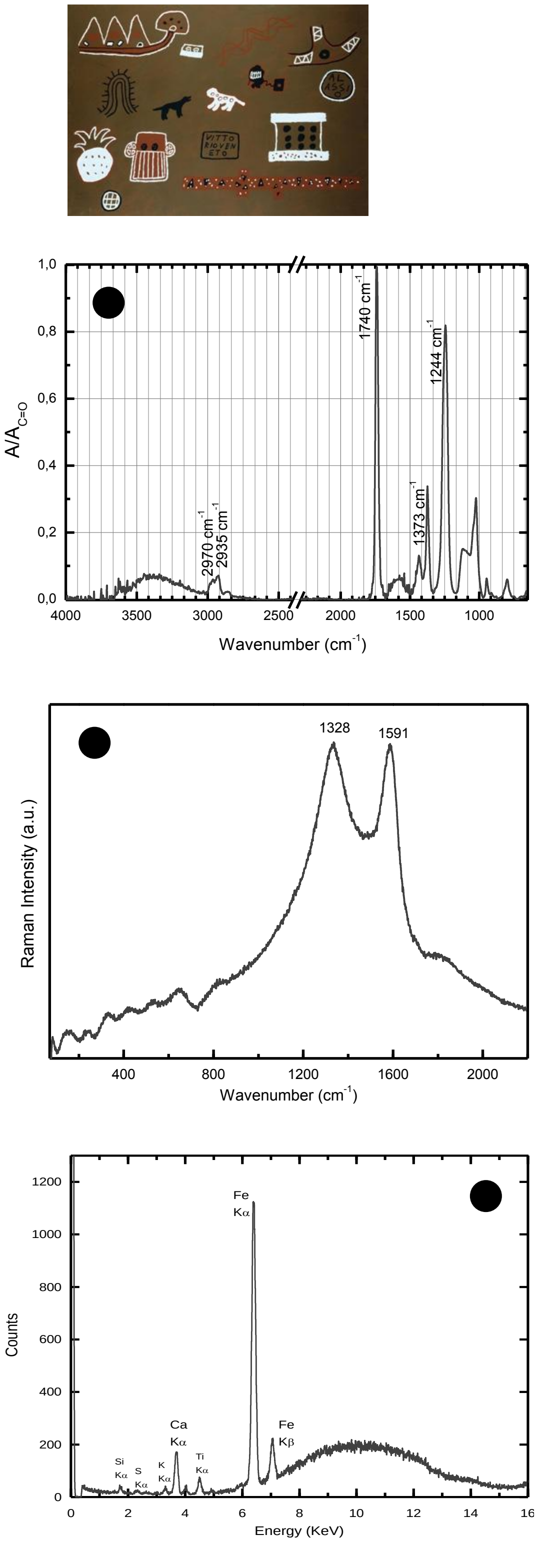


Figure V.29. Spectra of a black sample from *Alassio – Nice*, 1971: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

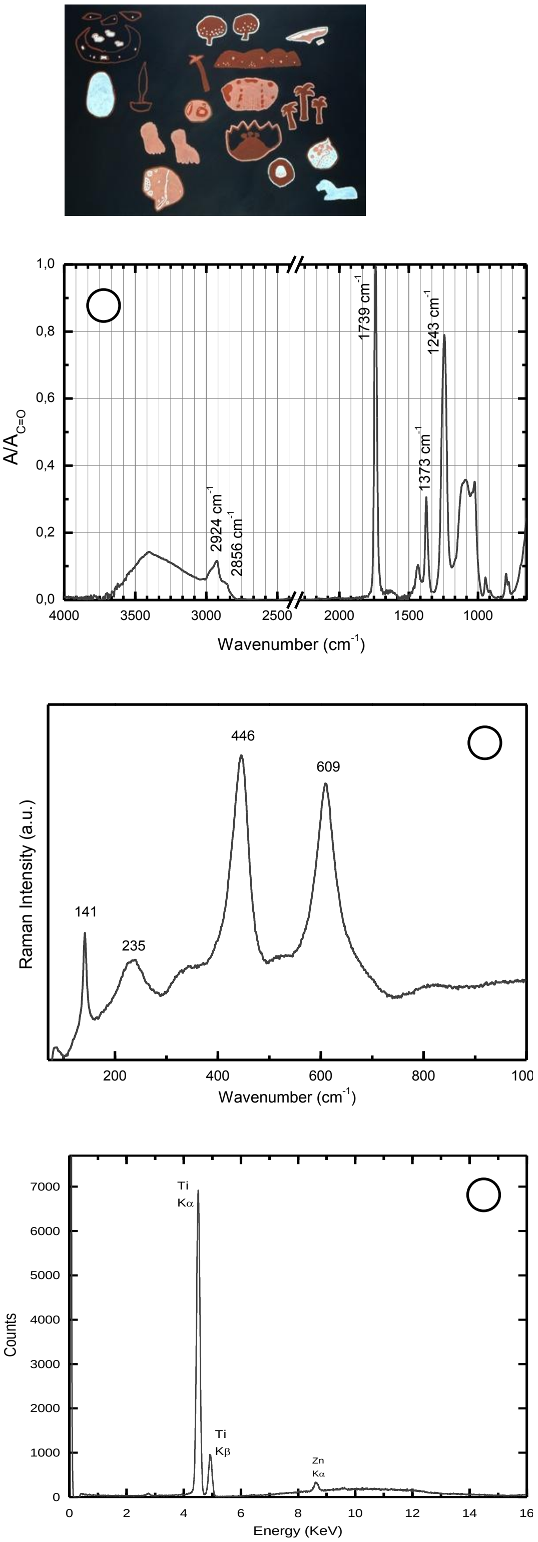


Figure V.30. Spectra of a white sample from *Port-Ligat – Granada*, 1980: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

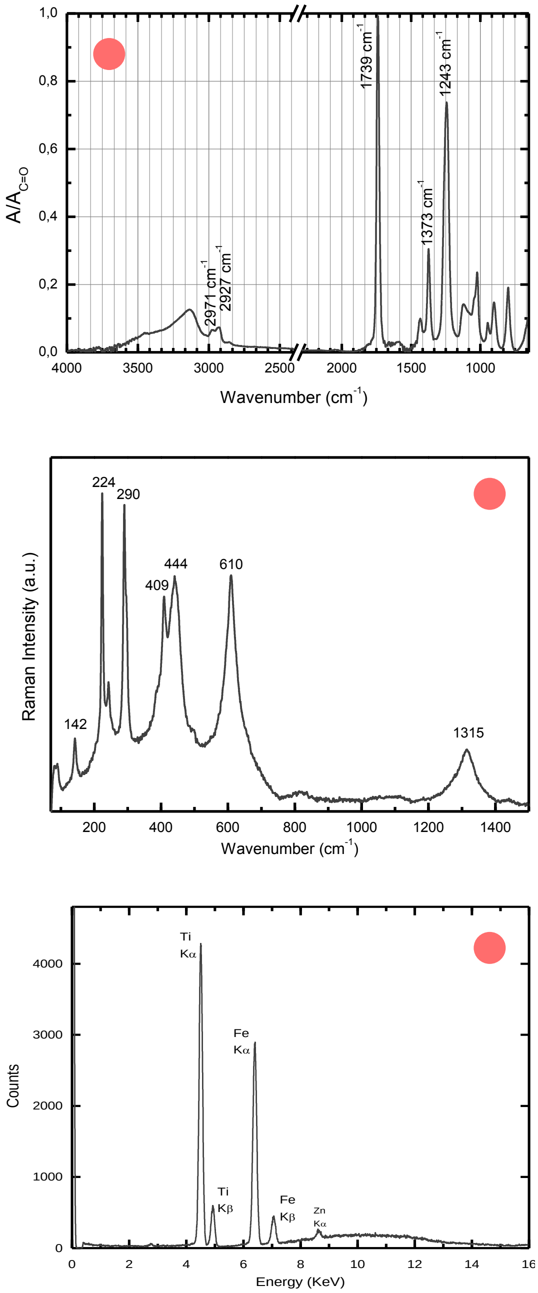


Figure V.31. Spectra of a pink sample from *Port-Ligat – Granada*, 1980: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

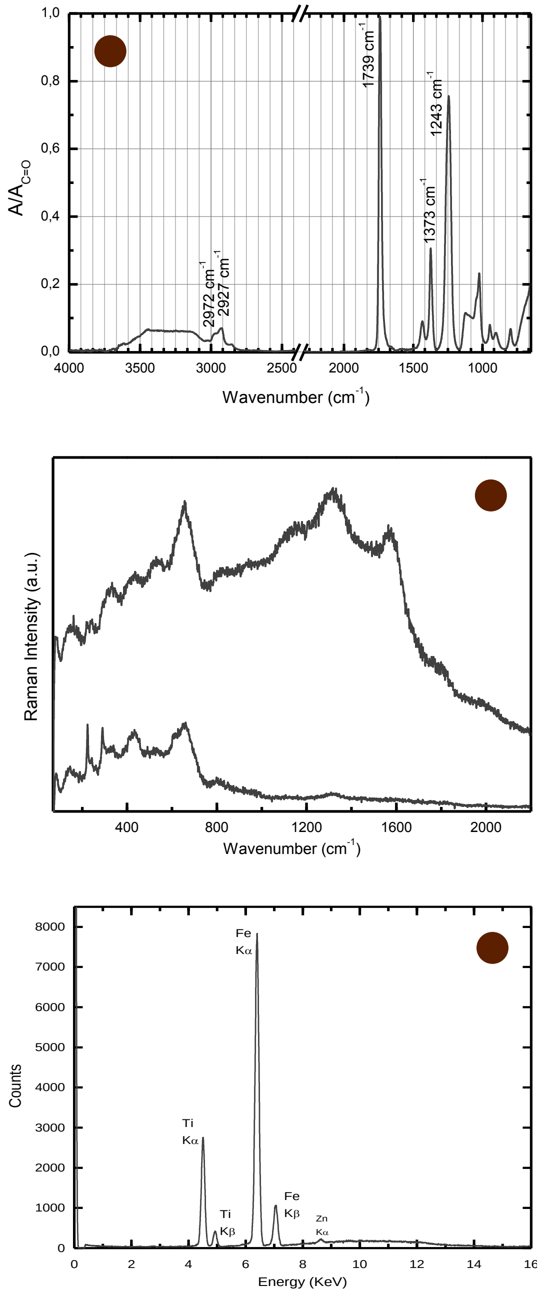


Figure V.32. Spectra of a dark brown/background sample from *Port-Ligat – Granada*, 1980: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

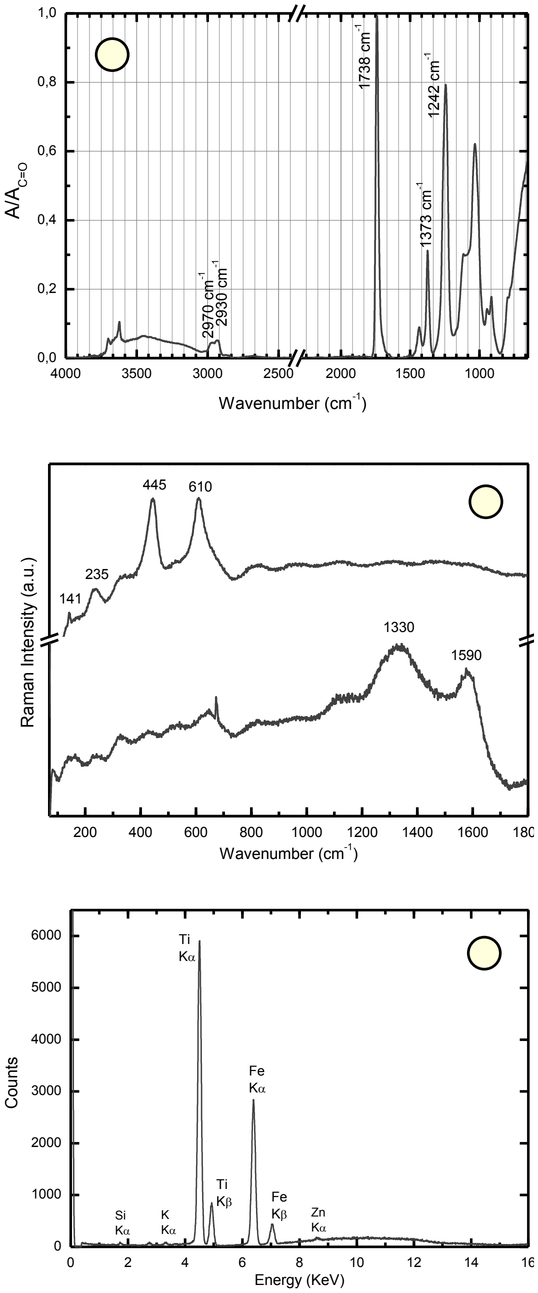


Figure V.33. Spectra of a off-white sample from *Os quintais*, 1989: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

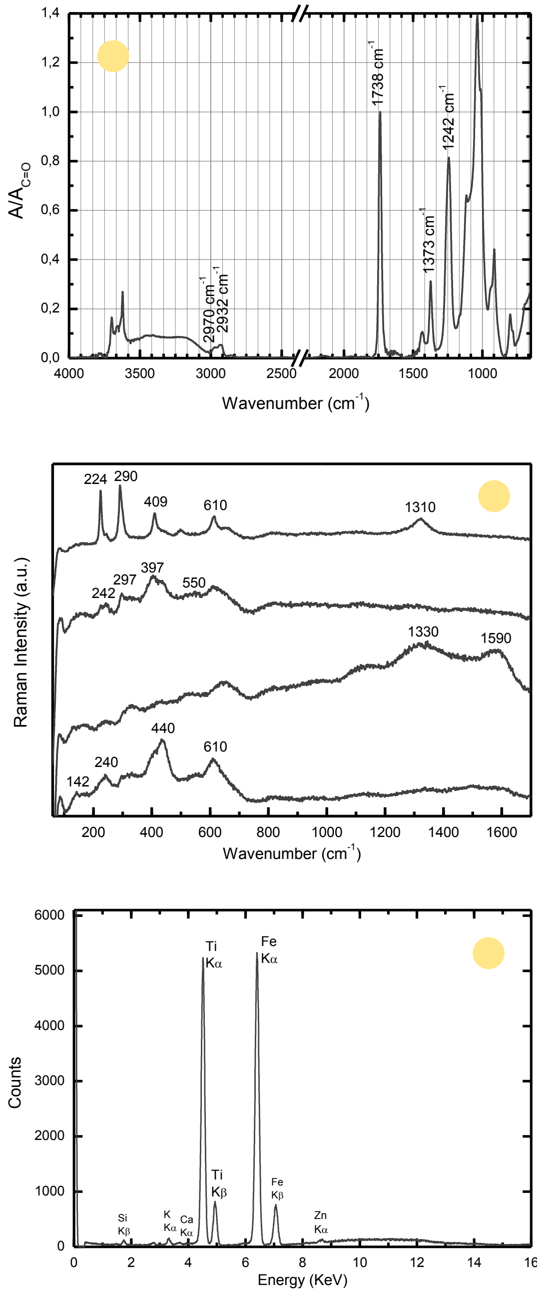


Figure V.34. Spectra of a background sample from *Os quintais*, 1989: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

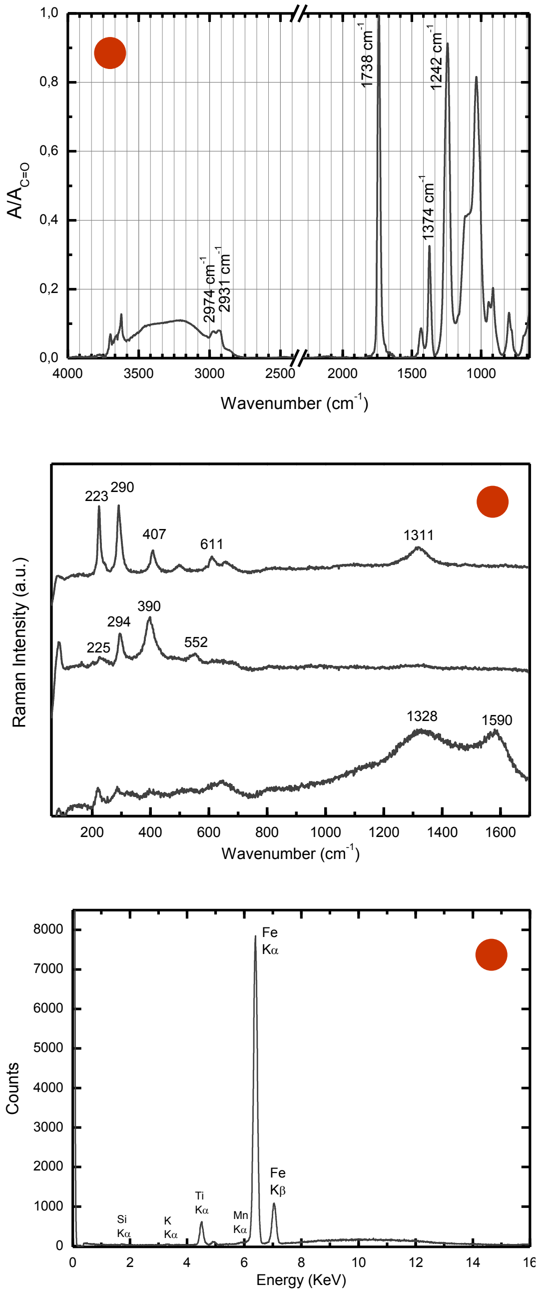


Figure V.35. Spectra of a red ochre sample from *Os quintais*, 1989: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

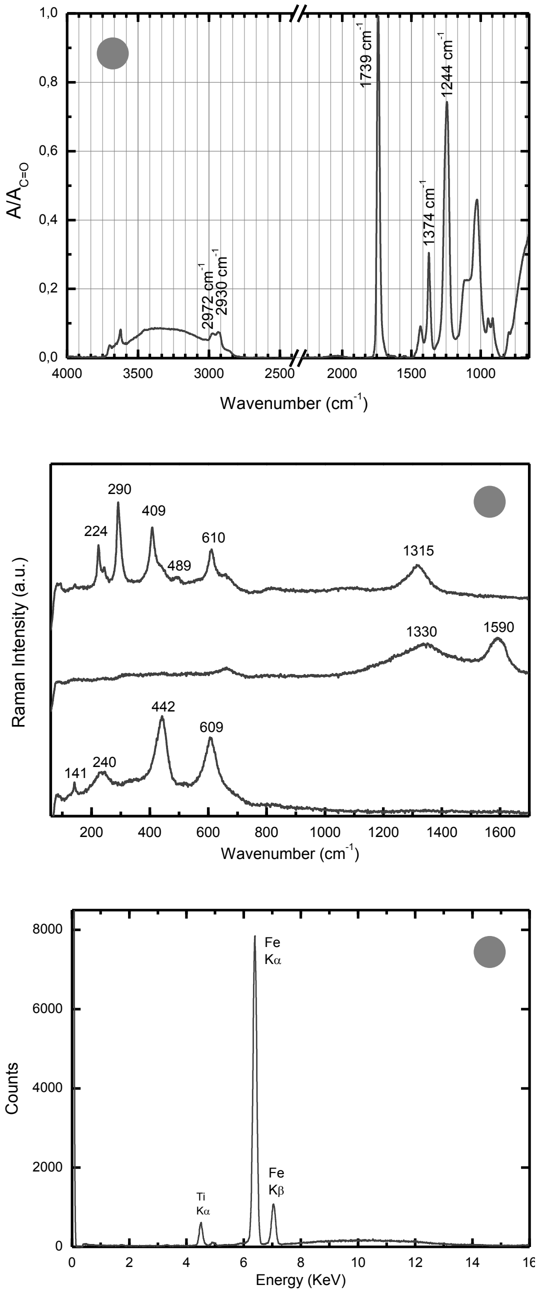


Figure V.36. Spectra of a grey sample from *Os quintais*, 1989: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

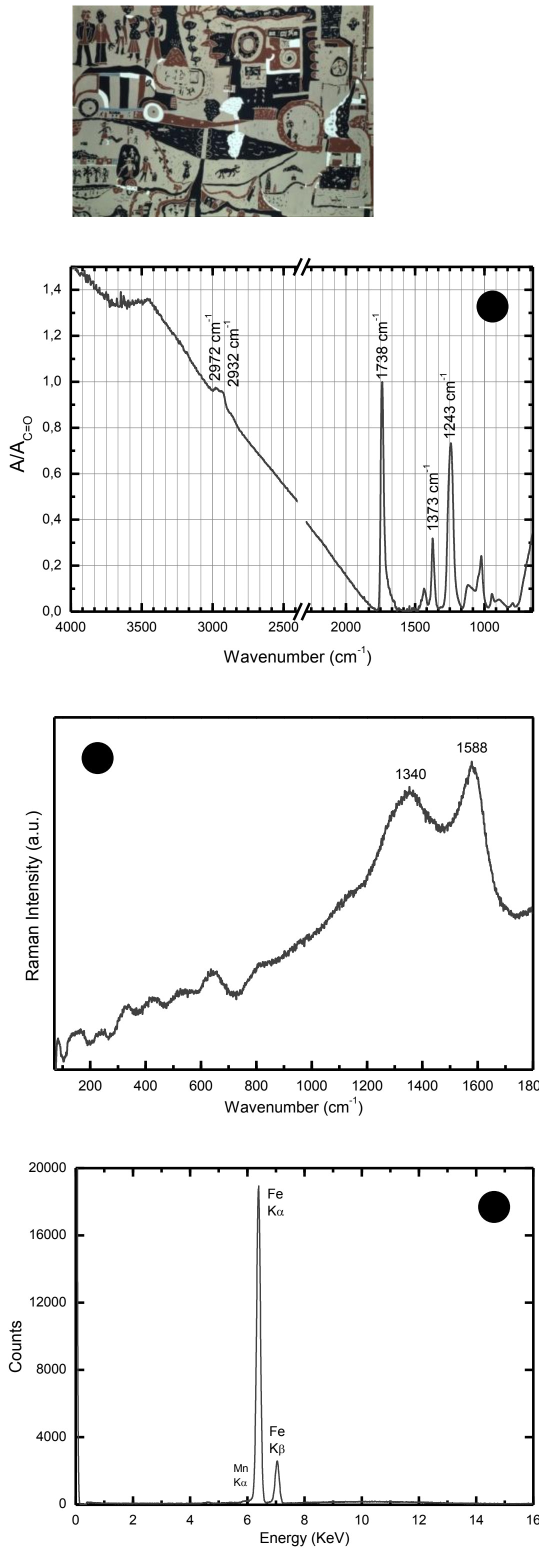


Figure V.37. Spectra of a black sample from *Os quintais*, 1989: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

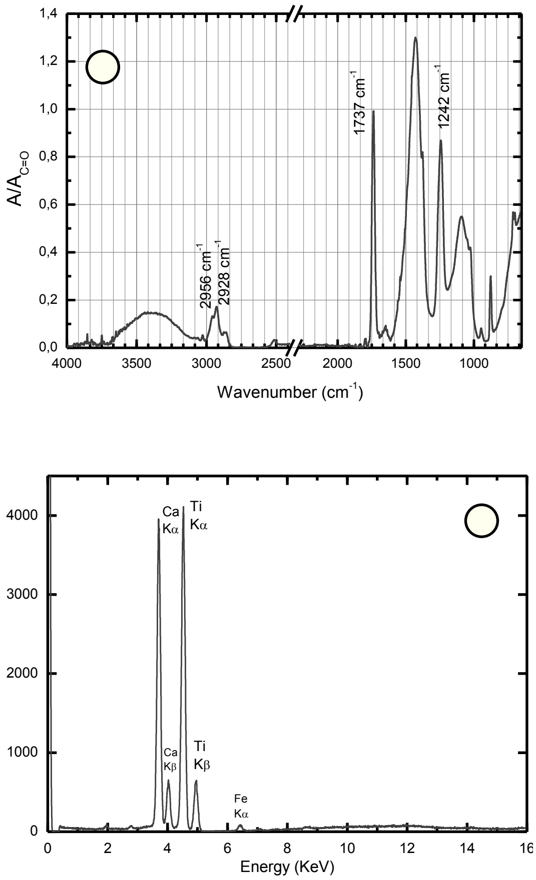


Figure V.38. Spectra of the final white left by the artist in his studio: top – infrared, with absorptions normalized for the C=O stretching; bottom – EDXRF.

