Journal of Cultural Heritage 16 (2015) 49–56

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Original article

Measurement of the reversible rate of conservation materials for ancient murals

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ARTICLE INFO

Article history:
Received 11 August 2013
Accepted 28 January 2014
Available online 26 February 2014

Keywords:
Dunhuang mural
Conservation materials
Removal
Reversibility
Reversible rate

ABSTRACT

The study of how to remove the ineffective conservation materials without damaging the mural's surface has been one of the hot issues of modern conservation science, and the reversibility problem of mural protective materials needs to be resolved instantly. In this article, we measured the reversible rates of 4 typical protective agents both on glazed tiles and model samples of Dunhuang murals, and used 3D microscopic system to observe the removal effect. The experimental results show that the cleaning agents should not contain water considering the water-soluble binding material of Dunhuang murals. All conservation materials are reversible, but their reversibilities are different. We obtained the best pairs of "conservation material-cleaning agent", which are "silicone-acrylic emulsion-p-xylene + propylene carbonate", "acrylic emulsion-p-xylene", "polyvinyl acetate emulsion-p-xylene + ethyl acetate" and "Paraloid B72-p-xylene + propylene carbonate". It is also found that the reversible rate of conservation materials declines after aging.

1. Introduction

Mogao Grottoes in Dunhuang, China, is a world-famous art treasury, with invaluable murals and sculptures made between the 4th and 14th centuries. In 1987, Mogao Grottoes was listed as World Cultural Heritage [1]. Dunhuang mural is a major component of Mogao Grottoes, it is well known as "a great miracle in the world art history". The structure of Dunhuang mural from inside to outside is conglomerate, earthen plasters (coarse plaster, fine plaster and lime layer) and paint layer [2]. Based on the information currently available [3–6], the binding material of pigments in Dunhuang mural is mainly animal glue.

However, after hundreds of years, a variety of diseases, such as flake, detachment, fumigation, discoloration and disruption, have emerged on these ancient murals because of local environment and human activities [7,8]. The conservators have applied a few protective agents, such as polyvinyl acetate (PVAc), acrylic and silicone-acrylic emulsions, to attach the paint layers back to the wall and consolidate the paintings. In 1932, Stout et al. [9] used polyvinyl acetate in murals, statues and other art works. PVAc was also used in Dunhuang to repair the flaked and disrupted murals since 1950s, and it was proved effective [10]. Paraloid B72 is also a reinforcing agent which has been widely used in murals, clay, stone and pottery conservation, especially in the United States and Europe [11].

Polymer materials will age with the action of light, heat, acid-base and bacteria corrosion in nature, and the aged materials will lose the protective function, even worse, they will produce damage to relics if they still remain. On the other hand, with the development of material science and technology, new and better materials for heritage protection will replace the old ones in the future. Therefore, the reversibility of conservation materials is an important and specific requirement in the conservation work [12]. Reversibility is referred to that when the material is applied, it can still be removed from the surface without damaging the art works by means of physical adsorption or chemical reaction after a period of natural variation [13]. It is a new problem in modern conservation science to seek an innovative and effective cleaning agent for removing the existing but ineffective conservation material without damaging the substrate.

For example, the fresco surface in the San Salvador Church in Venice (16th century) was affected by a thick layer of poly-EMA/MA (paraloid) applied 40 years ago. However, the coated surface appeared very shiny while the background was dark

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http://dx.doi.org/10.1016/j.culher.2014.01.010

because of the severe degradation of poly-EMA/MA. In consequence, it would damage the painted layer if they were still present on the painting's surface as coating [14]. Another wall painting in the Oratorio di San Nicola al Ceppo in Florence, Italy (17th century), was polluted accidentally by a thick and hard layer of insoluble black crusts composed of a mixture of $CaSO_4 \cdot 2H_2O$ and asphaltenes (inlet) stemmed from the deposition of undissolved fraction of mineral combustibles during the Arno's flood in 1966 [15]. It was impossible to extract the inorganic contaminants successively and remove them completely because the crusts were insoluble in pure solvents. Carretti et al. [14] developed a new procedure to get rid of the insoluble organic and inorganic materials without producing side effect on the heritage site.

The microemulsions and micellar solutions were used (neat or combined with gels) for the removal of contaminants and polymers applied in the past restorations because of their good thermodynamic stability and decontamination ability to dissolve polymer-based conservation materials [16,17]. The first application of amphiphile-based nanostructured microemulsions can trace back to 1980s, which was performed by E. Ferroni and P. Baglioni during the restoration of the Renaissance paintings in the Brancacci chapel in Florence by Masaccio, Masolino and Lippi [18]. They also devised, prepared and measured several oil-in-water microemulsions during the last 20 years, which are regarded as the most performing media to remove the organic polymers from porous structures, especially to eliminate the hydrophobic coatings from the mural's surface. They tested these oil-in-water microemulsions on both laboratory replicas and real art works and found that they appeared to have better performances compared with the traditional cleaning tools such as organic solvent or solvent mixtures [14,19–23].

