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The clean and evaluation methods for the paint pollution on the surface of masonry relics

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Abstract: *The immovable cultural relics such as masonry relics, sometimes become targets of vandalism due to their long-term exposure to the outdoors and difficult to regulate. Therefore, it is very important to study an effective treatment method after these accidents. In this work, 3 types of organic solvents were evaluated for their efficacy in cleaning three common types of paint. Through the paint film softening effect assessment, cleaning pressure selection, paint removal rate calculation, andcleaning safety evaluation, a systematic evaluation of the cleaning effect was carried out. The results showed that the paint cured for 24 h was applied with a cleaning agent primarily composed of methyl-carbonate to soften paint, followed by rinsing with water pressure at 0.1MPa. After repeated cleaning, the paint removal rate could reach up to 97 %, with the rock surface damage was less than 1.5% (invisible to the naked eye). For the paint cured for 72 h, a cleaning agent mainly consisting of dichloromethane was used, which provided better cleaning effects and higher safety for the cultural relics themselves.*

Keywords: *Paint; Cleaning; Masonry relics; Methyl-carbonate*

1. Introduction

In recent years, as people's understanding of the value of cultural relics has increased, cultural tourism has become a hot topic. However, as more cultural relics are displayed to the public, there has been a rise in the problem of cultural relics being deliberately damaged by humans. Especially those immovable cultural relics that are exposed outdoors for a long time are more vulnerable to vandalism compared to those movable cultural relics that can be placed in display cases or storerooms. Some stone immovable cultural relics at scenic spots have even become targets for individuals to vent their frustrations, being spray-painted with paint. For example, the stone monument of Su Xiaoxiao at West Lake in Hangzhou, the monument of Broken Bridge and the monument of Broken Snow, the Touji Temple, the Okyodo, and the Gudenin Temple in Kyoto City, Japan, the Lincoln statue at the Washington National Cathedral in the United States, and the Little Mermaid sculpture in Denmark, all of which have experienced similar incidents. In response to such events, in addition to increasing regulatory efforts, it is also necessary to study effective methods following the occurrence of these accidents.

Currently, the commonly used methods for cleaning paint pollution on cultural relics can be categorized into three main types: 1)mechanical and physical removal[1]. 2)cleaning with instruments such as lasers [2-3]. 3)solvent cleaning[4-5]. Careddu et al.[6] studied the efficiency of cleaning graffiti from buildings using high-pressure water jet technology. Through microstructural analysis and surface roughness tests, they found that water pressure and cleaning distance had a direct impact on cleaning efficiency and the safety of cultural relics. Mateo et al.[7] researched the application of laser cleaning technology to remove varnish and contaminants from copper artifact surfaces. By observing samples before and after cleaning using microscopy and infrared spectroscopy, they found that this technology could completely remove these pollutants without causing any damage to the body of the copperware. Natali et al. [8] prepared a peelable organic aqueous cleaning material using partially hydrolyzed polyethylene and borates, and discovered that this material was effective in removing varnish from the surface of cultural relics. Germinario et al. [9] investigated the ability of lipase to remove marker ink, and the results showed that using lipase in combination with gentle physical or chemical methods could

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achieve ideal results in removing marker ink.

In practical work, stone cultural relics defaced with spray paint often have characteristics such as large contamination areas and thick pollutant layers. The most commonly used cleaning method is to rinse with large amounts of organic solvents like turpentine or thinner before the paint has cured. This method is cost-effective and achieves a high rate of paint removal. However, there are not many scientific studies on this method, and the large-scale use of these highly toxic organic solvents will pose a great threat to the environment, operators and tourists' health. Franzoni et al. [10] had used the LCA (life cycle assessment) analysis method to study the reasonableness of the current cleaning materials and techniques used in the preservation of historic buildings from the environmental perspective, and concluded that the current commonly used organic cleaning agents had greater safety risks. Therefore, finding a cleaning agent that causes no or minimal damage to cultural relics and is non-toxic or low-toxic to humans and the environment, along with a reasonable cleaning method, is of great significance in dealing with such incidents.

In this work, the cleaning efficiency, method, and safety of cleaning agents prepared with dichloromethane, ethyl acetate, or dimethyl carbonate as the main agent were investigated. It is hoped that this work can provide a feasible reference for dealing with the problem of paint pollution of cultural relics.

