UNIVERSITY POLITEHNICA OF BUCHAREST
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Ph.D. Thesis Summary

CONTRIBUTIONS TO THE STUDY OF AGING PROCESSES IN PAINTING LAYERS BASED ON SYNTHETIC RESINS

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ABSTRACT

The present paper brings contributions to the study of ageing process in painting layers based on synthetic resins using data provided by Fourier Transform Infrared (FTIR) spectroscopy. The main directions of the study were focused on the characterization and identification of the constituent components of tested materials, the dynamic analysis and degradation mechanisms in the same set of samples subject to a controlled accelerated ageing protocol, the evaluation of the influence of pigments (and of the other components in the formulation) on the effects induced during the accelerated ageing tests, and the possibility of highlighting the existence of degradation markers that could assist in the identification of severely degraded samples. The analytical procedure was applied to a set of 150 laboratory samples representing acrylic emulsion paints and a series of polymeric adhesives and consolidants used in current conservation and restoration procedures. The research study was complemented by a comparative analysis of the degradation mechanisms in natural polymers. Experimental notes on the FTIR analysis of complex pictorial systems are also reviewed via some case studies represented by samples coming from various art objects executed in classical techniques. On a secondary direction, the present work aimed to evaluate the ATR-FTIR technique in the analysis of tested paint materials in terms of the identification and discrimination capability of the organic component when investigating complex pictorial samples – in general mixtures of organic and inorganic compounds affected by different degrees of ageing. The results highlight the first large-scale and systematic FTIR studies investigating the ageing of polymer systems in modern paint materials (following long-term monitoring trials) that highlight the main degradation pathways, and the use of chemometric techniques respectively on large data sets that emphasize specific binder-pigments interactions.

Keywords: synthetic resins, acrylic paints, pigments, organic binders, FTIR analysis, material characterization and identification, accelerated ageing, UV radiation, degradation processes, paint materials, natural polymers, conservation and restauration, cultural heritage

INTRODUCTION

The widespread use in the last decades of the new classes of synthetic materials raised an important issue within the field of conservation and restoration of the 21st century art, the variety of physicochemical properties and characteristics related to these types of materials having direct implications on the artworks behavior and response over time, under the action of different stress factors or to different applied treatments. Acrylic and alkyd resins, polyvinyl acetate, cellulose nitrate, polyurethane or epoxy resins are just a few of the most important classes of synthetic binders which are currently used in the formulation of paints, varnishes or other types of materials dedicated to the conservation and restoration applications. The unique set of characteristics associated to them (fast drying time, flexibility, etc.) includes nevertheless, beyond the immediate benefits to traditional materials and techniques, an increased factor of complexity with respect to the conservation potential of the artefacts over time.

Thus, with regard to the modern and contemporary art, among the major and difficult situations that the curators and the restorers face at present, we may include the lack of complete documentation regarding the new techniques and modern materials, the lack of experience concerning the application of appropriate restoration treatments, the rapid degradations which lead to significant damages and fragility due mainly to the incompatibility of the materials or to the inaccurate exposure and storage of the artworks and, not least, the difficulty regarding conservation of the artefacts without affecting their artistic expression.

Apart from the inward significance of any artwork, its outer dimension is inevitably affected over time, the natural aging processes associated to the constituent materials setting up a life cycle which imparts the transition to its form, degrading it. To this dynamic aspect of the matter which is in a continuous process of change are the conservation methods addressed, that need to be developed and adapted to current situations in order to be able to anticipate, quantify and extend the lifespan of an artwork. In the case of the conservation and restoration procedures of contemporary artworks, the very starting point of creation must be considered, which fundamentally differs from that of the classical artworks. If the traditional techniques have in the foreground materials which are devoted to each artistic genre, with contemporary art, the materials used receive new valences and interpretations that do not allow a clear delimitation. Along with the conservation problems which occur in the existence of each artwork over time, in the case of modern art we can notice a deficit area, which is given on one hand by the materials which are used, and often, by inaccurate overlaps and mixtures of the pictorial layers, the non-compliance with a performance methodology or the technical experiments causing various specific degradations.

The study and understanding of the aging phenomena associated to painting materials is essential in view of a good conservation practice, both for the identification of different degradation products resulting over time and for finding some methods of intervention, which could slow down, break or prevent the action of the aging processes. Due to free-radicals reactions – thermally or photo-chemically initiated auto-oxidations; ionic reactions - predominantly acid and autocatalytic hydrolysis; as well as the enzymatic biodegradations, the substances (especially organic ones) in the pictorial layers degrade over time, generating specific problems given by the characteristics of the material.

Apart from the seemingly stable aspect and the generally high level of conservation of traditional oil paintings, extensive studies carried in the last decades, which focused on the microstructural changes associated with artifacts under the signature of the great masters of the 16th-19th centuries, have demonstrated the surprising dynamics of these systems, with various physicochemical processes occurring at micromolecular levels. These processes, inherent to the technique and working materials, are triggered and/or accelerated by a series of external factors – storage and exposure conditions (microclimate parameters), previous conservation treatments or restoration interventions, which, over time, affect the aesthetic quality of the artwork in a more or less perceptible manner.

Even if in the case of traditional materials and techniques historical sources may be consulted for a better assessment of the problems that may be encountered, the understanding of the complexity of the reactions due to local characteristics – molecular structure, chemical reactivity, activation energy; as well as the natural aging phenomena, often involve a comprehensive and detailed research, at the interface of various fields: physics, chemistry, conservation, art history.

The study of pictorial layers raises major issues especially regarding the difficulty to physically separate these layers due to their micrometric thicknesses (1-200 μm) and not least due to the heterogeneous nature of these complex systems defined by various interactions between different

constituent compounds, impurities and/or degradation products resulting from the aging phenomena. In the case of traditional oil paintings research has shown that most surface-induced changes are due not only to the nature of the materials which were used, but also to the layout of the existing layers. The high complexity of these systems is directly reflected at the level of a material study, the understanding of the degradation mechanisms associated with traditional oil-based binders being based on studies of over 30 years.

Returning to the new generation materials, all these issues will receive new valences, mainly in terms of material particularities, to which is added the novelty component, the research in the field being still open towards several directions. When talking about the stability of modern pictorial materials an important aspect which must be considered is the chemical nature, respectively the combined effect of all the major and minor compounds which are used within the synthesis, the way in which they react and interact during the aging process, and not least the way in which these changes affect the basic properties of the material.

The ability to identify and characterize in detail the pictorial layers, especially the binding medium, is an essential aspect in view of their adequate conservation and restoration. Based on its chemical features, each pictorial material will show a different response to different cleaning agents (solvents, reagents) and therefore, for a good practice, a characterization is imposed prior to the application of any conservation treatment.

