Chapter

Response Surface Model Applied to Fine Arts: The Case of the Restoration of Paintings

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Abstract

Cleaning polychrome paintings and sculptures is an essential task in restoration treatment, since it irreversibly affects the appearance and material structure of such works of art. It is a completely "analogical" process consisting of removing surface dirt, aged varnishes or repainting (paints added to the original) based on the restorer's experience and knowledge, as well as on different internationally accepted criteria for such interventions. In this chapter we are presenting an example of the adaptation of the response surface model to this field, which is complex and difficult to adapt to quantitative parameters and has never before been studied with this approach. Using the MODDE Go® experiment optimization and statistical design software, the effectiveness of cleaning pictorial works of art has been studied using various formulas composed mainly of water and a low-toxicity monoterpene: limonene. The model's statistical validity is demonstrated, as well as its ability to determine the main factors that affect the cleaning by means of different responses (methods) to evaluate its effectiveness: an expert's opinion using visible light and ultraviolet light, the amount of varnish removed using gas chromatography coupled with mass spectrometry, and the effects on color, lightness and gloss. The main influential factors were the concentrations of the two main components of the proposed formulations, water and limonene, which regulate the cleaners' level of hydrophilia and lipophilicity, followed by the types of pigments and type of varnish used, and aging. Using an *in silico* simulation, the proposed model also enables specific compositions to be formulated for different scenarios and cleaning applications that are potentially effective and harmless to the pictorial materials and the restorers' health.

Keywords: cleaning, oil paintings, water, limonene, response surface

1. Introduction

Since the second half of the 20th century, works of art have been restored based on a fundamentally scientific perspective, using a great variety of products and methods for analysis that have enabled the materials to be characterized in detail, and the results of the restoration treatment to be experimentally proven. However, the results obtained have yet to be correlated with empirical models that adequately back them, which has not yet been studied enough [1–8].

The approach in this study uses an innovative model that compares the nature and conditions of the artwork to be cleaned, the composition of the cleaner and the results obtained after cleaning from multiple perspectives. This involves representing the complex phenomenon of cleaning and stripping varnishes over oil paint by using a model of surface responses. This model can be simulated *in silico* to highlight the synergistic and antagonistic relationships among the main factors involved in cleaning of oil paintings: the type of varnish, degree of aging, type of oil pigment and composition of the cleaner. To do so, different responses (methods) have been brought together to evaluate the cleaning's effectiveness: an expert's opinion using visible and ultraviolet light, the amount of varnish removed using gas chromatography coupled with mass spectrometry, and the effects on color, lightness and gloss. The simulation will also allow optimal cleaning products to be developed for specific cleaning treatments.

1.1 Cleaning works of art

Cleaning is one of the fundamental treatments used in restoring paintings and other types of works of art, and also one of the most controversial ones, since it is the one that most affects their appearance. The term refers to three types of tasks [9]:

- Surface cleaning: removal of non-adhering dirt.
- Varnish cleaning: total or partial removal. Resistant, greasy dirt and the oxidation of a varnish can create a layer where the two are intimately related. These layers can be removed together during the cleaning treatment.
- Lifting of repaints added to the original work and which it has been decided to remove, also known as stripping.

From classical antiquity to today, the criteria used in applying cleaning treatments to artworks have changed along with the development of concepts and theories as regards conservation and restoration.

The lack of control in using cleaning substances has led to the complete or partial loss of polychromy in many artworks. The substances used included highly aggressive products such as soap, diluted bleach and ash. Soda, urine, salt, alum, acids, ox gall, milk and egg yolk, for example, were also products commonly used in the 17th and 18th centuries. Gradually, an awareness of the potential aggressiveness of some of these substances for paints emerged [10].

In the 20th century, a great boost was given to the theory and practice of cleaning cultural assets, mainly due to what had been learned from the alterations caused by many of the products over time, and the risk involved in using solvents. The greatest stimulus came from the scientific advances made after the First World War, which provided a wide variety of products with physical and chemical properties that enabled problems to be solved and new techniques developed [11]. The research carried out in the second half of the century then laid the foundations for more scientifically based restoration work, concentrating on the main solvents' solubilization power as regards the materials to be removed [12–15]. There is now a growing awareness of the danger that cleaning can bring about for the artwork's integrity and the restorers' health.

One alternative to solvents are water-based cleaning systems that include surfactants and other additives in complex detergent formulas [16–18]. It is essential to know the composition of the detergents and the surface to be cleaned in order to determine the effectiveness of the detergent, but even so it is difficult to choose the best cleaner in each case, even for highly trained and experienced restorers.

1.2 Strata involved in cleaning paintings: dirt, varnish and painting layer

The main factors that can alter the appearance of an artwork's color over time are the accumulated dirt on the surface, the darkening and yellowing of the varnish and oil, pigment migration, and the effects of visible and ultraviolet light. When the cleaning is carried out for a polychromy, there are three layers that are affected (**Figure 1**): the dirt, the layer of varnish and the underlying pictorial layer (which in our case study is oil paint), which can alter the artwork's visual appearance [19]. We will briefly review their characteristics.