2. Experimental Design

2.1 Materials

2.1.1 Cleaning Agents

Ethyl acetate, methylene chloride, triethanolamine, analytically pure, Sinopharm Chemical Reagent Co. Ltd; dimethyl carbonate, sodium dodecylbenzene sulfonate, analytically pure, Shanghai Aladdin Biochemical Technology Co. The cleaning agent formulation was shown in Table 1.

Table 1. Cleaning agent formulations

Number	Main agent	Auxiliary agent		Proportion
①	Dichloromethane	Triethanolamine	Sodium dodecyl benzene sulfonate solution（5%w)	90: 5: 5
②	Ethyl acetate			
③	Dimethyl carbonate			

2.1.2 Paint

Water-based wood paint (acrylic resin), metal anti-rust paint (acrylic resin), and epoxy floor paint (epoxy resin), all in red color, purchased from the local building materials market. These three paints are commonly available commercial products.

2.1.3 Simulated Atone Artifacts

Two types of sandstone with different hardness levels were used as simulated stone cultural relics in this study (gray sandstone with a Leeb hardness of 37.8 HV0.5 and red sandstone with a Leeb hardness of 98.3 HV1). The sandstone was first cut into test blocks approximately 1 cm thick. These blocks were then soaked in clean water for 48 h, followed by ultrasonic cleaning for 30 min, and finally air-dried for later use.

2.2 Preparation of Simulated Samples

A brush was used to dip a suitable amount of water-based wood paint, epoxy floor paint, or metal anti-rust paint and applied it evenly onto the surface of the sandstone. The thickness of the uncured paint layer was controlled to be approximately 0.5-1 mm, with the paint layer area being about 1-2 cm². The samples were then left in a laboratory environment (T = (28±2) °C, RH = (60±3) %) for 24 and 72 h before cleaning experiments.

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2.3 Cleaning operation

Wet the nonwoven fabric with cleaning agent, then apply it to the surface of the paint layer. Wrap the sample with plastic wrap to reduce the volatilization rate of the cleaning agent. After 5 min, remove the cover, and rinse with a high-pressure water jet at a certain pressure for 10 s. The above steps were repeated until there were no significant changes on the surface of the sample, and the number of cleaning cycles was recorded.

2.4 Evaluation and Analysis

2.4.1 Softening Effect of Paint Film

The softening effect of different cleaning agents on the paint film was evaluated using a microhardness tester (HVS-1000Z, Wenzhou Weidu Electronics Co., Ltd.). First, the microhardness of the paint film cured for 72 h was tested. Then, after applying the cleaning agent for 5 min, the microhardness was tested again at intervals of 10, 30, 60, and 120 min following the removal of the cleaning agent.

2.4.2 Removal Rate

The removal effect of contaminant on cultural relic surfaces is commonly analyzed using methods such as weighing [11], color difference [1], spectroscopy [7, 12], and microscopy [13]. However, these methods often provide only qualitative or indirect evaluations. In this study, a video microscope (T993D, Taiwan XianTai) and Image J software were used to conduct both qualitative and quantitative analyses of paint removal effectiveness [14].

The quantitative analysis process was as follows: first, 10 random areas (each area approximately 1.5 mm × 1.2 mm) on the cleaned sample surface were selected and photographed using a video microscope. Then, the area of the red areas (un-removed paint) in the photographs was calculated using the image J software. The images before and after processing with ImageJ software were shown in Figure 1.