This analytical approach to understand the chemistry of the material is imposed also in the case of studies which target the processes and the aging rate of the pictorial materials. Oxidation reactions, cross-linking or chain cleavage reactions are processes which gradually affect the physicochemical properties of the paint film, and their knowledge is particularly important both from the preventive conservation point of view as well as in terms of making the most informed decisions regarding the adequate conservation/restoration treatments.

The aim of this thesis is to bring contributions to the study of aging processes in modern pictorial layers using data provided by Fourier transform infrared spectroscopy (FTIR). An extensive palette of painting materials intended for creation (new generations of pigments and paints), as well as materials dedicated for conservation/restoration treatments (polymer adhesives and consolidants) was investigated.

The analysis and the comparative study of some laboratory samples represent a fundamental step, which allow the establishment of some reference points in the analysis and the comprehension of the artwork; not least, these pilot studies allow the evaluation of the response and the detection sensitivity within the applied analytical techniques of different materials and/or compounds of interest.

Also, on a secondary direction, apart from the contributions which strictly target the study of material, the present work proposes an approach in the sense of simplifying the analytical methodology. The choice of the ATR-FTIR method is not random; the rapid analysis, the non-destructive aspect, the high sensitivity, and the low cost that such a method implies in relation to other techniques, place it in an area, which is, first of all, accessible to most of laboratories – from research institutes, universities, museums or private companies.

Studies in recent years confirm the potential of the ATR-FTIR technique in the analysis of modern pictorial materials. In relation to the traditional technique in transmission, ATR offers information regarding the superficial layers of the film being an ideal method in the study of surface chemical changes - caused by aging of the film or as a result of conservation treatments such as cleaning procedures.

In the attempt to improve the sensitivity, the resolution, the detection limit or the reproducibility and the accuracy of the results, the number of analytical techniques applied to the study of art and cultural heritage objects has seen a tremendous development over the last decades, the trend in the field being directed towards non- or micro-invasive investigation methods. In most cases, the determinations show however some difficulties in the analysis and the interpretation, considering that most of the analyzed samples include complex, often degraded mixtures. For a complete, in-depth analysis, a multi-analytical approach is most often needed, but this involves significant resources (equipment, specialists, analysis time), and, on the whole, the costs involved by a diagnosis study may exceed the real possibilities (financial or infrastructure ones) that a possible beneficiary might have.

It is understood that a single technique cannot respond to all issues that a material study may raise. However, the direction is not restrictive, but constructive in the light of the principle *less is more*. The intention was to use and explore the FTIR data in order to maximize the provided

information, but also in the sense of understanding the aspects relating to the correlation possibilities in the case of large datasets with the chemometric analysis.

This thesis is structured in five chapters:

Chapter 1 includes general information regarding the chemistry of modern pictorial materials. Fundamental notions for the industry and technology of organic coatings are presented, the structure of the formulation and the main classes of synthetic resins used as binders in order to obtain new generation conservation paints or materials. Pigments, mineral fillers and additives are also cross-referenced in the light of the accessible literature. The data provided in the last part of this section are completed by a synthesis on the issues of the conservation of modern pictorial layers, respectively on the current state of the research in the field.

Chapter 2 summarizes the fundamental theoretical aspects of the infrared spectroscopic techniques and the experimental aspects of the ART-FTIR technique. Both the advantages and the limitations of the method are discussed; the observations are completed by an overview of the optical properties associated to polymeric materials. Chemometric techniques used for spectral data analysis are also discussed, with a focus on Principal Component Analysis (PCA).

Starting with **Chapter 3 – *Analysis and the characterization of some acrylic paints,*** we move to the presentation of the personal contributions represented by the results obtained within the study of the new generation pictorial materials, which make the subject of this thesis.

Subchapter 3.1 describes the working methodology and the main stages within the analytical protocol. The accelerated aging treatments used to induce the degradation mechanisms along data processing mode are presented.

Subchapter 3.2, presents aspects regarding the analysis and interpretation of FTIR data towards the identification and characterization of the major constituent components within the analyzed paints: results regarding the characterization of the binder, pigments and mineral fillers are presented. The study continues with the analysis of the kinetics of the degradation processes (**subchapter 3.3**), the discussion of the results being done on two directions: aspects of physical aging, respectively aspects of the photodegradation processes associated predominantly with the acrylic binder.

In the last part of this chapter, the efficiency of infrared spectroscopy was tested in conjunction with the PCA analysis in order to highlight latent variables, the existence of some specific binder-pigment interactions, and the discrimination capability for complex situations, in which the comparison and the direct visual analysis of the IR data is not sufficient.

Chapter 4 deals with the analysis of the aging characteristics of some adhesives and polymer consolidants, which are frequently used in current conservation/restoration procedures. Similar to the study performed on acrylic paints, chemical and structural changes which occurred during the accelerated aging treatments were analyzed. The obtained spectral data were correlated to the stress factors in order to identify the processes and the degradation rate, respectively the main chemical species involved in the reaction.

Chapter 5 presents a series of case studies for a comparative analysis regarding the degradation dynamics in natural polymers. The analysis in relation to traditional techniques – oil, tempera, was achieved by presenting some case studies carried on various art objects. The aim of the study was to investigate the existence of aging markers that may assist in the identification of highly degraded samples, and secondly, the study of the main degradation mechanisms that lead to the loss of the original characteristics of the material.

The last section of the thesis presents **general conclusions**, personal contributions and prospects for future development. References are preceded by the list of the author's publications and a series of appendices which contain mainly tabulated data, of practical interest, regarding physicochemical characteristics of modern pictorial materials, respectively supplementary experimental data.

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CHAPTER 1. MODERN PAINT MATERIALS

1.1 SYNTHETIC RESIN PAINTS. GENERAL ASPECTS

1.1.1 Brief history of modern artists' paints development

The first synthetic paints, known as lacquers or enamels, were obtained from nitrocellulose or by adding alkyd resins in traditional oil colors. In 1933, Henry Levison was founding the company Permanent Pigments®, which would produce two decades later, under the name Liquitex®, the first range of water-based acryl paints (emulsions) (*Marontate, 1996*). Towards the mid-'50s, the acryl emulsions knew an extraordinary development and they were gradually adopted as painting materials by numerous artists such as Andy Warhol and Helen Frankenthaler (*Chiantore, 2013*).

1.1.2 The chemistry of modern paints. Introduction to polymer physics

Almost all modern paint binders are formed of polymers – macromolecular compounds resulting by the binding of several identical structural chemical units *(mers)* linked together by covalent bonds. The relationship between the molecular structure and the physical and chemical properties of the film is of great importance (*Blaga, 1981*), the knowledge of this relationship being essential for understanding the mechanisms through which the polymer acts as a binder and not the least in order to correctly choose it according to the purpose.