1.2.1 Dirt

The dirt that we may find on the surface of a painting is a difficult concept to define and varies considerably depending on the circumstances. Surface dirt is understood to mean the sediments that are deposited on an artwork's surface in multiple layers and bound by different forces of attraction [20]. This generally includes particles of dust, carbon and other solid materials such as sand, soil, corrosive products and salts. It is responsible for the grayish veil over the pictorial surface and sometimes causes mechanical damage or reactions with the materials within it as its components

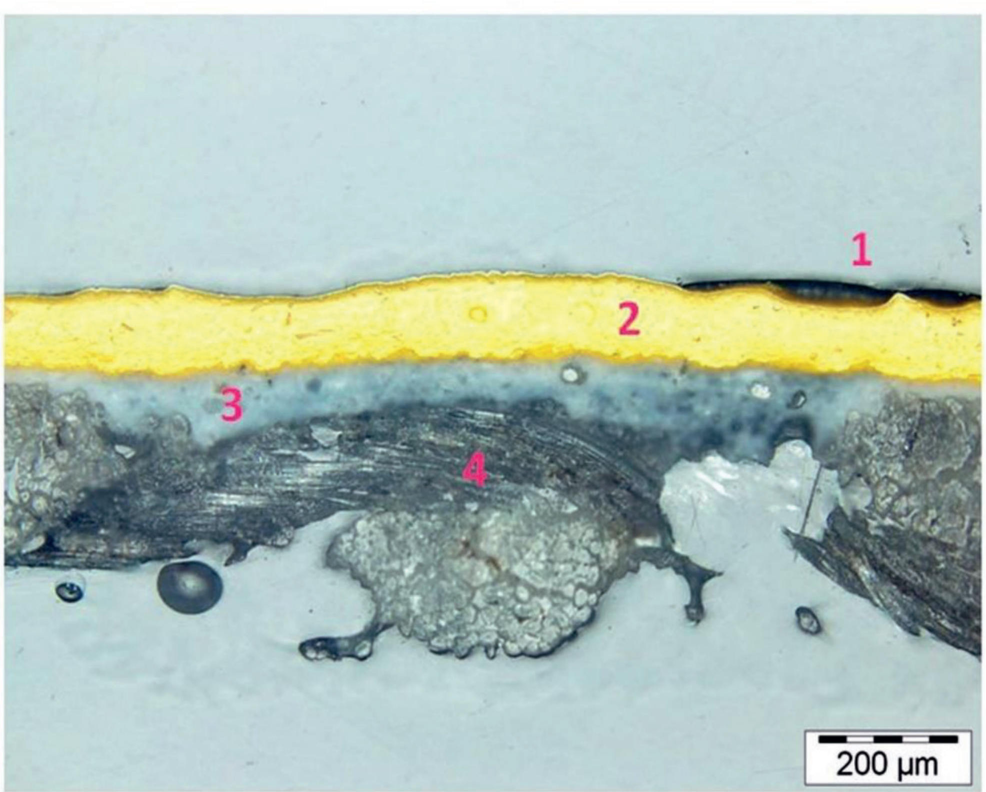

Figure 1.
Strata of a standard sample: [1] varnish layer [2] oil layer, [3] preparation layer, [4] canvas.

absorb some pollutants from the atmosphere. Non-polar surface dirt particles are bound together by weak intermolecular forces, and polar ones by stronger dipolar forces. It is usually sufficient to apply mechanical means and detersive substances in order to remove surface dirt [9].

Surface dirt on works of art is usually associated with fatty deposits made up of a complex mixture of components [21], predominantly natural lipids (triglycerides), which contain unsaturated fatty acids (susceptible to oxidation by air). This type of dirt remains attached to the surface after surface cleaning due to the greater strength of its molecular bonds and interactions [22]. To remove it, it is common to use organic solvents, which can damage the paint layer, both when it is applied and in the long term.

1.2.2 The varnish layer

A varnish is a liquid which, when applied to a solid surface, dries forming a transparent film with varying degrees of gloss, hardness, flexibility, and protection depending on its composition [12]. It is a material of prime importance in the sphere of artistic techniques, which must have an even finish and be transparent, stable and reversible, while preventing efflorescence from developing. Its main purposes in a work of art are for protection and esthetics [23]. The natural varnishes traditionally used in painting are terpenoids, which undergo oxidation processes and other chemical changes that cause them to yellow and lose mechanical and optical properties [24–27]. One of the most frequent painting restoration tasks is to remove aged varnishes by using solvents and replace them with polymeric varnishes, generally acrylics, which are much more stable.

1.2.3 The pictorial layer: oil paint

Oil painting has dominated the artistic sphere since the fifteenth century until today due to the variety of pictorial resources it offers as regards opacity, transparency and chiaroscuro [28]. A layer of oil is made up of finely ground particles of pigment evenly dispersed in a vegetable-based drying oil.

A drying oil is a liquid vehicle or binder composed mainly of triglycerides of fatty acids with 16 or 18 carbon atoms: palmitic, stearic (saturated) and mainly polyunsaturated ones. Among the unsaturated fatty acids, oleic acid (C18, one double bond), linoleic acid (C18, two double bonds) and linolenic acid (C18, three double bonds) are the most notable [29, 30]. The most widely used oils since ancient times have been walnut, poppy and especially flax, since they form transparent films after the drying process, with optimal mechanical and optical properties [31].

The oils dry by oxidation and subsequent polymerization of the triglycerides' unsaturated fatty acids, until they form a relatively hard yet elastic film. After a series of complex chemical reactions involving processes of crosslinking, oxidation of unsaturated acids and the hydrolysis of glyceride bonds, a new substance is formed that is usually called linoxin, with very different physical and chemical properties from the original liquid oil, and which will not return to its initial state by any means [32, 33]. Although the oil film dries out to the touch in weeks, it undergoes new chemical reactions throughout the life of the painting [19]. Natural aging makes the pictorial film less flexible and causes cracking and changes in opacity.

When one intends to clean or remove a varnish from a polychrome surface, it has to be taken into account that the pictorial layer may be altered [34], especially when glazing techniques are applied in the painting's finishing, in which the pictorial medium is a fine mixture of oil, pigments and varnish, and therefore has a composition and polarity that closely resemble the protective varnish that is going to be removed.

Solvents can also give rise to changes in the oil's properties and composition, fostering leaching of components with a low molecular weight such as ketones, alcohols and dicarboxylic acids, like azelaic acid. This process affects the physical properties of the pictorial layer, reducing its volume, increasing its density, and making it brittle and opaque [23].