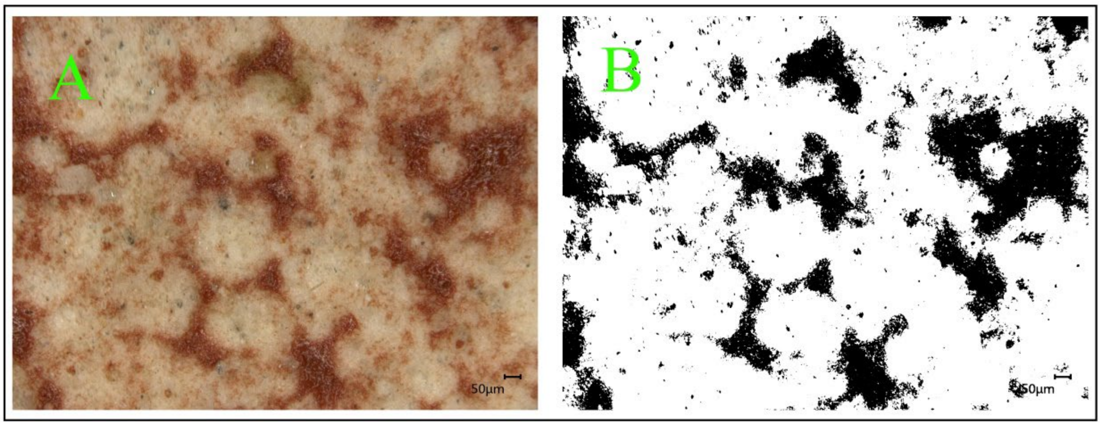

Fig.1. The edition of pictures by Image J (A. original micrograph; B. binary image)

The rate of complete paint removal was expressed as follows:

$$TC(\%) = \frac{\sum_{i=1}^{10}(sq_{totali} - sq_{redi})}{\sum_{i=1}^{10} sq_{totali}} \times 100\%$$

where TC: total clearance rate, sqtotal: Total photo area, sqred: Area of red area in photo.

2.4.3 Safety Evaluation

The cleaning safety was analyzed using microhardnessand microscopic structural comparison [6]. Microhardness: First, conduct microhardness tests on the two types of sandstone before cleaning. Then, apply the cleaning agent for 5 min, followed by continuous rinsing with water at pressures of 0.05, 0.1, and 0.2 MPa for 30 s. Finally, perform microhardness tests after cleaning. Structural Comparison: First, the samples before cleaning and after cleaning by different methods were photographed using a video microscope; then, the pictures before and after cleaning (as shown in Fig. 2) were compared using

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Beyond Compare software, and then the degree of difference was calculated using image J software. The smaller the difference, the better the cleaning safety.

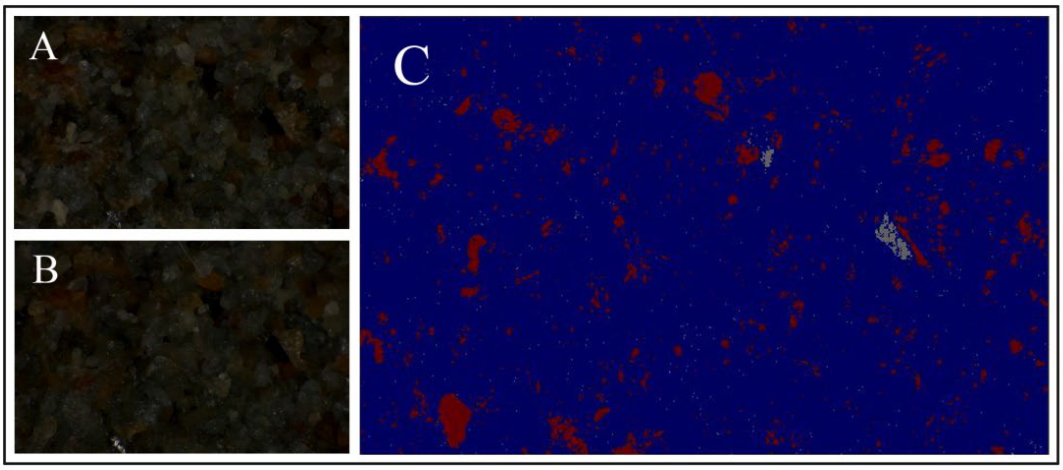

Fig. 2 Beyond compar, comparison analysis images (A. Microscopic image before cleaning; B. Microscopic image after cleaning; C. Processed comparison image)

2.4.4 Infrared Analysis

The mechanism of action of cleaning agents on cured paint films was analyzed using Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet iS20, Thermo Fisher Scientific). The procedure was as follows: First, prepare a paint film cured for 72 h and immerse it in the cleaning agent for 5 min. After removal, immediately rinse the sample with anhydrous ethanol. Afterwards, conduct FT-IR testing promptly. The spectral resolution was 4 cm^{-1}, and the testing range was 4000 to 400 cm^{-1}.

