

CLEANING AND RESTORATION OF AN OIL PAINTING WITH A POLYMER GEL IN IRAN

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1. Introduction

Imagining a world with no polymer materials is difficult, as these materials have now become an integral part of our lives and are used in the manufacturing of different objects, from general everyday tools to complex, medical and scientific instruments of precision. Polymer science has also proved advantageous in the conservation and restoration of historical artworks. The main question examined in this article concerns the properties of polymer gels used in the cleaning and restoration of paintings, the techniques they require, and the optimum results expected of them. This study seeks to present a different application of polymers, that is, the preparation and use of a polymer gel for the removal of surface layers of stains and unwanted substances accumulated on the varnishes formerly used on easel and mural paintings as a protective coating in the restoration of oil paintings. Over time, these coatings undergo physical and chemical alterations that reduce their reversibility and solubility and change their refractive indices, thus preventing viewers from seeing the true colors used by the painter due to changes in the pigments. These coatings have other adverse effects too and need repeated restoration; their elimination from artworks, therefore, appears essential.

In the proposed gel system, a gel formed by a polymeric compound is used to dissolve synthetic and natural substances on the porous surface of paintings. The present study examines the use of a polymer gel in cleaning stains and varnishes that have lost their properties. In the past decade, gels have established themselves as a physical substance used in the conservation of art; Wolbers was the first to propose the use of gels for cleaning artworks (oil paintings) [1]. The use of solvents in gel form somewhat overcomes the adverse effects of using pure organic solvents that deteriorate paintings by penetrating deeply into their layers. Choosing the right solvent and controlling the cleaning stages are difficult and in many cases, the unwanted layers of material that have built up on easel and mural paintings present a real challenge. Gels reduce the capillary penetration of solvents into the layers of an artwork and the gel lattice keeps solvent evaporation constant. Cleaning with a gel is much easier than cleaning with any other solvent. The gel cleaning method can therefore be used for the removal of stains, varnishes and the synthetic polymers that were formerly used on a wide scale in the restoration of paintings and which are now found to be harmful, in and by themselves. To further learn about this type of gel and to carry out the study, an ap-

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plied, descriptive, exploratory method of research was adopted along with the use of library and experimental instruments and methods of data collection.

2. Background

In the last thirty years, the application of gels for cleaning has reached its pinnacle. A new group of organic liquid gels in solid form was identified in the Department of Chemistry (CSGI), at the University of Florence, in Italy. In the past five years, these new gels have been tested on 16th century triptych paintings and 18th century oil paintings with the purpose of reducing the adverse effects of cleaning on color surfaces; in both cases, yellowish rotten layers of oil were detected on the canvas. These experiments aimed to assess the applicability of gel systems for cleaning and addressing the problem of the conservation of old objects. The application of these gels on the painting samples was done using simple tests. First, a small amount of the prepared gel (a drop) was applied to the surface for a few minutes and then scraped off by palette knife. In general, the possibility of keeping the patina formed on the painting surface and the removal of stains after cleaning can be a real advantage, if this layer of oil is not harmful to the layers of the painting and does not prevent the real painting from being read correctly. The preliminary tests [2] were carried out on an 18th century painting of a nobleman from the Carcherano di Osasco family by an unknown painter and a 16th century portrait of the symbolic marriage of Saint Catherine. The gel made by researcher was then tested a second time on paintings with different color hues. Due to the use of a solvent gel, no other solvent was needed [2].

The microscopic changes in these gels were assessed during the course of the tests. The gels were easy to use and malleable, making their close contact with the surface possible and facilitating their application and removal. Results showed that the gels maintained their transparency after contact with the colored surface, therefore enabling better control of the effects of the cleaning on the surface. A small amount of the gel (a drop) suffices for the cleaning process and is subsequently easily removed by palette knife. These new cleaning systems provide a valid, new method for cleaning artworks [3].