The type of solvent used for cleaning is decisive. It is generally thought that the greater the polarity of the solvent, the greater the risk of leaching [15], since the oxidation and hydrolysis of the initial triglycerides over time causes changes in the oil paint's chemical structure, making it more polar [35]. The magnitude of the changes also depends on the length of exposure time. When solvents are applied repeatedly or in excessive amounts, they cause surface wear as pigments get washed away with the oily film protecting them. Finally, the nature of the pigment also influences the effect of the solvents on the oil. One well-known example of this is the effect of one of the most significant pigments in art history, lead white, which minimizes the action of solvents even on fairly young oil layers [19].

1.3 Oil painting cleaning treatments

1.3.1 Cleaning methods

Cleaning can be done mechanically or by means of solvents, or else by combining both approaches in mixed treatments. Mechanical cleaning is done with vacuum cleaners, dusters, soft paintbrushes, brushes, compressed air, rubber erasers, lasers or scalpels [36]. It is used for superficial cleaning and as a treatment prior to any intervention in the sphere of restoration, as well as in cases of varnishes, repainting or dirt that is impossible to remove by other means.

Physical and chemical methods involve cleaning with solvents to soften and disperse or solubilize the material to be removed, forming a homogeneous mixture with it. This is finished off with mechanical wiping using a cotton bud or inert media such as cellulose pads or gels that keep the product active for longer. In the sphere of conservation and restoration, these procedures are carried out following internationally accepted cleaning guidelines and standard solubility tests [31].

1.3.2 Solvent properties

There are two different, closely related processes in the action of solvents [37]:

- Initial softening of the substrate by swelling of its molecules' chains.

- Subsequent dispersion or solubilization of the particles that give rise to dissolution.

According to the principles of thermodynamics, each type of substrate must be dissolved by a solvent of similar polarity. It is therefore essential for there to be chemical similarity between the molecules of the solvent and the solute, defined by the predominant intermolecular forces. What is commonly known as "like dissolves like" therefore refers to the fact that a solvent will remove the layer of varnish and/or dirt when it interacts with it with the same type of intermolecular forces as those that hold its own molecules together. Hansen's solubility parameters and visual diagrams such as the Teas triangle are often used to characterize solvents and classify them for their use in restoration [38–40]. Other very important factors must also be considered, such as the penetration capacity, volatility and retention in the artwork, not forgetting the toxicity values for the restorer [12].

2. Response surface model

All the above gives an idea of how enormously complicated it can be to approach the cleaning of artistic paintings from a scientific point of view. There are factors involved that are related to the material, which is chemically very complex and divided into three layers: dirt, varnish and the painting layer. These factors can in turn be subdivided into internal micro-layers with different compositions, as happens when a painting is repainted, in other words, when a new pictorial layer is added to an already finished work. Organic materials also appear, such as binders and varnishes, and also inorganic ones, such as many pigments. We could also distinguish between components that are natural or synthetic, original or added, and polar or non-polar. Metals can even appear if the work includes gilding or silver-plating techniques. Likewise, factors such as aging of the materials to be treated, deterioration agents, or previous restoration treatments are all very important. Lastly, when solvents are being applied, a single product is seldom used, since the habitual values of polarity required in cleaning and stripping varnishes are usually achieved by using solvent mixtures [37]. In restoration practices today, we should also add the frequent use of surfactants, chelating agents or enzymes [14, 21, 37].

Our research aims to analyze the most important factors affecting the effectiveness of cleaning a pictorial work of art so as to be able to put forward effective cleaning methods with few adverse effects. Due to the number of variables present, we used the MODDE Go® (Umetrics) software for statistical design of experiments and optimization, run on a PC with a 64-bit Windows 10 operating system. An effort has been made to include the utmost number of factors and reduce the number of experiments to a minimum, while being as representative as possible of the complex phenomenon that we are attempting to analyze.

As a way of explaining the rationale behind this procedure, think for example of carrying out four experimental points of four different concentrations of five components of a cleaner, plus one point for each of, let us say, five pigments present and two points for each of the factors of aging and the type of varnish. This would mean carrying out at least 20,480 different cleaning tests in the laboratory (45 × 5 × 22 = 20,480). Using statistically designed experiments, the representative sample has been reduced to only 72 cleaning trials. This has meant an enormous saving in time and material resources, which if an attempt had been made to carry out all of the theoretical tests would have made it impossible to actually do them.

The proposed response surface model uses analytical techniques (responses).

of a physical, chemical and visual nature to study the effectiveness of low-toxicity formulations, taking into account the main factors that influence cleaning: the composition of the cleaners, types of pigments and varnishes, and their aging. It also enables in silico simulations in order to develop optimal cleaning products for specific cleaning treatments depending on the characteristics of the pictorial work of art to be restored. Furthermore, in future research, three-dimensional vector models can be developed to analyze: 1) the material and physical–chemical aspects of cleaning, 2) the restoration technique used, and 3) the visual appearance, which can be evaluated using optical methods.

Below, we explain the fundamental points in the proposed design of experiments and some examples of the results obtained. The full technical details of the study can be consulted in Bailón-Moreno et al. [41].

2.1 Preparation of samples

The proposed cleaning methods were tested on reference samples containing the usual layers in an oil painting: support (linen canvas), preparation, paint layer and protective varnish.

The preparation applied over the canvas was composed of animal glue, calcium sulphate ($CaSO_4{\cdot}2H_2O$) and zinc white (ZnO). The oil painting was handmade prepared with stand linseed oil and five different pigments, one for each type of sample: zinc white (ZnO), lead white $(PbCO_3)2Pb(OH)_2$, cadmium yellow (CdS), cadmium red ($3CdS{\cdot}2CdSe$) and cobalt blue ($CoO{\cdot}nSnO_2$). All these products were purchased at Manuel Riesgo, Madrid, Spain) except lead white, wich was produced by ourselves [42].

After a drying period of 3 months, the samples were varnished following two possible procedures: using a traditional terpenoid varnish composed of mastic resin diluted in spirit of turpentine or using an acrylic synthetic varnish by Lefranc & Bourgeois®. In both cases, they were allowed to dry naturally for 12 months (**Figure 2**). Aged terpenoid varnishes such as mastic are affected by

Figure 2.
Reference samples: cobalt blue, cadmium red, cadmium yellow and lead White varnished with mastic.

chemical processes of crosslinking and oxidation that make them more polar than the original ones, and more difficult to remove using solvents in cleaning processes.