V.5 Colourimetry

Figure V.39. Colourimetry mapping for *M. L.*, 1961.

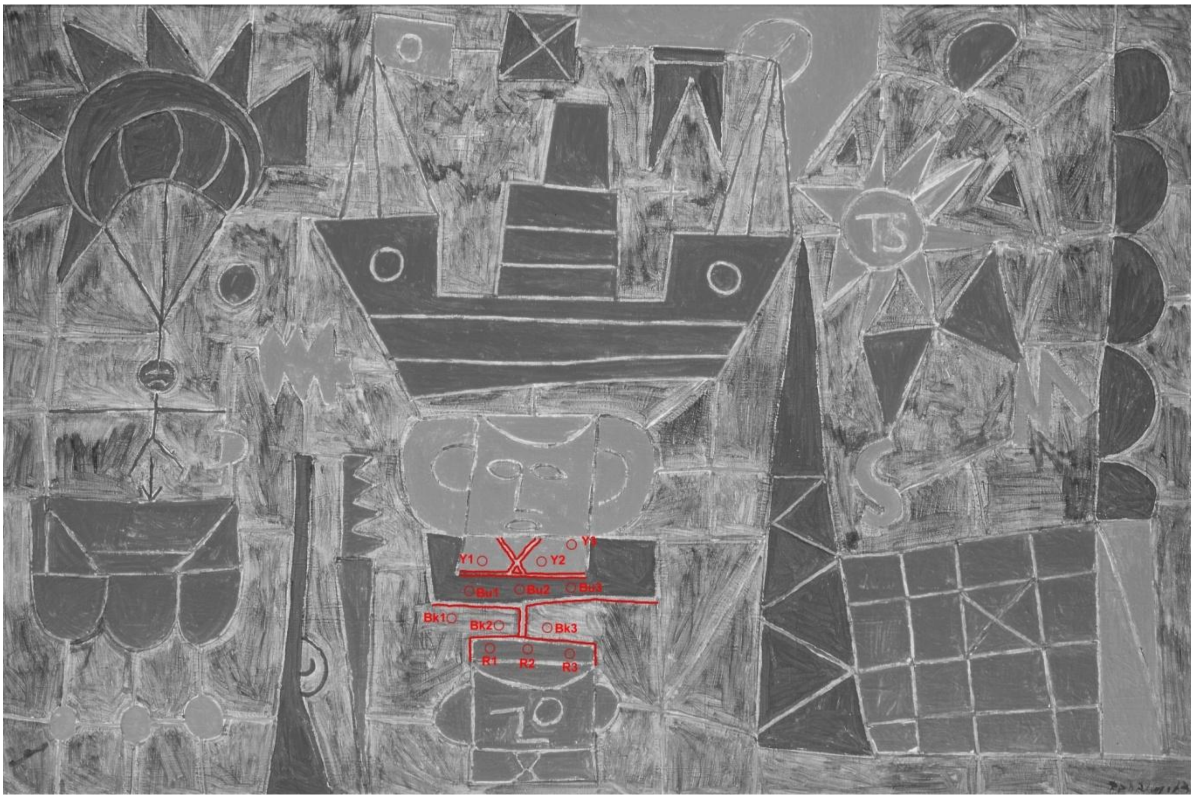


Figure V.40. Colourimetry mapping for *S. M.*, 1961.

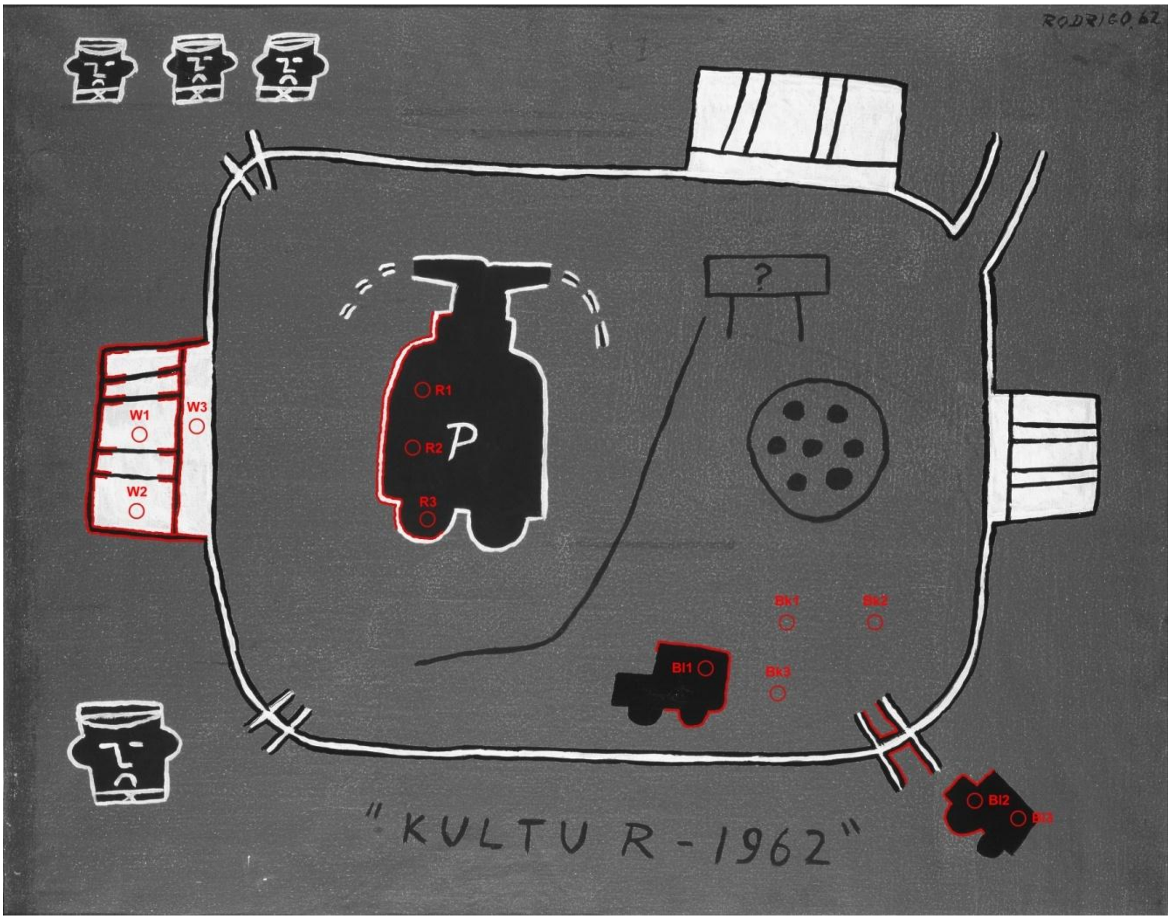


Figure V.41. Colourimetry mapping for *Kultur - 1962*, 1962.

Figure V.42. Colourimetry mapping for *Mondo Cane I*, 1963.

Figure V.43. Colourimetry mapping for *Liberté*, 1963.

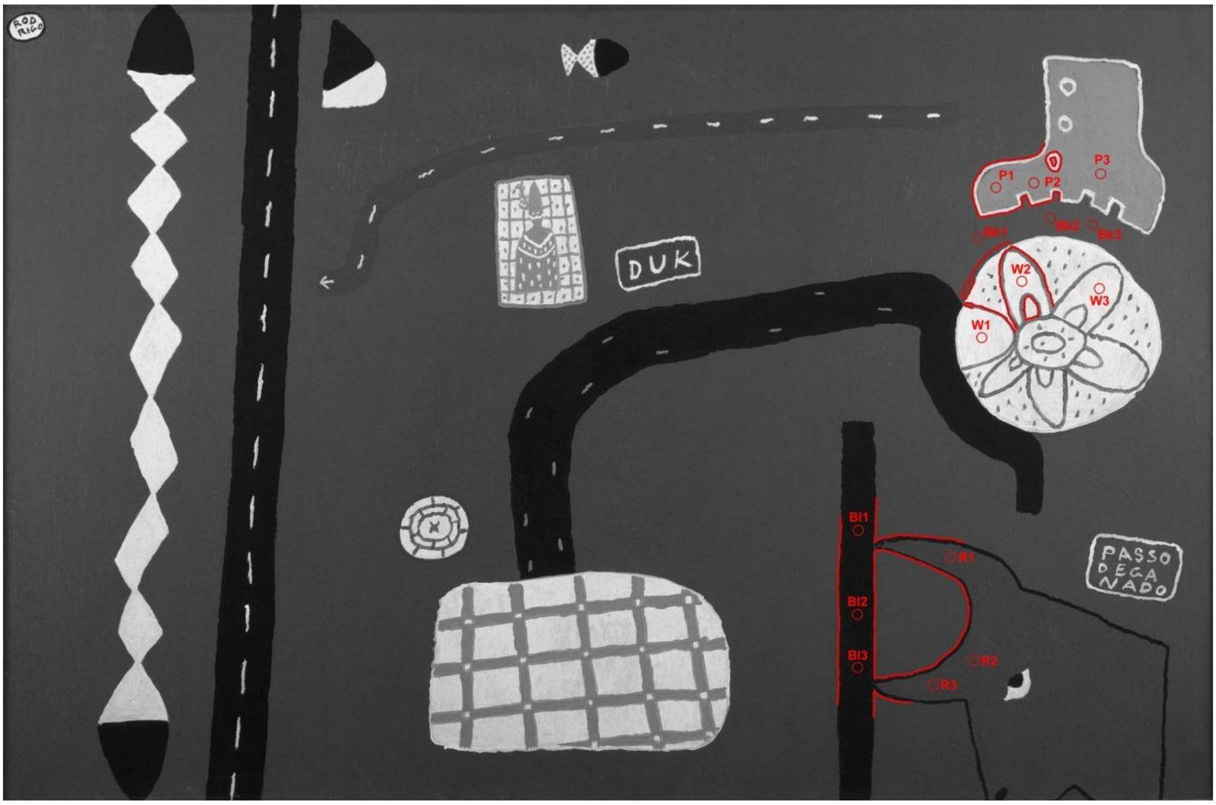


Figure V.44. Colourimetry mapping for *Lisboa – Oropeza*, 1969.

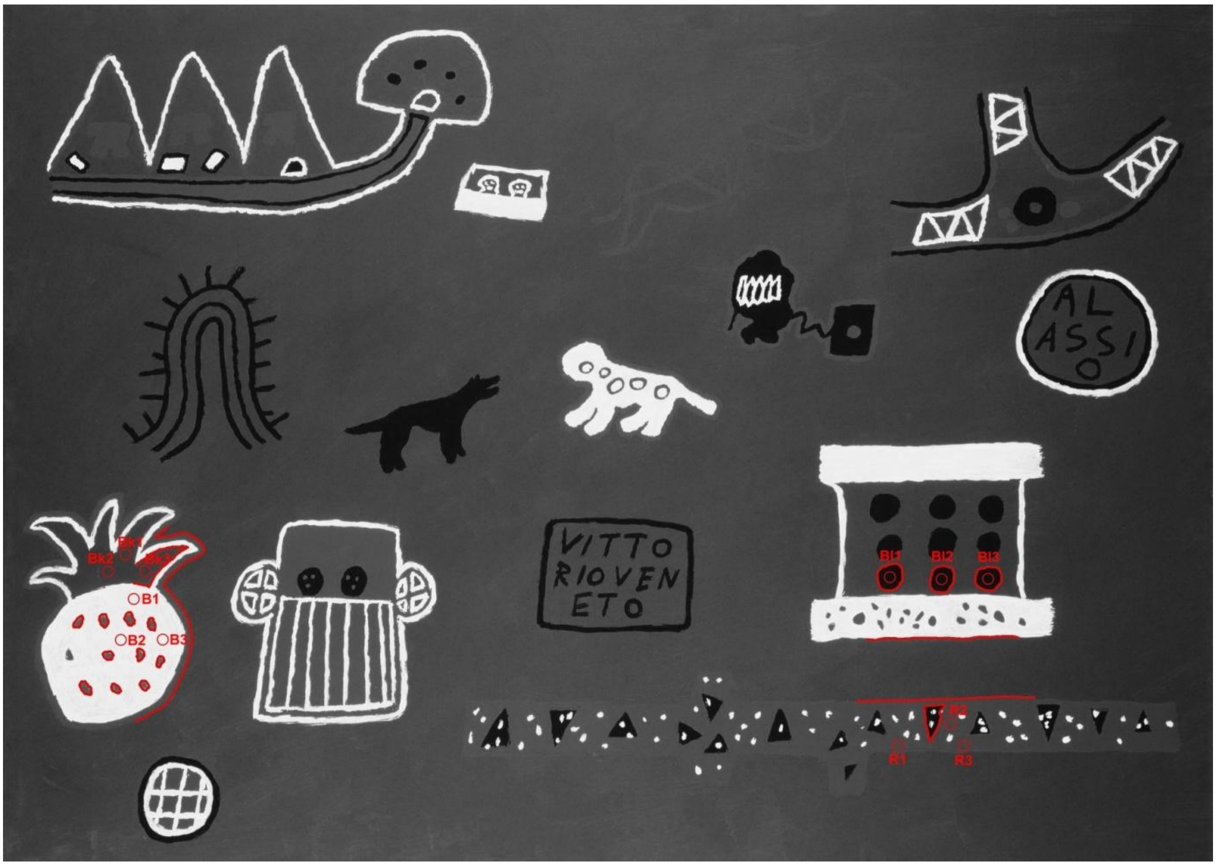


Figure V.45. Colourimetry mapping for *Alassio – Nice*, 1971.

Figure V.46. Colourimetry mapping for *Port-Ligat – Granada*, 1980.

Figure V.47. Colourimetry mapping for *Os quintais*, 1989.

Table V.11. Average *L*a*b** coordinates for each colour in Joaquim Rodrigo's paintings

Sample				***L****	***a****	***b****
M. L. 1961	White	○	Wa	79.56	0.83	12.40
			Wb	81.60	0.66	14.02
			Wc	80.15	0.60	11.17
	Red	●	Ra	38.13	28.24	20.23
			Rb	38.34	28.41	10.55
			Rc	38.28	28.40	20.33
	Brown	●	BRa	27.19	5.90	4.21
			BRb	29.08	10.22	7.57
			BRc	27.00	5.72	4.23
	Black	●	BLa	23.73	0.14	-0.33
			BLb	25.35	0.95	0.11
			BLc	24.61	0.64	0.01
	Background	●	BAa	31.00	12.49	9.57
			BAb	35.18	21.65	16.17
			BAc	34.77	20.70	15.35
S. M. 1961	Red	●	Ra	41.59	33.10	21.96
			Rb	41.62	33.01	21.82
			Rc	37.52	31.84	20.26
	Yellow	●	Ya	75.19	9.79	75.52
			Yb	73.15	11.23	75.28
			Yc	74.84	10.73	77.35
	Blue	●	BLUa	39.22	-11.85	-37.72
			BLUb	41.88	-12.80	-37.97
			BLUc	46.54	-14.34	-37.25
	Greenish Blue	●	GBa	60.82	-23.17	4.27
			GBb	67.39	-18.19	4.69
			GBc	67.46	-18.33	4.58
Kultur – 1962 1962	White	○	Wa	83.71	0.33	5.27
			Wb	85.72	0.20	6.54
			Wc	84.09	0.18	5.53
	Dark Red	●	DRa	30.12	8.90	7.86
			DRb	30.07	8.50	7.62
			DRc	30.11	8.29	7.36
	Yellow (background)	●	Ya	54.42	11.03	42.45
			Yb	53.72	10.17	41.04
			Yc	54.83	10.30	41.82
	Black	●	BLa	25.56	0.18	0.26
			BLb	25.47	0.20	0.34
			BLc	25.21	0.12	0.11
Mondo Cane I 1963	White	○	Wa	88.91	-1.21	4.74
			Wb	90.16	-1.06	5.06
			Wc	88.58	-0.84	5.57

Sample				***L****	***a****	***b****
	Yellow	●	Ya	75.60	11.65	81.94
			Yb	76.72	10.12	83.76
			Yc	77.94	9.68	84.53
	Red	●	Ra	39.94	33.56	22.30
			Rb	39.29	32.76	21.67
			Rc	40.80	34.33	22.61
	Blue	●	BLUa	38.12	-11.22	-40.15
			BLUb	40.17	-11.72	-39.19
			BLUc	37.84	-10.99	-39.60
Liberté 1963	White	○	Wa	83.64	-0.32	4.25
			Wb	86.45	-0.16	5.88
			Wc	86.83	0.16	7.52
	Light brown (yellow)	●	Ya	50.42	8.35	37.62
			Yb	49.91	7.89	36.70
			Yc	48.84	7.08	34.67
	Brown	●	BRa	32.24	3.92	9.82
			BRb	33.59	4.75	11.55
			BRc	33.12	4.74	11.52
	Black	●	BLa	24.80	0.19	-0.04
			BLb	24.63	0.13	-0.11
			BLc	24.38	0.24	0.04
Lisboa – Oropeza 1969	White	○	Wa	84.42	-0.49	1.00
			Wb	86.65	-0.45	2.06
			Wc	82.34	-0.40	4.23
	Pink	●	Pa	53.54	17.61	16.68
			Pb	52.89	17.92	17.08
			Pc	53.37	17.24	16.60
	Red	●	Ra	36.09	17.80	18.35
			Rb	36.65	18.11	18.56
			Rc	36.91	17.63	18.29
	Brown	●	BRa	40.20	6.30	10.12
			BRb	40.34	6.36	10.29
			BRc	39.99	6.43	10.37
	Black	●	BLa	24.49	0.06	-0.21
			BLb	24.07	0.25	0.38
			BLc	23.76	0.10	0.24
Alassio – Nice 1971	White	○	Wa	82.28	-0.50	-1.97
			Wb	86.37	-0.70	-0.88
			Wc	82.70	-0.58	-2.17
	Red Ochre	●	Ra	37.97	18.04	20.88
			Rb	37.92	17.64	20.29
			Rc	37.95	17.69	20.71
	Brown	●	BRa	37.58	8.13	16.38
			BRb	37.10	8.37	17.02

Sample				***L****	***a****	***b****
			BRc	37.58	8.36	16.95
Port-Ligat – Granada 1980	Black	●	BLa	21.84	0.14	0.19
			BLb	21.81	0.14	0.09
			BLc	21.36	0.14	0.29
	White	○	Wa	75.78	0.59	-3.08
			Wb	76.29	-0.69	-3.23
			Wc	72.96	-0.43	-3.00
	Pink	●	Pa	59.98	12.93	16.69
			Pb	59.14	11.83	15.47
			Pc	57.96	11.69	15.16
	Red	●	Ra	41.99	14.68	21.05
			Rb	41.03	13.60	18.99
			Rc	41.32	13.84	19.76
	Dark Brown (background)	●	BRa	31.60	1.47	2.85
			BRb	31.79	1.47	2.86
			BRc	31.44	1.48	2.57
Os quintais 1989	Off-White	○	Wa	68.50	7.28	16.23
			Wb	67.74	6.65	15.26
			Wc	68.40	6.66	15.23
	Yellow (background)	●	Ya	55.91	10.03	21.44
			Yb	55.37	10.04	21.35
			Yc	57.67	10.54	22.87
	Red ochre	●	Ra	33.82	12.73	10.89
			Rb	33.63	13.69	11.28
			Rc	33.91	13.98	11.94
	Grey	●	Ga	44.74	0.82	1.11
			Gb	46.15	0.96	1.96
			Gc	46.65	0.73	1.72
	Black	●	BLa	25.94	1.07	0.34
			BLb	24.12	0.87	0.52
			BLc	25.71	1.03	0.27

V.6 Fakes – a police case

In the framework of an apprehension by the Portuguese police (*Polícia Judiciária*) of paintings allegedly created by Joaquim Rodrigo, five paintings were analyzed at DCR for a molecular comparison based on the characterization presented in Chapter 4.2. In four of the five analyzed paintings all paints were identified as acrylics; most of the colours are organic with calcium carbonate being present as an extender. As previously discussed, from 1961 onwards Rodrigo prepared is own paints with a vinyl glue (PVAc), although in his books [105,112] he described it as acrylic. In which concerns the pigments, since 1969 a restricted palette of red and yellow iron oxides, titanium white and carbon based black was used. Also, those four paintings present evident formal, compositional and chromatic differences when compared to Rodrigo's works. According to the analysis results, and for the reasons described, the paintings could not be attributed to Joaquim Rodrigo.

On the other hand, the results obtained for the fifth painting analysed (*Triângulos*, Figure V.48) present a more complex interpretation and will be discussed bellow. In this painting the two larger triangles follow the construction precepts of the triangles series (1973) [22].

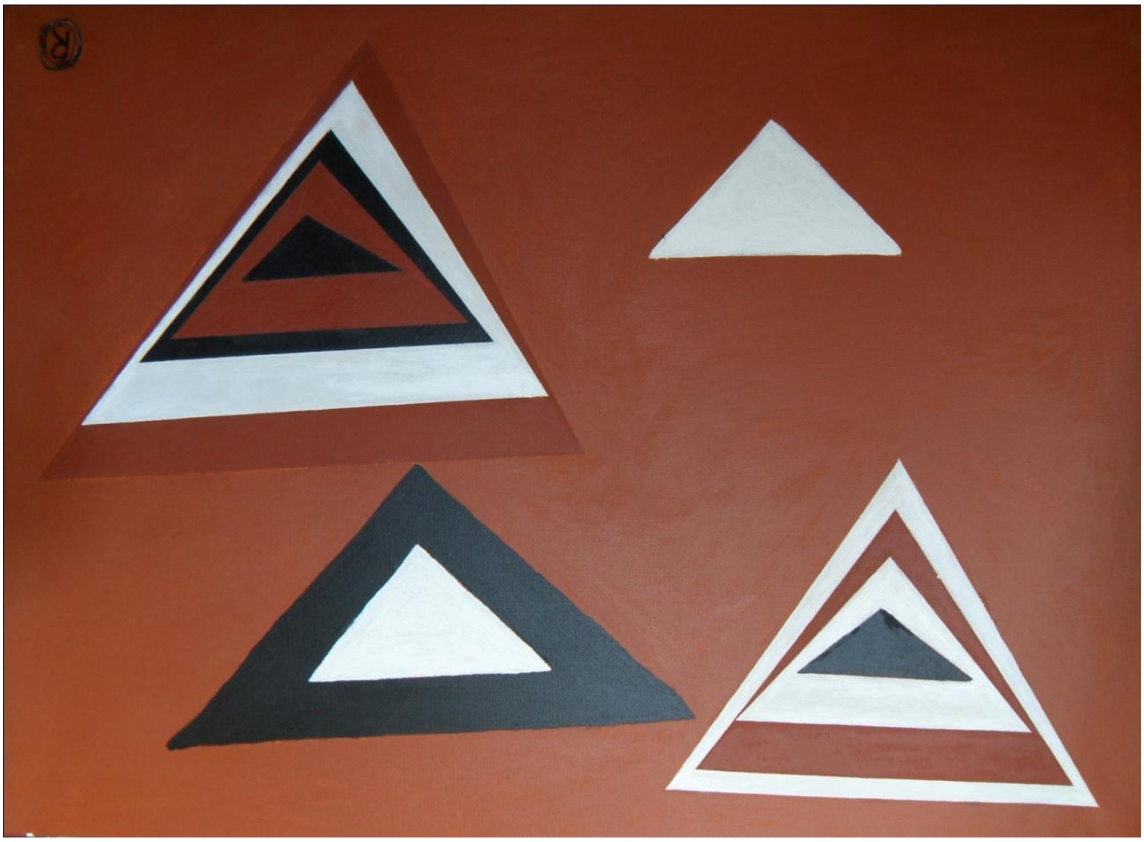
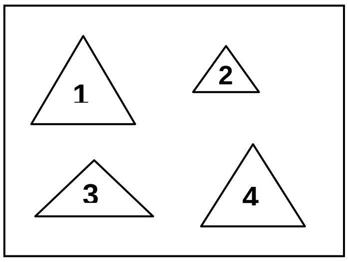


Figure V.48. One of the apprehended paintings (*Triângulos*). Although the signature is upside-down on the top-left corner, the image is presented with a rotation of 180º to be comparable to the triangles' paintings by Joaquim Rodrigo from 1973. Photo: *Polícia Judiciária*.