3. The application and disadvantages of solvents in the restoration of historical artworks

Solvents are mostly used in restoration tasks such as cleaning coatings (varnishes used on paintings and degreasing metallic surfaces) and removing organic matter from textiles. Solvents are also used for the dilution of adhesives and other substances. The use of a solvent in restoration tasks requires an evaporation rate appropriate to the painting. In cleaning the surface of a painting with a solvent, rapidly evaporating solvents (such as Acetone) tend to disappear before softening and removing the oxidized layers of varnish. In contrast, slowly evaporating solvents (such as Glycerin and Triethanolamine) remain in contact with the main layers of color in the painting for a prolonged duration and soften them. Under these conditions, mechanical operations can easily damage the layers of the painting. Another problem with solvents is that moistened surfaces attract dust. Most solvents are toxic and prolonged and frequent exposure to their fumes can cause serious harm to the operator's health. The degree

of hazard of a solvent is expressed as its maximum average airborne concentration, or Threshold Limit Value (TLV), in Parts Per Million (PPM), such that $TLV > 25$ indicates a relatively high solvent toxicity. Optimum care should be taken when working with solvents, especially in the process of cleaning paintings, when the person is exposed to the inhalation of solvent fumes for a prolonged period. Flammability is another problem regarding the use of solvents and fire precautions should be taken to avoid any possible risk, especially when large amounts of the solvent are being used. Using a volatile solvent fills the air with the solvent's fumes and a small spark or the lighting of a match can cause combustion [4].

4. Advantages of using the gel prepared by the researcher

Choosing the right solvent and controlling the stages of cleaning are also difficult; in many cases, cleaning unwanted layers of coating from easel and mural paintings causes problems [5]. Gels reduce the capillary penetration of solvents into the material layers of artworks, the gel lattice maintaining solvent evaporation constant. Cleaning with gels is much easier than cleaning with solvents. The gel cleaning method can therefore be used for the removal of stains, varnishes and the synthetic polymers that were formerly used on a wide scale in the restoration of paintings and which are now found to be harmful in and by themselves. The surface porosity of paintings has the effect of easily trapping solvents inside the micro-pores, which makes the cleaning process difficult. The special formulation of polymer gels is indicative of a major advantage over purely organic solvents that are still used today for cleaning and removing unwanted layers from oil paintings. The gel cleaning system has been developed to clean the surface of historical works of art without causing adverse effects on the artwork. The polymer gels developed, represent one of the main advances in the cleaning of paintings, as they leave no negative effects or residues on artworks [6]. Polymer gels can therefore represent a valid alternative in the conservation and restoration of paintings [6]. The prepared gel contains poly acrylic acid (PAA) compounds [7]. The past few years have witnessed an increased tendency to use hard gels made from liquid polymer compositions for cleaning artworks. A new group of organic liquid gels in solid form has been identified in the Department of Chemistry CSGI, at the University of Florence, in Italy. Over the past five years, these new cleaning compounds have been found to be associated with reduced adverse effects in cleaning on color surfaces [7]. The gels are formed by a polymeric network of polyvinyl alcohol-co-vinyl acetate and break up copolymers with different hydrolysis rates in transverse bonding with salt and borax in organic liquid solvents. These systems have special features, such as high concentration and strong elasticity; the former affects the spread of cleaning agents on all painted surfaces, and the latter enables the removal of cleaning agents from the surface, on first try [6].

5. Composition

The gel made by the researcher contains different percentages of different solvents, including Isopropanol, ethanol, Acetone, polyvinyl alcohol, metiletilketon, Borax (tetra sodium borate); it is also mixed with epoxy resin, titanium white, cyclohexane and other materials to produce a solid form. The technical knowledge behind this gel is owned by

a company in Iran and its formulation has been patented. This product was prepared and given to the researcher according to a request made to this company detailing the gel characteristics [3]. It should be noted that, due to the lack of means for preparation, this gel was prepared through trial and error and with continuous efforts made by the collaborating company and at the expense of the researcher involving great difficulties.