To imitate the deterioration of a layer of old paint varnish, some of the samples were subjected to artificial accelerated aging by exposure to ultraviolet light [31]. The rest of the samples were reserved to simulate a recent painting. The varnishes and oil color layers were applied with a micrometric adjustable paint applicator SH-1117/100 (Daesan CMC, South Korea).

2.2 Designing experiments. Software MODDE Go®

The model consists of a set of polynomials (one for each response), which have a constant value, a_0, representing the mean value of the response considered. These terms represent the linear effects of the factors on the responses, $\sum_{i=1}^{8} a_i F_i$, quadratic terms, $\sum_{i=4}^{8} a_{ii} F_{ii}^2$, and finally cross terms, $\sum_{i=1}^{8}\sum_{j=i+1}^{8} a_{ij} F_i F_j$, which represent the synergistic and antagonistic effects between the different factors. S is the response and the values of ai, aj and aij are coefficients that multiply the factors Fi, Fj.

$$\text{Response} = \text{Coeff.} + \{\textit{Lineal eqs}\} + \{\textit{Quadratic eqs}\} + \{\textit{Synerg.}\ \&\ \textit{antag.eqs}\}$$

$$S = a_0 + \sum_{i=1}^{8} a_i F_i + \sum_{i=4}^{8} a_i F_i^2 + \sum_{i=1}^{8}\sum_{j=i+1}^{8} a_{ij} F_i F_j$$

The model was adjusted with the MODDE Go® software from the company Umetrics using the Partial Least Square (PLS) technique with pseudo-components with non-scaled, non-centred values. Bailón-Moreno et al. [41] show the coefficients associated with each response, S, depending on the model proposed, the coefficient of determination, R2, and the coefficient Q2.

The proposed model considers the cleaning of painted artworks to be a procedure affected by a set of values or variables that is evaluated via a set of responses. The factors can be quantitative or qualitative, depending on whether they can be represented by quantity or not, and they can also be of the process or composition type. The factors chosen are as follows (**Figure 3**).

1. Quantitative composition factors: these define the composition of the cleaner, with different proportions of water, limonene, phenethyl alcohol, Findet ® 1214/N23 and Glucopon® 600.

2. Qualitative process factors: type of varnish (traditional: mastic; or synthetic: acrylic), aging (yes or no), type of pigment in the paint layer (zinc white, lead white, cadmium yellow, cadmium red or cobalt blue).

The cleaning was evaluated via seven possible sets of responses: the physical state, the chemical analysis via gas chromatography/mass spectrometry (GC/MS), cleaning from the point of view of an expert's opinion (observed with visible light and ultraviolet light), and also how the cleaning affects the painting from an optical and colorimetric point of view (color, lightness and gloss) [43, 44]. MODDE Go® (Umetrics), was used to establish a statistical design for experiments in keeping with

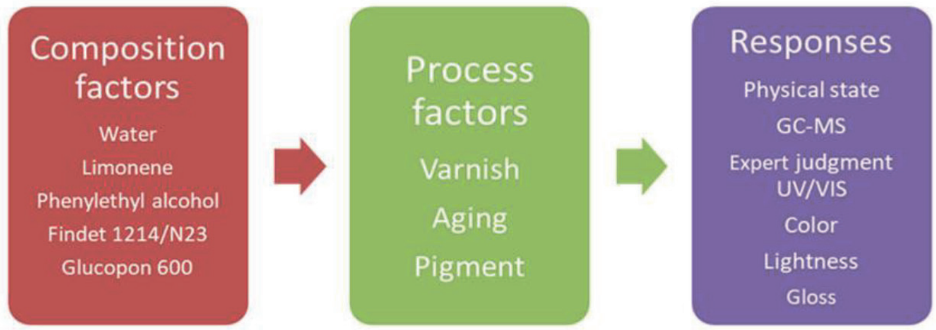

Figure 3.
Response surface model for cleaning oil paintings with composition factors, process factors and the responses studied.

the response surface model put forward. It has 72 statistically representative tests, whose experimental conditions can be consulted in Bailón-Moreno et al. [41]. Every test was performed once.

2.2.1 Quantitative composition factors

These are dependent on the composition of the proposed cleaning mixtures. Several criteria have been used in choosing the products [14, 21, 37].

1. Correct structure of the cleaners. The cleaners must be made up of components that enable stable, effective compositions to be formulated. To do so, the compositions may consist of:
    - One or two main solvents;
    - Optionally a co-solvent;
    - Optionally a surfactant with the possibility of a co-surfactant.
2. A wide variability in the mixtures' polarity. This variability lies in the two main solvents, one polar and one non-polar. Since substances of very different polarities cannot normally be mixed properly by themselves, it is important for there to be a co-solvent of intermediate polarity between the two main solvents, or else one or two surfactants to form an emulsion.
3. Non-toxic and low skin irritation.
4. Easily biodegradable components, in order to avoid environmental problems.
5. They should form compositions that are easy to prepare and use.
6. Industrially affordable and economical components.
7. Components that have already been tested in previous research with good results.