As in the other paintings analyzed, part of the paints were identified as acrylics. Nevertheless, vinyl paints were also found on one white (with an infrared spectrum similar to that of the white paint from the 1990 found in Rodrigo's studio), one black and two red ochres from the larger triangles; and also on white and ochre samples collected from two paint layers beneath the background. Table V.12 summarizes the main data collected from the infrared spectra. Furthermore, an acrylic varnish was applied on the painting and Joaquim Rodrigo always left the surfaces of his paintings unvarnished.

Table V.12. Summary of the main results from the infrared analysis of the apprehended painting *Triângulos*

Painting	**μ-FTIR**
  	*Whites*: PVAc (triangle 4[a] and inferior preparation layer[b]) + calcium carbonate + titanium dioxide Acrylic (triangle 1, superficial layer, triangles 2 and 3) + talc + titanium dioxide Oil + lead white + barium sulfate (canvas preparation) *Blacks*: PVAc (triangle 1) + gypsum [c] Acrylic + calcium carbonate (triangles 3 and 4) *Red ochre*: PVAc (triangles 1 and 4) *Background*: PVAc (inferior layer) Acrylic (superior layer) *Varnish*: Acrylic

[a] Spectra were collected from two layers, a vinyl white paint was identified on a layer found beneath the acrylic superficial one. The white vinyl layer presents several paint losses and was possibly repainted with an acrylic paint. [b] Spectra were collected from a stratigraphic sample of the background. A first layer (canvas preparation) was identified as being oil based, on top of which several layers were identified: vinyl white, vinyl red ochre, acrylic white; and acrylic red ochre (superficial background layer). [c] μ-Raman: carbon black.

Due to the several layers found and the presence of an oil based canvas preparation it is possible to consider that this painting is a reutilization of an old used canvas. Furthermore, its dimensions (81 x 116 cm) are comparable to those of the work *Triângulos I* (vinyl on canvas) painted by Joaquim Rodrigo in 1973 (see Table V.1). Nevertheless, in its present condition, this painting could not have been painted by the artist. In the triangles series painted by Rodrigo in the 1970s only one or two triangles are represented and correspond to a precise construction study [22]. Although four triangles are represented in this case, this is an attempt of creating a painting similar to those. Hypothetically, the canvas used could have been previously painted by the artist, where besides the background part of the triangles could be already present, Figure.V.49.

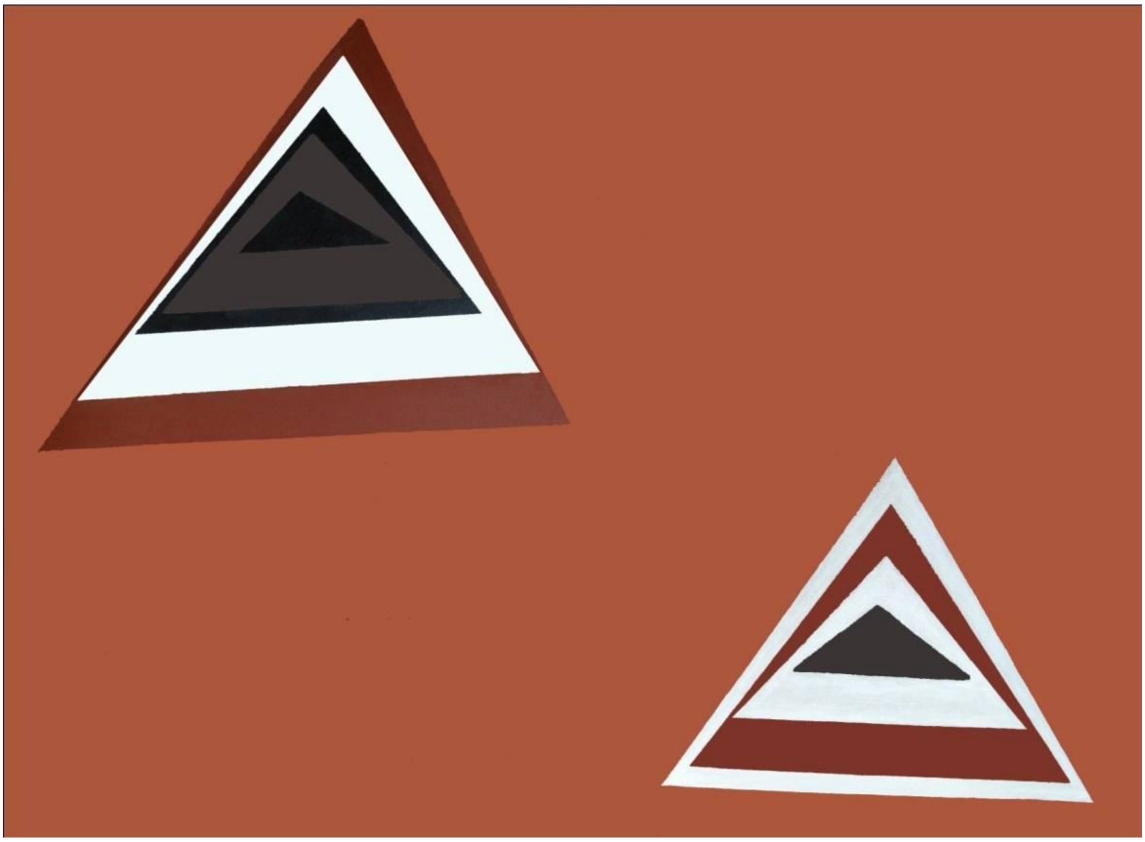


Figure V.49. Digital reconstruction of the hypothetic original vinyl painting for the apprehended *Triangles*; in grey are represented the colours not identified as PVAc.

V.7 Specific documentation

Specific documentation related to Joaquim Rodrigo's work was gathered and will be available for consultation at the DCR[1].

Out of print bibliography

Active

- Joaquim Rodrigo. *O complementarismo em pintura. Contribuição para a ciência da arte*. Lisbon: Livros Horizonte, 1982.
- Joaquim Rodrigo. *Pintar certo.* Lisbon: Edições Salamandra, 1995.

Passive

- José-Augusto França. *Joaquim Rodrigo* ou '*o pintar certo*'. Porto: Edições Galeria Nazoni, 1988.
  Including addenda (October 1982, January 1984 and July 1988) to Rodrigo's writings.

Related

- José Redinha. *Paredes pintadas da Lunda*. Lisboa: Companhia dos diamantes de Angola, 1953.
  Joaquim Rodrigo was introduced to this book in 1961 and it will be of decisive importance for his future work [22].

Other documentation

- Transcription of a talk (1965) with José-Augusto França, Fernando de Azevedo, José Blanc de Portugal, José Sasportes and Fernando Pernes.
  In this talk, Rodrigo explained his painting theory and the result was the basis for his future writings (*O complementarismo em pintura. Contribuição para a ciência da arte*, Joaquim Rodrigo, 1982) [22].
- Video (on digital support) of a conference by Joaquim Rodrigo about his work held at *Galeria Valentim de Carvalho* in 1994, with José-Augusto França, Rui Mário Gonçalves and António Rodrigues.
  The conference was organized in the framework of is solo exhibition *Uma viagem* [22].

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Appendix VI
Ângelo de Sousa Data[2]

VI.1 First interview with Ângelo de Sousa

Ângelo de Sousa, Joana Lia Ferreira and Maria João Melo
Porto, October 28th 2005

With Ângelo de Sousa at his place in a quiet afternoon. In this first conversation with the artist we tried to understand his choices and concerns about the materials. After we introduced our selves, Ângelo talked about a friend, who had died a short while ago and for a long time was his technical adviser for paints.

Ângelo de Sousa: O Joaquim Simões foi uma ajuda preciosa, era Eng.º químico e houve uma altura em que fazia tintas para a Escola[3]; acabei por ser o único freguês constante e ele fazia tintas quando eu precisava, agora não tenho a quem me agarrar. Sempre que eu precisava de qualquer coisa telefonava ao Simões e ele arranjava: 'Precisa de pigmento? Arranjo-lhe o *amarelo Hansa*. Meio quilo? 12-G? Qual é que quer? 6-G? Eu arranjo-lhe.' Ainda tenho ali uma latinha de *amarelo Hansa* do Simões, que é muito forte. Eu sei que os pigmentos que usam na indústria são misturas terríveis; no azul tem um bocado de preto para partir o azul, tem um bocadinho de ocre, vermelho, branco! Mas toda a gente trabalha assim; há uma aula de serigrafia na Faculdade de Belas Artes e havia um colega meu, o Nuno Barreto, que eu ia visitar e o que via era incrível! Havia montes de frasquinhos cheios de misturas complicadas e depois eu via os meninos e as meninas a deitar uma pinguinha de castanho e depois uma pinguinha de amarelo e depois uma pinguinha de azul da Prússia, depois um bocadinho de ftalocianina e depois um bocadinho de ocre e depois mexiam aquilo e ficava uma coisa terrível. 'Esta gente estraga tinta, mas porque é que não usam as cores mesmo? *Pantones* ou primárias?' Eu sempre fiz serigrafias só com as cores primárias, nunca usei outra coisa. Ninguém sabe que as cores não se misturam, sobrepõem-se; eu interessei-me por isso porque sempre fui coca-bichinhos.

Ligações Perigosas: Acabou de dizer 'azul da Prússia, azul de ftalocianina'. Uma das coisas que reparámos no inquérito a que respondeu é que tem muito cuidado em nomear correctamente os materiais que utiliza, o que não é muito comum num artista. Isso reflecte uma preocupação em conhecer o material?

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[2] The full interviews are presented here in Portuguese, the language in which they were conducted; the main information is discussed in the core of the thesis.

[3] Faculdade de Belas Artes da Universidade do Porto, antiga Escola Superior de Belas Artes do Porto.

A.S.: É porque me interessa que ao restaurarem as obras as não estraguem.

L.P.: Tem curiosidade em verificar a estabilidade dos materiais?

A.S.: Tenho e tenho lido alguns livros acerca dessa questão. Verifiquei que em condições normais de exposição, durante x meses, a 15º de inclinação, atrás de um vidro durante Agosto e Setembro; o acrílico, por comparação com os outros, tem uma determinada duração.

L.P.: E costuma testar o comportamento dos materiais que utiliza?

A.S.: Sim, tenho uma pasta com coisas dessas, com testes que tenho feito.

L.P.: Começou a experimentar vinílicos muito cedo, em 1961. No Porto isso já era comum?

A.S.: Não, não era. Fui eu e o Quadros, já nem sei quem foi primeiro. O António Quadros era futuro cunhado de uma Eng.ª Química (Ernestina Lima) e éramos os maluquinhos da tecnologia, comprámos livros; eu logo que cá cheguei[4] (vindo de Moçambique) comprei o livro do Dörner, custou 300 escudos, eu vivia com um conto e quinhentos por mês, foi um investimento do arco-da-velha!

L.P.: E o Dörner tem alguma coisa sobre vinílicos?

A.S.: Não, mas já fala em polímeros sintéticos.

L.P.: E o que é que o levou a experimentar os ligantes vinílicos?

A.S.: Não tinha dinheiro, vivia com uma bolsa relativamente restrita e aborrecia-me com o óleo que demorava anos ou meses a secar e comecei a experimentar coisas; primeiro foi o óleo, depois fazia caseína com pigmentos baratos que comprava, ainda era aluno da Escola, em 56/58. Preparava as telas com a caseína, não havia tela já preparada em Portugal, pelo menos cá no Porto não havia. Pendurava um bocado de pano-cru, que não era pano-cru, era pano de algodão daquele de lençóis baratos; pendurava na parede com *punaises*, passava-lhe caseína com branco de chumbo ou branco de zinco, tanto fazia; era

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[4] Quando comecei a pintar, ainda em Moçambique, não sabia nada de nada, de maneira que fui a uma livraria e encontrei a revista Pop & Club, colecção Pelikan, ainda a tenho, de um pintor da altura (chamado Norman Colchoun) e que depois desapareceu, em que falava sobre a questão dos pigmentos e das tintas que secavam devagar e depressa. De maneira que eu antes de começar a pintar comprei um livro sobre os materiais, talvez seja sintomático.

vendido como alvaiade[5]. Pintava uma série de quadros ao mesmo tempo, depois chegava ao fim, cortava, aproveitava dois e deitava o resto fora, isso desde 56.

L.P.: Comprava a caseína?

A.S.: Comprava na SUIL, que era onde se vendia os lacticínios.

L.P.: Era comum usar-se a caseína?

A.S.: Não, nem sei para que é que a vendiam. Um dia perguntei se tinham e até me perguntaram quantos quilos queria; ia lá comprar as manteigas e beber um leite de vez em quando, era mesmo ao pé da Escola.

L.P.: E isso passa-se quando?

A.S.: Eu vim em 55 e nessa altura estava num atelier com outras pessoas (em 56/57) e eu já pintava assim; eles compravam tintas de óleo, e também já pintava algumas coisas com tintas de parede da *Ripolin* ou semelhantes.

L.P.: E depois passou para os vinílicos?

A.S.: Depois, sim; também usava óleo, mas fazia eu o branco, com branco de chumbo ou de zinco, consoante houvesse na drogaria. Tenho algumas dessas coisas (estaladas) lá em cima, o pano não era grande coisa para aquilo ou então o óleo era ordinário; era óleo cozido. Entretanto pintava umas coisas a óleo, mas na Escola, como a tinta demorava a secar não dava jeito e às vezes pintava tudo com caseína com pigmentos comprados na drogaria, uns óxidos de ferro, uns amarelos, uns azuis, vermelhos não havia nada de jeito e aquilo secava logo; simplesmente para não me chatearem depois passava por cima um bocado de óleo cozido e aquilo ficava a cheirar a óleo. Fazia essas coisas para despachar. Também usei uns óleos que comprava mas ficava um bocado caro e não secava; como se sabe; o azul ultramarino demora várias semanas a secar, o azul da Prússia amanhã está seco... Fiz umas experiências de preparar a caseína mais concentrada mas aquilo estalava tudo. Às tantas comecei a pintar com cera, a encáustica (1958 a 1960/61), comprava cera de abelha e ainda pintei alguns quadros assim; punha em banho-maria e em areia para manter o calor e ia pintando. Também fazia pigmentos castanhos tirados da terra. Uma vez fiz um pigmento cinzento, porque num pinhal descobri uma mancha cinzenta num corte de terreno. Se a cera tivesse algum mel era amarela e podia pintar directamente. Pintei até 61 / 62 assim e depois fartei-me porque aquilo era extremamente trabalhoso, era um cheiro

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[5] Definição estrita de alvaiade: branco de chumbo (carbonato básico de chumbo) [Claro, A…].

terrível a petróleo queimado, e ainda tinha que comprar petróleo; deixei-me disso. E foi nessa altura que pensei nos vinílicos; eu tinha visto numa revista inglesa chamada *The Studio* um quadro de um senhor chamado Sidney Nolan que é australiano, e dizia PVA; ele pintava com tintas baratas, usava aquela *Ripolin* que era um esmalte alquídico e que já se usava há muitos anos e depois começou a pintar com o acetato de polivinilo. Um dia comprei uma cola para madeira para colar qualquer coisa, vi PVA e pensei que era capaz de ser o que o Nolan usava[6]. Depois aquilo ficava esbranquiçado, mas misturado com pigmentos, com guache ou com aguarelas não se notava, comecei a pintar com isso e pintei durante muitos anos.

L.P.: Lembra-se qual era a marca?

A.S.: A uma certa altura era da fábrica *Soberana*; pedi à Tina (Eng.ª Ernestina Lima) para me arranjar um meio mais transparente e ela arranjava um latão para mim e para o cunhado (António Quadros) e nós dividíamos aquilo a meio para preparar telas. Depois comecei a misturar com coisinhas para imitar a textura da cera, papel higiénico desfeito para fazer massa e serradura fininha. Também experimentei misturar com pigmentos e ficou bestial, entretanto ia trocando ideias com o Quadros e nem sei quem fez primeiro ou depois, sei que passei a fazer assim a partir de aí; entrei para a Escola como professor em 62 ou 63.

L.P.: E a *Soberana*?

A.S.: Era uma fábrica de tintas industriais, de interior e exterior, para barcos, etc. Eu penso que ainda existe.

L.P.: Sempre usou os vinílicos da fábrica *Soberana*?

A.S.: Primeiro usei a cola de carpinteiro para madeira que havia e depois o que a Eng.ª Ernestina Lima arranjava na fábrica *Soberana*, mais transparente.

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[6] Ainda há uma outra anedota. Eu tinha um amigo que era arquitecto, estudante de arquitectura, que me disse: ‘eu tenho um parente na *Robbialac*’; fui lá à *Robbialac* e apareceu um senhor muito alto com uma costela estrangeira, ‘tens que arranjar para este meu amigo uma amostra de polivinilo e amostras de pigmentos’, ‘eu só posso arranjar uma latinha e umas amostras de pigmento’. Arranjou uma lata do polivinilo, ‘isto fica transparentíssimo’, e uma série de latinhas pequeninas com vermelho, azul e amarelo em pó: ‘Não posso arranjar-lhe mais, nós estamos proibidos de vender matéria-prima, o senhor leva isso e não me aparece cá mais, não fica chateado?’ – ‘Não, não fico nada chateado’. De maneira que usei o *medium* enquanto durou e a lata até começou a enferrujar, experimentei uma vez os pigmentos – ‘isto é sagrado’ - ainda devo ter aí as latinhas. Sabe quem era o senhor? Encontrei-o no outro dia, nunca mais o tinha visto. É o pai do Zé Pedro Croft, Croft de Moura. Isso foi logo talvez em 60, 61. E depois é que encontrei a tal cola de carpinteiro, ‘*auf Wiedersehen Robbialac*’.

L.P.: Já analisámos umas amostras microscópicas do seu quadro que está no Museu do Chiado e não é um homopolímero de PVA.

A.S.: O branco do fundo é um branco de parede industrial, não sei se é da *Robbialac*, se calhar é da *Barbot* que ficava ali ao pé da Escola ou talvez fosse ainda da *Soberana*; possivelmente era da *Barbot*. Mas a pintura propriamente dita, aquela cor que dizem que é preta mas não é preta, era feita com cores primárias de impressão, magenta, cyan, amarelo e um bocadinho de preto, que eu tinha comprado e que eram para serigrafia. Um banco tinha convidado 3 ou 4 artistas para fazer a capa de um relatório de contas e eu tive a ideia de fazer em serigrafia, quer dizer com um tramado, mas não ia fazer o tramado à mão com tracinhos. Com um tira-linhas?! Morria velho! Mandei fazer um écran de serigrafia que ainda devo ter aí, mandei tramar aquilo de grosso até fininho. Experimentei passar com polivinilo, mas entupia a rede e como não tinha solventes para aquilo... Pensei que deviam vender tintas para serigrafia, que era para imprimir em qualquer coisa, creio que era para imprimir em papel, só que em papel a camada seria mais fininha do que acabei por usar no quadro; porque a tinta era muito translúcida, até o preto era transparente, e por isso é que dei aquelas camadinhas por cima umas das outras, era dado à espátula. Tenho ideia que era de uma marca holandesa chamada *Van Son*.

L.P.: Disse que não tinha solvente para o PVA, não misturava com água?

A.S.: Claro, com água. Mas se fosse preciso limpar, na altura não tinha nada com que pudesse limpar, remover o que não interessava. Agora uso tricloroetileno, ou algo semelhante, e sai a tinta toda. Ou então um truque que descobri há uns anos; tinha que limpar uns quadros e experimentei acetona, mas como a acetona evaporava tentei metade acetona e metade água, depois com um pincel velho aquilo saía tudo em película sem atacar a parte debaixo. Talvez porque tem muito titânio ou muito pigmento e é mais resistente.

L.P.: Então a preparação era industrial, feita com *Robbialac* ou *Barbot*. Porque é que não usava a cola da *Soberana*?

A.S.: Porque é que eu havia de estar ali horas a moer aquilo? A tinta já estava feita. Era para tapar e tinha cargas, talvez sulfato de bário ou titânio. Onde é que eu arranjava titânio? Portanto usava a tinta de lata. Hoje em dia, para além da tinta branca dou uma camadinha de gesso da *Talens*; para ficar tudo da mesma família, o gesso *Talens* as tintas da *Talens* e depois fica o verniz *à tableux Talens*, se alguém quiser limpar a sujidade passa um pano com *white spirit* e está o quadro pronto a receber verniz outra vez.

L.P.: Isso é o que usa agora?

A.S.: Já há muitos anos.

L.P.: Tem experimentado muitos materiais. A escolha desses materiais é fortuita ou corresponde a uma busca?

A.S.: Corresponde a uma maneira de ser. Quando faço qualquer coisa tento sempre saber como é que ela funciona, desde pequenino.

L.P.: Vai à procura destes novos materiais? Selecciona-os?

A.S.: Isso é uma questão de sorte. É evidente que se não tivesse comprado aquele frasquinho de cola de madeira, daí a cinco anos havia de aparecer alguma coisa. Já temos a ideia na cabeça. Por exemplo é evidente que a cera vai apanhar a porcaria (atmosférica) toda e na altura não havia verniz *à tableaux*; fui ao Dörner ver uma receita e fui a uma drogaria química e havia verniz *Dâmar* e *Mastique* (que depois não usei, era mais frágil), então fiz verniz *Dâmar* para dar nos quadros a cera e ficavam protegidos. Quando fazia as coisas de polivinilo misturadas com guache, aguarela ou pigmento, não podia dar o verniz *Dâmar*, primeiro porque era chato de preparar e não tinha muita confiança naquilo e como estava a pintar em papel não podia dar o verniz porque ficava com um aspecto engordurado. Então nessa altura comecei a dar cera de abelha dissolvida e diluída em aguarrás dava uma boa protecção e até se podia puxar o lustro. Houve uma altura que fiz uma exposição na galeria *Divulgação*, que hoje é a *Leitura*, e eles ficaram lá com uns quadros para ver se vendia, passados uns anos fui lá à procura e eles tinham deixado um quadro ao pé do exaustor, estava com uma cor totalmente diferente. Levei-o para casa e verifiquei que o lixo se tinha incrustado no acetato de polivinilo e no papel, estava tudo castanho e pensei que não podia ser assim; às vezes também dava uma camadinha de polivinilo sobre o papel para depois dar a cera, porque se não a cera manchava aquilo tudo, o que quer dizer que a cera não protegia e o polivinilo por si atraía as moléculas de sujidade todas. Daí para a frente é que passei a dar o polivinilo ou o acrílico a seguir e depois o verniz *à tableaux* quando passou a haver; assim se houver porcaria fica agarrada ao verniz, que não está directamente sobre o quadro, por cima do quadro está uma camada fininha de medium e por isso pode deitar o que quiser, *white spirit*, aguarrás, gasolina... que não acontece nada ao boneco.