3. Results and Discussion

3.1 Paint Film Softening

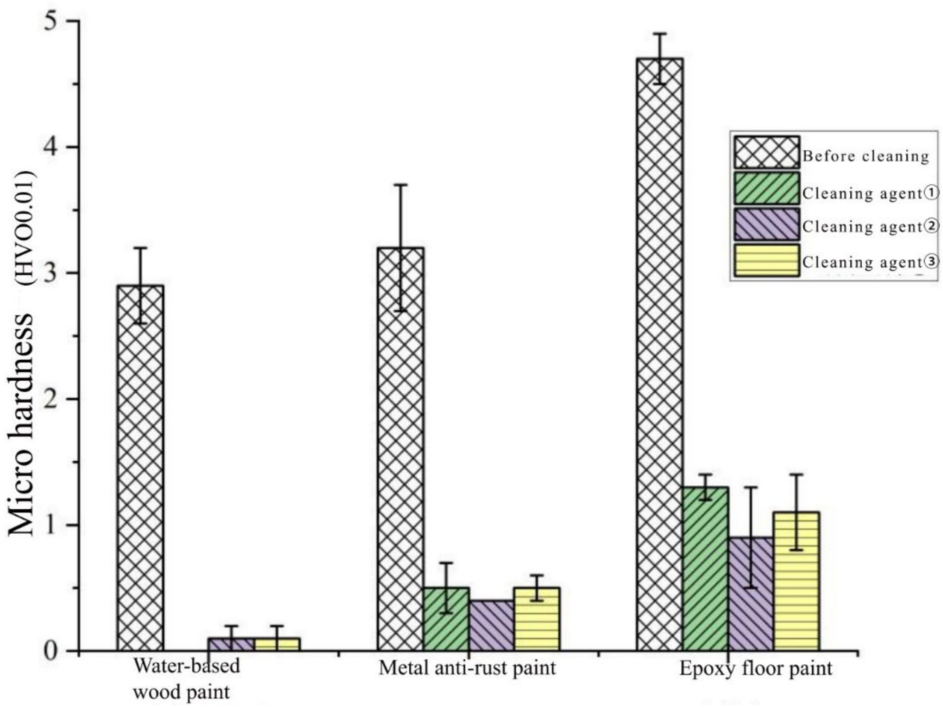

Fig. 3. Microhardness test results of different paint films before and after cleaning

The microhardness test results of cured paint films before and after treatment with different cleaning agents were shown in Figure 3. The results indicated that the initial microhardness of the

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waterborne wood paint, anti-corrosion metal paint, and epoxy floor paint before cleaning were 2.9, 3.2, and 4.7 HV0.01, respectively. Within 30 min after treatment with the cleaning agents, the microhardness of all three cured paint films remained below the minimum detection limit of the instrument. After being left for 60 minutes post-cleaning, the microhardness of the paint films gradually recovered. Among them, the microhardness of the water-based wood paint recovered by 0-3%, the metal rust-proof paint by 12-15%, and the epoxy floor paint by 19-27%.It was evident that the three cleaning agents demonstrated d a good softening effect on the three types of paint that had been cured for 72 h, and the softening effect remained quite good within 60 min. Therefore, there was sufficient operating time for practical large-area paint contamination cleaning.

3.2 Cleaning pressure

The cleaning pressure test results were shown in Table 2. The results indicated that for the relatively loose-structured gray sandstone, continuous washing at a water pressure of 0.05-0.1 MPa for 30-60 s didn't affect its apparent microhardness. However, when the water pressure increased to 0.2 MPa, the microhardness of the gray sandstone decreased by 4.5%. For the relatively compact-structured red sandstone, continuous washing at a water pressure of 0.05-0.2 MPa for 30-60 s had no impact on its apparent microhardness.

The calculation results of structural change rates (Table 2) showed that for both types of sandstone, the surface structural change rate increased with the increase in cleaning pressure. This indicated that higher cleaning pressure intensified the destructive effect on sandstone. Therefore, lower cleaning water pressure should be used during cleaning. However, the results of single-action cleaning on softened paint film (water-based wood lacquer) under different cleaning pressures (Figure 4) indicated that a water pressure of 0.05 MPa had low paint removal efficiency. To achieve a desired cleaning effect, the number of cleaning cycles needed to be increased, which would significantly increase the risk of damage to the sandstone.The paint removal efficiency at 0.1 and 0.2 MPa water pressures was similar and significantly better than the cleaning results at 0.05 MPa water pressure.

Therefore, taking all factors into consideration, this study adopted a cleaning pressure of 0.1 MPa.