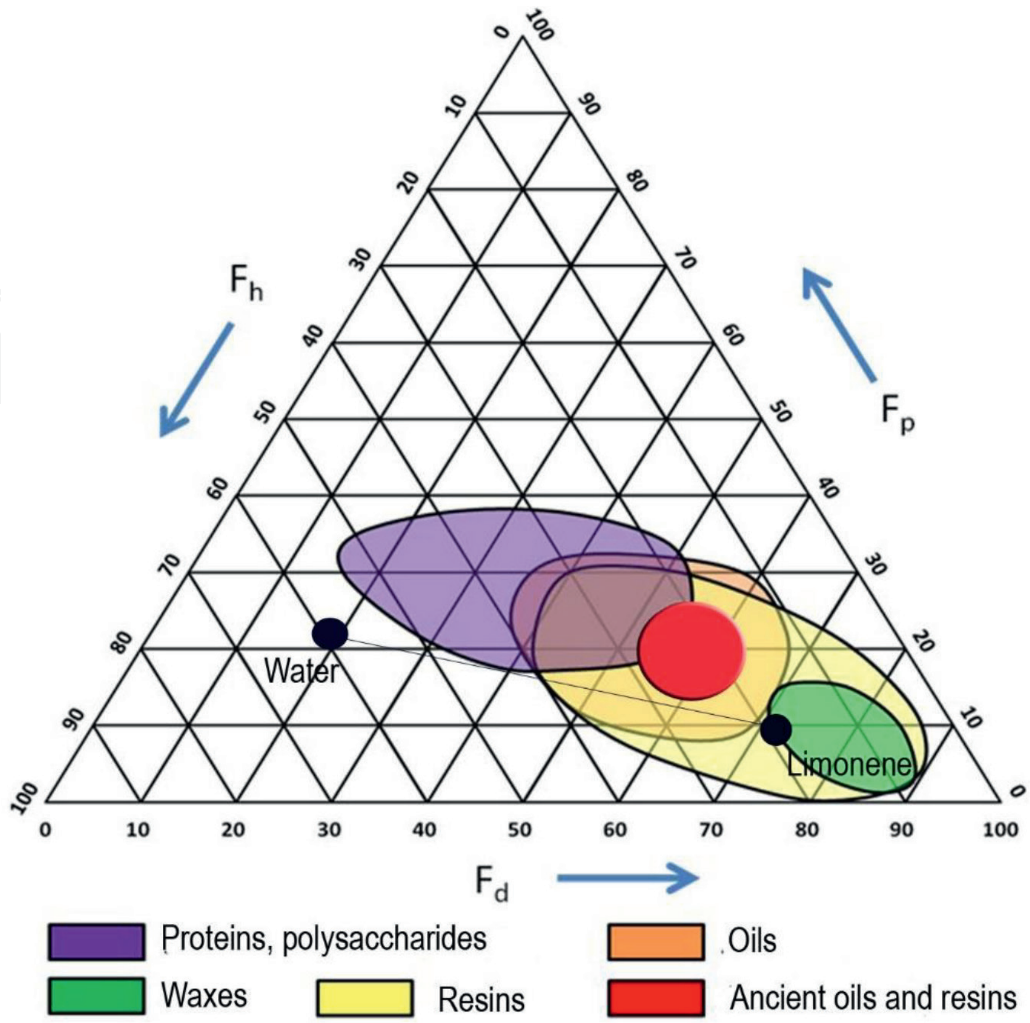

Figure 4.
Masschelein–Kleiner diagram: Solubility of natural film-forming substances and position in the triangle of the two main components of the proposed cleaning formulas: water and limonene. Note how there is partial overlap between resins and oily layers.

In keeping with these general requirements, five substances have been chosen. The proposed cleaning method is based on a mixture of two main components: one clearly polar, water; and the other strongly nonpolar, limonene (1-Methyl-4-(1-methylethenyl)-cyclohexene), a hydrocarbon (monoterpene) devoid of toxicity that is found as the main component in the essential oils of orange, lemon and other aromatic plants. The relative proportion of these components marks the polarity of the mixture and its greater or lesser effectiveness in dissolving each type of material (**Figure 4**).

The formulations have been stabilized by the presence of three products: Findet® 1214/N23 (KAO Chemicals Europe, Barcelona, Spain), comprised of a vegetable-based narrow-range ethoxylate with a C12-C14 fatty chain and 11 moles of ethylene oxide; and Glucopon® 600 (BASF, Barcelona, Spain), a non-ionic surfactant of the alkyl polyglycoside type, specifically a lauryl glucoside with 1.3 moles of glucose.

The cleaning compositions used contain, according to the response surface model, variable amounts of these substances that are statistically representative in all of their possible cleaning formulations. The concentration ranges for each component were Water and limonene: from 0 to 100%, Phenethyl alcohol: from 0 to 5%, Findet ® 1214/N23 and Glucopon® 600: from 0 to 10% [41].