L.P.: E compra sempre a mesma marca?

A.S.: Sim, já uso há muitos anos o verniz da *Talens*. Isso também foi influência do Quadros, ele pintava a óleo umas velaturas e usava *Talens*; na altura, havia poucos óleos e aqueles tinham uma paleta completa, havia sempre alguém que mandava vir. Mesmo assim, deixei de usar óleos há muitos anos (desde 1961).

L.P.: Houve uma altura em que passou a pintar a acrílico.

A.S.: Mas ainda houve outra coisa pelo meio. Como era pobrezinho e também por uns hábitos diferentes que tenho, talvez da formação científica liceal, já sabia como é que se fazia tetracromia ou tricromia e pensei que estava a ser burro, a comprar tantas cores, a comprar uns pigmentos foleiros e a misturar polivinilo com isto ou aquilo, se há pigmentos de *offset* que devem servir. Falei com um senhor que me arranjou uma lata de 1 Kg de cyan para *offset*, uma lata de magenta, uma lata de amarelo, uma lata de branco, uma lata preto e uma lata de *medium*; o preto usei muito pouco, ainda devo ter aí, o branco nunca usei. Comecei a pintar com aquilo porque tinha a vantagem de misturar, com gasolina que era mais barato; a terebentina era cara e tinha um cheiro horrível, a gasolina também, mas eu tinha um quarto ventilado; pintava com aquilo e vinte minutos depois estava seco, embora a espessura fosse maior que no caso do *offset*. Preparava umas cartolinas com tinta de parede *Robbialac*, não sei se já seria acrílica ou talvez fosse ainda polivinílica, tinta mate de parede e depois pintava com aquelas cores, amarelo, azul, magenta e de vez em quando punha um bocadinho de branco, mas depois deixei de dar porque demorava um bocadinho mais a secar e, de vez em quando, um bocadinho de preto. Assim num dia preparava umas dúzias de cartolinas que custavam 15 tostões cada uma, não era barato, era o preço de meio maço de cigarros. Fazia aquilo directamente no papel e depois mandava colar os que me interessavam, os outros deitava fora; nessa altura passei a trabalhar só com tintas de *offset*, cores primárias e isso durou muitos anos, só usava o polivinilo ou o acrílico para a base, durante talvez 6 ou 7 anos. De maneira que, quando usei a tinta de serigrafia para o tal quadro preto e branco, já sabia que aquilo funcionava. Durante muitos anos, naqueles quadros monocromáticos (com acrílico), usava só um vermelho da *Talens*, mas não havia e não há nem um que seja magenta e, os que são parecidos penso que são pouco resistentes à luz; às vezes interessava-me um vermelho de cádmio médio, outras vezes interessava-me vermelho de cádmio claro, geralmente usava azul de ftalocianina...

L.P.: Pigmentos em pó?

A.S.: Não, nessa altura eram os acrílicos da *Talens*. O amarelo que usava era o amarelo mais forte que eles tinham que era o amarelo de cádmio médio, como aquilo era muito diluído, muito disperso, tinha muito medium, muita água, ficava bastante transparente.

Portanto nos quadros chamados monocromáticos era só isso, amarelo, azul e vermelho, o mais primários possível. Entretanto ia fazendo outras coisas, também arranjei umas minas de lápis de aguarela de cores primárias, não sei de que marca eram, talvez uma marca suíça, talvez fossem *Caran d'Ache*; ou então comprava lápis, partia-os, tirava-lhe as minas que metia nas lapiseiras e levava-as comigo para todo o lado. Depois, aqui há uns 4 ou 5 anos disse para comigo 'mas isto é uma chatice, vou passar a usar acrílicos de todas as cores' e agora tenho para aí sessenta e tal cores diferentes, de diferentes marcas ali no atelier; é raríssimo usar os primários, a não ser para serigrafia, em algumas coisas feitas com lápis de aguarela ou com pastel de óleo, aí geralmente também uso as cores primárias. Agora uso tudo o que me dá na bolha!

L.P.: Mas voltando aos vinílicos. Disse-nos que quando começou a usar vinílicos preparava as tintas com o pigmento moído.

A.S.: Isso eram os tais pigmentos que a Tina Lima vendeu para aí em sessenta e um, ela depois foi para Inglaterra talvez em 64; eram pigmentos de muito boa qualidade que já não interessavam industrialmente, porque ninguém usava vermelho de cádmio que era caríssimo, punham vermelho de qualquer coisa para durar seis meses ou um ano; não usavam o amarelo Hansa é evidente, deitavam um amarelo de crómio ou qualquer coisa, também ninguém usava ftalocianina. De maneira que eram tudo cores boas, porque ninguém ia usar; propôs aos patrões e vendeu-nos 30/50 Kgs e depois foi tudo vendido em saquinhos, espero que ninguém tenha morrido a cheirar aquilo! Ainda tenho frasquinhos disso. Depois do 25 de Abril, quando as pessoas se queixavam imenso, a Escola arranjou duzentos contos e eu e outro colega descobrimos uns vendedores de pigmentos, tudo embalagens de 50 Kgs; fizemos uma lista para aí de dúzia e meia de cores, as que de facto são necessárias. Pusemos um gabinete lá na Escola com um empregado e uma balança, as pessoas chegavam lá e podiam comprar 50g. Mas pensam que resultou? Qual quê! Chegavam lá: 'Não tem o azul (não sei quê)? Não?!? Mas então, afinal não tem nada! Não tem aquele vermelho? Não?!? Não tem aquele verde (não sei quantos)? Não?!? Mas, isto afinal é uma porcaria!' E assim, ao fim de seis meses o homem disse 'estou aqui apanhar moscas, sou encarregado do Museu, tenho que limpar aquilo, tenho que arrumar aquilo, vamos liquidar esta porcaria'. E eu disse-lhe para fechar; eu não precisava de pigmentos, por acaso já não sei se na altura também comprei alguns. Eram pigmentos de boa qualidade que vinham directamente do importador, cada um vinha com uma tabela de reacções a isto e àquilo, alcalinos, sulfurosos. Na mesma altura, ou pouco depois, apareceu o tal rapaz, o Simões, o tal que era Eng.º químico e que era colega do rapaz que dava serigrafia, o Nuno Barreto, que no-lo apresentou: 'o meu amigo Simões, estivemos juntos em Lisboa, num lar universitário'. Com ele combinámos fabricar tintas acrílicas[7] para responder às exigências dos alunos; na altura as pessoas diziam 'isto é um roubo, somos pobres, os alunos perseguidos, os alunos são a classe operária', aquelas tretas, 'a Escola tem que dar tintas, a Escola tem que dar tintas!'. Fizemos uma paleta de 12 cores com médios e tudo, com pigmentos bons, pusemos aquilo à venda. Uma vez até fui a Lisboa, com o Nuno Barreto e com o Joaquim Simões, numa furgoneta da fábrica onde ele trabalhava, creio que era a CIN; fomos aos Coruchéus, preveni toda a gente, apareceram lá duas dúzias de artistas, com estas conversas:

- 'Só isto? Em boiões?! Eu só uso os da *Liquitex*! Estou à espera que me tragam um verde da *Liquitex*. Uma rapariga que é aero-moça quando vai lá traz-me.

- E vais estar três meses até a aero-moça trazer um verde?

- É assim, cá não há nada! Isto é uma porcaria, sei lá o que é isto!'

Custava cem escudos o boião, o *Liquitex* era 800 mas ninguém pegou naquelas tintas, e na Escola também não. Aqui há um tempo, 1 ano ou 2 antes de o Simões morrer, acabou por me oferecer uma caixa com as tintas que tinham sobrado.

L.P.: E essas tintas, de quando são?

A.S.: Talvez sejam de 1978, tenho uns quadros feitos com isso. Durante vários anos usei só as tintas do Simões. Ele arranjava-me um azul de ftalocianina, um vermelho misturado com um bocadinho de cor-de-rosa, que dava uma espécie de magenta, etc.

L.P.: Numa entrevista o Ângelo diz preferir os acrílicos aos vinílicos, ou mais correctamente, diz que usava o poli(acetato de vinilo) porque era a única coisa que havia.

A.S.: Não os posso comparar porque neste momento já não há vinílicos (julgo eu).

L.P.: Há.

A.S.: Não sei se há, mas não são anunciados como tal. Por exemplo eu estive na RDA, chamada Republica Democrática Alemã, em 81; numa rua perto do hotel vendiam materiais para artistas, tinham lá uma academia, e o que eles vendiam não eram acrílicos, eram tintas de polivinilo em tubo. A patente de lá era PVA, não era acrílico.

L.P.: O Ângelo não conhece a *Favrel*? São vinílicos.

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[7] Análises de infravermelho efectuadas mostraram que tintas produzidas pelo Engº Joaquim Simões eram vinílicas. Sobre esta questão Ângelo de Sousa afirma não se recordar se o Eng.º Simões se referia de facto a tintas acrílicas ou vinílicas.

A.S.: Conheço, mas nunca usei. Na altura a *Favrel* tinha uma fama desgraçada, eram umas cores para os meninos de escola pintarem. Houve uma altura em que tive medo que me faltasse, antes de aparecer o Simões, e mandei vir uma data de pacotes de pigmentos desses da Varela, paguei uma fortuna.

L.P.: E o ligante deles, o V7, nunca usou?

A.S.: Não, não me dava jeito ir a Lisboa comprar isso. Ir a Lisboa era uma aventura, era uma viagem da meia-noite às 7 da manhã.

Isto foi o meu percurso em termos tecnológicos. Além disso também usei acrílicos em escultura, para aí em 64; depois passei para o metal que era todo pintado por mim.

L.P.: Também pintava os acrílicos, ou usava exclusivamente a cor do *plexiglas*?

A.S.: O vidro acrílico, foi adquirido numa loja, de um senhor que ia ao Magestic, que se dava com um rapaz arquitecto do meu tempo e com uma rapariga escultora que era minha colega. E um dia diz: 'Tu sabes que um tal tem uma loja ali perto do Liceu Carolina Michaelis, que vende placas de acrílico.'

L.P.: Isso quando?

A.S.: 64 ou 65, provavelmente em 65. Aquilo era usado por exemplo por fabricantes de botões para fazer botões de fantasia com cores. Comprámos algumas placas e fizemos umas esculturas. Na altura não havia secadores de cabelo, de maneira que eu usava umas luvas e usava uns aquecedores que se costuma dizer que são de quartzo, têm um tubo de quartzo com uma resistência lá dentro; a resistência fica incandescente e aquecia a placa, cortava e dobrava assim. Depois deixei-me disso porque aquilo partia-se constantemente e comecei a fazer em ferro; o ferro era muito barato, simplesmente o ferro enferruja e não tem resistência mecânica nenhuma.

L.P.: Não fazia nenhum polimento à zona onde recortava?

A.S.: Limava. Para pintar as esculturas de ferro usava o que se chamava subcapa, que eram esmaltes baços.

L.P.: Sabe onde é que os acrílicos eram feitos? Tinham algumas amostras?

A.S.: Não, chegávamos lá e comprávamos o que havia e ninguém sabia onde é que aquilo era feito, não faço ideia. Mas há pouco tempo tinha aí uma escultura que se partiu e pensei em tornar a fazê-la, era uma escultura porreira, e fui a uma loja ali no Largo do Camarão, que fica mesmo ao pé da Escola e que antigamente era o atelier do Lagoa Henriques e do Carlos Amado e estava lá a loja de plásticos equivalente a essa; foi caríssimo, meia dúzia de placas e gastei trinta contos.

L.P.: E eram parecidas?

A.S.: Eram. Uma delas era exactamente igual, vermelho e prateado de fantasia.

L.P.: E das suas antigas?

A.S.: Ainda tenho aí algumas.

A primeira vez que fui a Paris, em 57, fui ao *Sennelier*, que era o paraíso, e queria comprar uns pastéis, tinha comprado uns pastéis de uma marca alemã, uma marca que também tinha tintas, eram umas cores muito vivas, se calhar ainda tenho essa caixinha em qualquer lado, eu não sou muito gastador. E então pensei 'vou comprar uma *Flo-master* (que era um marcador inglês com uma tinta que resistia à luz e que tinha pigmento além de ter corante, como se podia verificar com o passar dos meses) e uma caixinha de pastéis'. O senhor da loja perguntou-me 'o que quer, paisagem ou figura?'. Pensei, 'paisagem, devem ser uns verdes porreiros', mas acabei por levar para 'figura'. Ainda hoje estou arrependido, nunca consegui usar aquilo, são umas cores tão feias, tão 'pastel'! Eu tentei insistentemente, mas é um cor-de-rosa desgraçado! Já tentei nos últimos meses, num desenho que tenho estado a fazer: 'vou usar um bocadinho deste cor-de-rosa horrível'. Depois partem-se, não têm cola nenhuma, pega-se e parte-se na mão; depois pega-se noutro, um castanho: 'que castanho tão feio', parte-se.

VI.2 Second interview with Ângelo de Sousa

With Ângelo de Sousa, Joana Lia Ferreira and María Jesús Ávila

Lisbon, June 5th 2008

With the previous interview as a start point, as well as our knowledge about Ângelo's work and also with what some art historians and critics have said about it, we outlined several questions aiming to understand the possible relations between the technical issues raised by the use of certain materials in period of his work and the merely aesthetic aims.

Ligações Perigosas**:** Começando pelo início. E o início, se deixarmos de lado experiências escolares e algum exemplo disperso de óleo sobre tela (como aquele que abre o catálogo [23] da sua retrospectiva), é a encáustica sobre platex ou aglomerado de madeira que utiliza entre 1958/9 e 1960/1. Como o próprio Ângelo explicou, era uma técnica muito trabalhosa, muito suja e lenta. Porque partiu já em 58/9 para esta técnica? Quais as vantagens e como se adaptou àquilo que era o seu projecto artístico neste momento?

Ângelo de Sousa: Eu sempre tive tendência para planificar umas actividades. Fica tudo estudado, os problemas todos e depois em geral desinteresso-me. Naquele caso não me desinteressei logo e que acabei por fazer.

L.P.: Foi um interesse por experimentar a técnica?

A.S.: Não, não sei. Lembro-me de ter visto no Louvre as pinturas do delta do Nilo, com figuras cristãs e não cristãs, do fim do primeiro milénio antes de Cristo e do início do primeiro milénio, e achei graça. Havia uma questão que me aborrecia, o óleo tinha irregularidades a secar; era facílimo comprar, mas sabia que demorava muitos dias a secar e a cera endurecia logo. O óleo aborrecia-me… também não gostava do cheiro. De modo que resolvi experimentar, com um certo optimismo, creio que foi isso, se tivesse percebido que as possibilidades técnicas eram tão reduzidas, talvez não tivesse avançado. Tive a ilusão de que estava a ver os problemas todos. E um problema, por exemplo, era não haver cores estáveis para misturar na cera; não podia ir a uma loja como se fosse em Paris e pedir 50 gramas de qualquer cor. Só havia algumas cores para pintar paredes, para misturar com cal; não tinham aproveitamento possível (algumas talvez resultassem). Não tenho nada com cores vivas nessas obras. Em alguns casos tinha qualquer coisa pintada por baixo, creio que com caseína, ou alguma coisa desse género, de forma que se via uma cor. À partida não havia nada a fazer; a não ser óxidos de ferro, preto, algumas coisas tiradas do chão, a paleta era mesmo reduzida. Também podia jogar com a relativa transparência, translucidez ou opacidade da cera, dependendo da forma como era aplicada.

L.P.: Em termos plásticos seria um dos principais atractivos.

A.S.: Se fosse um determinado branco era translúcido, se fosse outro branco era opaco... e às vezes até aplicava a cera sem nada. Habituei-me a explorar essas coisas.

L.P.: O endurecimento era rápido, o processo é que era demorado.

A.S.: Exactamente.

L.P.: O Ângelo disse numa entrevista [121], em relação aos expressionistas, que lhe interessavam mais os austríacos do que os alemães, que parecia estarem apenas interessados em pôr fora as mágoas e que não tinham prazer na questão pictórica. Também disse nunca estar interessado em crises histéricas, que gosta de ver as coisas acontecer enquanto está a trabalhar, mas isso implica uma margem de espontaneidade, que com a cera de abelha é difícil. Referiu que esteve um mês e meio a trabalhar numa obra que fez em Ponte de Lima.

A.S.: Sim, demorava muito tempo a fazer, um ou dois meses, trabalhava em dois ou três quadros ao mesmo tempo. Eram coisas muito vagarosas.

L.P.: Existia um plano inicial? Como é que se pode conciliar esse ‘acontecer’ com um processo tão demorado?

A.S.: Não, não havia plano, as coisas apareciam. Por exemplo, nesta obra (Figure VI.1), a superfície é lisa porque foi esculpida com uma goiva de gravura; estava muito irregular e como não queria que ficasse assim, ia desbastando, ficavam algumas fendas e vê-se a cor diferente. Isto demorou várias tardes com muita paciência, quando estava aborrecido pegava noutro trabalho. Em contrapartida, havia pormenores muito rápidos. Grande parte deste trabalho era uma aventura, não tinha plano.

L.P.: Ou seja, era o que estava a acontecer, o resultado de cada fase do trabalho, que ia provocando as intervenções seguintes.

A.S.: Em certa medida sim. Esta paisagem (Figure VI.2) acho que foi relativamente simples porque à partida já tinha um desenho e não tem muita invenção; excepto ter sido pensado na vertical, era uma árvore, mas depois pensei que deitado ficava muito melhor e pintei esta zona mais pesada em baixo para ‘pousar’ o quadro. Para o outro nem sei se tinha desenho, talvez um esboço simples, não me lembro de onde veio o verde da bola. Era verde por baixo, talvez fosse têmpera, se eu o visse era capaz de perceber. Há quase sempre coisas que vão acontecendo. Na Paisagem nem por isso, mas no outro quadro aconteceram coisas do ‘arco-da-velha’ enquanto pintava.

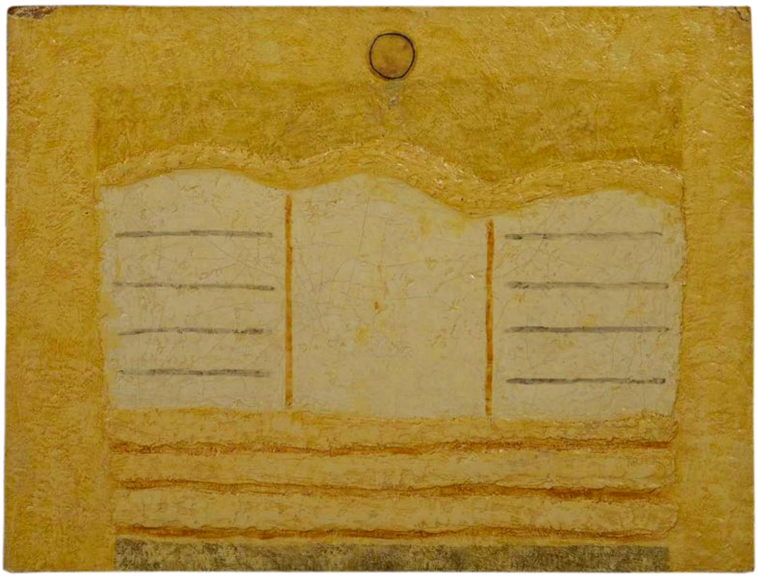

Figure VI.1. (Cat. 4.) *Paisagem com bola azul*, 1959. Wax on hardboard, 45 x 60 cm. TEMM collection, Porto. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Figure VI.2. (Cat. 3.) *Paisagem*, 1959. Wax on hardboard, 29.5 x 40.5 cm. Author’s collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: O Ângelo disse na altura em que deu aquela entrevista, 'tenho meios para fazer outras coisas, já não vou voltar a pintar com cera'.

A.S.: Ceras fiz talvez 12 ou 13.

L.P.: Mas havia alguma coisa, talvez a textura, que o atraía. Quando utilizou os vinílicos, misturou a tinta com papel desfeito para ficar com a mesma textura.

A.S.: Era um papel que os arquitectos usavam para fazer esboços, 'papel cebola'. Uma espécie de papel de arquitecto mas baratinho, servia também para embrulhar bolos, era uma espécie de papel vegetal, que eu usava para fazer esquissos. Esta pintura tem relevo (Figure VI.3), que provavelmente foi feito com gesso e um bocado de branco; se fosse cortado parecia um quadro de cera, tem uma altura considerável. Os ramos foram colados primeiro, foi feito com polivinilo mas com umas aguadas ainda a imitar o óleo.

L.P.: Embora estivesse a usar o polivinilo, a textura deste material naquele momento não lhe interessava. Interessava-lhe mais a textura do óleo, a da cera...

A.S.: Não. Ainda fiz mais um ou dois quadros, em que tentei com polivinilo e com branco jogar dentro do branco só com relevos e fazer aquele efeito de ser translúcido ou opaco, de que falei em relação à cera. Por exemplo, aqui (Figure VI.3) podia ter sido pintado de branco e depois riscado, mas foi com muita paciência, com uma espátula. Era uma coisa imensamente trabalhosa porque isto, apesar de tudo, ainda era para imitar as coisas de cera. No fundo era uma solução exactamente igual à da cera. Até as cores são parecidas com as da cera. Fiz mais dois ou três e depois achei que chegava. Estive em Moçambique três meses no Outono de 60; até ali eu pensava que a questão das cores era muito complicada. Inicialmente estava a evitar o problema com a pintura a cera. Em Lourenço Marques comprei

Figure VI.3. (Cat. 15.) *Plantas*, 1961/62. Poly(vinyl acetate) on hardboard, 70 x 50 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Figure VI.4. (Cat. 9.) *Fonte*, 1960. Oil on plywood, 76 x 45 cm. *Museu Municipal Amadeo de Souza-Cardoso*, Amarante. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

uns óleos, comprei papel e alguém me ofereceu um bocado de contraplacado muito bom, que foi pintado a óleo enquanto lá estive. Na mesma altura estava a pintar um quadro (Figure VI.4) à primitivo, tem um violeta por baixo e depois ia pondo branco, no fundo não é muito diferente. Foi tudo esbranquiçado. A lista era violeta, que é uma cor que eu não gosto, e tinha um azul bastante vivo. À partida eram umas cores muito giras mas não jogavam bem, de forma que eu ia manchando com branco. Com o papel cavalinho estava à vontade, se tivesse vinte folhas e estragasse quinze, talvez aproveitasse cinco. Enquanto que aquele contraplacado era uma placa que eu tinha preparado com muito trabalho, por isso era uma responsabilidade, era um ‘investimento’ enorme. Fiz umas coisas que não têm importância nenhuma mas que, de repente, me fizeram perceber como tudo funciona. Depois desatei a trabalhar; estes são óleo sobre papel (Figure VI.5), não têm gordura, estão óptimo. E então disse ‘acabou, já não tenho medo’. Já tinha 22 anos.

L.P.: É curioso. Primeiro com cera de abelha, depois passa para o óleo mas, já nesta fase inicial, surge um esquema de composição muito particular durante algum tempo no seu trabalho: um elemento central, as barras laterais e depois é muito frequente a fragmentação em faixas horizontais progressivas. E depois passa a utilizar o mesmo tipo de esquema com o PVA e com as tintas de *offset*.

A.S.: Sim. É feito mais tarde mas é, em certa medida, um *remake* daquelas coisas iniciais. Na altura estava a pensar tentar com o polivinilo fazer como as coisas de cera, porque apesar de tudo eu tinha alguma pena de ter abandonado.