1.2 BASIC ASPECTS OF MODERN PAINTS TECHNOLOGY

The applicability for the use of a synthetic resin as a medium for art paints or varnishes is directly determined by its physical features, especially by those related to resistance and flexibility (for example the resistance to cracking or fracture), aspects which are related to the value of the glass transition temperature (T_g) of the polymer. In the formulation of the paint, a pigment (or several) will be added to the basic binder consisting in fine, insoluble particles with a diameter between 0.2 and 20 μm, which give color and opacity to the paint, respectively fillers (in general inert minerals), for volume, texture or luminosity effects (*Learner, 2004; Croll, 2007*).

1.2.1 Synthetic binding media

Generally speaking, the term acryl includes a large range of polymers with high molecular weight, derivatives of the acryl, methacrylic and chloroacrylic acids, the effective monomeric species that are included in the acryl polymers being most often esters of the above-mentioned acids, known by the name of acrylates and methacrylates. The first acryl emulsion-based products were mostly based on copolymers of ethyl acrylate (EA) and methyl methacrylate (MMA), which have recently been replaced by copolymers of n-butyl acrylate/ methyl methacrylate (nBA/MMA) (*Learner, 2004*).

1.2.2 Siccative oils

From a structural point of view, oils are complex mixtures of triacyl glycerols – esters of glycerin and fatty acids, generally ranging between C_{16} and $C_{18:3}$. The properties of each type of oil and consequently its features as a painting medium are largely determined by the nature and the relative proportion of the constituent fatty acids.

1.2.3 Pigments

The most important classes of pigments of the 20th century include cadmium-based pigments (shades of red, orange, yellow), iron-based synthetic oxides (ochre, red), azo pigments (mono or disazo), polycyclic pigments (of phthalocyanine, oxazine, quinacridone, perinone etc.), a series of blue synthetic pigments (Prussian blue, ultramarine blue, cobalt blue), earth pigments, titanium white, carbon black and black iron (*Learner, 1998*).

1.2.4 Mineral fillers

Fillers are inert, powdery minerals, which were introduced in order to increase consistency, adhesion and the thermal stability, respectively in order to lower the manufacturing costs. The mineral fillers most frequently found in the formulation of art paints are: calcium carbonate, hydrated aluminium silicate, barium sulphate, hydrated calcium sulphate, and silicone dioxide.

1.2.5 Additives

Apart from the already mentioned basic compounds (binder, pigments, fillers), the acryl emulsions contain a large range of additives, which are introduced both during the production of the polymer emulsion (1) and subsequently, during the formulation of the paint (2), and except for the volatile compounds, all these chemical species shall be found in the final paint film (*Learner, 2000; Jablonski, 2003*).

1.3 CONSERVATTION AND RESTAURATION OF MODERN PICTORIAL LAYERS
1.3.1 Properties of modern pictorial layers

The surfactants on the surface of the film can determine changes of the optical properties – gloss, opacity and/or of the mechanical properties – they prevent the adhesion of the varnish layers (*Golden, 2002*), favor dust deposits and biological attacks. Also, they may cause foaming effects, which are difficult to remove by classical cleaning procedures (*Chiantore, 2002; Golden, 2002*).

1.3.2 Behavior under conservation and restoration treatments

The cleaning procedures which are currently used cover both dry and wet methods (*Murray, 2001*), including the use of organic solvents, and the main problems are centered on the following directions: the difficulty to remove the dust deposits; the sensibility of the pictorial layers to the cleansing agents which are used in the classical treatments; the solubilisation of the pictorial layers during the wet cleaning treatments; identification and characterization of the compounds and of the chemical species present in the binder.

1.4 CURRENT STATE OF RESEARCH

Due to the presence of the additional compounds, mostly contributions given by pigments, the analysis of binders in a pictorial layer has always raised problems. In the case of modern paints, apart from the pigments, the presence in large quantities of some fillers, but also of some stabilizers in small concentrations, may cause an even greater complexity factor in relation to the possible identification of the present chemical species (*Learner, 1998*).

The present stage of the research in the field points out the presence of several directions of study (*Domenech-Carbo, 2011; Wolbers, 2013; Di Crescenzo, 2014; Pintus, 2016; Ciccola, 2017*):

- in-depth analysis regarding the general structure of synthetic resin-based binders (mostly acryl emulsions), but also of the individual compounds within the formulation;
- analysis of the characteristics and the way of interaction of the minor compounds in the formulation: pigments, fillers, additives; their effect upon the behavior of the film to aging;
- study and evaluation of the degradation kinetics under the action of different stress agents (UV radiation, microclimate parameters, air pollutants);
- monitoring of the material features along with the natural aging processes;
- studies regarding the interaction of the paint film with other materials, respectively the film response to different conservation/restoration treatments.

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CHAPTER 2. FTIR TECHNIQHUES FOR THE ANALYSIS OF PAINT MATERIALS

2.1 THEORETICAL ASPECTS

The specialized literature points out the strong character of the FTIR technique in the analysis of modern paints and the specificity in differentiation based on the spectral signature of the fingerprint region of the various chemical classes existing at the binder level (*Domenech-Carbo, 2001; Learner, 2004*). The main advantage of this technique is given by the fact that the generated spectra give information both regarding the organic compounds and also regarding the inorganic compounds, which are present in the investigated samples. Also, they provide complex datasets, which can be handled by multivariate analysis techniques, thus offering the possibility to extract extremely valuable latent information (*Sarmiento, 2011*). In general terms, the ability of different functional groups to absorb IR radiation at specific frequencies stands at the base of the method (*Herzberg, 1991; Smith, 1998; Griffiths, 2007*). The absorption involves discrete, quantified energy level, the characteristic frequencies for a given molecule being determined by the masses of the constituent atoms, their spatial arrangement and the strength of the bonds between them.

2.2 EXPERIMENTAL ASPECTS. THE ATR TECHNIQUE

Basically, the technique is based on the internal total reflection phenomenon. The attenuation of the internally reflected radiation is the result of the penetration of the so-called evanescent wave in the sample which is in direct contact with the reflecting surface, and the basic characteristic of this wave is that its energy decreases rapidly with the increase of the depth of penetration (d_p) into the sample, according to the expression:

$$d_p = \frac{\lambda}{2\pi(n_1^2 sin^2\theta - n_2^2)^{1/2}}$$

where λ is the wavelength of the IR radiation, n_1, n_2 are the refractive indices (of the ATR crystal and the sample), and θ is the angle of incidence.

In relation to other IR acquisition techniques, the ATR mode offers the following advantages:

- it is a non-destructive technique (the samples can be recovered and reanalyzed or given for analysis to other complementary techniques) (*Willneff, 2014*);
- it does not need a sample preparation protocol in view of the analysis and thus, it is recommended as an extremely rapid technique;
- provides high spatial resolution data; allows investigation of an extremely small area due to the magnification factor of the ATR crystal (*Maryse, 2009*);
- it gives information at the level of the superficial layers and it is ideal for film characterization, surface layers being practically the most vulnerable areas, as it reflects the interaction with the environment and / or with conservation treatments;
- it involves relatively low costs (of ~10 times lower compared to micro-FTIR).