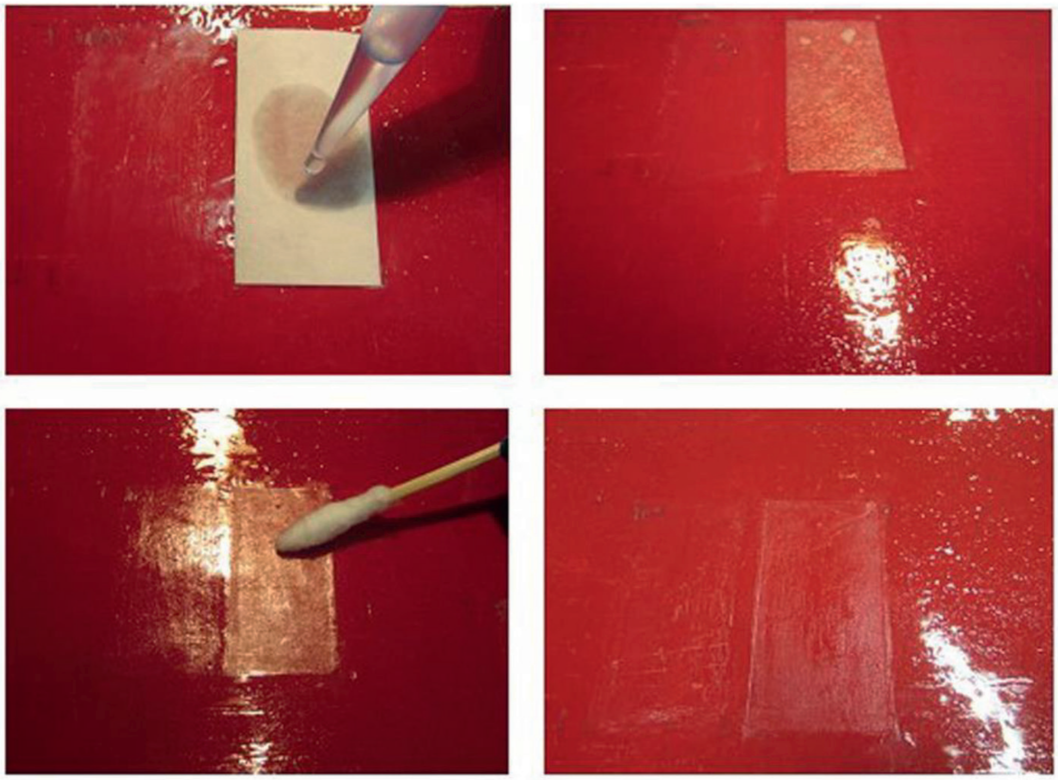

Figure 5.
Cleaning process of unaged mastic varnish on cadmium red oil with formulation N44.

2.2.2 Cleaning trials

The cleaning formulations were applied to the samples and allowed to act for 5 minutes. Afterwards, possible residues of the formulations were eliminated by washing with distilled water and subsequently White spirit (Talens). The process was repeated three times on each sample (**Figure 5**).

2.2.3 Responses

The cleaning was evaluated via seven possible sets of responses: the physical state, the chemical analysis via gas chromatography/mass spectrometry (GC/MS), cleaning from the point of view of an expert's opinion (observed with visible light and ultraviolet light), and also how the cleaning affects the painting from an optical and colourimetric point of view (color, lightness and gloss). The complete description of the analytical study can be found in Bailón-Moreno et al. [41] (**Figures 6–8**).

3. Results and discussion

3.1 Validity of the model and most important factors

In order to confirm the validity of the model, the predicted values for the model were compared with the values observed experimentally for each response, achieving very good concordance between the values observed empirically in the 72 experiments actually

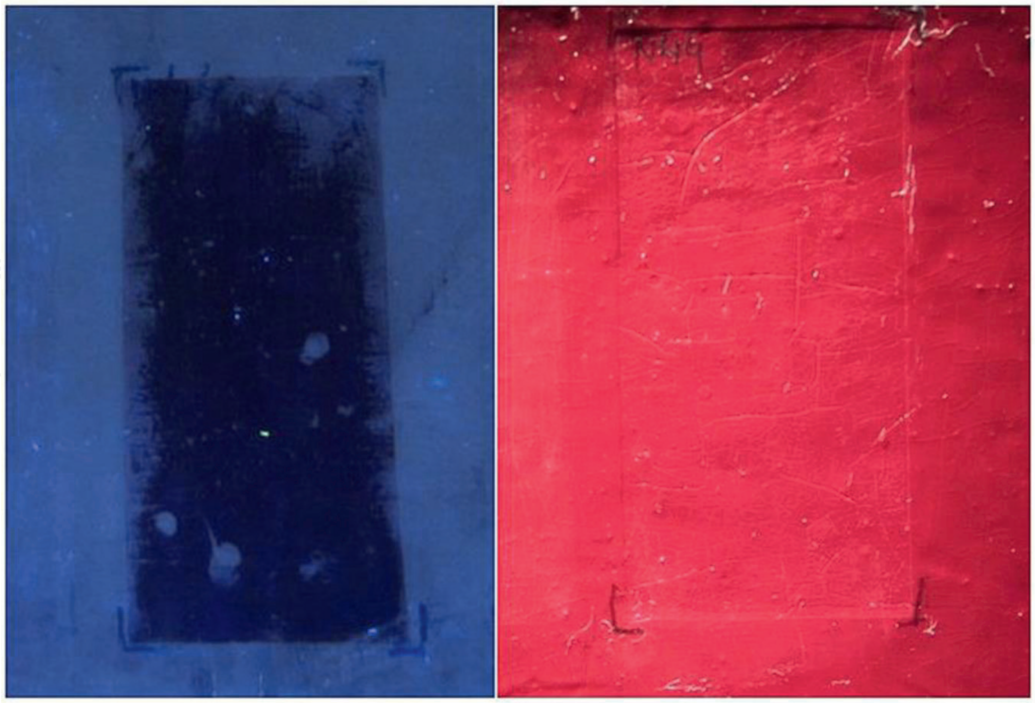

Figure 6.
Photographs with UV/(left) and oblique visible light (right) of the standard sample varnished with mastic on cadmium red oil after cleaning with formulation N44.