Figure VI.5. (Cat. 11.) *6 espectadores*, 1961. Oil on paperboard glued on hardboard, 50 x 65 cm. Author's collection; (Cat. 12.) *Plantas*, 1961. Oil on paper glued on hardboard, 65 x 50. Private collection, Matosinhos; (Cat. 13.) *Plantas*, 1961. Oil on paper glued on hardboard, 50 x 35 cm. José Mário Brandão's collection; (Cat. 14.) *Plantas*, 1961. Oil on paper glued on hardboard, 56 x 45 cm. João Perry collection. Photos: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: É interessante. São várias séries, a das fontes, a das árvores, a das plantas; o esquema é o mesmo, portanto, o motivo em si é quase uma desculpa, um pretexto para experimentar e depois vai passando por diferentes materiais. Que diferenças encontra dentro destes mesmos esquemas em função do uso de um material ou outro?

A.S.: Eu andava à procura de alguma coisa que fosse relativamente barata e com qualidade. Nestes quadros (Figure VI.6) eram tubos de guache ou aguarela que ainda apareciam misturados com o PVA, são lisos. Este (Figure II.3) tinha uma matéria qualquer, talvez fosse gesso ou um bocado de branco de chumbo misturado com o PVA; tinha relevo, era branco e depois é que foi colorido de verde.

Figure VI.6. (Cat. 17.) *Plantas*, 1962. Poly(vinyl acetate) on paper glued on hardboard, 65 x 50 cm. Author’s collection. (Cat. 18.) *Plantas*, 1962. Poly(vinyl acetate) on paper glued on hardboard, 65 x 50 cm. Author’s collection. (Cat. 19.) *Flor que ri*, 1962. Poly(vinyl acetate) on chipboard, 90 x 49 cm. Author’s collection. Photos: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Estes (Figure VI.7) não, eram uns restos de tinta que lá estavam, que fui tirando com um bocadinho de água morna de um vidro que usava para misturar a tinta, depois colei e pintei o fundo de branco. Isto (Figure VI.8) também é uma volta atrás, porque foi pintado de branco e depois dei uma aguada de vermelho, no fundo como quem está a pintar a óleo à moda antiga. E depois eu estava sempre com a ideia de que queria alguma coisa para trabalhar depressa e não muito caro, que pudesse usar à vontade, como tinha feito com o papel: se tiver muitos papéis funciona. A ideia, neste caso, era ter a mesma abundância e à-vontade com o material de pintar. Primeiro o polivinilo e depois a ideia de usar as tintas de *offset*. Tinha quatro latas; o preto, que eu usava, as três primárias e branco. Mas tenho impressão que nem cheguei a abrir a lata branca. E havia mais uma espécie de verniz para dar transparência que também não cheguei a usar muito. Tinha papel que podia gastar com toda a irresponsabilidade e tinha uma tinta que era só tirar uma colher da lata, e era barata relativamente às outras tintas.

Figure VI.7. (Cat. 25.) *Plantas*, 1964. Collage and poly(vinyl acetate) on chipboard, 40 x 30,5 cm. Private collection, Porto; (Cat. 26.) *Flores*, 1964. Collage and poly(vinyl acetate) on chipboard, 40 x 31,5 cm. António da Rocha Melo collection, Porto. Photos: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: A escolha foi determinada por essas razões. Mas uma vez que começa a utilizá-los, há alguma coisa nesses materiais que determine uma mudança em termos puramente plásticos e que faça mudar ou adaptar o seu trabalho a outras coisas?

A.S.: Sim, tenho pinturas feitas com tinta à moda antiga.

L.P.: A tinta de *offset* fica com uma textura próxima da aguarela, fica mais diluída. O seu trabalho ao longo destas séries é cada vez mais subtractivo, cada vez reduz mais os elementos formais, cada vez simplifica mais as composições. Mas, por exemplo com o polivinilo, adensa mais a matéria.

A.S.: Sim, naturalmente. Seca bem, faz matéria, não tem fissuras, não tem problemas. Se eu fosse pintar a óleo demorava muito tempo e depois estalava. Cheguei a tentar criar espessura com as tintas de *offset* mas não dá, não seca bem. Nem tentei a sério, não há nada feito com espessura. Habituei-me a puxar a tinta e ficar por aqui.

Figure VI.8. (Cat. 21.) *Grande Árvore*, 1962. Poly(vinyl acetate) on hardboard, 100 x 70 cm. private collection, Porto. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: O material que utiliza, seja *offset*, seja o polivinilo, condiciona os resultados do seu trabalho.

A.S.: Sim, claro. Esta obra (Figure VI.9) (polivinilo) tem altos e baixos, com uns cordões submersos por baixo desse preto, porque a tinta naturalmente ficava lá, depois secava, ficava dura e com relevo. O que não acontece nas obras a tinta de *offset*, simplesmente porque não podia ser.

L.P.: E em termos estéticos, nesta fase, qual era a sua preocupação?
A.S.: Já que tinha aquelas quatro cores queria aproveitar toda a gama.

L.P.: O seu trabalho é muito experimental, muito sobre a própria matéria, sobre a própria pintura.

A.S.: Por exemplo aqui (Figure VII.9), como é de polivinilo, há uns altos e baixos, provavelmente é gesso ou branco dado com uma espátula ou com um pincel muito grosso. Neste não (Figure VI.10), isto é *offset*, portanto tem que ficar magrinho, fininho, mesmo fino fica uma coisa berrante, de forma que não vale a pena estar a fazer mais.

Figure VI.9. (Cat. 23.) *Pintura*, 1963/64. Poly(vinyl acetate) on hardboard and collage, 125 x 85 cm. Private collection, Porto. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

Figure VI.10. (Cat. 34.) *Plantas*, 1965. Offset ink on treated paperboard glued on hardboard, 100 x 70 cm. Isabel Maria Abrunhosa de Brito, Porto. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: Quando começava uma série e pensava trabalhar sobre determinado aspecto em polivinilo, o seu projecto mental antes de começar moldava-se em função deste material?

A.S.: Isso era natural. Normalmente eu não tinha desenho prévio para trabalhos em *offset*, não fazia ideia do que ia sair.

L.P.: Mas nos trabalhos de polivinilo sim?

A.S.: Às vezes, porque depois dava para voltar atrás, experimentar. Agora com tintas de *offset*, ou acertava em meia hora ou numa hora, ou então ia para o lixo. Tinha muitas folhas destas preparadas e gastava muitas, rasgava algumas. Mas acontecia assim, não tinha nada pensado. Este (Figure VI.11) ia ser uma paisagem, dei-lhe a volta e ficou uma mulher, parece a República Francesa, com esta coisa na cabeça. Achei engraçado, 'a liberdade conduzindo o povo'! Mas à partida não fazia ideia o que era. Isto (Figure VI.12.) já foi feito como se fosse a óleo, com muitas camadas; depois é colado em cima de um platex grande, mas era uma folha de papel que foi feita com tinta de *offset* e depois é que resolvi, achei muito pequenino e tinha esta prancheta, que era grande e pensei colar com jeitinho e o homem lá colou e eu pintei de branco à volta.

Figure VI.11. (Cat. 51.) *Cabeça*, 1965. Offset ink on treated paperboard, 100 x 70 cm. Maria Nobre Franco collection, Porto. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

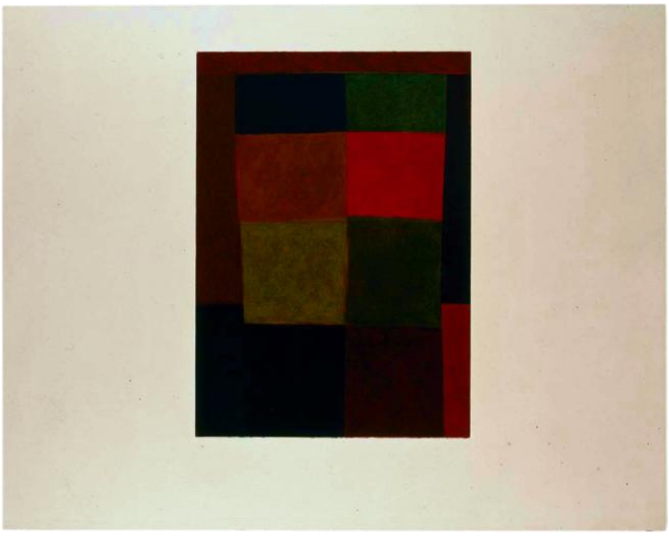

Figure VI.12. (Cat. 53.) *Janela*, 1965/67. Offset ink on treated paperboard glued on hardboard, 137 x 170 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: O Ângelo faz muito isso. Utiliza uma técnica para imitar os efeitos matéricos, texturais de outra técnica.

A.S.: Isto (Figure VI.12.) foi pintado à quadro holandês, com uma série de camadas. Demorou imenso tempo, devo ter andado meses com isso pendurado na parede enquanto ia fazendo outras coisas. Dava umas pinceladas de vermelho e depois estava um mês sem olhar para aquilo e fui pondo mais camadas. Como ficou tão sombrio, achei que a única maneira era pôr em cima de um painel branco.

L.P.: Na primeira entrevista, o Ângelo disse que tinha visto pela primeira vez o polivinilo numa obra do Sidney Noland, tinha visto uma reprodução…

A.S.: Sim, a preto e branco, na *Studio*, que era uma revista com tudo a preto e branco e a capa era verde. É uma revista muito antiga. Achei graça e nunca mais me esqueci do polivinilo, já sabia que servia para fazer tinta e andei à procura.

L.P.: O que lhe chamou a atenção nessa obra? Foi alguma coisa em termos de textura?

A.S.: Não. Não se via nada, aquilo era uma reprodução pequena a preto e branco. O que me interessou foi ver que não pintavam só a óleo, que era caro, aborrecido, mal cheiroso, demorava…

L.P.: O polivinilo tinha algumas vantagens. Económicas, disponibilidade. Mas também disse que era um meio mais transparente.

A.S.: No caso do polivinilo pode fazer-se o que se quiser, enquanto no caso do óleo ficamos cativos. Se aquilo é opaco, o que é que faço? Vou pôr-lhe verniz? Como às vezes as pessoas faziam, e depois não ficava transparente nem opaco. Nunca usei verniz para pintar a óleo, eventualmente deitava um bocado de aguarrás para ficar mais fino. Mas no caso do polivinilo podia fazer-se praticamente tudo, sem que o material se queixasse. Claro que não se pode agarrar numa coisa e esperar que por usar polivinilo fique transparente; não fica, mas vê-se 'através de'. Se for a óleo, só com muito verniz e depois nunca mais seca ou estala. Com o polivinilo era a impunidade total. Ninguém me castigava, não havia maus resultados. Dava uma sensação de bem-estar formidável. E não estava à espera que secasse e à espera que estivesse disponível na loja. Interessava-me ter uma certa independência, autonomia e não estar dependente da alfândega, do homem que vendia as tintas… A vida já é tão complicada, pelo menos nisso tentava simplificar ao máximo. Ainda hoje isso interessa-me muito.

L.P.: Em temos de suportes, muitas vezes utiliza papel que depois cola sobre platex ou sobre contraplacado. Independentemente de utilizar sobre o papel óleo, PVA, acrílico ou cera, quando utiliza papel parece que assume mais uma das características que esteticamente melhor marca o seu trabalho, que é a natureza de desenho que a sua pintura adquire. Isto é condicionado pelo suporte? Este aspecto mais branco, mais gráfico, acentua-se quando o suporte é papel. Há alguma relação directa?

A.S.: Não. Repare, de uma forma ou de outra isto vai parar também ao branco. Por exemplo, depois há uma recaída (Figure VI.13), isto era juta de fazer cortinas baratas, é um tecido grosso de uma fibra vegetal qualquer, e que foi preparada com polivinilo e esteve para lá abandonada durante anos, porque acabei por não a usar de imediato. Nessa altura eu andava a fazer desenhos.

L.P.: De algum modo, esta é precedida pelas experiências de desenho.

A.S.: Estas coisas eu já tinha feito… alguns motivos foram pintados com *offset*, tintas para serigrafia, outros com polivinilo e mesmo com um lápis de pastel d'óleo… e depois foi fixado. De maneira que voltamos no fim a ter outra vez branco opaco e um branco muito transparente ou translúcido, um certo tipo de matéria no branco que durante muito tempo não me interessou. Foi só para esta obra, porque estava lá e de vez em quando acrescentava um bocado de tinta, depois estava semanas sem fazer nada ou então estava uma tarde inteira a pintar isto de branco ou a fazer gatafunhos e depois ia fazendo outras coisas. Quando demora, normalmente há uma tendência para ir acrescentando e tirando coisas. Enquanto nos outros ou acerto ou não acerto, faz-se um intervalo e depois faz-se outro, numa tarde ou num dia faz-se uma série deles. Pelo meio, estes coitados vão estando, até que um dia: 'já chega'.

Figure VI.13. (Cat. 94.) *Catálogo de algumas formas ao alcance de todas as mãos*, 1970/71. Mixed media on white canvas, 150 x 121 cm. Manuel de Brito/*Galeria 111* collection, Lisbon. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: No conjunto de desenhos que fez nesta altura, é quase um experimentar de formas primordiais das obras anteriores: as espirais, as fontes, as plantas…

A.S.: Sim e este (Figure VI.13) é um catálogo de coisinhas. E depois tem uma série de nomes escritos. Nessa altura, na minha ingenuidade, estava com a mania das pontes; devia estar no café e comecei a escrever as coisas que já tinha feito: pontes e outras formas, eram talvez umas sete ou oito ou mesmo uma dúzia. Depois fui escrevendo outras coisas que me ocorriam, penso que não se consegue ler, e às tantas tinha: cruz, cavalo… uma série de substantivos concretos. Porque não me apetecia fazer nada naquele momento e pensei tentar o truque de encontrar um tema. Por exemplo: cruzamento; depois pode fazer-se coisas com cruzes, estradas a cruzar, etc. Às tantas já tinha 30 e tal, e estão aqui mais de 30 substantivos concretos, e guardei o papel. Passado muito tempo, já estava no fim e creio que foi a última coisa que pintei neste trabalho, lembrei-me da lista e decidi copiar os nomes da lista. Passei polivinilo, ficou fixado e acabou. Mas nessa altura eu estava tão desesperado que pensava fazer cavalos, ou cães, ou gatos, papagaios, árvores, coisas concretas, podia ter continuado ou ia a um dicionário e era capaz de ter sido mais simples! Mas também me interessava ver o que me ocorria, é uma questão de associação. Não iria certamente ocorrer-me pintar sobre futebol ou guindastes. Depois acabavam por ser trabalhosos, ter texturas e ter os tais branquinhos… Há uma parte que foi feita com uma esferográfica daquelas que tinham 12 cores, que a minha mãe achou muita graça e comprou no supermercado.

L.P.: Este projecto surge primeiro sobre papel, com lápis de cera, pastel de óleo, com técnicas de desenho. Antes disto a sua obra torna-se um pouco mais abstracta. Aqui há uma intenção de reproduzir um gesto, formas essenciais do processo da escrita, do traço.

A.S.: Sem dúvida.

L.P.: Esta sua obra é muito trabalhada.

A.S.: Estava sempre a ver se havia mais coisinhas, mais motivos destes que eu pudesse usar. E acabei por fazer motivos que não existiam, há um ou dois aqui que eu nunca tinha feito; ou que tinha feito mas de outra maneira. Chegou uma altura que queria encher isto tudo mas já não tinha mais motivos e comecei a acrescentar outras coisas, por exemplo um resto de branco…

L.P.: Mas sempre mantendo muito branco de fundo para manter o natureza de desenho.

A.S.: Sim, era um bocado.

L.P.: Procurou essa ideia de folha branca?

A.S.: Interessava-me que ficasse branco, claro. Tem o fundo branco e só podia funcionar com o fundo branco. Mas era uma coisa muito morosa. Acho que demorou mais de um ano, estava sempre à espera que aparecesse mais qualquer coisa e chegou uma altura em que já não conseguia fazer mais nada. Depois ia haver a exposição no Brito, na galeria 111, ao pé do Palácio Cristal, e pensei que tinha que acabar porque precisava de um quadro grande para lá. E lembrei-me da lista e acrescentei; 'acabou, fica vazio, não ponho mais nada, até fica melhor assim'.

L.P.: Antes desta série de trabalhos fez estes outros (Figure VI.14).

A.S.: Isso foi antes de ir para Inglaterra.

L.P.: Pode dizer-se que de alguma forma é a primeira vez que assume o polivinilo, sem imitar outras texturas?

A.S.: Sim, isso era mesmo uma espécie de esmalte. Era polivinilo misturado com aguarela ou com guache, normalmente era guache. Era mesmo só isso, não estava a fazer texturas.

L.P.: Digamos que esta série abstracta é muito mais rigorosa…

A.S.: Era quase pintura industrial, já tinha feito as esculturas. E depois fiz este (Figure VI.14., Cat. 71.) porque tinha uma prancheta deste tamanho, fiz mais um que tenho lá em casa e outro que não sei onde está e os pequeninos, fiz tamanhos pequenos porque não tinha pranchetas nem tempo. Estas obras (Figure VI.14., Cat. 77/78.) foram feitas em papel colado, papel de máquina que eu usava para desenhar. Primeiro cortei as fitas de papel.

L.P.: As colagens que aparecem em algumas fichas, são colagem de papel pintado de branco?

A.S.: Em alguns casos sim. Mas nestes trabalhos já não, é mesmo o platex pintado de branco. Aqui (Figure VI.14., Cat. 75/76.) são bolinhas das máquinas de furar papel.

L.P.: É papel pintado onde depois faz os furinhos?

A.S.: Sim, pintei umas folhas e depois furei. Se eu tivesse telas e tempo teria feito em enorme. Não havia telas, tinha que ser em platex. Pesa vinte e tal quilos (Figure VI.14., Cat. 72.), porque tem uma armação atrás, está óptimo, nunca estalou, é madeira seca.

Figure VI.14. (Cat. 71.) *Geométrico Grande*, 1967. Poly(vinyl acetate) on hardboard, 170 x 138 cm. *Caixa Geral de Depósitos* collection, Lisbon; (Cat. 72.) *Sem título*, 1967. Poly(vinyl acetate) on hardboard, 170 x 120 cm. Author's collection; (Cat. 74.) *Pintura*, 1967. Poly(vinyl acetate) and watercolour pencil on canvas, 42 x 29 cm. Author's collection; (Cat. 75.) *Pintura*, 1967. Poly(vinyl acetate) on canvas and collage, 42 x 32 cm. Author's collection; (Cat. 76.) *Pintura*, 1967. Poly(vinyl acetate) on canvas and collage, 42 x 32 cm. Author's collection; (Cat. 77.) *Pintura*, 1967. Poly(vinyl acetate) on canvas and collage, 45 x 38 cm. Author's collection; (Cat. 78.) *Pintura*, 1967. Poly(vinyl acetate) on canvas and collage, 42 x 32 cm. Author's collection. Photos: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: Aqui (Figure VI.14., Cat. 77/78.) o fundo também é polivinilo? O papel é pintado com polivinilo e depois colado…

A.S.: Sim, são coisas pequeninas. Eram uns painéis de aglomerado e depois tinham um pano esticado por cima. Isto foi feito em 67, antes de ir para Inglaterra. Até à primeira metade do ano fiz estes quadros grandes (Figure VI.14., Cat. 71/72) e muitos pequenos, uma dúzia ou mais. Ou eram muito pequeninos ou muito grandes, um tamanho intermédio não me interessava. Ou é pequenino e funciona ou é grande e funciona, um metro já não resultava.

L.P.: Estes trabalhos (Figure VI.14., Cat. 77/78.) tinham algum esquema prévio?

A.S.: Não. Quero dizer, fazia as formas, depois cortava com uma navalha, numerava por trás e depois misturava todas e pintava com cores vivas. Eu não sabia onde é que ia parar. Estava tudo misturado e, por exemplo, punha um verde e depois tinha que encontrar uma ordem… 1, 2, 3 ou a, b, c. Era o destino deles.

L.P.: Mas obras de composição como esta (Figure VI.14., Cat. 71), por exemplo, já tinham um esquema?

A.S.: Não. Comecei num certo ponto e desenvolvia a partir daí, depois passava para outro ponto porque trabalhar sempre a mesma área era aborrecido e às tantas tinham que se encontrar, tinha que encontrar soluções.

L.P.: Portanto, uma obra supostamente muito racional, muito geométrica, ia acontecendo…

A.S.: Exactamente. Era para partir de um ponto, não sei de onde, sei que não foi do bico. Mas achei que nunca mais acabava se fosse crescendo… e decidi começar em mais pontos. Às tantas tinha várias zonas começadas. E depois tinha que arranjar um triângulo ou outra forma, tinha que encontrar uma solução. Um bocado como um jogo de paciência. Tinha regras, mas dentro das regras tentava tornar o processo mais rápido e mais eficiente. Era divertido.

L.P.: Curioso! Estes trabalhos são antes de ir para Londres[8], já tinha começado a escultura.

A.S.: As esculturas estavam todas feitas. Depois quando vim de lá só fiz aqueles trabalhos de fitas. É por isso que eu digo que isto já tem a ver com as obras das fitas. Quando fui para

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[8] Setembro de 1967 a Junho de 1968. Bolseiro do *British Council* na *St. Martins School of Fine Art.* Neste período trabalhou durante cerca de um mês na *Slade School of Art*.

Londres tencionava fazer esculturas de fitas. Até levei um bocadinho de aço e andámos à procura daquele material e ninguém sabia o que era. Não havia, não consegui comprar.

L.P.: Há uma clara relação entre o seu trabalho no campo da escultura e da pintura. Como se relacionam? Por exemplo, a escultura aqui (Figure VI.15.) tem um carácter geométrico mas orgânico ao mesmo tempo. Também elas são feitas, digamos, um bocado ao acaso? Vão surgindo ou existe um desenho prévio do trabalho?

A.S.: Por exemplo esta (Figure VI.15., Cat. 64.), era uma chapa grande e muito comprida. Tracei uma risca a meio, e depois dividia, por exemplo em segmentos de 10 cm, e cortava com comprimentos diferentes, o que permitia manobrar as orientações. Se a ponta fosse para lá dobrava de uma maneira, se ficasse para cá dobrava de outra. Havia um jogo que eu já sabia no que dava.

L.P.: E o material com que pintava…

A.S.: Isso é tinta industrial, é um esmalte para pintar portas. Pintava depois de estar tudo cortado, porque senão a tinta estalava. Era muito trabalhoso, dar as voltas todas para conseguir pintar.

L.P.: Na escultura o Ângelo também não usou materiais nobres. Sempre foi utilizando materiais que ia encontrando e com os quais ia trabalhando… com a curiosidade de experimentação.

A.S.: Barro não gostava, colava-se às mãos. Eu sempre tive as mãos secas e a certa altura parecia que ficava com as mãos mumificadas. Também gosto de trabalhar com gesso, mas fica tudo sujo e eu não podia trabalhar com gesso no quarto onde vivia, o senhorio não gostava. Ainda tentei, cheguei a fazer umas coisas em gesso (por acaso não estiveram nesta exposição). Primeiro fiz uns trabalhos em plástico, com chapas de acrílico, mas isso era caro, custava 25 escudos cada folha (tínhamos que ir de automóvel lá acima ao pé do liceu). Eu dava aulas de gravura e tinha que comprar chapas, havia uma loja onde se comprava as chapas para os alunos, de modo que comprei umas chapas de alumínio para eles fazerem ponta seca e pensei ensaiar com aquele material, que era menos provável. De maneira que comecei a fazer coisas em alumínio. Pelo meio aconteceram coisas que não tinham como vocação o alumínio, eu não ia deitá-las fora. O acrílico (Figure VI.16) é aquecido e depois dobrado, ficou assim como podia ter ficado com outra forma.