2.3 INFRARED OPTICAL PROPERTIES OF POLYMERS

All polymers are characterized by their own frequencies, in which the incident radiation comes into resonance with certain internal vibrations of the given body. Infrared absorption spectra contain a valuable volume of information on the state or modification of macromolecules. The extraction and interpretation of this information implies the understanding of some fine notions related not only to the molecular structure of the analyzed polymer material, but also to the aspects regarding the statistical mechanics of the macromolecules, their configuration and conformation, or the flexibility of the chain and the factors which influences it (*Volintiru, 1980*).

2.4 CHEMOMETRIC TECHNIQUES FOR THE ANALYSIS OF SPECTRAL DATA

Often, by direct spectral analysis it is difficult to discriminate the compounds present in different painting layers, especially in the case of complex mixtures; however, the FTIR spectra contain information that could be highlighted by multivariate techniques. The use of some statistical mathematical methods allows the differentiation between similar vibration spectra for complex situations where the comparison and the direct visual analysis of the fingerprint area is not sufficient. The chemometric analysis of spectroscopic data is a powerful instrument, which allows extracting some extra interpretable information within the investigated systems, emphasizing the most important variables, which are involved in the process.

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CHAPTER 3. ANALYSIS AND CHARACTERIZATION OF SOME ACRYLIC PAINTS

3.1 WORKING METHODOLOGY

3.1.1 Analytical procedure

It was characterized the molecular structure and investigated the ability to identify the constituent components for a series of acrylic art paints.

Taking into consideration the specialized literature regarding the investigation and the characterization of pictorial layers by spectroscopic techniques (*Meilunas, 1990; Domenech-Carbo, 2011; Azemard, 2014*), an experimental setup was approached which underwent the following stages:

(1) investigation and characterization of known macroscopic samples; identification of diagnostic bands which allow for a clear assignment when analyzing an unknown sample (with similar chemistry);

(2) analysis of the degradation dynamics in the same set of macroscopic samples subjected to a controlled accelerated aging protocol;

(3) tracking of degradation markers that could assist in the identification of severely degraded samples;

(4) assessing the influence of pigments (and other components within the formulation) on the induced effects during the accelerated aging tests.

3.1.2   Accelerated aging treatments

The photosensitivity of the materials was tested by exposure under different UV spectral regions. The following steps were followed in establishing of the testing protocol: (1) defining the problem: establishing the necessary framework and infrastructure; material characterization; identifying critical functional characteristics and properties that could act as indicators of possible degradation; identifying possible degradation factors; estimation of possible degradation mechanisms; establishment of a testing model; (2) pre-testing: designing and performing preliminary tests done in extreme conditions for the rapid demonstration of the degradation effects and mechanisms; (3) testing: designing and performing long-term monitoring tests in pre-established conditions for the determination of the degradation rate; (4) interpretation and validation of the results establishing patterns of degradation processes and correlating laboratory data with theoretical data; assessing the stability of the tested materials; predictions regarding the behavior of the tested material over time.

3.2 IDENTIFICATION AND CHARACTERIZATION OF THE MAJOR COMPONENTS

The limited data within the literature on the new types of synthetic materials, as well as the lack of some dedicated databases, determined that the first stage of the present study should be oriented towards the construction of a library with reference spectra, respectively towards the identification and the characterization of the main constituent compounds within the analyzed paints.

3.2.1 Molecular characterization of the binder

Spectra of the analyzed paint films are dominated by the acrylic emulsion absorption bands. The analysis of the identified characteristic IR bands indicate the presence of an p(nBA/MMMA) copolymer - poly(n-butyl acrylate/methyl methacrylate).

3.2.2 Molecular characterization of the pigments

Most of the organic pigments will be characterized by a spectral signature with strong and sharp absorption bands located both in the fingerprint area as well as in the large wavenumber region (3300-2900 cm^{-1}) characteristic for the C-H, O-H and N-H stretching vibrations (*Newman, 1979; Derrick, 1999; Learner, 2004*). Vibrations associated to the aromatic compounds will be visible in the 3100-3000 cm^{-1}, 1600-1585 cm^{-1} and 1520-1400 cm^{-1} region, respectively within the lower wavenumber region: 900-675 cm^{-1}. The absorption of the carbonyl groups are positioned for most synthesis organic pigments in the 1705-1730 cm^{-1} range.

In contrast with the general spectra associated with organic pigments, inorganic pigments are characterized by a simplified spectral signature, or sometimes even devoid of features (*Nyquist, 1997; Vahur, 2009; Vahur 2010*) in the mid-infrared region. For example, titanium white (PW6) will present a single absorption band, broadened, at lower wavenumbers – 900-400 cm^{-1}, similar to the black iron oxide (PBk11) (peak at 544 cm^{-1}), this last one showing also a strong Christiansen effect which significantly distorts the spectrum. FTIR spectra of earth pigments will be dominated by the absorption bands related to the constituent materials (generally bands with a slightly broadened profile), information regarding the oxides which give the pigmentation being observable in the fingerprint area and only for certain situations of quantitative ratio.

3.2.3 Molecular characterization of the mineral fillers

In terms of the mineral fillers, the careful analysis of the fingerprint region allowed for the identification of the presence of calcium carbonate in most of the acrylic paints analyzed.

Summary

The FTIR analysis performed on the acrylic paints selected in this study points out a high sensitivity from the point of view of the molecular characterization capacity. Starting from a minimum level of information (according to the data supplied by the producer: acrylic emulsion-based paint + pigment index) it is possible, by a systematic analysis of the samples, to identify the type of emulsion,

respectively to highlight the diagnostic bands associated with the others components in the formulation: pigments, fillers, additives.

By building a spectral library with reference samples including spectra recorded on pure pigments, the analysis of the obtained data allowed for the identification of the specific absorption bands in the case of the majority compounds present within the analyzed paints. The high complexity of the samples given by the large number of present components generates an impressive number of absorption bands. Although from the theoretical point of view "the more vibrations noticeable in the spectrum, the more obtained information", in practice the bands overlap, minimizing the interpretation. Thus, even if a series of specific bands related to the pigment can be detected in the spectrum, the contributions due to the carbonyl groups, respectively to the C-O stretching vibrations assigned to the acrylic binder, significantly hinder the interpretation.

However, there are situations when the present compounds exhibit extremely specific absorption bands that make it possible to identify and individually assign bands through a classical visual analysis. Band overlaps can also provide semi-quantitative information and most of the times the relative proportion of two compounds present in a mixture can be estimated. For situations where more than one pigment and/or multiple fillets are in the formulation, a higher complexity is expected and consequently a significant difficulty in the assignment of the absorption bands.

Compared to laboratory samples, the analysis complexity significantly increases for samples coming from art objects. The analysis of an unknown sample will be extremely problematic, and in this respect, any information regarding the sample history is extremely valuable because it restricts the research range and consequently the analysis time.

