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THE ESSENTIAL OF ESSENTIAL OILS IN THE PRESERVATION OF PAINTINGS ON CANVAS, AND RISKS OF FALLING INTO THE ATTRACTIVENESS OF THEIR ESSENTIALITY

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Abstract: The awareness of toxicological risk issues as a search for a substantial improvement in the quality of life, has progressively allowed the development of lines of research in Conservation and Restoration of Cultural Assets. One of these premises is the reduction of toxicity parameters, as for example happens with the use of natural and innocuous preservatives and biocides for the restorer, but that used without criteria can pose a clear risk to the conservation of the work. This research analyzes the incorporation of new natural materials for microbiological control, focusing the study on the inclusion of essential oils and extracts, which allow to promote the future conservation of the adhesive mixtures used in different restorative treatments of paintings on canvas. The aim is to make known the advantages and disadvantages that the inappropriate use of this type of substances can cause for the conservation of works, which currently present an upward projection of use in the conservator's workshop. For this, its fundamental characteristics are exposed, not only taking into account toxicity parameters, but also assessing its chemical composition and biocidal behavior against critical microbial pathogens. Gone is the primacy of the artistic work over the restorer, where the development of formulations free of harmful agents, facilitates friendly working environmental environments, seeking the perfect balance between heritage conservation and health.
Keywords: Restoration canvas paintings; sustainable conservation; Natural extracts; Natural biocides; green chemistry; Toxicology.

INTRODUCTION

Talking about biodeterioration in the conservation of paintings is a complex issue due to the framework of materials that make up the works, which complicates the prediction of their future aging and the pathologies that they may manifest. The driving vehicles for the development of biological species of deterioration are fundamentally the materials used by the artist, the organic materials used by the restorers throughout the material life of the work and the environmental factors that surround it, all fundamentally guided by the ambient temperature and humidity of the piece. (Matteini and Moles, 2001).

Therefore, adhesives, pigments, varnishes, and the textile support itself are organic components susceptible to being attacked by heterotrophic agents such as fungi and bacteria. The damages that they can cause in the works are in most cases irreversible, since they affect the chemical composition of the materials.

(Caneva, *et Al*, 2000).

It is unavoidable that the trophic relationship that they maintain with the work itself, favors their proliferation, being able to cause changes in the mechanical properties that they presented in origin (with loss of tension and initial elasticity). Modification of the chemical properties of cellulose, irreversibly weakening its internal structure. (Fig.1) And damage of an aesthetic nature, caused by the staining of the textile support when the irreversible staining of its fibers occurs.

Figure 1 – Affectation of the polychromy of a painting on canvas by biological pathogens.

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FUNGUS

It is a very unequal group of organisms, being able to be unicellular or multicellular. With a similar structural composition to cellulosic vegetables, they show a different chemical composition as they are made up of chitin. Metabolically, they are chemoorganotrophic compounds with simple nutritional needs, being very simple the formation of spores in very diverse media. (Vaillant, 2003)

Its development in artistic works on canvas is determined by the acidity that the textile support manifests with its aging, and the great capacity of the fibers to retain the humidity of its environment, being two fundamental aspects for its growth. Infestation occurs with the formation of hyphae, with spores of pigmented mycelia of various shades depending on the species, with Aspergillus niger and Penicillium crysogenum being two of the families of fungi that most commonly affect works with a cellulosic support. (Roche, 2012)

The development of fungal strains causes a general loss of its initial mechanical resistance in the work. The fungus progressively weakens the textile fibers of the canvas, until it completely deteriorates, possibly causing its breakage due to the rotting of the support, and due to parallelism, the detachment of the pictorial layers. (Roche, A. 2012; Vaillant, M. 2003)

The fungal agents generate deterioration in the canvas by chemical and mechanical action, being able to solubilize components of the materials, complexing cations in glucose-rich media, producing organic acids such as gluconic acid. ($C_6H_{12}O_7$), cítrico ($C_6H_8O_7$), and oxalic ($C_2H_2O_4$). Bacteria reduce the essential properties of pictorial materials from the oxidation of compounds with reduced sulfur (sulfides, thiosulfates and elemental sulfur), weakening their structure, and endangering the correct conservation of the work. (Fig.2) (Zhong et al. 2011).