Figure VI.15. (Cat. 64.) *Escultura*, 1966. Iron, 50 x 90 x 60 cm. Author's collection; (Cat. 65.) *Escultura*, 1966. Steel, 35 x 43 x 26 cm. Author's collection; (Cat. 66.) *Escultura*, 1966. Steel, 36 x 67 x 31 cm. Author's collection; (Cat. 67.) *Escultura*, 1966. Aluminium, 21.5 x 71 x 42 cm. Author's collection; (Cat. 68.) *Escultura*, 1966. Steel, 41 x 80 x 44 cm. Author's collection. (Cat. 70.) *Escultura*, 1966. Iron, 35 x 90 x 100 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

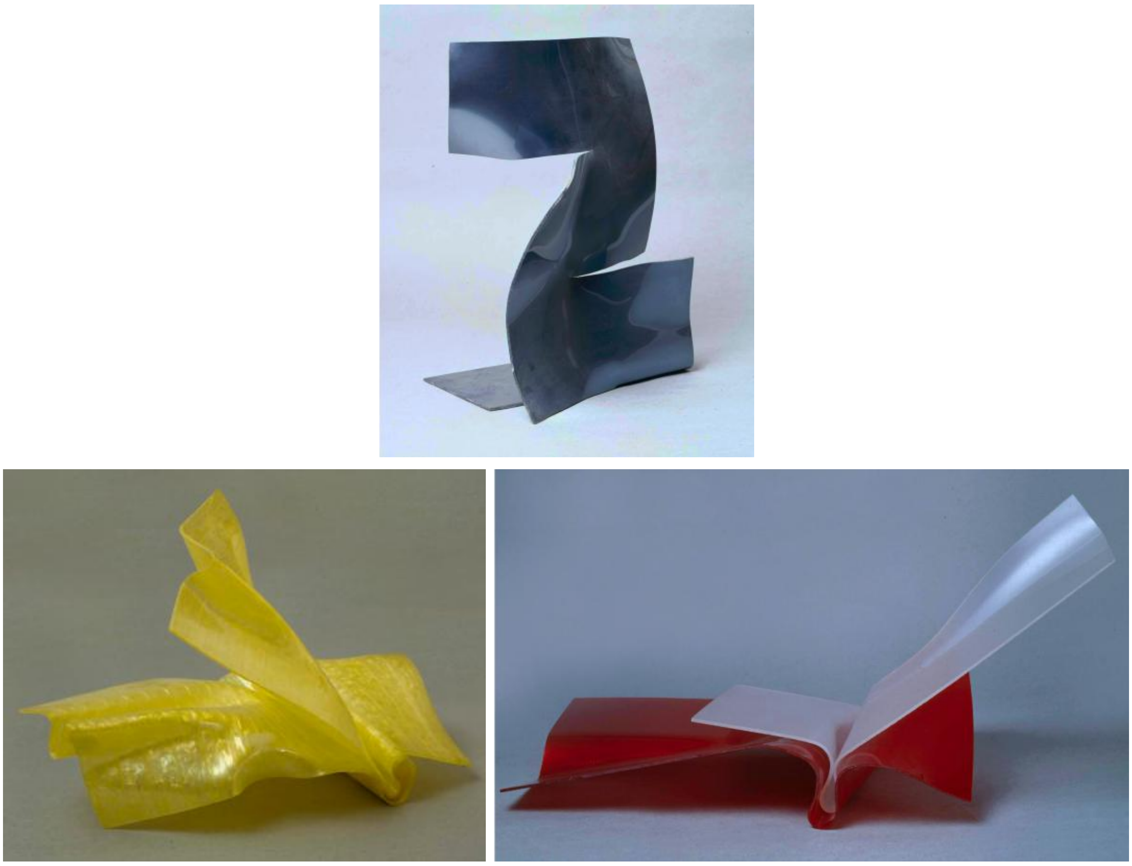


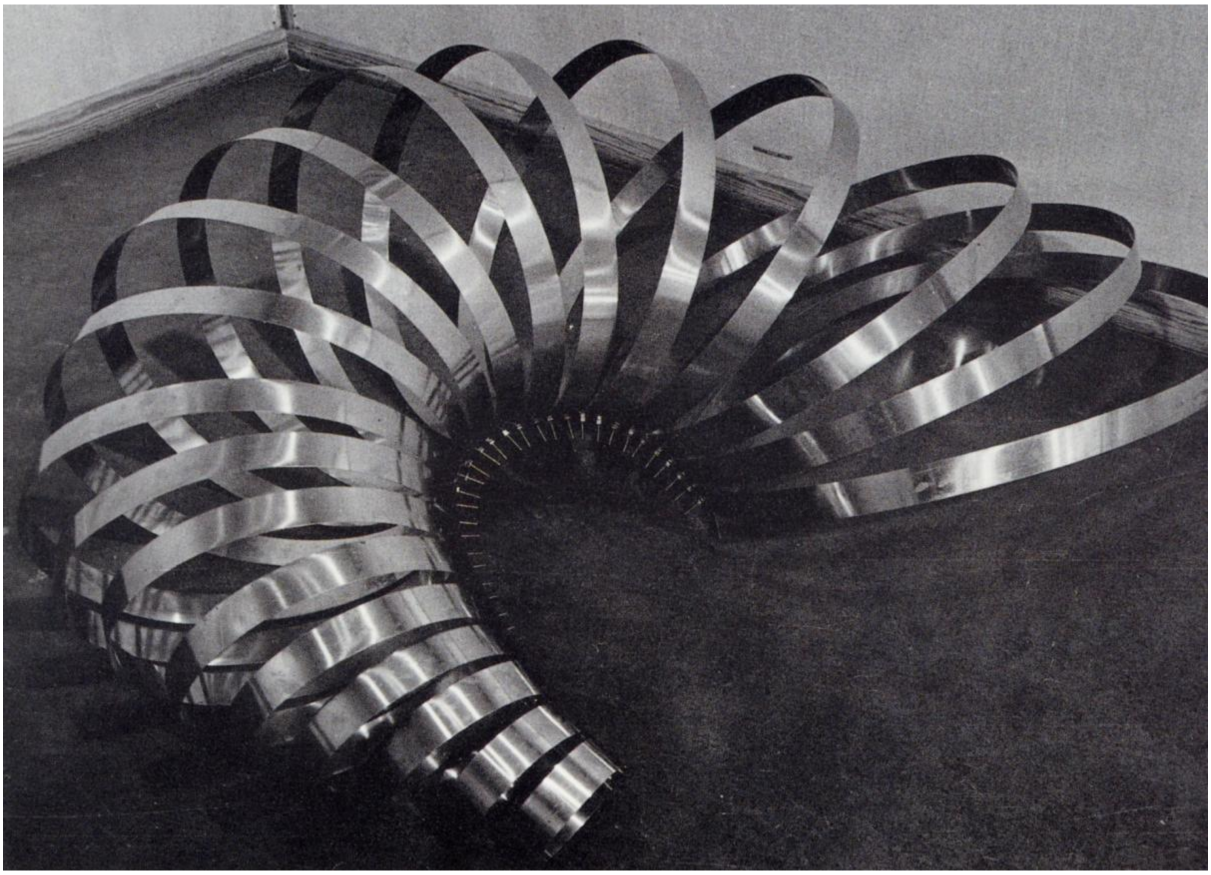
Figure VI.16. (Cat. 61.) *Escultura*, 1966. Acrylic, 41 x 30 x 20 cm. Author's collection; (Cat. 62.) *Escultura*, 1966. Acrylic, 36 x 51 x 30 cm. Author's collection; (Cat. 63.) *Escultura,* 1966. Acrylic, 28 x 55 x 30 cm. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: É um efeito menos propositado, há uma certa 'margem de manobra' que o material proporciona e que é mais difícil de controlar…

A.S.: Claro, mas com o alumínio não. Normalmente fazia um esboço e já sabia. Portanto pelo meio começou a acontecer coisas que já não tinham nada a ver com as proporções das chapas de acrílico que eram de cerca 40 cm e eram mal cortadas, nem sequer eram quadradas. Umas eram em bico e outras não. Então, decidi que já não ia fazer as esculturas em acrílico. Pensei usar ferro, porque era muito barato e vendia-se na loja onde comprava os alumínios e as chapas de zinco e latão para a escola para eles fazerem gravura.

L.P.: Aqui procura o material existindo já uma ideia de trabalho. Mas por exemplo nas fitas (Figure II.17), encontra primeiro as fitas e depois pensa o que fazer com elas.

A.S.: Era uma casa de ferro-velho e eu ia lá comprar ferro. O ferro era 7 escudos, decidi comprar aço que era 25 escudos o quilo, mas não se estragava. Era um aço esquisito que ninguém sabia exactamente o que era, mas disseram-me que era francês. Era uma 'bobine' com uma fita fininha, ficava em 200 escudos e decidi levar. Levei para casa e fiquei a pensar no que ia fazer com aquilo.



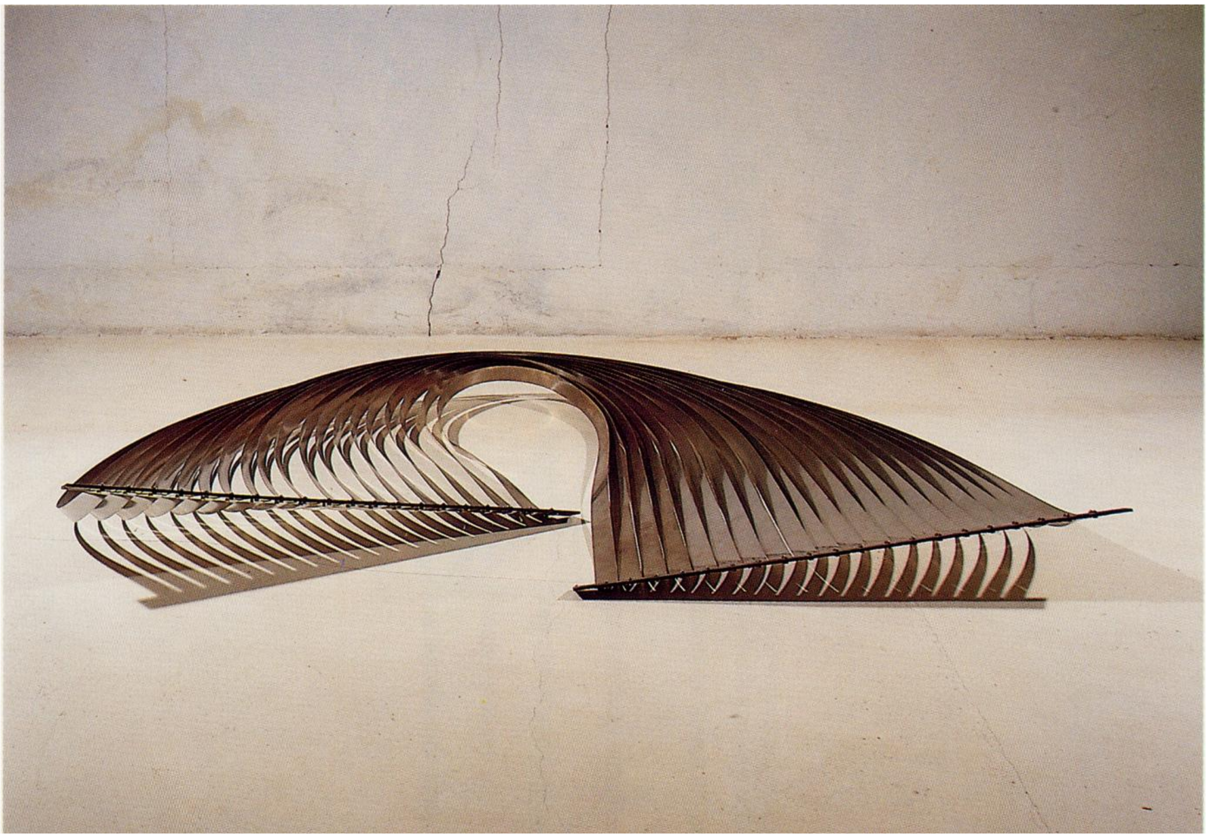


Figure VI.17. Cat. 79. *Escultura*, 1968. Stainless steel, variable dimensions. Author's collection; Cat. 80. *Escultura*, 1968. Stainless steel, variable dimensions. Author's collection. Photo: *Fotografia Alvão*, courtesy *Fundação de Serralves.*

L.P.: O Ângelo fala como se fosse tudo muito casual… Parece que depois o resultado é casual.

A.S.: Não. Primeiro comprava ferro lá ao pé de casa. Mas o ferro enferruja, é chatíssimo de pintar, não tem resistência – de repente vai a baixo. Decidi trabalhar em aço; era uma casa onde comecei a comprar chapas de aço e depois vi estas fitas.

L.P.: O Ângelo é curioso, gosta de experimentar os materiais.

A.S.: Eu tinha uns cadernos *Moleskine*, como os da minha mãe, com papel quadriculado azul e branco. Tenho uns 17, andava sempre com um. E durante muito tempo sempre que tinha uma ideia tomava nota e escrevia a data. Passados uns dias abria o livro e via, por exemplo, uma ideia para umas fotografias, que tinha escrito em determinado dia. Se tivesse aqui esses livros era muito fácil despistar qual a ordem em que essas coisas aconteceram.

L.P.: É claro que o Ângelo é capaz de aproveitar as possibilidades todas dos materiais, em termos formais e estéticos. Porque estas obras não são escultura no sentido tradicional; procura as 3 dimensões a partir de um volume que já existe ou construindo o volume. Procura muito bem o modo em que uma forma plana se desenvolve tridimensionalmente no espaço, quais as possibilidades de isso acontecer ou de conferir essa mesma mobilidade e conferir qualidades diferentes à escultura, como o som ou o movimento.

A.S.: Se me tivessem dito eu tinha trazido, ainda tenho uma gaveta cheia desses cadernos. Agora há anos que já não tomo notas, ou faço ou não faço. Mas percebia-se, há muitas coisas destas que não fiz antes de ir para Londres; achei que ia para Londres e ia arranjar lá fitas: ‘em Londres tem que haver’ e claro que não havia. Podia se calhar ter feito em borracha, mas a borracha é mole e depois apodrece… Eu na altura já tinha uma série de projectos para estas coisas, agora não posso garantir sem os tais livrinhos se aquele já estava desenhado, ou as regras daquele ou as regras deste.

L.P.: Mas primeiro aparece a fita e depois o modo de trabalhá-la.

A.S.: Algumas coisas sim. Por exemplo, uma parte tem um determinado comprimento mais pequeno e depois aumenta x por cento, só que x vai aumentando. Era quase só um princípio aritmético. Tinha uma regra de crescimento dos valores, eu não sabia ao certo no que ia dar, mas podia imaginar. Por exemplo, a mais pequena tinha 100 cm e a variação era de 5 cm cada uma… era só isto.

L.P.: Mas as pinturas já se relacionam com estes trabalhos das fitas.

A.S.: As pinturas foram feitas em 67 antes de ir para Londres. Nós fomos para lá em Setembro e isso foi feito durante a Primavera e Verão. E tinha os projectos de desenhos nos livrinhos.

L.P.: Mas as fitas foram feitas depois de Londres.

A.S.: Sim, já foi feito cá. Porque lá não podia fazer, tinha uma oficina primorosa com tudo o que era preciso, mas não havia o material. Eu mostrava o pedaço de fita, diziam que era aço inox, mas não é bem. Há uns anos mandei analisar isso e não é aço inox, é *um* aço inox, mas não é o que se chama *o* aço inox. O aço inox não é magnético e este é. Tinha coisas estranhas, também tinha crómio e níquel, mas não tinha nada a ver com as proporções do aço inox vulgar. Além disso, o aço inox vulgar molda-se, é assim que se faz as banheiras, os lavatórios… e este não dá para moldar, parte. Se lhe der uma pancada forte parte-se. É flexível e o outro não é, se o dobrar fica com essa forma. Uma vez experimentei abrir um buraco numa fita com um punção, saltou aos bocadinhos. Portanto, não tem nada a ver com o aço inox.

L.P.: Durante estes anos em que trabalhou muito a escultura, trabalhou menos a pintura.

A.S.: Parei mesmo de pintar, só em 1972 é que recomecei.

L.P.: Aqui nesta fase, nestas obras mais abstractas (Figure VI.14.), está a pintar com polivinilo. Escolheu-o por alguma razão? Por esse aspecto mais industrial relacionado com a escultura?

A.S.: Não, foi na continuação de pintar com o polivinilo. Isto era tudo pintado de preto (Figure VI.14., Cat. 72.), colei umas fitas adesivas bastante ao acaso e depois pintei de branco, grosso para tapar o preto, depois ainda passei umas aguadas, tirei a fita adesiva e aqui está o quadro. Aqui nem pensei sobre o que estava a fazer… se cruzava, se não cruzava, por exemplo há um triângulo muito pequenino que mal se vê, ficou assim. Há uma parte muito grande de acaso nisto tudo. A ideia é ter regras do jogo, regras para o jogo, mas não uma rigidez de não sair dali, isso não faço.

L.P.: Nesta fase também usou a tinta de *offset* e no entanto para estas obras abstractas utiliza polivinilo.

A.S.: Por acaso podia ter feito isto com tinta de *offset*, mas era impossível pintar em *offset* aquilo lisinho, ou então teria que dar uma camada, deixar secar e ir acrescentando, como agora faço. Mas de uma vez não se conseguia, porque aquilo secava muito depressa, a tinta é feita para dar umas voltas na máquina e quando sai está seca. Para pintar áreas com uma cor não dá, porque seca logo e depois começa a fazer manchas mais grossas e nunca fica certo. Naturalmente tinha que ser com polivinilo que seca mais devagar, consegue-se controlar. Ou então pintar à pistola, só que eu nunca tinha pintado à pistola.

L.P.: E depois então em 72 regressa à pintura.

A.S.: Sim.

L.P.: E regressa com acrílico.

A.S.: Sim. Eu tive que fazer o concurso na Escola de Belas Artes e durante 3 meses deram-me uma sala, com sol a entrar, e fiz uma séria de quadros. Nessa altura, pela primeira vez, havia tela à venda em Lisboa.

L.P.: Não havia tela à venda? Mas os artistas sempre pintaram sobre tela.

A.S.: No Porto não se vendia tela e em Lisboa havia mas eram telinhas.

L.P.: Mas o Resende e outros artistas não pintavam sobre tela?

A.S.: Não sei como é que pintavam… provavelmente iam comprar a Lisboa. Mas eu não tinha dinheiro para comprar um rolo de tela, até essa altura. E então disseram-me que o senhor Varela estava a fabricar tela e eu mandei vir um rolo de tela, que era muito boa, era grossa. Depois o senhor Varela morreu e começaram a mandar vir as telas belgas, que têm um nome flamengo, eram umas telas com 10 metros e eu mandei vir. E então já as usei para o concurso e para estas pinturas. Antes, a única coisa que eu usava era juta, que é uma coisa para os cortinados de montra, muito peluda, muito grossa, depois pinta-se e aquilo vai dando de si, de maneira que às tantas o quadro já tem mais uns centímetros de comprimento, que é uma coisa repugnante. Além disso, não tinha resistência nenhuma.

L.P.: Mas deixou o polivinilo?

A.S.: Sim.

L.P.: E porquê? Podia ter pintado com ele sobre tela.

A.S.: Porque começou a haver acrílicos à venda.

L.P.: Aqui as cores como são? São também primárias por cima umas das outras?

A.S.: São as cores ‘primárias’. É vermelho (de cádmio médio), azul (de ftalocianina) e amarelo (de cádmio médio), mais nada, por baixo era branco.

L.P.: E isto não poderia fazer com polivinilo?

A.S.: Podia. Só que os acrílicos já vinham misturados, eram todos da mesma marca e havia os produtos para misturar. Enquanto que com o polivinilo usava um guache de uma marca e outro de outra… o acrílico eu já sabia que era material de confiança, sabia que tinha 3 estrelas ou 2 estrelas (aquelas coisas que lá põem, como a durabilidade). Sempre usei os acrílicos da *Talens*, é uma mania no Porto. Não sei porquê toda agente começou a usar *Talens* e tenho-me dado bem. Actualmente já não uso as cores primárias e tenho umas gavetas com 50 e tal ou 60 tubos. Sempre que vejo uma cor ou um tom diferente: ‘Que marca é esta? Vou levar para experimentar’. Vou fazendo colecção de tubos variados de todas as marcas.

L.P.: Continua então com a mesma curiosidade.

A.S.: De facto, o azul ultramarino de uma marca não é igual ao de outra.

L.P.: Estes pretos também são feitos da mesma maneira?

A.S.: São camadas, é vermelho, azul e amarelo (como o que está no Museu do Chiado). A única diferença é que comprei umas latas novas de tinta, porque pediram-me para fazer uma serigrafia e a tinta de *offset* já estava seca.

VI.3 Micro sampling

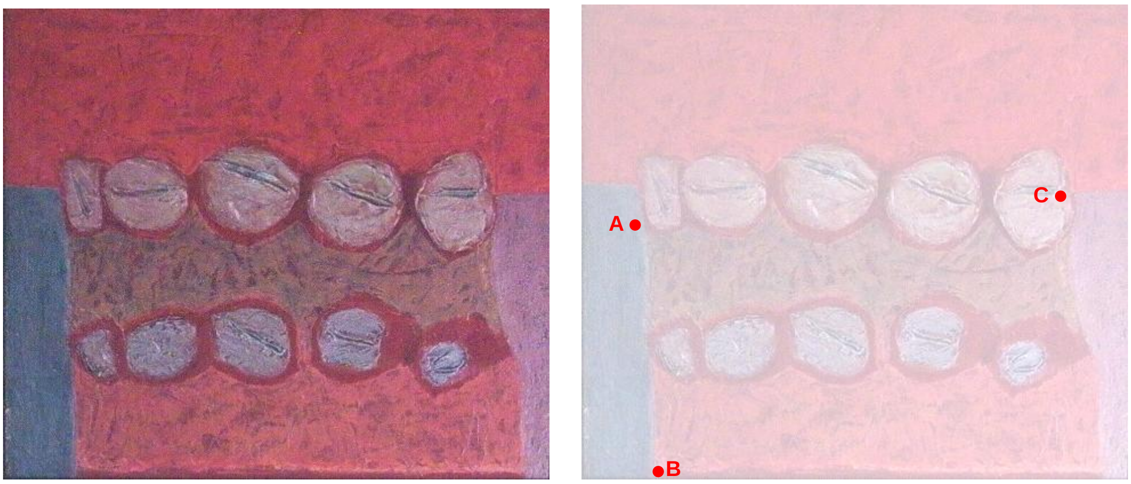


Figure VI.18. *Untiled*, 1961/62. Poly(vinyl acetate) on hardboard. Author’s collection.
μ-sampling: A – green sample; B – red sample; C – whitish sample.

Figure VI.19. *Plantas*, 1962. Poly(vinyl acetate) on hardboard. Author’s collection.
μ-sampling: A – green sample; B – red sample.