6. Application of the gel

The gel was tested on the sample (an old oil painting named “*Qajar Princess*” by an unknown Iranian artist, from the Qajar period), for a duration of 5 and 10 minutes. It was then removed in a thin layer with no mechanical pressure once it was dried out. It is possible to reuse the gel once in certain cases. Prior to the application of the gel, it is necessary to have accurate information about the composition of the paints and the materials used in the painting. To do this in my workshop, it was not necessary to perform chemical and physical analyses of the paint because the paints used in the Qajar period were known and were produced using organic and mineral substances, such as azure, vermilion, lead etc. The maximum duration for leaving the gel on a painting is 10 minutes, a longer time has no further positive effects. Two five-minute applications will produce better results than a longer 10-minute application. Application of the gel at the recommended duration will reduce harmful oxidized layers of stain and varnish that have lost their color. Overall, the possibility of preserving the fine uniform patinas on the surface of the artwork after cleaning is considered a huge advantage. In fact, the application of this gel makes cleaning a fully controllable procedure. The diffusion of liquids is directly linked to the hardness and concentration of the gel, and the gel structure of the substance facilitates the long storage of liquids. This product can be applied to artworks with simple tools such as a palette knife and, due to its elasticity, it can be successfully removed from surfaces. It spreads well on surfaces and makes close contact with the surface layer of the painting. After application, it slowly dries out with little discoloration, since it progressively absorbs the layers of stain and yellowed varnish through its particular composition and dissolves them. The transparency of this product enables the effective control and monitoring of the surface of the artworks throughout the cleaning process.

7. Storage of the gel

Considering that this gel is an air-dry product and should not be exposed to direct light, certain conditions are necessary for its storage. The gel packaging should be airtight and protect the product from exposure to light; otherwise it will change color and lose some of its solvent through exposure to air, consequently losing its effectiveness. The gel should be kept at room temperature. If all these conditions are met, the gel can be stored for a maximum of one year.

8. Sample test

The gel was tested on a Qajar-style oil painting on canvas depicting a Qajar princess and showing yellowed varnish, surface staining and dust (Table 1).

As can be seen in Figure 1, the second test was performed to examine the effect of the reduced drying time on the outcome of the cleaning. A warm blow-dryer was then used to accelerate drying time, which caused some peeling of the paint. It was therefore concluded that the gel should be allowed a certain time to air dry with no interference in order to avoid damage to the colors. The third test was performed to detect residues. After removing the gel from the painting, a pH test was used to confirm the absence of residues (Figures 1-3).

Figure 2 shows the painting depicting the Qajar Princess before the cleaning process. Figure 3 A shows the researcher-made gel sample; in Figure 3 B the part of the painting surrounded by tape is the part used for the test; after applying the researcher-made gel, we waited for 5 minutes for the gel to dry and then, carefully removed it (Figure 3 C); Figure 3 D clearly shows the difference between the cleaned part and the uncleaned parts around it.

Table 1. Sample dimensions.

Length	Width	Wooden frame profile
60 cm	40 cm	2x4 cm



Figure 1. Measuring pH before and after gel application and results for each test.



Figure 2. The sample painting depicting a Qajar princess (unknown artist).



Figure 3. A) Using the gel prepared by the researcher for cleaning; B) first test of the gel for cleaning painting; C) removing the gel from the surface of the painting after testing on a sample; D) segments of the painting cleaned with the gel are clearly distinguishable from other segments.

9. Examining the gel residue on artworks

Residue is a major problem with such compounds, especially solvent gels. The peel-off property of gels reduces the need for mechanical action on the surface and cleaning is accomplished without leaving any residue. The cleaning of painting surfaces is associated with certain problems, and aesthetic decisions need to be made with regard to the complete or partial removal of dirt from the varnish and paint layers. Expert analyses include choosing a technique that facilitates maximum control over the cleaning process, so that the undesirable layers of oil are removed from the surface without damaging the layers underneath.

Old cleaning methods involve mechanical cleaning or the use of organic solvents or liquid alkaline solutions. Some cleaning techniques allow for greater control over the cleaning process by slowing down evaporation or reducing its spread to other parts. Art experts use solvent adhesives made of wax and antiques experts use thickening agents such as wood paste, clay wax and a variety of cellulosic substances.

The main issue with using gels concerns residues. Any residue remaining on the clean surface is a potential risk for the artwork, including increased color solubility or changes in paint composition. The present study examined potential gel residues on sample paintings selected as a result of a comprehensive study of the subject; the initial results showed that active substances on the surface break down relatively quickly. These results were presented at an IIC Melbourne Congress. David Miller, an art expert and professor of chemistry at California State University Northridge (CSUN), ran cleaning tests on sample oil paintings at the chemistry lab in his department so as to determine the amount of residue on the painting surface after cleaning with the gel. Just as in previous tests, these tests also emphasized the negligibility and the rapid break-down of residues with the use of the gel cleaning method.