Figure 2 – Stained on the back of a painting, caused by a fungal attack by Aspergillus Niger. (20th century canvas, cotton).

BACTERIAL AGENTS

It is its trophic relationship with the materials that make up the paintings on canvas that promotes its development, being able to use carbon sources derived from both organic and inorganic pictorial compounds as food. Specifically, bacteria of the chemoorganotrophic heterotrophic nutritional group are the most common in this type of artistic work.

There are numerous genera of existing bacterial agents, Bacillus, Nocardia and Pseudomonas to mention some of the most common. Although the main causes of cellulosic deterioration are the bacteria of the genus Erwinia and some Pseudomonas, which produce pectinases capable of breaking the outer layer of vegetables by means of extracellular hydrolytic enzymes, reaching the point of colonizing the internal tissues of the fabrics. (Gómez, 1998 ;Roche, 2012)

Bacterial agents decompose the cellulose of the pictorial support in alkaline media, requiring a high degree of environmental humidity for its development, without the need for light energy as it lacks a chlorophyll function. They cause irreversible chemical

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deterioration in textile fibers, by transforming cellulose into glucose. (Fig.3) (Doménech, 2013)

Figure 3 – Accumulation of environmental dirt and remains of insect droppings, on the back of a painting on canvas.

The materials that have been used up to now in restorative treatments to alleviate the deterioration caused by these agents have always yielded high toxicity data, as we will see later. The prevention of chemical risk is one of the fundamental axes of study at present by interdisciplinary research groups, which value the substitution of these ecotoxic substances, by others of less or no danger until the practical disappearance of the danger in the workshop is achieved. conservative.

THE RESTORATION PROFESSION UP TO THE 20TH CENTURY: HIGH RISK WORK

Until the first half of the last century, the artistic work was the key element that appeared as the main element to take into account, without considering the danger of the materials that the restorer used in its restoration. Starting in the second half of the 20th century, the search for friendly working environments facilitated the development of formulations free of harmful materials, which did not pose a risk to the restorer or to the correct conservation of the work.

The analysts John Warner and Paul Anastas at Green Chemistry have already established the essential points to reduce the dangers associated with non-eco-friendly products and processes, with which our society can usually find itself immersed. (Contreras, 2007).

Although a slight advance has been made formulating proposals for the eradication of toxic products in some restorative processes (such as polychrome cleanings), carcinogenic compounds continue to be used in other intervention treatments such as color protection, or the use of preservative substances added to the adhesive mixtures intended for the consolidation of pictorial layers and artistic supports.

These preservatives are substances of natural or synthetic origin, intended to neutralize the action of harmful microorganisms. Its action is focused on the destruction of the cellular systems of the pathogens, annulling the biochemical reactions that allow the life of this organism. (Sanchez, S.; Barahona, M. 2009). Unfortunately, these substances currently used by restaurateurs are mostly dangerous due to their emission products in the form of gases and vapors. Its use without proper individual protection (such as glasses and gloves) can cause the development of respiratory allergies which in turn can lead to bronchial asthma, rhinitis, eye irritations (conjunctivitis) and mucous membrane damage. (Fig.4) (Moreno, M.D. 2003)