3.3 ANALYSIS OF ACCELERATED AGING INDUCED DEGRADATIONS
3.3.1 Aspects of physical aging
Comparing the reference spectra with the data recorded at different UV exposure thresholds, we can notice a series of spectral variations regarding the relative intensity of the absorption maxima. These variations, translated by decrease or enhancement effects of the absorption rate are a general feature for all tested samples and they can experimentally be related to a relaxation of the polymer chain segments. This relaxation effect is explained (*Robertson, 1984)* based on reorganizations at the molecular level, especially in the areas characterized by a high free volume, as a direct response achieved during the thermal fluctuations. Regarding the relaxation dynamics, the spectra, acquired at different exposure thresholds, point out the non-linear nature of these processes (*Struick, 1980*).

Summary
The analysis of the experimental data registered on the aged samples revealed in the case of all tested acrylic paints a similar behavior to that of glassy materials, where physical aging can be considered a slow, time-dependent, structural reorganization to the amorphous state of metastable equilibrium. From a qualitative point of view, the obtained FTIR data points out alterations in the packing geometry of the chains generally determined by phase transitions. It has been shown that the effects induced by aging depend both on the thermal history of the polymer and on the experimentally induced stress as aging occurs. Investigation of relaxation times at successive exposure thresholds has revealed a relaxing dynamics that progressively decrease with aging time and the reset of the aging process for prolonged exposure of the samples.

Describing and assessing the effects of physical aging pose major difficulties in terms of the complexity given by the non-linear nature of the processes that take place and of the relaxation dynamics, which follows a Kohlrausch-Williams-Watts (KWW) function.

The term of *spectral signature* should be reevaluated in the case of polymeric materials, the spectrum recorded for such materials being a unique signature specific for that particular moment. In other words, the infrared spectrum of a polymeric material will be given by the characteristic absorption bands of the constituent molecular groups *found in the physical and morphological state from the moment of the spectrum acquisition,* to which the effects due to the sample preparation technique, respectively the acquisition techniques sum up.

3.3.2 Aspects of chemical degradation
Changes induced at the chemical level were evaluated by direct comparison of the FTIR spectra recorded before and during the UV exposure. Starting from the changes observed in the spectrum, we can notice a relatively similar degradation dynamics in the case of all sets of aged acrylic paints, regardless of the nature of the pigment in the formulation. The similarity of the spectra recorded at the

level of the investigated samples, suggests the presence of some related aging mechanisms at the level of the acrylic binder. In terms of wavelength specificity, we can notice the similar response of aged samples exposed under 300-380 nm UV radiation, compared to the samples exposed below 300 nm, in the latter case a much higher degradation rate being recorded.

The evolution of the spectral elements during the accelerated aging tests highlights the existence of several alteration processes that affects the polymeric structure of the acrylic binder. The main spectral elements observed are:

- amplification of the absorptions from the hydroxyl region (3600-3100 cm^{-1}) related to the formation of new OH groups;
- progressive decrease of the absorption bands related to the stretching vibrations C-H (aliphatic) within the 3000-2800 cm^{-1} region, respectively a slight shift of their position towards higher wavenumbers;
- progressive decrease of the carbonyl band (peak at 1730 cm^{-1}) and its symmetric broadening;
- overall decrease of the absorption bands related to the polymer and loss of spectral elements in the fingerprint area for high exposure thresholds.

Due to their photochemical stability, mineral fillers can be used as an internal standard as no changes at their level are induced during the irradiation. For the semi-quantitative evaluation of the chain scissions within the acrylic binder, the integrated IR band area ratios A (ν C-H) / A (ν CO$_3^{2-}$), A (ν C=O) / A (ν CO$_3^{2-}$) and A (ν C-O) / A (ν CO$_3^{2-}$) were calculated corresponding to the stretching vibrations of the CH groups present within the hydrocarbon skeleton, the C-O and C=O stretching vibrations present in the ester functional groups of the polymer, respectively the stretching vibration of the carbonate groups within the calcium carbonate used as a mineral filler (*Domenech-Carbo, 2011*). For the majority of the analyzed samples the binder/filler ratio value lowered.

At the level of the acrylic emulsion we can notice based on the recorded data side-chain reactions resulting in the loss of the CH$_3$ groups and the decrease of the carbonyl bands. For quantifying these processes, the integration of the IR bands area corresponding to the stretching vibrations related to CH$_3$ groups in the 3000 - 2900 cm^{-1} region and the stretching vibrations of the C=O groups in the 1740 - 1714 cm^{-1} range, was calculated.

Spectral analysis of the carbonyl area is problematic, changes recorded at the level of the carbonyl groups being irregular during the UV radiation exposure. These uneven changes are probably based on complementary reactions: on one hand the loss of the ester groups, and on the other hand oxidation processes with formation of new carbonyl species.

Influence of the aging conditions. Wavelength specificity

We can notice, depending on the irradiation source used within the aging tests, extremely different degradation rates. For exposures under high energy radiation (λ below 300 nm), the main induced reactions will be homolytic (at the level of all involved bonds) which will cause the relatively rapid fragmentation of the polymeric structure (*Melo, 1999*). For samples exposed to broad-spectrum UV radiation (305-380 nm) a slight amplification of the carbonyl area can be recorded at the initial exposure thresholds, which may indicate the presence of some moderate processes of oxidation. Compared to the samples exposed to high energy UV radiation, for the same initial thresholds, the general fingerprint of the investigated samples is, however, predominantly preserved.

Influence of the compounds within the formulation
• *The effect of pigments*

It was observed the catalytic effect of the organic pigments within the general degradation processes related to the acrylic binder, for samples exposed below 300 nm. Considering that the entire set of test samples has been subjected to the same aging protocol, and in terms of acrylic emulsion the sample show the same structure, the preferential oxidation with formation of new species in the carbonyl area can be related to the particular effect given by the nature of the other components in the formulation.

• *The effect of additives*

During the aging, the surfactants segregate at the level of the film surface. For a semi-quantitative evaluation of this effect, the ratio of the peak area centered at 1065 cm^{-1} (associated with the surfactant present in the formulation) to the peak centered at 1238 cm^{-1} (associated with the acrylic emulsion) was calculated, this ratio being an indicator of the surfactant concentration at the surface (*Chiantore,*

2007). Obtained data shows a high concentration of the surfactant at the surface of the analyzed films especially in the case of the samples exposed below 300 nm UV radiation, compared to the other two UV aging regimes, for which the induced changes are significantly lower. Analysis at successive exposure thresholds points out a non-linear evolution, which can be related to achieving a disintegration threshold, the aging time being sufficiently long for the surfactant molecules to undergo degradation processes.