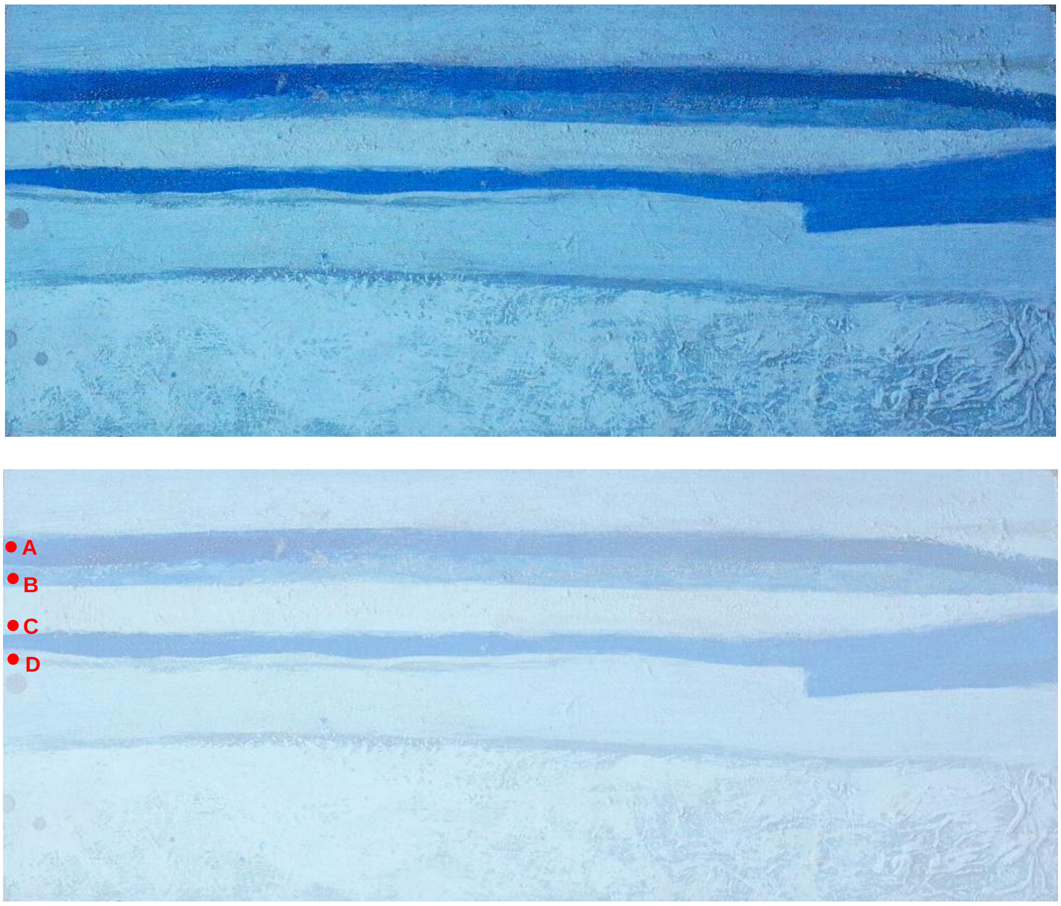


Figure VI.20.*Untitled (study)*, 1963. Poly(vinyl acetate) on hardboard. Author’s collection.
μ-sampling: A – dark blue sample; B – light blue sample; C – white sample; D – green sample.

Figure VI.21. *Árvore*, 1962. Poly(vinyl acetate) on hardboard (wax protection layer). Author’s collection.
μ-sampling: A – wax sample.

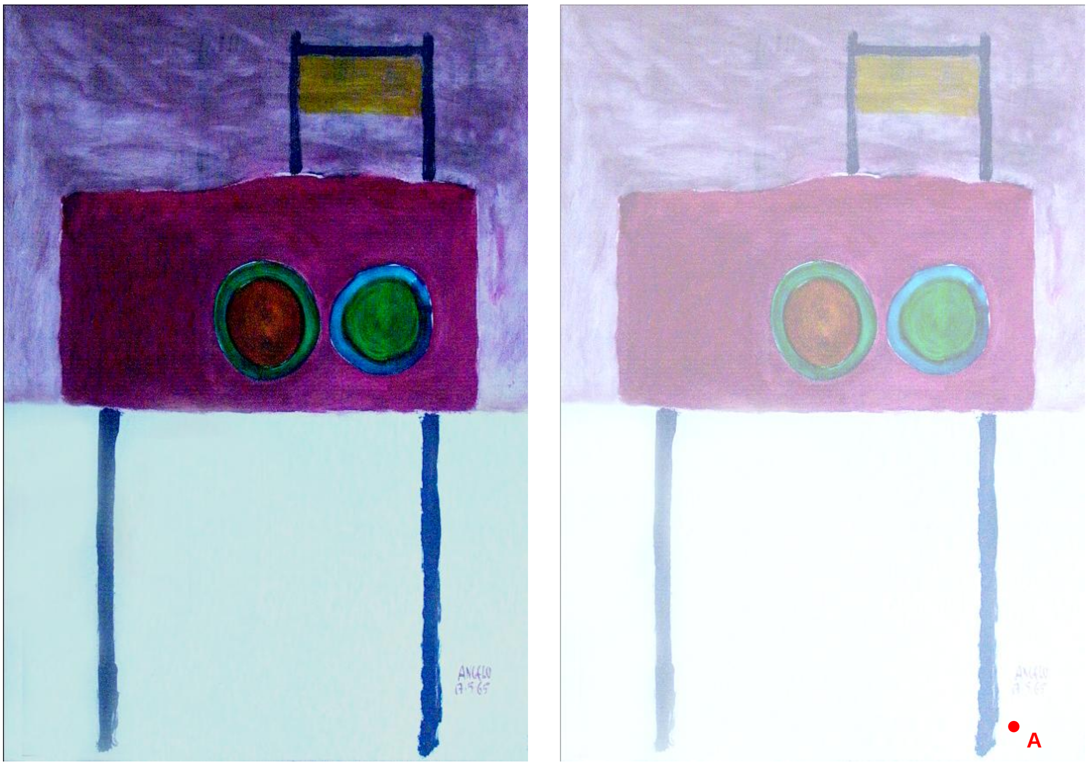


Figure VI.22. *Natureza Morta*, 1965. Offset ink on paperboard (prepared with white PVAc) glued on hardboard. Author's collection.
µ-sampling: A – white sample.

VI.4 Spectra

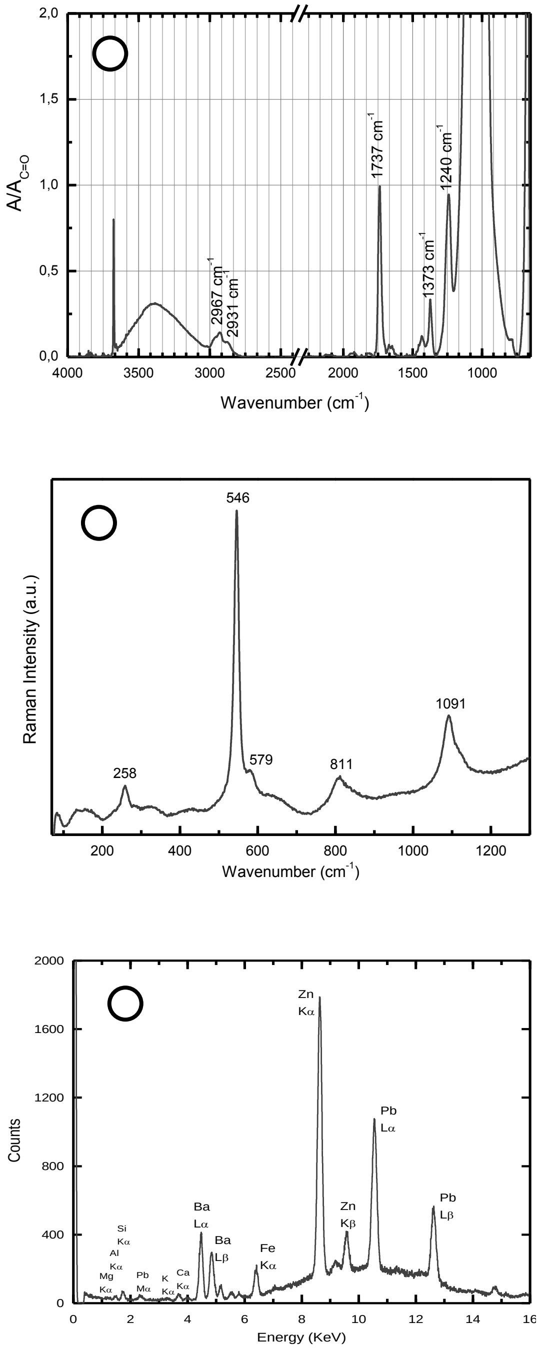


Figure VI.23. Spectra of a white sample from *Untitled*, 1961/62: top – infrared with absorptions normalized for C=O stretching; centre – Raman; bottom – EDXRF.

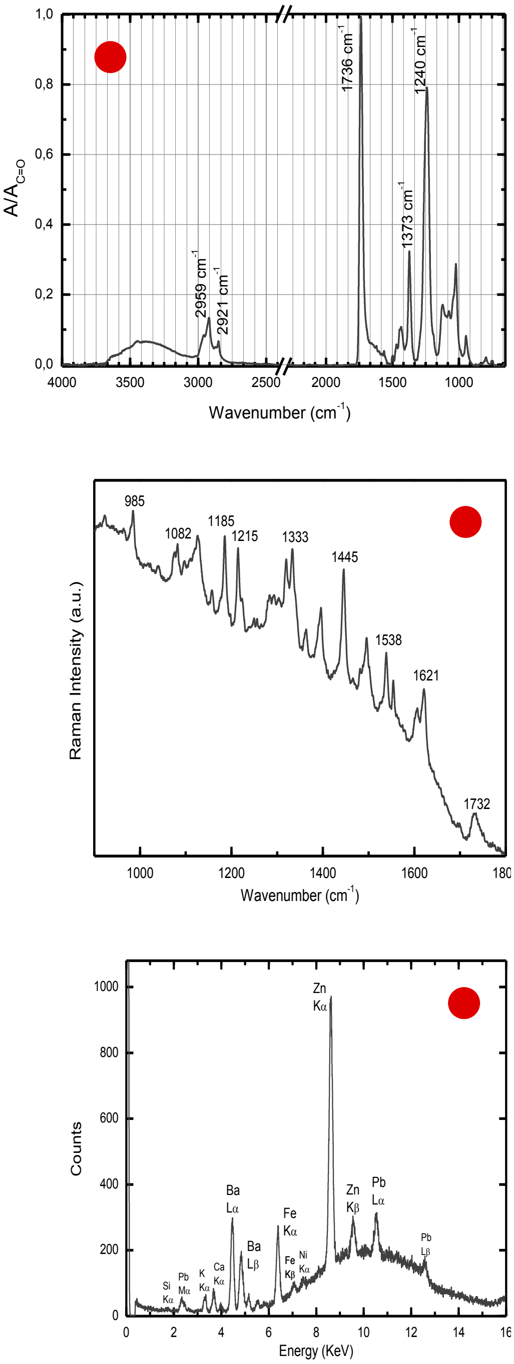


Figure VI.24. Spectra of a red sample from *Untitled*, 1961/62: top – infrared with absorptions normalized for C=O stretching; centre – Raman; bottom – EDXRF.

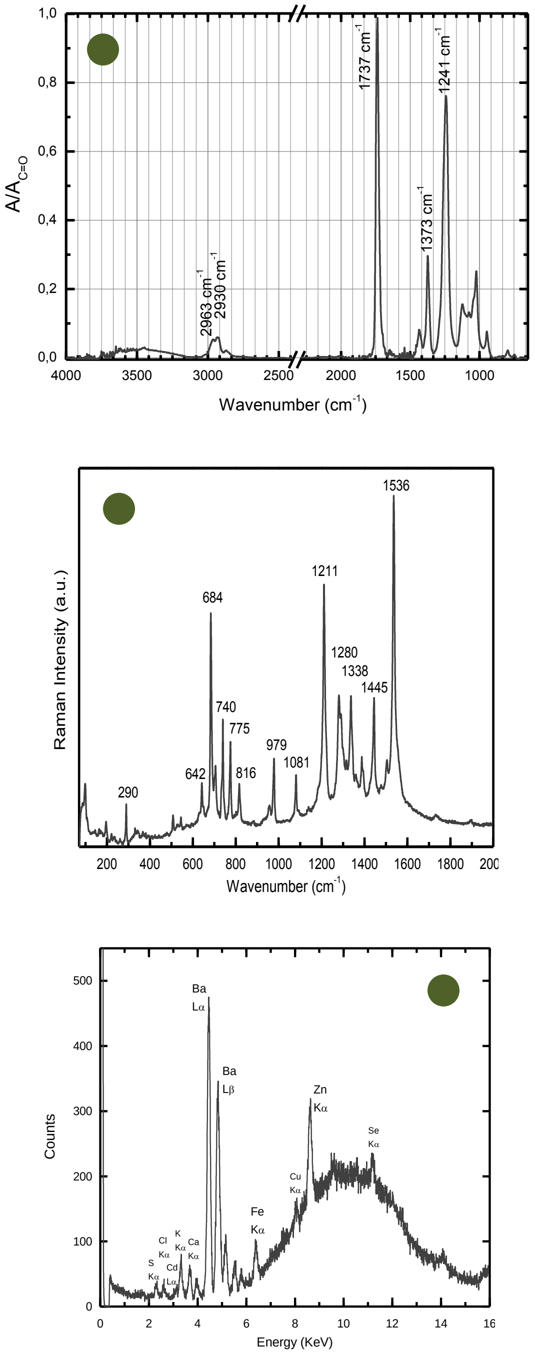


Figure VI.25. Spectra of a green sample from *Untitled*, 1961/62: top – infrared with absorptions normalized for C=O stretching; centre – Raman; bottom – EDXRF.

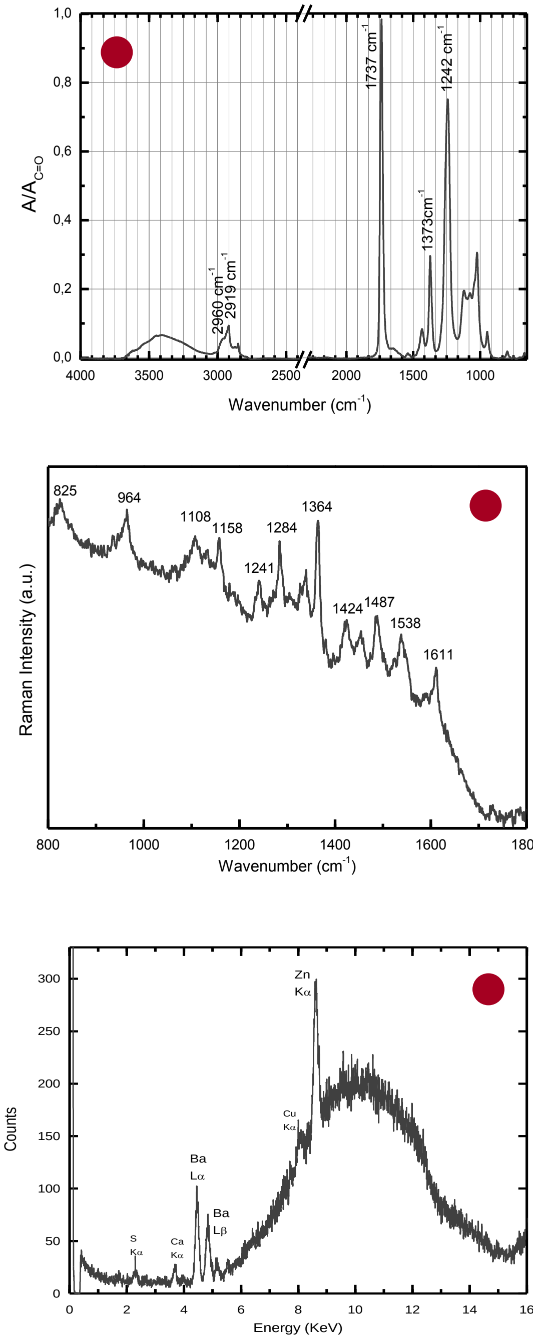


Figure VI.26. Spectra of a red sample from *Plantas*, 1962: top – infrared with absorptions normalized for C=O stretching; centre – Raman; bottom – EDXRF.

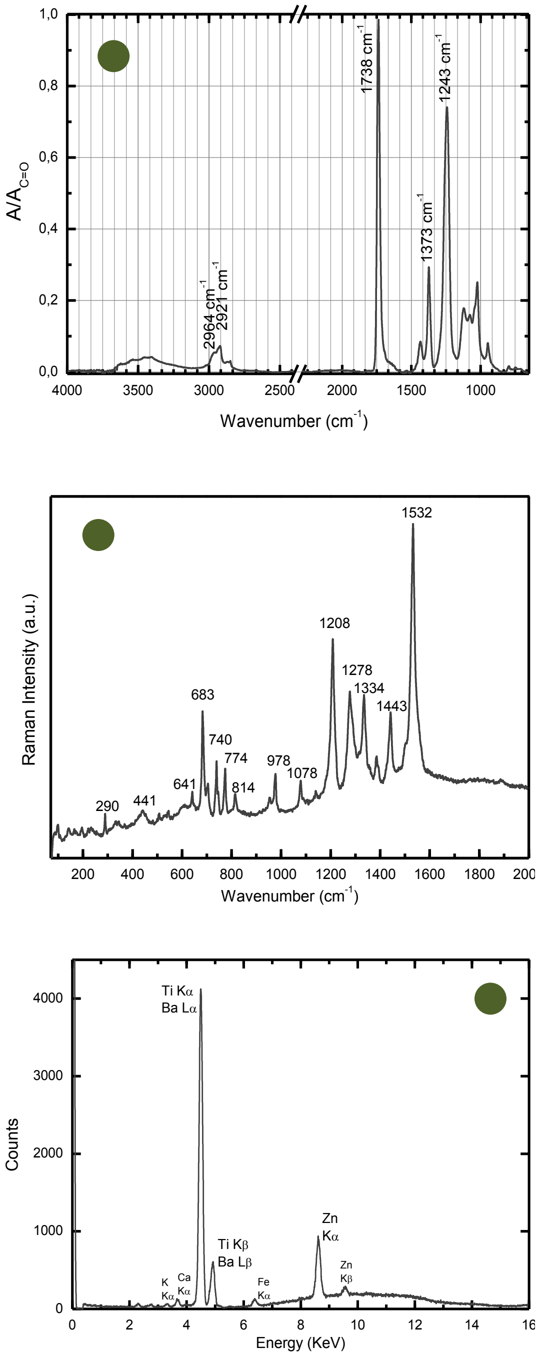


Figure VI.27. Spectra of a green sample from *Plantas*, 1962: top – infrared with absorptions normalized for C=O stretching; centre – Raman; bottom – EDXRF.

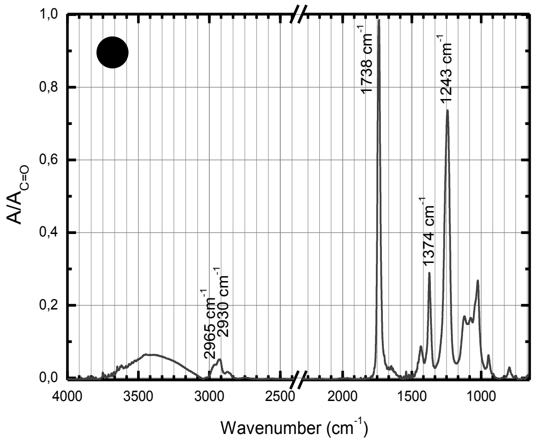


Figure VI.28. Infrared spectrum of the binding medium from *Plantas*, 1962, with absorptions normalized for C=O stretching.

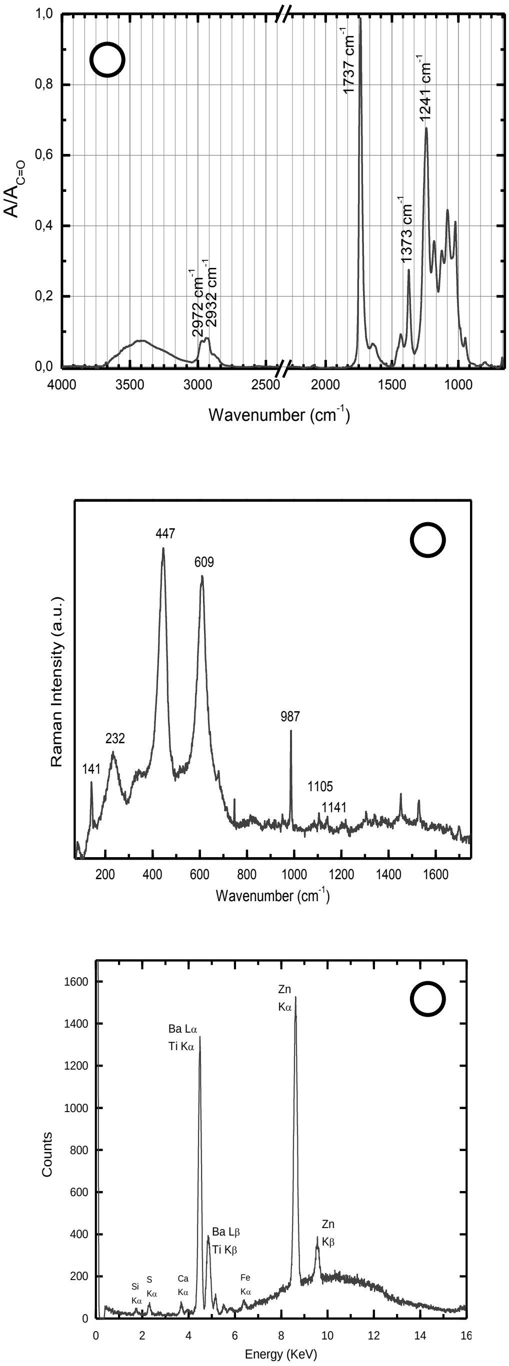


Figure VI.29. Spectra of a white sample from *Untitled (study),* 1964: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

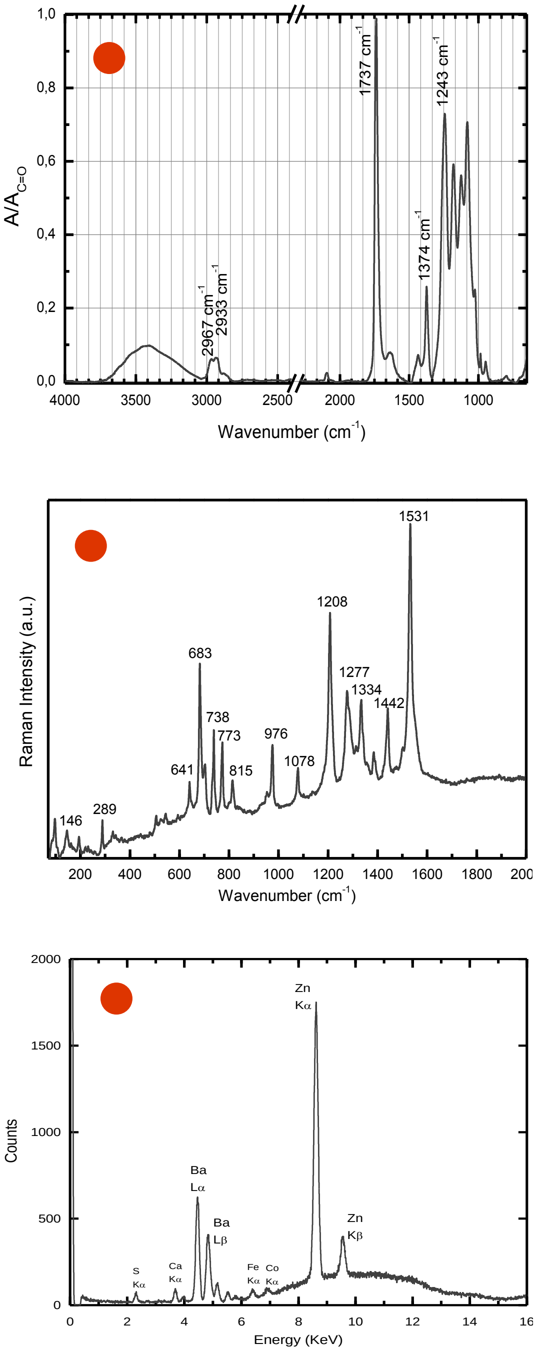


Figure VI.30. Spectra of a red sample from *Untitled (study)*, 1964: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

