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Original article

Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings

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ABSTRACT

Today, acrylic emulsion paint is widely used in the artistic area as an alternative to the traditional oil painting. However, after a short time of painting exposure to the environment, the acrylic tends to accumulate surface dirt for inherent reasons to its composition. This phenomenon creates a conservation problem, because the usual cleaning methods are hindered by the acrylic film soft morphology and its high sensitivity to organic solvents. To date, few aqueous solutions based cleaning systems have been investigated as alternatives to the traditional methods. This paper proposes the use of oxalic and tartaric acid solutions for acrylic paints cleaning as alternatives to citric acid. A series of titanium white acrylic paint films were subjected to immersion tests in different aqueous solutions and their weight change was monitored to determine the effects produced by the solutions according to pH (3.5, 5 and 8.5) and conductivity (4, 6 and 12 mS cm^{-1}). Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), X-ray diffraction (XRD), and scanning electron microscopy (SEM-EDX) techniques were used to evaluate the acids effects on the films before and after the tests. The results obtained showed that oxalic and tartaric acids exhibit similar properties to citric acid, resulting as a valid alternative for aqueous cleaning treatments on acrylic paintings.

1. Research aims

During the last years, the cleaning of contemporary acrylic paintings has represented a great problem for the conservation area. The objective of this work is to propose the use of organic acid solutions that can be an alternative to those already used in the cleaning of polychrome surfaces, as the common citric acid. An important objective for the present conservation is to increase the knowledge about the aqueous cleaning methods, because they can replace organic solvents in the resolution of complex intervention problems. In addition, due to the lower toxicity of aqueous solutions, these cleaning systems are safer for conservators and friendly with the environment. The purpose of the first part of the work is the characterization of an acrylic paint to know its polymer composition, extenders and additives. The second part evaluates the behaviour of young acrylic paint films through immersion tests in different aqueous cleaning solutions. The results help to have a better understanding of the aqueous systems effects and its versatility as chemical cleaning agents in the conservation area.

2. Introduction

The use of acrylic emulsion paints emerged in the artistic field on the second half of the 1950's with a wide degree of acceptance. Its low toxicity, versatility of use and rheological properties, were decisive for their quick incorporation as a new medium of artistic expression [1]. Since then, their presence has grown in all art collections, making it one of the most representative painting techniques used by contemporary artists [2].

The first commercial brand to produce acrylic solution paints (poly butyl methacrylate dissolved in turpentine) for artists' use was Magna® in 1949 [1]. But it was not until 1956 when Liquitex® [3] appeared, the first acrylic paint in aqueous dispersion with the copolymer poly ethyl acrylate/methyl methacrylate (EA-MMA) [4]. Currently, this copolymer is present in the artists' acrylic paint

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market with the poly butyl acrylate/methyl methacrylate (BA-MMA) and the acrylic-styrene resins (MMA-2EHA-Sty).

Basically, acrylic emulsion paint is a mixture of pigments dispersed on acrylic emulsion or *latex*, and a large amount of additives. On the one hand, the acrylic emulsion is defined as a dispersion of "tiny beads of solid, amorphous polymer suspended in water" [1], with biocides, buffers, emulsifiers and other ingredients [4] that stabilizes the product and gives to it the optimal use properties. On the other hand, the pigments are added to the acrylic resin in paste format, an aqueous medium with wetting agents and dispersants too [5].

Non-ionic surfactants, polyethylene glycol type (PEG), are the most problematic additives for the acrylic paintings conservation as they may affect both the optical and mechanical paint properties [6]. Non-ionic surfactants have high mobility and they migrate to the surface from the acrylic bulk film [7] by different mechanisms associated with the coalescence process, its acrylic polymer incompatibility, or the glass transition temperature (T_g) [8–10]. Over time, surfactant surface accumulation modifies the paint saturation and brightness caused by the formation of semi-crystalline groups that have the ability to catch and embed environmental soil. These water-soluble groups may also be formed into the polymer matrix, creating hydrophilic 'pockets' that favour water absorption by capillarity [11,12]. It is considered that a combination of non-ionic and anionic surfactants added as resin stabilizers may include between 2 and 6% of the total acrylic dry film weight [13].

The amount and type of the additives present in the painting determines the acrylic film behaviour in absorption and water-soluble materials extraction. Certain additives as buffers (ammonium hydroxide) or coalescing agents (glycols) are evaporated during the drying process, but other water sensitive compounds remain in the paint affecting film absorption and swelling [14]. It is considered that associative thickeners (hydrophobically modified ethylene oxide urethane [HEUR]) and poly acrylic acids (PAA) can rehydrate depending on the pH of a solution, causing big dimensional changes inside the paint [15]. This can result not only in an irreversible deformation of the polymer matrix, but also in a high extraction of water-soluble components [3,8,16]. These materials loss, mainly water-soluble surfactants, is translated in the appearance of acrylic film micro-perforations and a reduction of their original elasticity and adhesion [5].