Aspects regarding the chromatic stability

Changes at the level of the CIE (L*,a*,b*) color coordinates were registered for most of the analyzed samples; these changes are mainly related to a surface discoloration effect following the induced aging processes. The observed overall trend points out a decrease of the general chromatic variation, its rate and direction being directly dependent on the photosensitivity of each pigment. The colour coordinates seem to be associated to the changes that the pigment undergoes, while the variation of the luminosity provides information particularly regarding the changes which take place at the level of the binder.

Summary

FTIR data recorded on the aged paint samples shows a typical evolution of the photodegradation processes encountered in acrylic polymers. The most obvious aspect in the FTIR spectra is given by the oscillatory variations in the intensities of the carbonyl peak – related to the loss of the ester groups, respectively to the formation of new species following oxidation. The progressive decrease of the bands in the 1450-1470 cm^{-1} region could suggest the abstraction of the hydrogen within the CH_2 groups present in the basic polymer skeleton. An oscillatory trend is also recorded for the absorptions bands within the CH region and the bands in the C-O region respectively, mainly related to structural relaxation processes. Most of the tested materials shows wavelength specificity. Under UV radiation with λ in the 300-380 nm range, the photodegradation processes of the acrylic binders are significantly lower compared to wavelengths below 300 nm, which will generate the most harmful effects in the situation where there are also specific chromophores capable to absorb the radiation. For high exposure thresholds, following the cross-linking and the fragmentation of the polymer chains a monomer is generated (generally below 300 nm UV radiation).

3.3.3 Advanced data processing. Chemometric analysis of FTIR data

The use of PCA analysis on large spectral datasets allowed the identification of some specific binder-pigment interactions, based on the score plots in the CH and carbonyl region. Specific binder-filler interactions could be also emphasized. The results indicate that the structural changes due the binder-pigment or binder-filler interactions are extremely specific, in the sense that for some situations it is possible to group and separate the samples – aspect which could be used in the future to develop a model that could assist in the discrimination/identification of some unknown samples.

PCA analysis on aged datasets indicates the existence of some correlation between the scattering degree of the data within the score plot and the degradation degree related mainly to the acrylic binder, and the possible influence of the binder-pigment interactions at the level of the degradation processes dynamics.

The low scores generated within the tested PCA models on regard sample grouping and discrimination reflect the existence of several variability sources and the complexity (heterogeneity) of the dataset. Even for low scores however, in some cases a relatively good separation of selected acrylic paints is possible based on the chemical class of the pigment within the formulation, both in the case of the reference samples (non-aged) as well as in the case of the UV aged samples.

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CHAPTER 4. ANALYSIS AND CHARACTERIZATION OF SOME POLYMERIC MATERIALS USED IN CULTURAL HERITAGE CONSERVATION AND RESTORATION

4.1 POLYMERIC MATERIALS USED IN CONSERVATION

Among the most common classes of synthetic materials used at the moment within the conservation and restoration field we can mention polyacrylics, polyvinyls, poliesters, polyamides, polyolefins or epoxi resins. (*Horie, 2010; Down, 1996; Asensio 2009*).

4.2 EXPERIMENTAL RESULTS

4.2.1 Notes on the identification of synthetic resins via FTIR techniques

Unlike natural resins (complex mixtures of multiple components, impurities, etc.), synthetic resins are relatively pure, this molecular structure providing intense sharp absorptions bands, extremely well resolved. Structurally, synthetic resins are generally composed of long chains based on a relatively small number of functional groups. For the characterizations of these materials all spectral regions should be analyzed and an exact identification must include cross-checking of the data.

4.2.2 General aspects regarding the ageing mechanisms of selected resins

The general aspects observed in the FTIR spectra of aged samples are:
- oscillatory variations at the level of the intensity of the absorptions bands both in the CH region and carbonyl region, that points towards competitive effects between different processes and ageing mechanisms;
- amplification of the absorptions within the 3600-3100 cm^{-1} region, characteristic for hydroxyl groups;
- broadening of the carbonyl peak (aspect correlated with the formation of some degradation compounds following radical reactions);
- formation of new bands in the spectra during the UV exposure, mostly new bands positioned in the carbonyl region associated with the formation of oxidation species;
- gradual broadening of the absorption bands within the fingerprint region and the loss of some spectral elements - aspects that can be correlated with a severe degradation of the polymeric network;

Summary

The analysis of the new generation materials dedicated to conservation and restoration interventions is of real necessity, the problem of material identification being especially emphasized in the case of modern artworks which are actually based on the same class of synthetic materials. The objectives of the study were mainly focused on the capacity of identification and discrimination by FTIR analysis of the various synthetic resins, respectively on the changes induced within the spectral signature with aging.

Although complex, the FTIR spectra of synthetic resins can provide relevant information, careful analysis of the fingerprint region showing diagnostic spectral elements. Assignment with a high degree of certainty is possible especially in the case of the main absorption bands. For complex samples (mixtures or aged samples), a material identification implies the need to solve the bands due to the multitude of the present organic compounds (and inorganic ones). In the case of synthetic resins, the C-C stretching vibrations, respectively the C-H bending vibrations, which are important in the analysis, fall in a relatively narrow range (1600-1000 cm^{-1}), which often results in spectral overlaps and/or spectral interferences. In addition, from the perspective of practical applications, experimental data emphasizes the difficulty of identifying diagnostic bands for low concentration solutions due to signal interferences with the substrate.

From the preventive conservation point of view, we can notice that the response of the material under UV radiation action is selective and preferential, based on the nature of the polymer binder in the formulation. Physical aging can be defined as changes generated in the spatial arrangement of macromolecules and side chains. These structural reorganizations can generate various changes at the level of the thermodynamic properties, which further on can determine possible changes at the level of solubility and of the optical properties, respectively the change of the mechanical properties such as flexibility.

The morphological changes induced at the level of the film surface are related to the observable changes at the level of the molecular structure. The photodegradation of the tested materials determine the emergence of an oxidation area at the level of the superficial layer, which, as the degradation of the polymer skeleton takes place, generates local heterogeneities (high concentrations of oxidation species), which further determines changes in the topography of the superficial layers. The general trend of diminishing reflectance (spectrophotometric data) along the decrease of the intensity of the IR absorption bands, suggests the increase of the surface roughness along with the exposure time (increased surface scattering).

Both physical aging and photodegradation processes lead to the loss of the elasticity of the consolidants; following cross-linking new tensions are generated in the sub-layer which can determine the emergence of micro-cracks at the level of the surface. The impurities, which are present in the formulation, respectively the additives, may act as UV absorption centers and therefore as initiators of the degradation processes. A certain product can be therefore unstable as a direct effect of the minority compounds embedded in the formulation and not necessarily of the basic polymer compound.

Similar to the tested acryl paints, the rate of the degradation processes achieves a peak under low wavelengths UV exposure. Even if aesthetically the UV irradiated samples do not exhibit at low exposure thresholds sign of alteration, the molecular analysis points out a rich reaction kinetics, the spectral changes being assigned to multiple processes running simultaneously - chain breaks, crosslinking and oxidative processes with the formation of new chemical species. Part of these aspects may stay hidden because these changes are not exhibited from the beginning at the optical or mechanical levels.