Table 2. Effects of cleaning pressure on the structure and hardness of sandstone

Grey sandstone						
Hydraulics(MPa)	0.05		0.1		0.2	
Duration of action(s)	30	60	30	60	30	60
Structural change rate(%)	0.36	0.55	1.11	1.97	3.15	6.33
Micro hardness(HV0.5)	37.6	38.1	37.9	37.6	36.6	35.7
Red sandstone						
Hydraulics(MPa)	0.05		0.1		0.2	
Duration of action(s)	30	60	30	60	30	60
Structural change rate(%)	0.1	0.15	0.52	0.78	1.36	2.07
Micro hardness(HV1.0)	97.9	98.1	97.5	97.9	98.3	97.7

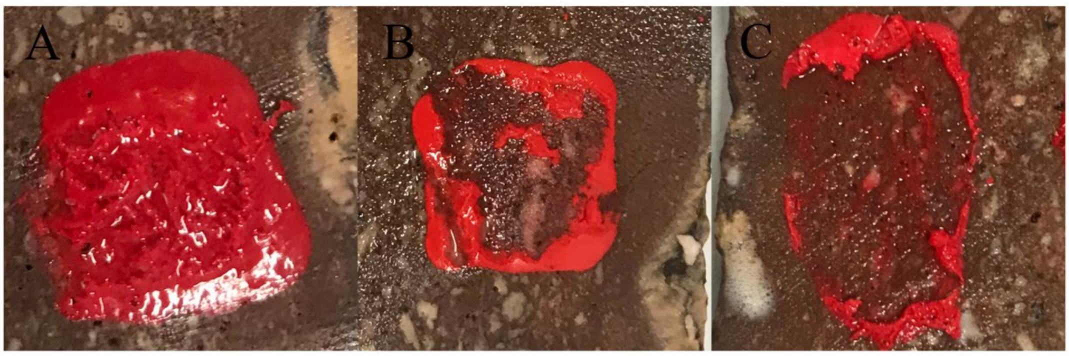

Fig. 4. Single-action results of different cleaning pressures on softened paint film (Water-based wood lacquer) (A. 0.05MPa; B. 0.1MPa;C. 0.2MPa)

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3.3 Paint removal rate

a) Water-based wood paint

The removal efficiency of three cleaning agents on cured water-based wood lacquer was shown in Figure 5. First, among the three cleaning agents, Cleaning Agent ①, with dichloromethane as the main component, demonstrated the highest cleaning efficiency, requiring 5 and 6 cleaning cycles to completely remove water-based wood lacquer cured for 24 h and 72 h, respectively. Second, the cleaning efficiencies of Cleaning Agents ② and ③ were similar, requiring 6 and 9 cleaning cycles to fully remove water-based wood lacquer cured for 24 h and 72 h, respectively. Finally, the extension of paint curing time had a minimal impact on the cleaning efficiency of Agent ①, while it significantly affected the cleaning efficiencies of Agent ② and Agent ③ (efficiency decreased by 50%).The safety test results for the removal of cured water-based wood lacquer (Table 3) indicated that the surface structural change rate of sandstone after paint removal was influenced by the type of cleaning agent and the curing time of the paint. Among them, Cleaning Agent ① had the least impact on the surface structural change rate. After removing the water-based wood paint cured for 24 h, the surface structural change rate of sandstone is only 0.69%. Cleaning Agents ③ and ② followed, with surface structural change rates of 1.18% and 1.37%, respectively. As the curing time of the paint increased, although no visible changes were observed on the sandstone surface after cleaning, microscopic examination revealed a significant increase in the surface structural change rate (1.73%, 3.55%, and 4.17% for Cleaning Agents ①, ②, and ③, respectively), indicating an increase in cleaning-induced damage.