There are several other cases of using microemulsions and micellar solutions to protect cultural heritage. The surface of a Renaissance wall painting by Spinello Aretino was coated with hydrophobic acrylic copolymers during a restoration in the 1960s in the Cappella Guasconi in San Francesco Cathedral, Arezzo, Italy, and nanocontainer solutions were used to remove them completely as well as the poly (vinyl acetate) resins, which was applied on the Renaissance frescoes decorating the external wall of the Cathedral of Conegliano, Northern East Italy during a restoration in the 1950s. So, it is a new, safe and efficient way to remove the aged polymers from surfaces of art works [20]. Another cleaning agent called M1/hmHEC system was tested on a mural surface coated with 35-year-old EMA/MA from a previous restoration treatment in Santa Maria della Scala Sacristy, Siena, 15th century. The result indicated that the glossy coating disappeared completely, so it was appropriate for cleaning the aged polymers [23]. Besides, this system can be used to remove the aged organic varnishes [24], for example, an 18th century gilded frame covered with a layer of a natural aged varnish was treated with M1/hmHEC system, after that, the dark patina on the surface was removed completely [23]. Baglioni et al. [25] compared two cleaning systems, EAPC and XYL, and found that different from XYL, a "classical" oil-in-water microemulsion, the EAPC system was neither a microemulsion nor a simple micellar solution, with the cosolvents partitioned between the dispersing phase and the disperse droplets. They tested these two systems on the paintings of the Annunciation Basilica in Nazareth (Israel), which were treated with different polymeric materials in the 1970s, and it turned out that EAPC system showed better results compared with XYL system, confirming its brilliant cleaning capability. They [26] also successfully applied the EAPC system to clean acrylic and vinyl/acrylic copolymers from Mesoamerican frescoes in the archeological site of Cholula, Mexico. To clean the wax contaminations on the murals, an oil-in-water microemulsion composed of sodium dodecyl sulfate (SDS), pentanol (PeOH), and organic solvent dodecane was proved to be significantly effective [27].

Gel materials can also be used to clean murals, since it can reduce the swelling effect on the paint layers by slowly releasing the active solvent and the dissolved dirt/grime segments can be trapped in its special 3D network structure [28]. In addition, gel materials may be combined with a variety of cleaning agents, such as enzymes, chelates and microemulsions, obtaining very effective tools in the field of mural cleaning. Currently, lots of studies are focused on responsive gels, reversible gels, magnetic gels and "peelable" gels [29,30].

These cases showed effective removal of coatings from artistic surfaces. Feller tests and Teas charts are used to determine the suitable solvent for the formulation of microemulsions and micellar solutions for a particular conservation material [31]. However, considering the potential different structure and composed materials, whether these innovative cleaning agents used in Europe are suitable for ancient murals in China is unknown. Therefore, based on our previous studies [32], the reversibility problem of Paraloid B72, silicone-acrylic, acrylic and polyvinyl acetate emulsion was investigated qualitatively and quantitatively on glazed tiles first; then we make model samples from the prototype of Dunhuang murals for qualitative and quantitative investigation with aged conservation materials; finally, three-dimensional microscopic system was used to offer experimental data and theoretical guidance for practical application.

2. Materials and methods

2.1. Instruments

Electric analytical balance (FA1004, Shanghai, Hunyuhengping scientific instrument Co., Ltd) was used for weighing materials and agents. Electric heating oven (DH-9070, Shanghai, Jinghong experiment facilities Co., Ltd) was used for sample drying. UV ageing oven (Common Wealth Industrial Corporation) was used for sample aging. Three-dimensional microscopic system (VHX-2000, KEYENCE China Co., Ltd) was used to observe the removal effect.

2.2. Materials

Red lead (A107), azurite (A29 14#) and mineral green (A22 14#) were all produced from Beijing Tianya Company. Lime ($Ca(OH)_2$) was obtained from Sinopharm Chemical Reagent Co., Ltd. Gelatin was purchased from Suzhou Jiangsixutang Pigments Company. Glazed tiles, with the size of $10 \times 10 \times 0.5$ cm, and clay blocks, with the size of $10 \times 5 \times 1$ cm were obtained from Hangzhou. Paraloid B72 was obtained from Germany, 49% silicone-acrylic emulsion, 49% acrylic emulsion and 48% polyvinyl acetate emulsion were purchased from Boshijiaofendeli (China) Binder Co., Ltd. SDS ($C_{12}H_{25}NaO_4S$, CP), water, ethylene glycol (EG, $C_2H_6O_2$, AR), Tween-20 ($C_{58}H_{114}O_{26}$, CP), ethyl acetate (EA, $CH_3COOC_2H_5$, AR), P-xylene (PX, C_8H_{10}, CP) and 1-PeOH ($C_5H_{12}O$, AR) were all obtained from Sinopharm Chemical Reagent Co., Ltd. Propylene carbonate (PC, $C_4H_6O_3$, 99%) was obtained from Aladdin Industrial Corporation. Silicone-acrylic, acrylic and polyvinyl acetate were diluted to a concentration of 15% to 20%, and Paraloid B72 was dissolved in *n*-butyl acetate to prepare a solution of 20% concentration. The SDS were dissolved in water to prepare the 10%w solution and the other agents were used as received. The mixtures were prepared by mixing each two of the PC, EA, PX and 1-PeOH at the weight ratio of 50/50. The criterion behind the selection of the cleaning agents is that the agent should have no effect on binding material (gelatin) and can remove the protective agents efficiently according to the compositions of the microemulsions and micellar solutions mentioned in Section 1.