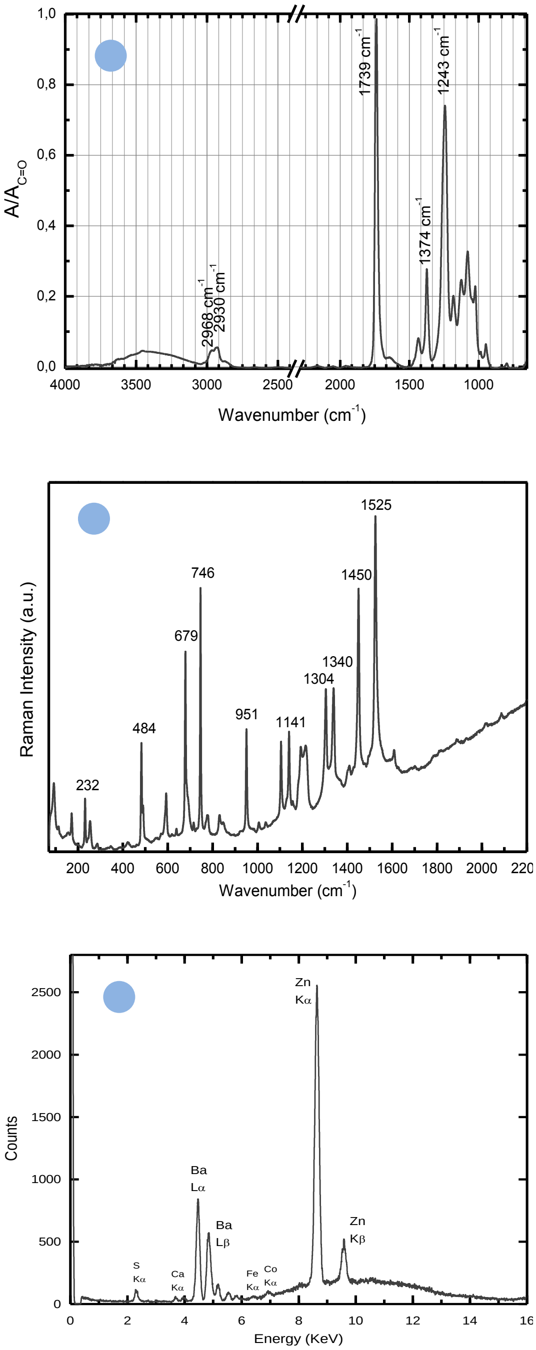


Figure VI.31. Spectra of a light blue sample from *Untitled (study)*, 1964: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

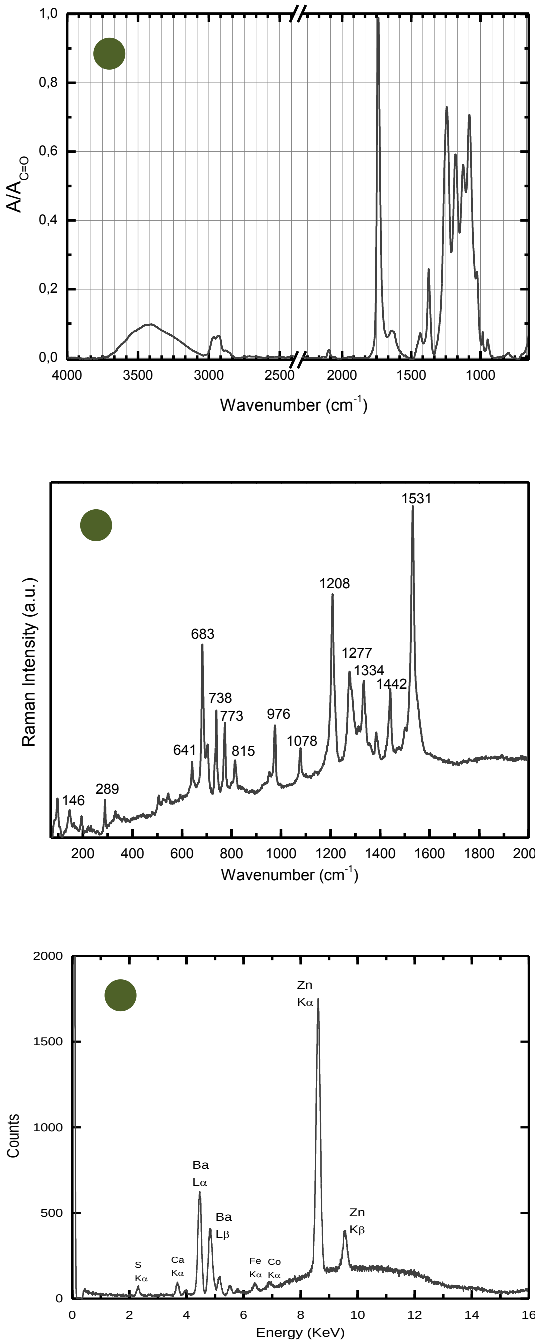


Figure VI.32. Spectra of a green sample from *Untitled (study)*, 1964: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

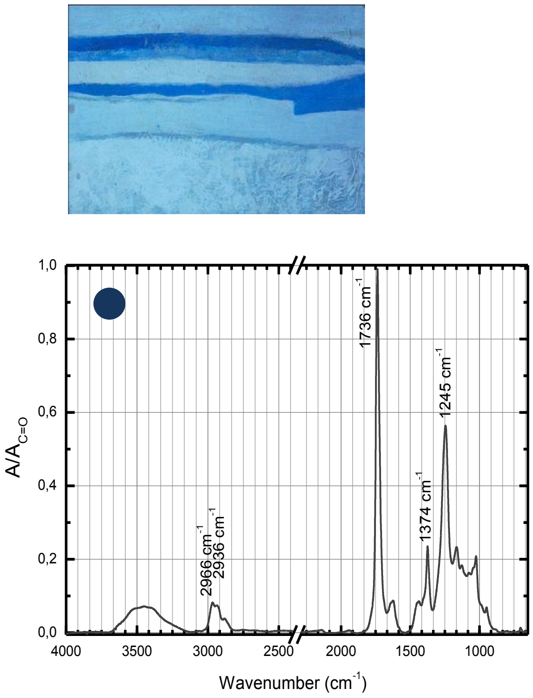


Figure VI.33. Infrared spectrum of a dark blue sample from *Untitled (study)*, 1964, with absorptions normalized for the C=O stretching.

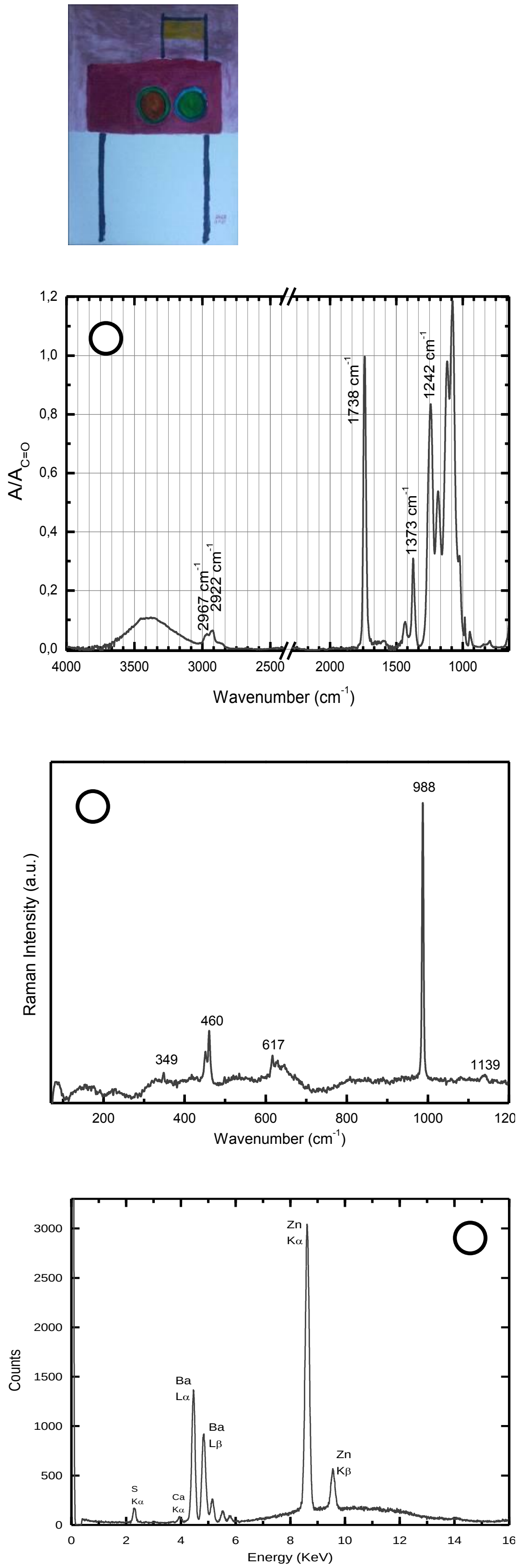
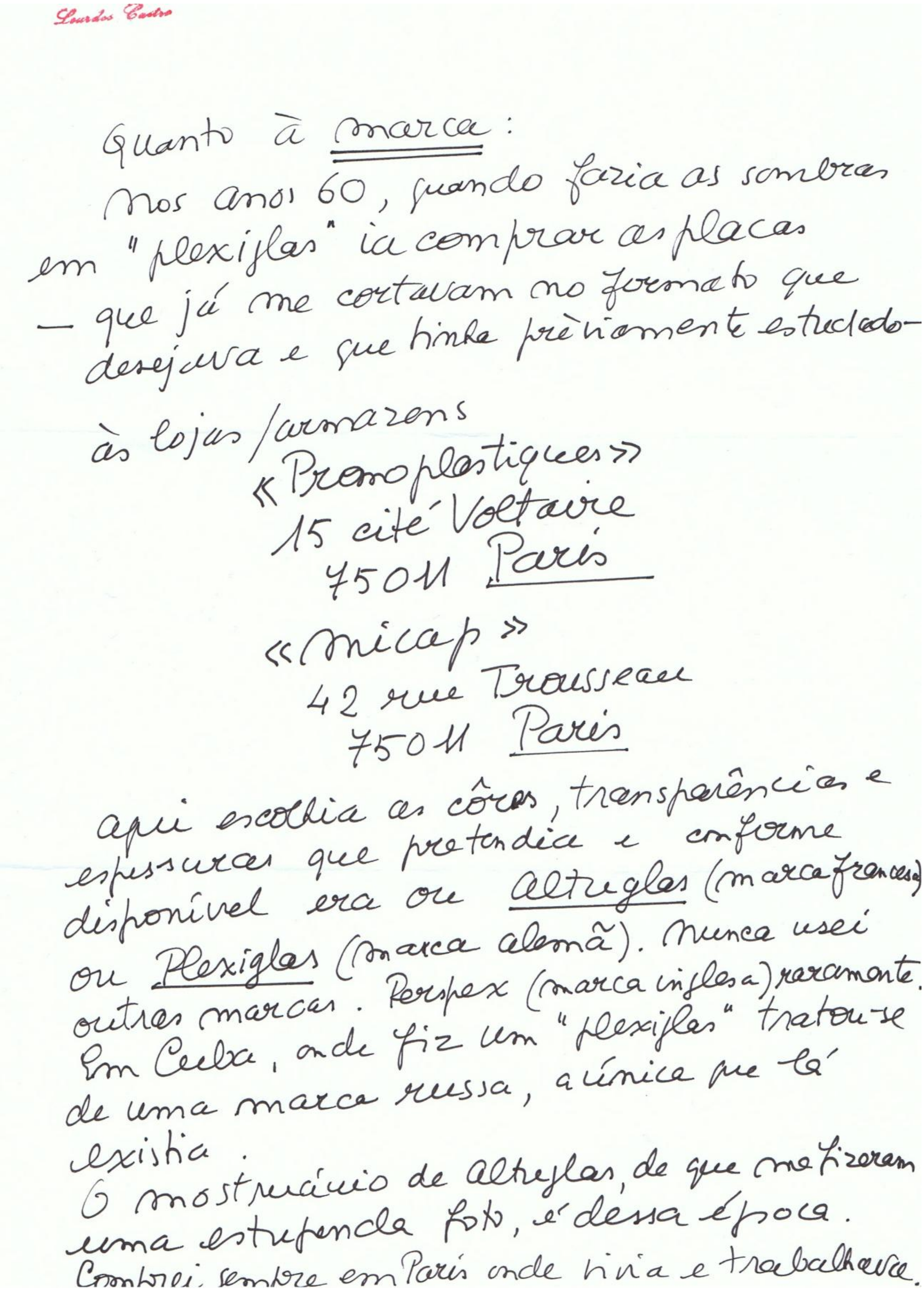


Figure VI.34. Spectra of a white sample from *Natureza Morta,* 1965: top – infrared, with absorptions normalized for the C=O stretching; centre – Raman; bottom – EDXRF.

Appendix VII

Lourdes Castro Data

VII.1 Information on the PMMAs brands used



Lourdes Castro

Quanto à <u>marca</u>:

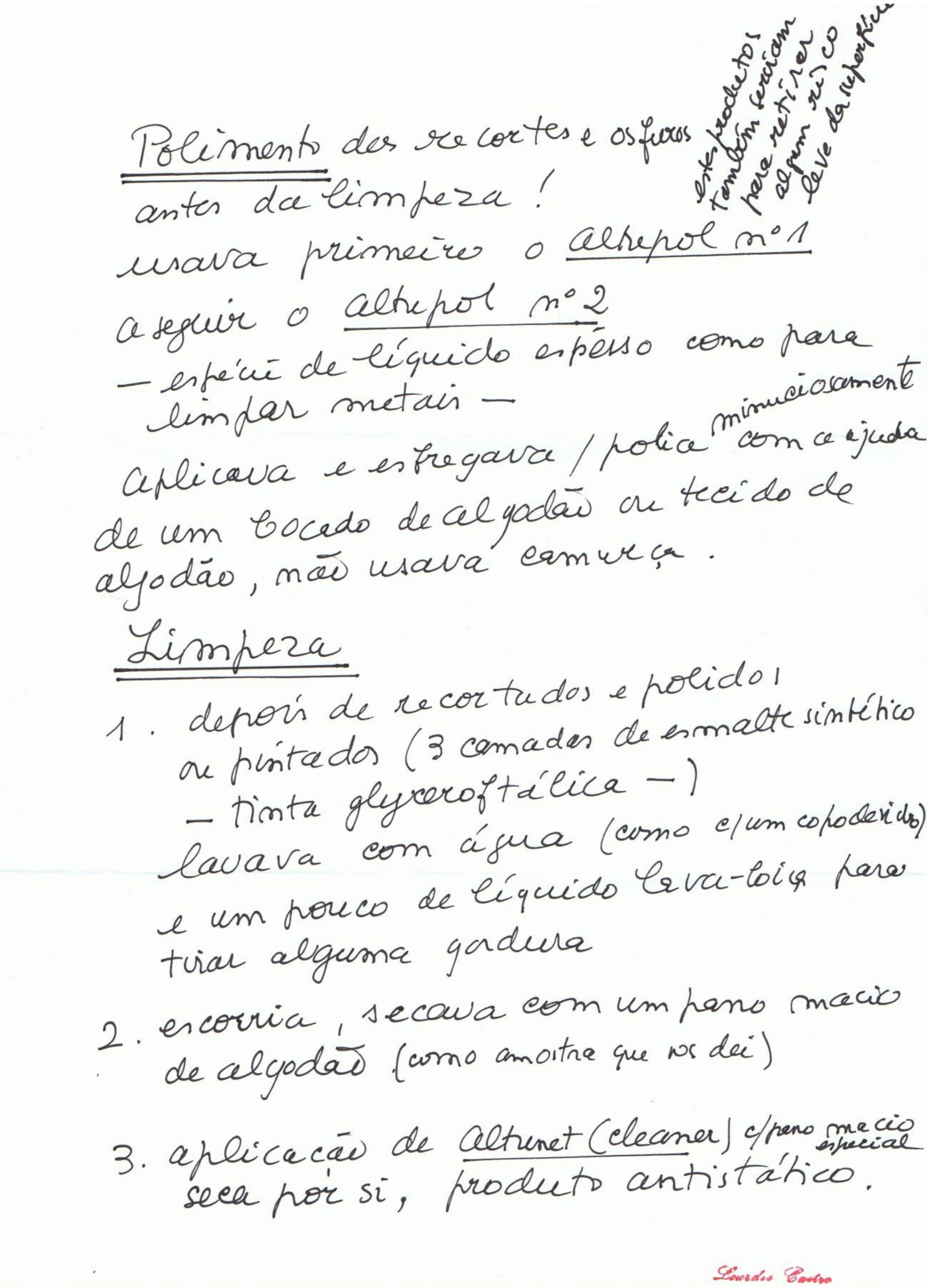
Nos anos 60, quando fazia as sombras
em "plexiglas" ia comprar as placas
— que já me cortavam no formato que
desejava e que tinha prèviamente estudado—

às lojas/armazens
«Promoplastiques»
15 cité Voltaire
75011 <u>Paris</u>

«Micap»
42 rue Trousseau
75011 <u>Paris</u>

aqui escolhia as côres, transparências e
espessuras que pretendia e conforme
disponível era ou <u>Altuglas</u> (marca francesa)
ou <u>Plexiglas</u> (marca alemã). Nunca usei
Perspex (marca inglesa) raramente
outras marcas. Em Cuba, onde fiz um "plexiglas" tratou-se
de uma marca russa, a única que lá
existia.
O mostruário de altuglas, de que me fizeram
uma estupenda foto, é dessa época.
Comprei sempre em Paris onde vivia e trabalhava.

VII.2 Information on the polishing and cleaning procedures



estes productos
também serviam
para retirar
algum risco
leve da superfici

Polimento dos recortes e os furos antes da limpeza!

usava primeiro o Altrepol nº1
a seguir o Altrepol nº2
— espécie de líquido espesso como para
limpar metais —
aplicava e esfregava / polia minuciosamente com a ajuda
de um bocado de algodão ou tecido de
algodão, não usava camurça.

Limpeza

1. depois de recortados e polidos
ou pintados (3 camadas de esmalte sintético
— tinta glyceroftálica —)
lavava com água (como c/um copo de vidro)
e um pouco de líquido lava-loiça para
tirar alguma gordura

2. escorria, secava com um pano macio
de algodão (como amostra que vos dei)

3. aplicacão de Altrunet (cleaner) c/pano macio especial
seca por si, produto antistático.

Lourdes Castro

andijo altuenet:

« Altuglas White Cleaner »

1Kg

Batch No 2M 26 99 24

ATOHAAS
6 cours Michelet
92064 Paris La Défense
France

telf: 01 49 00 80 80

T 828 388

VII. 3 Size exclusion chromatrography (SEC)

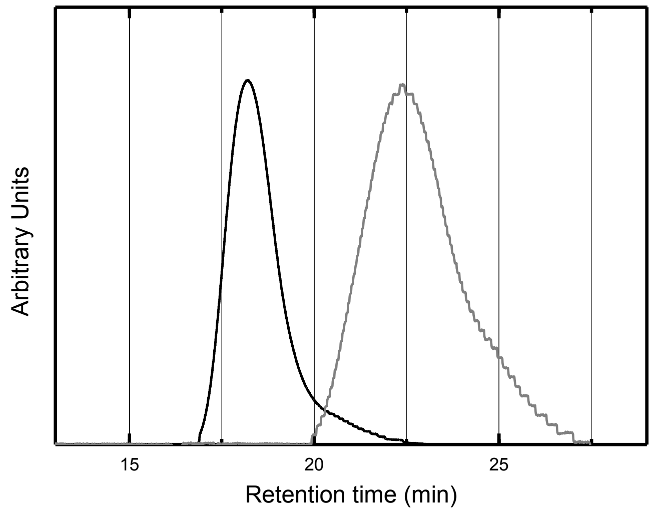


Figure VII.1. SEC chromatograms: left – cast PMMA sheet (*Mw* = 10.5 x 10^5; PD = 1.6); right extruded PMMA sheet (*Mw* = 1.2 x 10^5; PD = 1.9).

VII. 4 FTIR

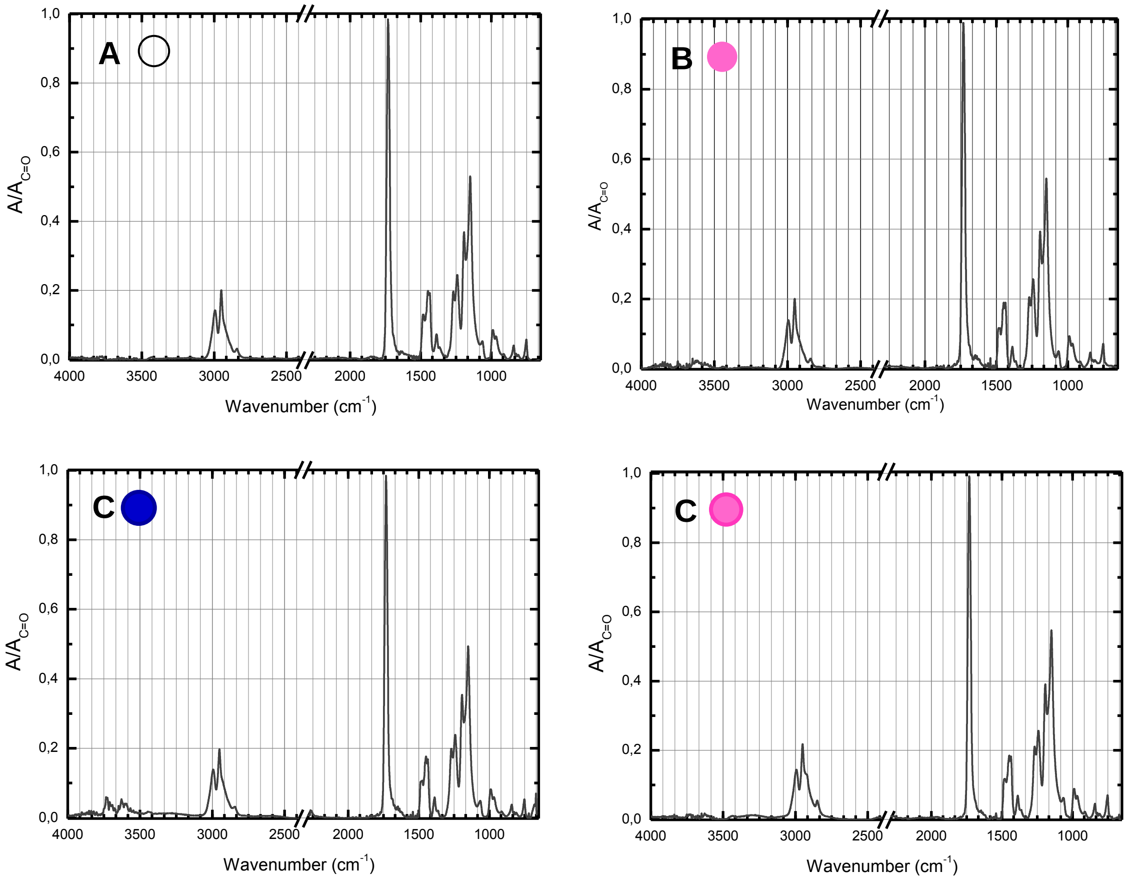


Figure 4.2. Infrared spectra of PMMA sheet from the sample collection belonging to Lourdes Castro: A – LC Transparent Alt S310; B – LC Fluorescent pink Alt T770A; C – LC Opaque blue; C – LC Fluorescent pink. Absorptions are normalized for the carbonyl peak.