Regarding the yellowing process we mention the fact that it has an oxidative nature, with chromophore formation, a reaction which is accentuated with the exposure time. The formation of some reaction products affect the solubility and consequently the reversibility of the material, aspects which are important from the point of view of the practical applications.

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CHAPTER 5. ANALYSIS OF DEGRADATION MECHANISMS IN NATURAL POLYMERS. CASE STUDIES

5.1 COMPARATIVE ANALYSIS IN RELATION TO TRADITIONAL TECHNIQUES
5.1.1 Notes on the FTIR analysis of traditional paint materials
Starting from a series of case studies, in this subchapter a comparative analysis of the degradation dynamics was made in a series of natural polymers frequently found within art objects. The research focused on the analysis of aged paint layers (made in classical techniques) and on the identification and discrimination capacity of the various organic compounds and of degradation markers respectively.

5.1.2 Experimental results
In addition to the characteristic bands associated with each material, in the FTIR analysis a series of absorption bands identified within the literature as specific degradation markers were considered: (*Meilunas, 1990; Pilc, 1995; van der Weerd, 2005; Azemard, 2014*):
- peak at 1778 cm^{-1} for the identification of aged siccative oils;
- absorption bands at 1620 cm^{-1}, 1636 cm^{-1} and 1586 cm^{-1} ascribed to the carboxylic acids generated by the reactions/interactions between the binder (oil) and the pigments;
- absorptions within 3500 cm^{-1} region (hydroxyl compounds), and peaks around 1776 cm^{-1}, 1734 cm^{-1} and 1714 cm^{-1} respectively (carbonyl species), degradation compounds due to the oxidation of the triglycerides;
- peaks at 3289 cm^{-1}, 3080 cm^{-1}, 1654 cm^{-1} and 1539 cm^{-1} for aged samples of egg yolk;
- peaks at 3525 cm^{-1} and 1300 cm^{-1} as indicators of secondary alcohol formation;
- peaks at 2940 cm^{-1}, 1464 cm^{-1}, doublet at 1394 cm^{-1} / 1364 cm^{-1}, 1246 cm^{-1}, spectral elements characteristic for aged natural resins.

Summary
In the case of most of the analyzed samples a complex spectral signature was observed, with absorption bands strongly broadened in the fingerprint area as a direct effect of the spectral overlaps, the various present compounds in the sample having similar absorption regions. In the majority of the

analyzed samples, the bands specified by the literature as degradations markers for identifying the presence of aged oil or aged egg yolk, respectively, are shifted and/or cannot be emphasized within the direct spectra. In the case of severely aged samples, the molecular signature presents a complex pattern given by the existence of components with different degrees of aging. For such cases, the interpretation must take into consideration the analysis of the characteristic IR bands related both to the reference material (not-aged) and also to the aged one, respectively multiple points analysis, as samples from relatively close areas may have for example different degrees of oxidation which will generate fine details in the spectrum making characterization more difficult.

In the case of linseed oil, its exact identification will consequently need the identification of the pigments present within the analyzed sample, the presence of different coloring agents having a specific influence at the level of the degradation chemistry and kinetics of the oil, aspects which are reflected in the spectrum. The most important changes observed at the level of the infrared spectra are the broadening of the absorption area related to the carbonyl groups following the formation of new bands in the 1800-1700 cm^{-1} region, respectively formation of metal salts in the 1600-1500 cm^{-1} region. These bands can be highlighted by spectral resolution improvement techniques, the profile of the second derivative of the spectrum allowing to solve these peaks even in situations where fine structures and/or shoulder bands are not observed in the direct spectrum. With rare exceptions, this region is not masked by bands due to other components, which allows the use of these absorptions as a criteria in the classification and identification of the binder.

At the binder's level, we noticed that most of the diagnostic bands disappear as a result of aging processes and after a specific threshold of degradation, an exact identification of organic materials is no longer possible through simple FTIR analysis. For particularly complex situations, the technique will allow therefore at the best only the identification of the classes of organic compounds. Methods to improve spectral resolution can clarify certain situations, and in order to reduce the degree of uncertainty (in assignment) it is recommended to correlate the original spectrum with the second derivative of the spectrum.

In the case of the complex multilayer samples, the ATR analysis is limited as the registered spectra will reflect mainly the chemical characteristics of the superficial layers and therefore the compounds present in the inferior layers can often remain unidentified. The strong absorptions and the signal interferences can also limit the interpretation in the sense of masking the weak bands associated with minor or weakly absorptive IR compounds. The correlation of data with complementary analytical techniques is often necessary for the confirmation of some particular situations, especially in terms of constituent pigments.

5.2 STUDY OF THE OXIDATION MECHANISMS IN NATURAL FIBERS
5.2.1 Notes on the FTIR analysis of natural fibers
Due to their internal structure, cellulosic fibers have a certain susceptibility to stress factors - microclimate variations, UV radiation, biologic attack; all these environmental influences leading to structural changes. Aged fibers (textiles) will therefore have different (modified) characteristics, aspects that can be correlated with specific mechanisms and processes of degradation: oxidation, hydrolysis, macromolecule fragmentation, cleavage of intermolecular bonds (*Garside, 2004*).

5.2.2 Experimental results
The degree of structural organization was assessed by calculating the crystallinity index (TCI), the lateral order index (LOI) and the hydrogen bond intensity (HBI) respectively. Obtained data could be related to specific degradation processes: under microclimate stress the evolution of the IR parameters indicates a slight depolymerization and the oxidation of the amorphous regions (*Garside, 2004*). Slightly more pronounced photo-oxidation processes were observed in the aged samples exposed to UV radiation, the kinetic of degradation showing wavelength specificity.

Summary
FTIR data registered on the aged samples allowed a qualitative interpretation of the main structural changes, as well as highlighting of fines details that can be correlated to the degree of ordering and changes of the ratio of crystallinity indices in these types of materials. It has been shown that the assessment of the degree of degradation induced by artificial ageing procedures requires a particular analysis depending on the nature of the applied stress factors. For high exposure thresholds surface photo-oxidation of cellulose with the generation of chromophores as well as phenomena indicating acid dehydration are highlighted.

5.3 COLLAGEN DENATURATION ANALYSIS

5.3.1 Notes on the FTIR analysis of protein structures

The peptide group, the repetitive structural unit of proteins, determines nine IR characteristic bands: amide A, amide B, amide I, II, ... VII. Representative for the infrared spectral signature of proteins are the bands associated with amide I and amide II structures.