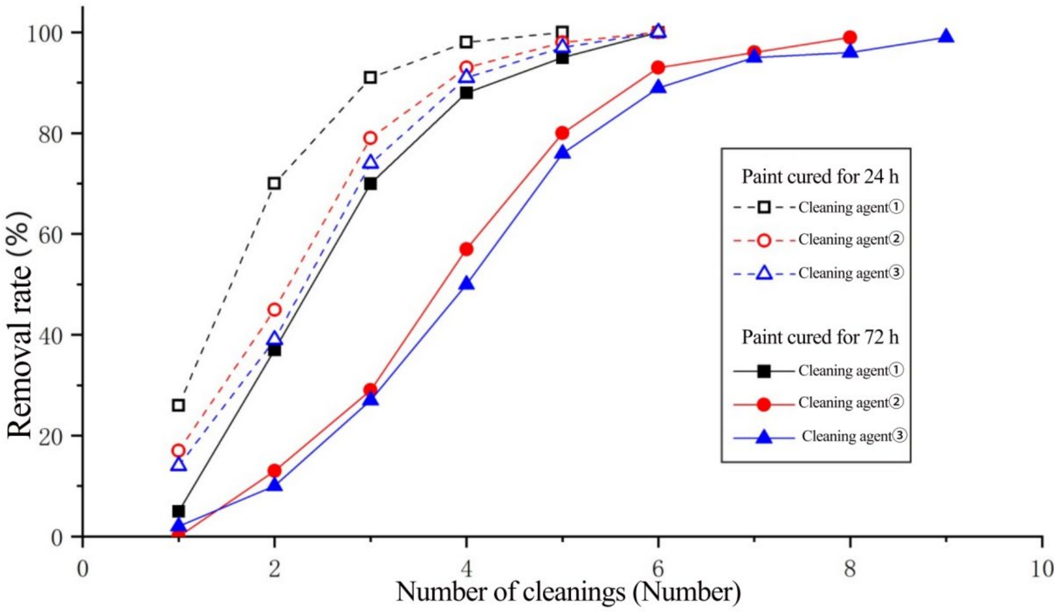

Fig. 5. Cleaning results of different cleaning agents on cured waterborne wood paint

Table 3. Rate of change (%) of gray sandstone surface structure after removal of cured waterborne wood paint by different cleaning agents

Paint curing time		24h	72h
Cleaning agent	①	0.69	1.73
	②	1.37	3.55
	③	1.18	4.17

b) Metal Anti-rust Paint

The removal efficiency of the three cleaning agents on cured metal anti-rust paint was shown in Figure 6. First, the cleaning efficiency of the three agents were in the order of Cleaning Agent ① > Cleaning Agent ② > Cleaning Agent ③. Second, as the curing time of the paint increased, the

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cleaning efficiency of Cleaning Agent ① remained almost unchanged, while the efficiency of Cleaning Agents ② and ③ decreased (required one additional cleaning cycle). This indicated that all three cleaning agents demonstrated good removal capability for this type of paint.The safety test results for the removal of cured metal anti-rust paint (Table 4), indicated that for metal anti-rust paint cured for 24, all three cleaning agents demonstrated good safety performance. The surface structural change rates of sandstone after the application of Cleaning Agent ①, ②, and ③ being 0.41%, 0.55%, and 0.83%, respectively. For metal anti-rust paint cured for 72 h, Cleaning Agent ① was still relatively safe, while the destructive effects of Cleaning Agents ② and ③ increased.

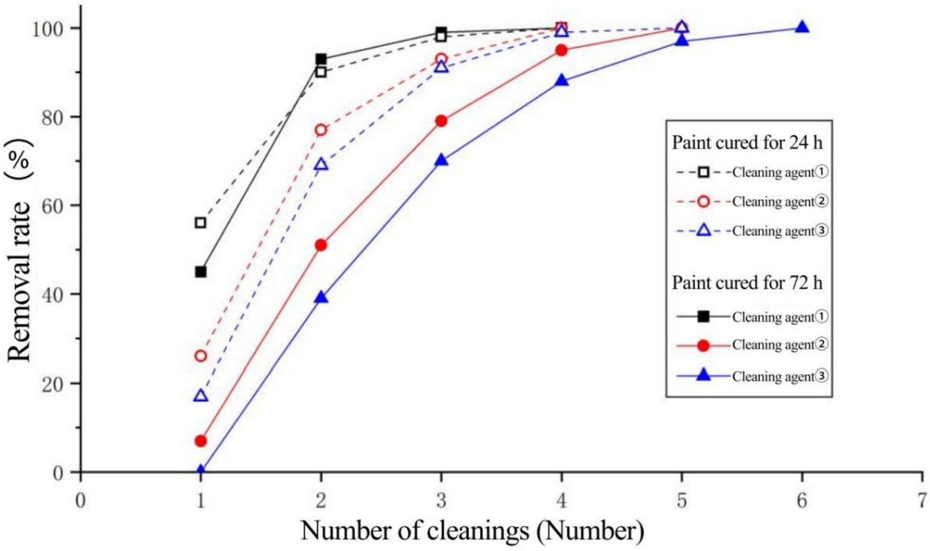

Fig. 6. Cleaning results of different cleaning agents on cured metal anti-rust paint

