



## Research Article

# Paints analysis and conservation treatment of painted sculpture: Jean Dubuffet, *Guard Dog II*



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Received: 26 May 2021 / Accepted: 11 October 2021

Published online: 24 October 2021

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## Abstract

**Abstract** *Guard Dog II* (1969–1970) by Jean Dubuffet is an artwork that shows the characteristics of the artist's l'hourloupe period (1962–1974). This study revealed the materials and manufacturing techniques used by the artist at the time through material analysis of *Guard Dog II*, and suggested an appropriate conservation treatment method for the work through a cleaning test. Dust, stains, discoloration, cracks, etc. were observed on the surface of the artwork and stains were particularly severe and discoloration required conservation treatment. Prior to treatment, multiple analytical approaches such as Fourier transform infrared spectroscopy, Raman spectroscopy and gas chromatography/mass spectrometer were applied to identify the materials of the paint layers and confirm the state of the conservation of the artworks. As a result, it was confirmed that polyurethane paint was used in the artwork, and the pigment used for each color was also identified. For the stable conservation treatment of the artwork, the chromaticity, glossiness and workability of the cleaning materials were evaluated, and it was found that isopropyl alcohol and nonionic surfactant were suitable for cleaning. The conservation treatment was performed based on results from the cleaning test, and the artwork was restored cleanly. Since most of the existing research on cleaning methods has been focused on painting, this study contributes to the conservation of sculptures by suggesting cleaning methods suitable for three-dimensional colored objects.

## Article highlights

- The materials and production techniques used in Jean Dubuffet, *Guard Dog II* were confirmed.
- As cleaning materials for deteriorated artworks, isopropyl alcohol and non-ionic surfactants are effective.
- Hydrogels are not suitable for this work due to the type and characteristics of the gels.

**Keywords** Painted sculpture · Paint analysis · Conservation treatment · Cleaning · Jean Dubuffet

## 1 Introduction

Since the twentieth century, various types of paints have been produced and artists have created artworks using synthetic paints on materials such as metals, wood, and plastics. Adding various colors to three-dimensional

objects to create painted sculptures can further enhance their artistic and aesthetic value. Various sculptures using synthetic paints have been produced, these painted sculptures by twentieth century artists such as Alexander Calder, Niki de Saint-Phalle, Jean Dubuffet, and Roy Lichtenstein are now exhibited in museums, art galleries,

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outdoor sculpture parks, around the world. Sculptures with synthetic paints started appearing in the 1960s and were produced in large numbers in the 1970s and the 1980s. As approximately 50 years have passed since then and therefore, many of these artworks require conservation treatment.

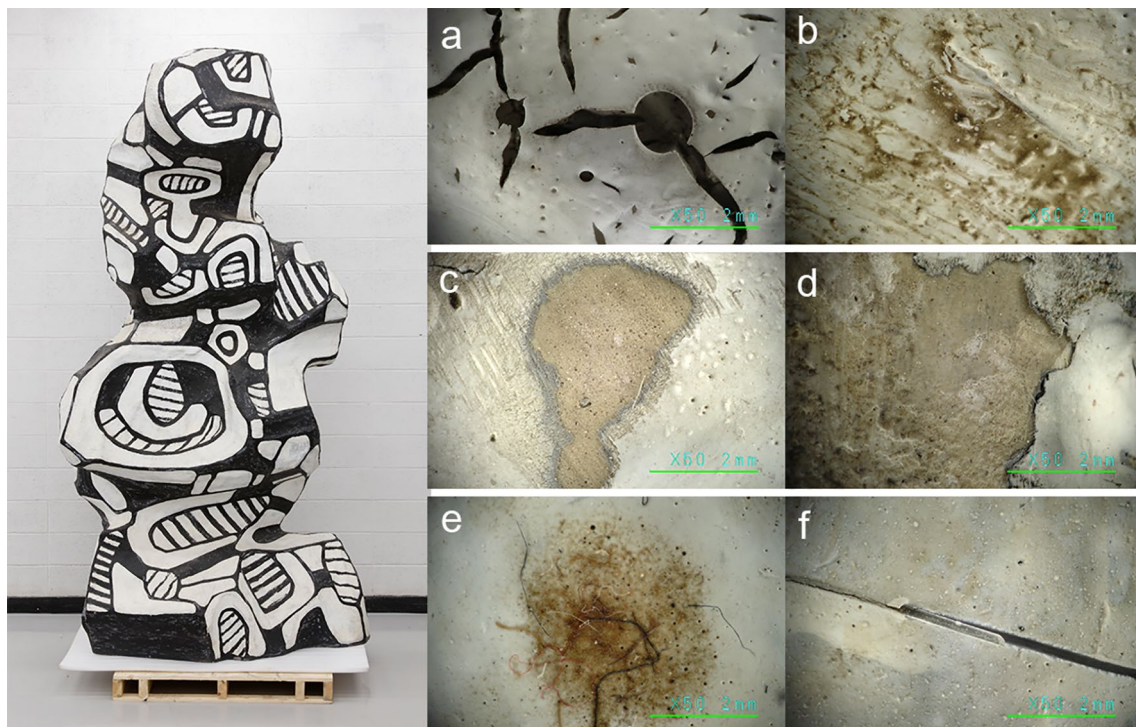
Since the 2000s, studies on the conservation of sculptures using synthetic paints have been conducted, with a focus on the material analysis of painted artworks and conservation treatment materials. Conservation treatments have also been performed using various techniques, such as partial repair and repainting [1–4]. Specifically, in the case of outdoor painted sculptures in severely deteriorated conditions, the method of removing the original paint layer and applying new paints is used for conservation [5–7]. In addition, Getty provided guidelines for reproducing and documenting the characteristics of the painting by reflecting the original painted sculpture as much as possible [8]. Recently, many studies have been conducted on the material analysis of synthetic paints applied to the surface of polyurethane foam artworks. Multiple analytical approaches such as SEM–EDS, FTIR and Py–GC/MS were applied to identify the materials of the paint and the cause of degradation and confirm the state of conservation of the artwork [9–11].