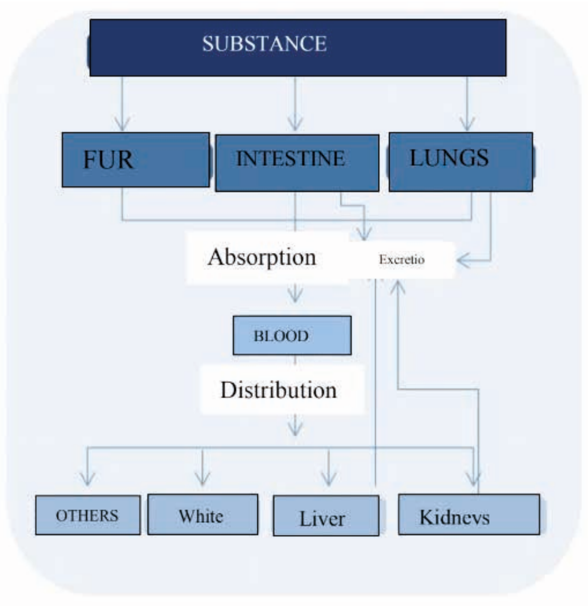

Figure 4 – Routes of entry and distribution of xenobiotics in the organism.

The risk to which the restorer is exposed will depend on the type of substance used, the exposure time and the dose that he manages to assimilate. This way, the materials could be classified as carcinogenic (nitro compounds), teratogenic (nitro compounds), mutagenic (nitrosamides), or produce metabolic disturbances (sulfur dioxide and benzoic acids).

TOXICITY OF A MATERIAL WHAT ARE WE TALKING ABOUT?

The toxicity of a compound refers to its ability to cause damage through negative biological effects, being able to alter the biochemical or enzymatic processes of an organism [Millet, I. 1991]. All substances, natural or synthetic, are toxic, that is, they produce adverse effects for our body depending on the exposure conditions, so it is incorrect to call some chemical substances toxic and others non-toxic. The exposure conditions and the dose are the factors that determine its toxic effects. This was already determined by Philipp T. Paracelsus (1493-1541), in his written work Opera, where he already warned of the danger of using materials such as lead, sulfur and copper: [...] *Every substance is toxic, there is none that is not Whatever it is, it is the dose that makes the difference between a toxic substance and a medication* [...]

Currently it is determined that the toxicity of the substance will depend on the physical-chemical properties of the material, the duration of exposure to it and the dose, together with the mechanisms of action. All this will determine the final toxic effect, depending on the factors of each individual. The innocuousness of a substance will be determined by the protection used for its handling, since there is no material that can be considered 100% innocuous. [Moreno, M.D. 2003]

At present, the two large groups that include the biocides used in the formulation of adhesive mixtures in intervention of paints on fabric, are materials of phenolic origin and quaternary ammonium compounds, with different levels of carcinogenicity and environmental hazards. (Rossmoore, H.W. 1995)

Regarding biocides of phenolic origin, these are the first compounds that were used as biocides around the 1930s, where phenol itself was taken as the reference substance. The most widely used have been pentachlorophenol (PCF) and dinitro-ortho-cresol (DNOC). Today both compounds are prohibited as biocides due to their great harmfulness to human health and the environment, destining their use only for research

Since the first decade of the 21st century, quaternary ammonium compounds (QAC) have been the alternative to phenolics for many restorers, although their chemical composition continues to show worrying traces of carcinogenicity.

These are substances with a broad biocide spectrum, widely used as disinfectants in the food industry, for sanitizing surfaces and facilities. The most commonly used compounds are didecyldimethylammonium chloride (DDAC) and benzalkonium chloride (BAC). They are produced by chemical synthesis by reacting ammonia with alkyl halides (such as methyl iodide), generating a mixture of primary, secondary, and tertiary amines. (Caneva G. et al. 2000)

The health risks associated with the emission of volatile organic compounds (VOCs) affect both the environment (due to the deterioration that occurs in the atmospheric ozone layer) and the restaurateur's environment. The use of compounds such as chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), trichloroethanes and carbon tetrachloride constitutes a problem that extends to most of the member countries of the European Union, where they are already prohibited substances or have a maximum period established for the eradication of its use, contemplated in the so-called Montreal Protocol. The European Chemicals Agency (ECHA) is in charge of supervising the risk derived from chemical substances that pose a danger to environmental health in the European Union, while pursuing their replacement by other healthier alternatives. [https://echa.europa.eu/en/regulations/reach/authorisation]