Although in the last years the research on acrylic paintings characterization and its aging behaviour has increased, few studies have focused on the cleaning aqueous solutions effects on acrylic films. In this sense, several authors agree that the modification of the pH and the conductivity in a cleaning solution can help to control water absorption and materials extraction [14,15,17].

It is known that the organic solvents, commonly used in the conservation area, produce the film swelling and soften the acrylic [1,18], so its cleaning use is restricted to non-polar solvents. In general, solvents penetrate into the acrylic paint and are retained for long periods causing pinholes, surface erosion, material displacement and polymer chains break [16]. As an alternative, some research in conservation [19,20] proposed dry cleaning methods, aqueous systems with artificial saliva, or deionized water with additives as ammonia, ethanol or triammonium citrate (between 1–2% v/v. or w/v.) [18,21]. Other methods included the use of aqueous solutions with additions of surfactants (Triton® X-100), rheology modifiers (thickeners, gels) or chelating agents (citric acid or ethylenediaminetetraacetic acid [EDTA]) [22,23].

The first approaches to the organic acids use in conservation were the incorporation of citric acid for insoluble salts removal on mural painting and other inorganic surfaces (ceramic, metal, etc.) [24,25], and the use of oxalic acid for metal objects passivation [26]. Afterwards, the use of weak acids was also incorporated into the cleaning systems for polychrome surfaces conservation [27,28].

Table 1
Painting technic data declared by Grumbacher®.

	Titanium white
Opacity	Opaque
Lightfastness	I–Excellent [33]
Medium	Acrylic polymer emulsion
Pigments	Titanium dioxide TiO_2 – PW6 [34]

Weak organic acids (acetic, malic, citric, tartaric, etc.) were proposed by Cremonesi [29] for the elaboration of compatible cleaning solutions with different pictorial layers, while Wolbers and others authors [14,17] explore the use of this acids as chelating agents for surface dirt removal. Chelates are compounds that can interact in solution with metal atoms, forming or dissolving complexes according to the chemical environment in where the chelation process is produced [30]. Other compounds derived from citric acid, have also been studied for cultural heritage cleaning such as EDTA (a strong chelator) [31], or ion citrate salts as triammonium citrate (TAC) or triethanolamine (TEA) [32].

Despite these works, there is a significant lack in the aqueous systems study for polychrome surfaces cleaning yet. This paper proposes the use of oxalic and tartaric acid compared to citric acid for the acrylic paints cleaning, since they have a similar nature in terms of chemical composition, chelation effects and low toxicity. Organic acids were used in aqueous solution to evaluate their behaviour on young titanium white films according to certain parameters of pH and conductivity.

3. Materials and methods

For the proposed cleaning solutions evaluation, 20 min and 24 h immersion tests were performed on titanium white acrylic paint films. Visual analysis, colorimetric measurements and scanning electron microscopy were carried out to determine possible surface changes before and after the immersion tests.

3.1. Acrylic paint samples

A titanium white acrylic paint was selected from the artists' professional line Academy® Acrylic, from Grumbacher® (USA). In Table 1 are presented the main paint characteristics declared by the manufacturer.

Films were prepared as drawdowns on a glass substrate in laboratory conditions. The films obtained were 300 mm long and 40 mm wide, while the average thickness was 130 μ after drying. After a period of 72 hours, acrylic films were removed from the glass and dried in total darkness and dust-free environment during 90 days prior to analysis.

3.2. Acrylic paint films immersion tests

In order to determine the acrylic films water absorption and desorption, a series of 9 aqueous solutions were prepared for each acid: citric, oxalic and tartaric (Table 2). The values of pH 3.5, 5 and 8.5; and conductivities of 4, 6 and 12 mS cm^{-1}, were obtained in proportion of 0.01 g of acid by 100 mL of deionized water for the pH 3.5 and 5, and the addition of a 1 M solution of sodium hydroxide (NaOH) to adjust to the desired value. For the pH 8.5 was used 0.1 g of acid and 0.5 g of sodium borate, with the addition of 1 M of NaOH for the adjustment. The conductivity was modified with sodium chloride (NaCl), adding 0.1 g until the desired value was reached. The solution *number 0* (reference solution) correspond to pure deionized water.

Titanium white acrylic paint films (50 × 20 mm) were immersed for 20 min in beakers with 50 mL of each solution. The weight of

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