10. Conclusion

As shown by the studies and practical tests conducted on the sample paintings, the preparation of polymer gels is a difficult and complex process that is still in its early stages in Iran. However, the gel prepared in this study did have the cleaning properties discussed, allowing better control over the operation and facility of use. Moreover, the amount of dirt stains removed depends on the length of time the gel remains on the surface. The minimum and maximum times required for this gel are 5 and 10 minutes. The gel will produce no further positive effects after the maximum 10-minute duration. Two applications of the gel for a shorter length of time will produce better results than a single prolonged application. According to the results obtained from the first and second samples tested, this gel is well capable of dissolving oxidized varnishes and maintains its transparency in contact with colored surfaces, thereby enabling better control over the cleaning effects of the gel on the surface. A small amount of the gel can be easily applied to surfaces and then be easily removed using simple tools such as a palette knife. The resultant cleaning is completely superficial and does not penetrate the lower layers of the artwork, which is considered an important advantage of this gel. Furthermore, examining the gel residues after the cleaning process shows that no further solvents are required to remove the gel itself from the surface, as this process leaves no residues, making for another advantage in using this technique. The

application of this gel reduces art restoration experts' contact with volatile chemicals that are physically harmful, and also minimizes any damage to artworks caused by the use of these chemicals. The storage of this product does not require any special conditions besides room temperature and airtight packaging. The gel can be stored for a maximum of one year. This cleaning method can be used at the conservator-restorer's discretion and with his careful scrutiny, as an alternative or adjunctive method of cleaning paintings.

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Biographical notes

Siyamak Alizadeh, born in 1963, is a Faculty member at the Faculty of Art, Shahid Chamran University, Ahvaz, Iran. He is a researcher, teacher, art work restorer, sketcher, and painter. He has a Ph.D in art research, Tehran University of Art, 2007; an MA degree in buildings and historical textures repair, Isfahan University of Art, 1995; Bachelor degree in restoration of ancient artifacts, Isfahan University of Art, 1989; wall painting preservation and repair course license from Venice European Center, 2004. He has cooperated with *Tehran Museum of Contemporary Art* in painting restoration since 1999. He has taught restoration and art in several university art faculties in Iran, including Shahid Chamran University, Ahvaz, Iran, since 2010.

Summary

One of the major stages in the conservation and restoration of a painting is to clean its colored surface of unwanted stains, and old and darkened varnishes. Various solvents have been used to date for this purpose; however, new cleaning materials have also come onto the market in the past decade that are still unknown and may never have been employed in Iran. The present study aims to introduce a polymer gel and use an *in vitro* sample of the substance for cleaning and to then present the results of the tests carried out. Applying a polymer gel in the cleaning of paintings yielded better results and greater advantages over the solvents previously used to clean artworks. The advantages include: performing on the surface without penetrating the lower layers, the absence of residues after application, flexibility, solubility and the gentle removal of old stains and varnishes, maintaining clarity and cleaning the surface by simple removal of the thin dried layer, which requires no mechanical pressure. Microscopic examinations and pH testing showed that this new alternative technique can be of use in cleaning the color layers of oil paintings.

Riassunto

Una delle fasi principali della conservazione e del restauro di una pittura riguarda la pulitura superficiale del film pittorico con la rimozione delle macchie indesiderate e delle vernici invecchiate per le quali vengono utilizzati diversi solventi. Tuttavia, negli ultimi dieci anni nuovi materiali per la pulitura sono entrati sul mercato, ancora sconosciuti e che potrebbero non essere mai stati impiegati in Iran. Il presente studio intende introdurre l'uso di un gel polimerico e utilizzare un campione con lo scopo di effettuare la pulitura, per poi presentare i risultati delle prove. L'applicazione del gel polimerico durante la fase di pulitura ha dato risultati migliori e maggiori vantaggi rispetto ai solventi precedentemente utilizzati per le opere d'arte. I vantaggi includono, agendo in superficie senza penetrare gli strati inferiori, l'assenza di residui dopo l'applicazione, la flessibilità, la solubilità e la leggera rimozione di vecchie macchie e vernici, mantenendo chiarezza e agendo sulla superficie mediante la facile rimozione degli strati sottili senza richiedere pressione meccanica. Le indagini microscopiche e il pH test hanno mostrato che questa nuova tecnica alternativa può essere utile per la pulitura degli strati di colore delle pitture ad olio.