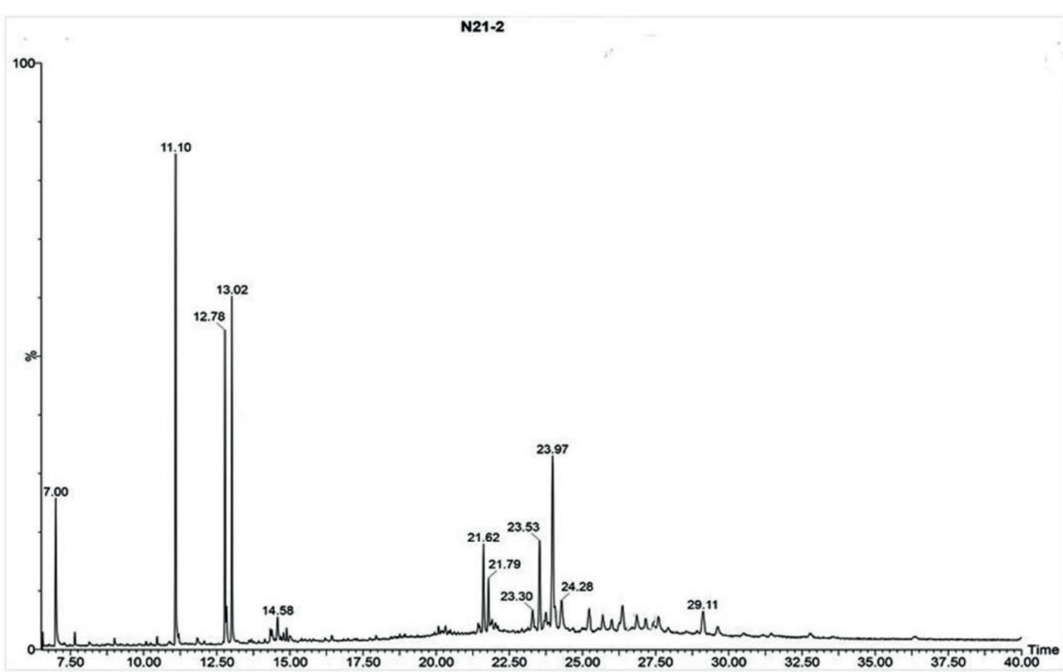

Figure 7.
Chromatogram of a standard sample composed of cadmium yellow oil and aged mastic varnish after cleaning with formulation N21. The peaks corresponding to the fatty acids are observed as main markers of the oil on the left (azelaic acid tR:7, palmitic acid tR:11.1, oleic acid tR:12.78 and stearic acid tR:13.02) and to the triterpenic resin acids as main resin markers on the right (ursonic acid tR:23.53, ursolic acid tR:23.97, moronic acid tR:25.99 and oleanonic acid tR:26.37).

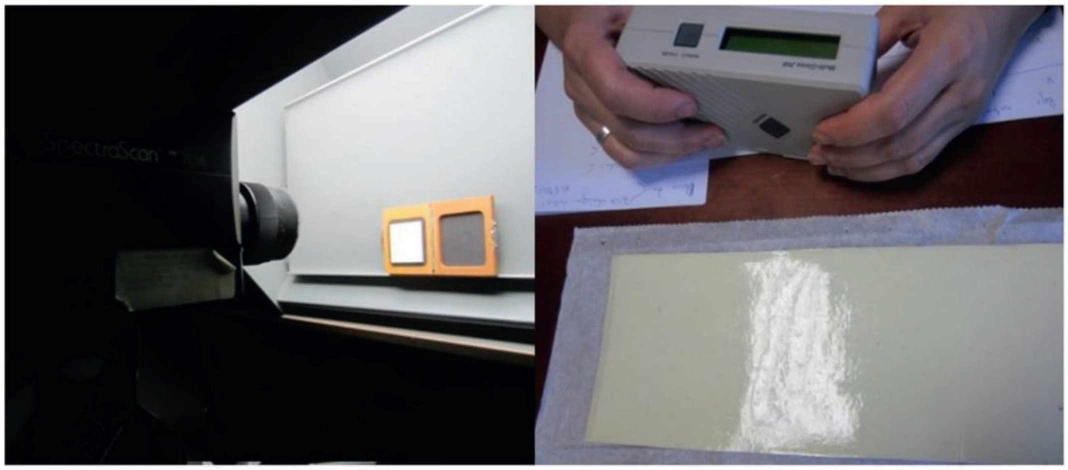

Figure 8.
Gloss measurement of reference white (left) and zinc white varnished with mastic (right).

carried out, and those predicted with the model. The absolute and relative errors were also calculated, correlating the latter with the experiments' order of implementation (run) so as to discard any bias related to the way and order in which they were implemented. Equally, they were correlated with the value of each response, either in their observed values or in their predicted values, so as to also discard any possible bias [41].

MODDE Go® provides an indicator based on the relative weight of each factor or a combination of factors over all of the responses as a whole, called VIP (Variable Importance in Projection). In the oil painting cleaning model and as the most important factors, the following stand out in order of importance:

1. Water
2. Limonene
3. Pigments (lead white is the most important) and varnishes, and their synergies and antagonisms
4. Synergy-antagonism between water and limonene
5. Aging
6. Quadratic terms for water and limonene
7. Complex synergies and antagonisms between aging, pigments, varnish, water and limonene
8. Other components in the cleaner: Findet® 1214/N23, phenethyl alcohol and Glucopon® 600

The main factors that affect the cleaning process with the formulations proposed are water and limonene, as well as their synergies, antagonisms and quadratic terms. The concordance between the polarity of solvents and solutes is the fundamental matter in cleaning polychromies. Water acts as a modulator of polarity whereas limonene is a moderator of non-polarity, so their proportion in mixtures is decisive in the cleaning effect, as predicted by the model.

3.2 *In silico* cleaning simulations

After establishing the response surface model for cleaning varnishes on oil and having confirmed that the mathematical model is a good one, using the appropriate computer tools it is possible to carry out computer simulations, putting forward unlimited cleaning scenarios and analyzing them without having to carry them out physically. These types of techniques are often called "in silico", evoking the terms "in vivo" and "in vitro" common in the natural sciences and medicine.

The basis of these simulations has been created using the MODDE Go® 6.0 software, which allows triangular diagrams to be obtained that visually hold thousands of results in which all possible combinations of cleaner compositions have been simulated *in silico*, sweeping through all the ranges of concentrations of water, limonene, Findet® 1214/N23, Glucopon® 600 and phenethyl alcohol.

Figure 9 shows an example of a triangle diagram. In this example, the main solvents (limonene and water) and the main surfactant (Findet 1214/N23) are located at the vertices of each triangle. Within a triangle, there are colored areas corresponding to the different responses given by each cleaner depending on the type of varnish and pigment. Each level corresponds to the scale of values for the response in question: expert opinion with ultraviolet lighting and visible light; O/V cleaning with GC-ME; affectation from color as a distance, dELab, in the CIELAB space; affectation from lightness, ΔL; and affectation from gloss, ΔG.