PRESERVATIVE ADDITIVES: CURRENT 'ECO-FRIENDLY' ALTERNATIVES

Since the beginnings of the restorative practice of artistic works, preservative substances have been added in order to give durability to adhesive mixtures. Until the Industrial Revolution, these materials were of natural origin (such as garlic juice, onion juice or alkalis), but once science developed and industry in parallel, they began to be replaced by biocides processed in the laboratory, being mostly very harmful to the human organism, as we have seen in previous sections. In general, what is required of preservative substances is that, in addition to having high antimicrobial activity, they present non-ionic surfactant molecular properties. Due to these characteristics, they will provide antifoam and antioxidant qualities to the adhesive mix, being an important factor to take into account, to achieve quality joints. Similarly, they must present good long-term stability and a high capacity to be biodegraded. (Falya, Y. 2020)

When the fungal strain develops in a painting on canvas, a stain appears on the surface with different colors depending on the family and genus in question. That is why the contribution of cytotoxic agents is required to correctly protect the work, preventing deterioration from occurring. (Zhong, Y. et al. 2011)

At present there is great concern towards the use of natural substances, such as essences and oils, although their use has already been verified in Ancient Egypt (4500 and 3350 BC), being used in mummification techniques. Later, the Greeks and Romans applied it as purifiers for temple and home environments. It will be its greater or lesser phenol content that accentuates its bactericidal and fungicidal power. They are very complex mixtures that can reach up to a hundred components with groups of terpenes $(C_5H_8)_n$ and other compounds mostly always oxygenated. They are phenolic substances, acyclic, monocyclic, bicyclic and polycyclic hydrocarbons of low molecular weight.

Regarding the toxicology of these materials, it differs to a great extent from one compound to another, depending on the substances they contain and their percentage in the formulation. (Zuin, V. 2021)

Experimentation in laboratory mice has revealed the physiological phenomena of intoxication that these substances can cause, where terpene compounds (alcohols, aldehydes and phenols) in high doses (greater than 15%) and prolonged can cause pathologies of different degrees, phototoxic -Irritating to mucous membranes and epidermis due to the evaporation of its gases. (Zeggwagh, A.2013)

It deserves special attention from the conservative point of view, to analyze the influence that the volatile organic complexes of these materials can cause both in the pictorial layer and in the textile support itself. Fundamentally, it is intended to test the effect of oxygenated terpenes and sesquiterpenes formed through the phenylpropanoic acid route of the secondary metabolism of the plant, on the future conservation of the work. These substances are produced as secondary metabolites by maceration of the leaves and flowers of the base vegetable, being the one that will determine the type of denomination of the oil based on its nature. It is the aliphatic alkene chains that they contain in their composition, such as myrcene, linalool, citronellal, citronellol or geraniol, which enhance their antifungal effect. (Doménech, M.T. 2013)

This is a line of research currently under development, which must be expanded as a complement to the toxic study of the material derived from its use.

CONCLUSION

In general, all the substances currently used as biocides in antifungal treatments are very complex mixtures that can reach up to a hundred components. Specifically, natural extracts are made up of groups of terpenes $(C_5H_8)_n$ and other almost always oxygenated compounds such as: Phenolic substances, acyclic, monocyclic, bicyclic and polycyclic hydrocarbons of low molecular weight.

The possible chromatic changes that may occur in the polychromy of the paintings and the modifications that develop in the internal structure of the cellulose of the support are currently being determined. Paying special attention to flavonoids, aromatic aldehydes and phenolic triglycerides.

To conclude, it is worth highlighting how the search for the perfect balance between heritage conservation and health is currently pursued, with the disappearance of the primacy of the artistic work over the restorer, and progressively achieving increasingly friendly environmental environments in the conservative profile.

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