5.3.2 Experimental results

For the assessment of the collagen denaturation rate, the difference in positioning between the amide I absorption band (peak at 1627 cm^{-1}) and amide II (peak at 1538 cm^{-1}) was calculated. Aspects regarding collagen denaturation are also highlighted by the increase in the contribution of non-organized proteins with secondary structures - characteristic absorption band centered at 1625 cm^{-1} compared the helical component - absorption peak at 1655 cm^{-1} (*Kamińska, 1996*). Spectral details were obtained by mathematical refinement of the spectrum.

Summary

The most significant change observed in the FTIR spectra was the displacement of the amide II absorption band from 1550 cm^{-1} to 1538 cm^{-1}, this shift towards lower wavenumbers being associated with the conversion of collagen into the gelatin discorded structure. The use of spectral resolution improvement techniques has allowed extraction of information related to the secondary protein structure and on the local conformation of the polypeptide backbone. In terms of degradation dynamics, the collagen denaturation process can be related with changes in intramolecular hydrogen bonding as well as possible changes within the constituent amino acids that destabilize the ordered structures.

CONCLUSIONS

C.1 GENERAL CONCLUSIONS

The studies performed within this thesis highlight the importance of the formulations, the high complexity given by the multicomponent nature of these paint systems leading to major difficulties form a material study point of view. The results showed that the aging processes induced in the new-generation painting materials tested are due to a complex cumulative physical processes and chemical reactions that gradually affect the appearance of the pictorial surface, the film morphology and the reactivity of the polymer binder.

Regarding the synthetic resin-based binders, their aging could be seen as a degradation process, which depends, on one hand, on a series of inherent factors – the chemical nature of the constituent compounds, and on the other hand on the external factors and the interaction with the environment and/or with other materials. Whereas each of the compounds present in the formulation show their own characteristics, the specific mechanisms as well as the degradation rate will depend on multiple variables.

Experimentally it has been observed that the chemical aging of these polymer systems includes multiple mechanisms, which often overlap. The analysis of the recorded data revealed in the case of the photodegradation processes that they follow a non-linear function, situation explained by the coexistence of competitive reactions with different activation energies. The aging studies also revealed the importance of the entropic nature of the elasticity of the polymer systems in the evaluation of the molecular dynamics processes, another mechanism which affects the polymer materials being represented by the physical aging. Complex phenomenon, the physical aging results because all temperature-dependent properties change abruptly around T_g. Moreover, even for temperatures below T_g, the properties of these classes of materials continue to modify themselves during extremely long periods of time, even if at a low rate – aspect related to the molecular reorganizations within regions characterized by a high free volume. The physical aging phenomenon, which is thermodynamically determined, cannot be stopped and is rarely reversible due to the cumulative effects given by the chemical aging. All these processes and degradation mechanisms modify the spectral signature of the polymeric binder, which, even if it retains the macromolecular nature, will exhibit different physical and chemical characteristics.

The adopted ATR-FTIR methodology provides a detailed characterization of the present compounds with limitations regarding mixtures of multiple compounds with absorption in the same spectral regions. The technique allows for discrimination between the different classes of organic binders, but not the exact identification of their chemical structure. For complex samples which show large absorption bands in the fingerprint area, in order to discriminate the absorption bands of the existing chemical species, an advanced data-processing is imposed and/or the corroboration of the existing data with other analytical techniques.

Monitoring the degradation dynamics following accelerated aging treatments has highlighted an overview of the processes, reactions and changes taking place in the chemical and morphological structure of these materials. The ATR-FTIR analysis allowed the evaluation of the influence of different aging conditions on the properties of these materials and not least the correlation of the locally recorded results with the optical and structural changes occurring at the paint film level.

The analytical procedure was applied on a set of 150 laboratory samples representing acrylic emulsion paints (80 samples) and polymeric adhesives and consolidants (70 samples) respectively. The research study was completed by a comparative analysis with respect to the traditional techniques and the degradation dynamics in natural polymer compounds.

C.2 ORIGINAL CONTRIBUTIONS

In view of the applied research, the original contribution of the author can be summarized as follows:

- physicochemical characterization of a large range of new generation artistic materials (synthetic resin-based) through a rapid, efficient and relatively low-cost method;
- designing an aging protocol and performing long monitoring tests in pre-established conditions emphasizing the main chemical species involved in the reaction;
- assessing the effect of stress factors through comparative testing and analysis procedures;
- analysis of the oxidative degradation mechanisms related to several classes of synthetic resins by correlating the molecular effects with the macroscopic ones, observable at the film surface;

- use of chemometric techniques (PCA analysis) on large datasets emphasizing some specific binder-pigment interactions;
- building of a database specialized on acrylic paints and various polymeric materials used in current conservation/restoration practice which contains FTIR spectra registered on reference samples (not-aged) as well as on aged samples (at different exposure thresholds under the selective action of the induced stress factors);

The results point out the first FTIR studies investigating the physical aging of polymer systems within modern pictorial materials that highlights a similar behavior to glassy materials. The physical aging phenomenon was noticed in the case of all materials studied within this work -acrylic paints and various polymeric adhesives and consolidants. Since this phenomenon affects the mobility of the polymer segments, we can assume that it affects/interferes also with both swelling and relaxation processes, or photo-oxidation processes and crosslinking reactions associated with a wide range of macromolecular systems. Therefore, we draw the attention on the importance of recognizing and differentiating between physical aging processes and chemical aging processes affecting these types of structures in order to properly assess the distribution and degradation rate of these processes.

Overall, the present work brings contributions to a better knowledge of the chemistry and stability over time related to these new classes of pictorial materials. The study and the understanding of the degradation mechanisms supports a conscious practice of the restoration interventions. Not least, the obtained results supports authentication studies and detection of fakes within the art market through the ability to identify spectral diagnostic elements even in the case of complex, multicomponent samples.

C.3 FUTURE DEVELOPMENT PERSPECTIVES

Carried research confirms the potential of the ATR-FTIR technique in the analysis of modern pictorial materials, the recorded data and the achieved evaluations being confirmed by complementary studies which appeared in the specialized literature in parallel with the development of this thesis.

Regarding the processes and degradation mechanisms studies remain open, moreover as new polymers are embedded within the formulations of art and conservation/restoration materials.

Among the study directions that would significantly contribute to the understanding of the dynamics of these systems over time, and consequently to the conscious improvement and refinement of the existing conservation procedures, we can mention:

- in-depth studies regarding the structural relaxation processes in polymers;
- extending the study to a qualitative and quantitative analysis of the degradation processes by completing it with data provided by related techniques;
- study of changes induced at the level of modern pictorial layers under the influence of biological factors or interior and exterior pollutants;
- study of the changes induced at the level of the initial properties of the paint film following specific conservation/restoration interventions;
- study of these classes of materials in complex structures - modern and contemporary artworks;
- mapping of degradation products at the level of the pictorial layers with highlight of their distribution in order to optimize the restoration procedures and treatments;
- development of a portable fiber-optic ATR-FTIR equipment for in situ characterization.

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