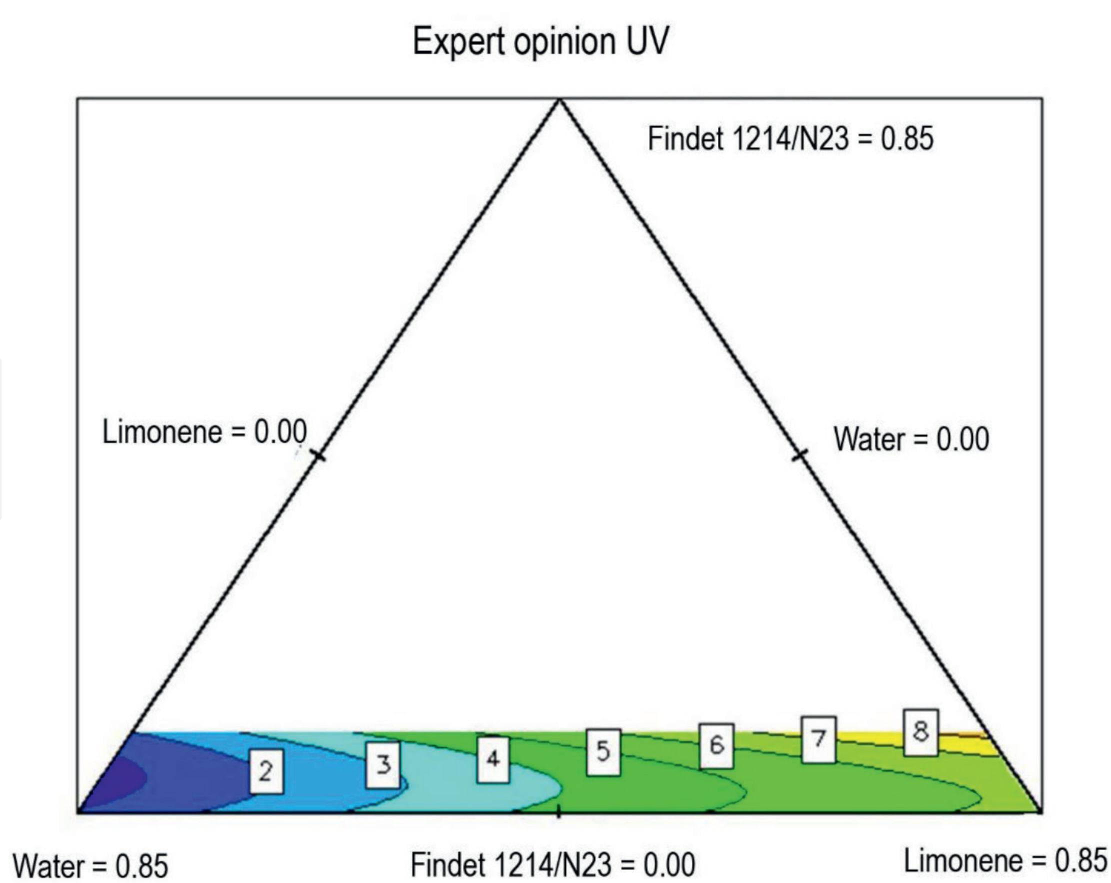

Figure 9.
Example of a triangular diagram of the results from cleaning with acrylic varnish according to expert opinion with ultraviolet light. Aging (Yes), Varnish (Acrylic). Pigment: Cadmium Red. Glucopon® 600: 0.1%. Phenethyl alcohol 0.25%.

The example in **Figure 9** comes from cleaning an oil painting made using cadmium red as a pigment and varnished with acrylic varnish that has undergone an aging process. The cleaners that have been simulated contain all the possible compositions of water, limonene and Findet® 1214/N23 (up to 10%) within the established ranges, in this case maintaining a fixed concentration of 10% of Glucopon® 600 (the maximum concentration established in designing experiments) and 2.5% of phenethyl alcohol (intermediate concentration in designing experiments). The response shown on the color scale is the expert's opinion using ultraviolet light, UV. To help with the analysis, the bottom section of the triangle is shown, where the cleaner's area of action is to be found, given the proportions of its three main components.

The simulations that have been carried out using this system are as follows:

1. Simulation in all ranges of the factors and for all responses. The results obtained are shown in triangular diagrams that enable a general "mapping" of the entire system to be obtained. This first approximation gives a general picture of the phenomenon of cleaning oil paintings, allowing us to visually find the main relationships between factors and responses.

2. Simulation for particular cases of cleaners that enable an evaluation of the complex relationships between the type of varnish, aging of the paint and type of pigment with the two main components of the cleaning compositions, water and limonene, using as a basis a cleaner with Findet® 1214/N23, Glucopon® 600 and phenethyl alcohol in fixed amounts (10%).

3. Tests to optimize the model in order to develop cleaning formulations with special characteristics that are optimum for performing their purpose.

4. Conclusions

1. A response surfaces model has been proposed for cleaning oil paintings with aqueous-based and limonene cleaning formulas using the MODDE Go® program, and its statistical validity has been demonstrated.

2. Thanks to the model, it has been possible to simulate a multitude of cleaning scenarios *in silico* and to determine the main factors that affect the cleaning, which is evaluated via the responses: O/V cleaning, expert opinion using visible and ultraviolet light, color affected, dELab, percentage of lightness affected, ΔL, and percentage of gloss affected, ΔG.

3. The main factors influencing the cleaning were the concentrations with water and limonene as the main solvents and which regulate the cleaners' level of hydrophilia and lipophilicity, followed by the type of varnish, aging and types of pigments. The cleaners' other components are less relevant. In decreasing order of relevance, they are Findet® 1214/N23, phenethyl alcohol and Glucopon® 600.

4. The cross-synergistic and antagonistic effects between the cleaners' components, the pigments, the varnish and the extent of aging have also been found to be very significant in cleaning.

5. Using *in silico* simulation, it is possible to formulate specific compositions for different scenarios and cleaning applications.

6. For future research, it is proposed to develop 3-dimensional vector models that include, firstly, the material and physico-chemical aspects of cleaning; secondly, factors related to the expert restorer; and thirdly, the visual dimension that can be evaluated with optical methods.

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