Table 4. Rate of change (%) of gray sandstone surface structure after removal of cured metal anti-rust paint by different cleaning agents

Paint curing time		24h	72h
Cleaning agent	①	0.41	0.77
	②	0.55	1.51
	③	0.83	2.38

(c) Epoxy Floor Pain

The removal efficiency of three cleaning agents on the cured epoxy floor paint was shown in Figure 7. Overall, the cleaning efficiency of the three agents on epoxy floor paint was similar to that on metal anti-rust paint. Among them, the cleaning efficiency of Cleaning Agent ① was close to that of Cleaning Agent ②, indicating that non-toxic dimethyl carbonate could completely replace the highly toxic dichloromethane as the main cleaning component for this type of paint.The safety test results for the removal of cured epoxy floor paint (Table 5) showed that for metal anti-rust paint cured for 24 h, Cleaning Agent ① demonstrated the highest safety, while Cleaning Agents ② and ③ were similarly. For metal anti-rust paint cured for 72 h, cleaning with Cleaning Agents ① and ② was safe, while Cleaning Agent ③ had relatively higher destructive effects.

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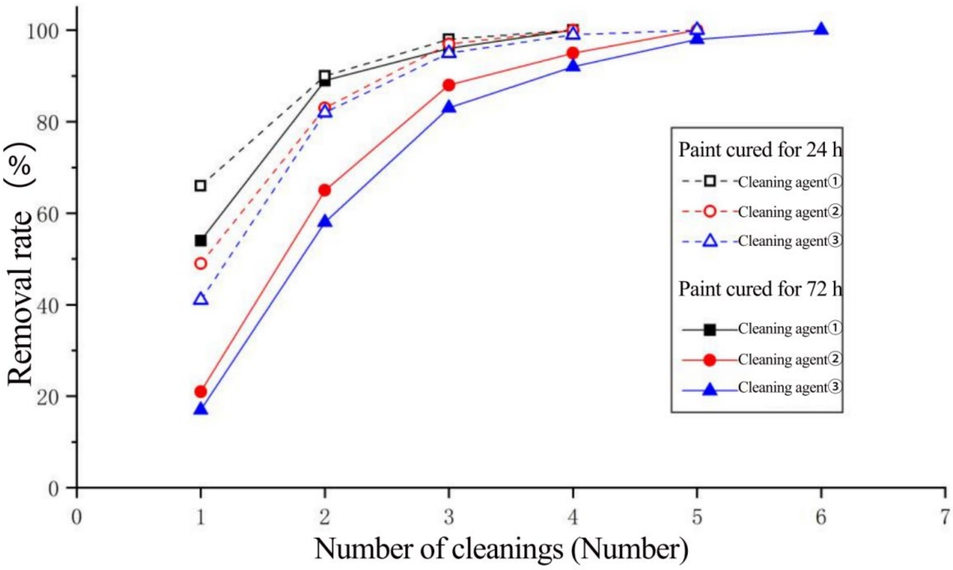

Fig. 7. Cleaning results of cured epoxy floor paint with different cleaning agents

Table 5 Rate of change (%) of gray sandstone surface structure after removal of cured epoxy floor paint by different cleaning agents

Paint curing time		24h	72h
Cleaning agent	①	0.39	0.67
	②	0.82	1.28
	③	0.77	2.23

3.4 Infrared spectroscopy analysis

The infrared spectroscopy results of the cleaning agent with dimethyl carbonate as the main component on three types of paint after patch treatment were shown in Figure 8. First, in the spectrum of the metal anti-rust paint, the peak at 3028 cm-1 corresponded to the =CH stretching vibration, the peak at 1673 cm-1 corresponded to the C=C stretching vibration, and the peak at 1728 cm-1 corresponded to the C=O stretching vibration, which were characteristic peaks of incompletely polymerized acrylic prepolymers. The peaks at 1600 cm-1, 1547 cm-1, 1493 cm-1, and 1452 cm-1 corresponded to the skeletal vibrations of the benzene ring, while the peaks at 757 cm-1 and 699 cm-1 corresponded to the out-of-plane bending vibrations of the benzene ring protons, indicating that this metal anti-rust paint used a polymer of acrylic and styrene. Second, the spectrum of the water-based wood lacquer also showed characteristic peaks of incompletely polymerized acrylic prepolymers, but there were no characteristic peaks of styrene. The peaks at 1417 cm-1, 873 cm-1, and 700 cm-1 were attributed to the stretching and bending vibration peaks of the carbonate group, suggesting that the paint likely contained light calcium carbonate fillers. Although both of these paints were acrylic resin-based, their compositions differ, which might be the underlying reason for the different cleaning effects. Finally, the epoxy floor paint did not yield a characteristic infrared spectrum due to the strong fluorescence effect, which indirectly suggested that the paint contained a large amount of filler, making its removal relatively easier.

Through infrared analysis, combined with the microhardness test before and after cleaning (Figure 3), we deduced that the cleaning agent used in this study removed the paint for two reasons: firstly, the paint film was not fully polymerized; secondly, the swelling of the paint film by the cleaning agent destroyed its structure and reduced its strength.

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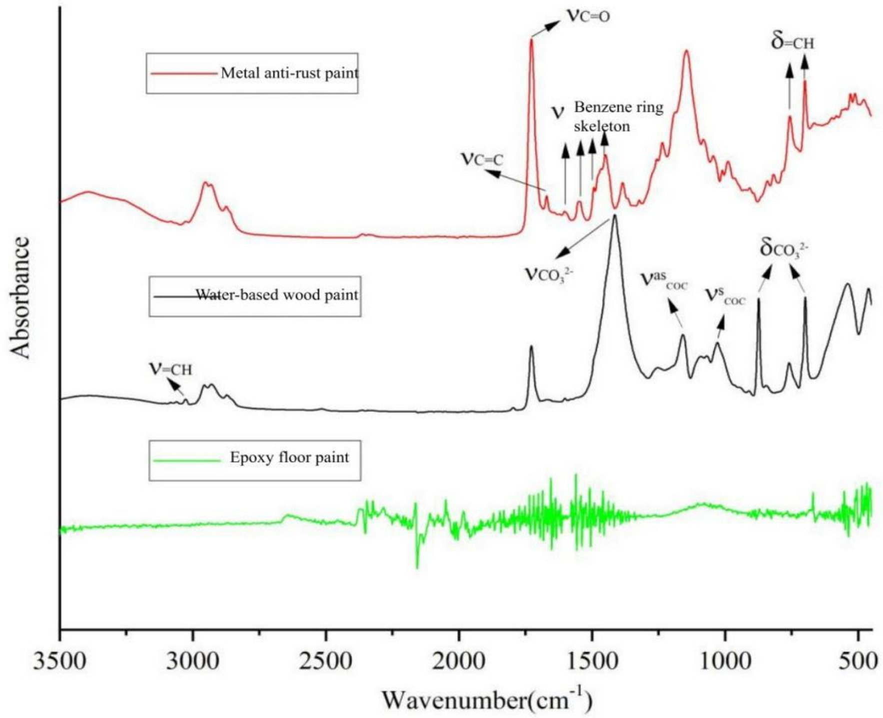

Fig. 8. Infrared spectra of the cleaning agent based on dimethyl carbonate as the main agent after the treatment of three paint pastes

4. Conclusion

1)The cleaning pressure test results showed that continuous flushing of softened paint films with a water pressure of 0.1 MPa could achieve effective paint removal while causing minimal damage to the rock.

2) Cleaning Agent ①, with dichloromethane as the main component, demonstrated excellent removal efficiency for metal anti-rust paint, water-based wood lacquer, and epoxy floor paint cured within 72 h. Cleaning Agent ②, with dimethyl carbonate as the main component, performed well for removing these three types of paint cured for 24 h, but less effectively for water-based wood lacquer cured for 72 h. Since dimethyl carbonate was harmless to both the environment and human health, it was recommended to use Cleaning Agent ②, with dimethyl carbonate as the main component, for paints with shorter curing times.

3)This study used two types of sandstone with different strengths as test substrates to evaluate the cleaning of three common types of paint. In practice, the surface properties of stone cultural relics were influenced by weathering and preservation conditions, resulting in individual differences. Therefore, in actual work, small-scale tests should be conducted based on actual conditions before proceeding with the cleaning work.

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