Various factors affect painted sculptures; these include the materials used, the keeping or exhibiting environment, and the conservation state. Therefore, it is important to

secure the basic data of the sculptures to identify their characteristics and prepare an appropriate conservation method for each artwork. However, the conservation treatment of painted sculptures mainly concentrates on repainting and restoration, and few studies have investigated detailed conservation treatment methods. In particular, studies on the materials and methods used in the cleaning process have mostly focused on paintings, with only a few researching the cleaning of painted sculptures.

Currently, the National Museum of Modern and Contemporary Art in South Korea has many painted sculptures that are exhibited indoors and outdoors, based on the exhibition plans. Among them, *Guard Dog II* (1969–1970) by Jean Dubuffet (1901–1985) is a large work—more than 3 m tall—produced in 1970, with paints applied to an epoxy resin layer.

Jean Dubuffet created a new art form by rejecting traditional art and culture. In particular, he showed a shift from paintings to sculptures through a series of works called “*l’hourloupe*,” starting in the 1960s. The *l’hourloupe* series goes beyond creating a distinction between paintings and sculptures and is based on three-dimensional objects breaking away from two-dimensional planes. Initially, he became interested in the industrial material polystyrene and used hot wire to cut lightweight polystyrene objects into flat and curved shapes; he then used red, blue, white, and black paint colors on these works [12]. However, polystyrene is very soft



**Fig. 1** Jean Dubuffet, *Guard Dog II* and microscopic images of the damage (a: cracks, b: pollutants, c: abrasion, d: loss, e: foreign substance, f: brush fiber)

and fragile and the artist therefore started investigating methods to increase its durability. As a result, he devised a “resin transfer molding.” This method was to transfer the original polystyrene work into a plaster mold and then remove the polystyrene, pour polyester into the mold, and transfer it again. Because of the problem of the original work being destroyed during this process, new methods were studied and Haligon, a mold-maker, developed an epoxy resin work method that allows unlimited replication without destroying the original. From December 1967, Jean Dubuffet used both techniques together in his work [13].

*Guard Dog II* is coated with black and white paints, and as 50 years have passed since its creation, it needs conservation treatment due to the presence of dust, discoloration, cracks, and exfoliation on the paint surface (Fig. 1). In particular, the surface of the artwork was heavily contaminated by dust and stains, which may induce degradation, and therefore proper cleaning was required. The conservation treatment was performed based on the test results to ensure that the work was conserved and managed stably. Through scientific analysis of the paints used in the work, this study confirmed the materials originally used by the artist when producing it. Moreover, through a cleaning test of the painted sculpture, the most suitable cleaning method and materials were applied to proceed with conservation. In particular, aiming to address the paucity of studies on the appropriate cleaning materials and methods for painted sculptures, this study proposes a practical conservation method for painted works.

## 2 Method

### 2.1 Paint analysis

A sample was required to obtain information about the paint layer used in the sculpture. Fragments were collected from where the surface of the work was peeled off, and cross-sectional samples were produced using them. The samples were made one for each color (black and white). An imaging microscope (RH-2000, Hirox, Japan) was used to observe the cross-sections and measure the coating thickness of the paint layer.

The paint analysis proceeded as follows (Table 1). To estimate the pigments contained in the paints, we performed a component analysis using Raman spectroscopy (LabRAM HR, Horiba, JP) and an energy-dispersive analyzer (EDS, X-MAX, Oxford Ins., UK) mounted on a scanning electron microscope (SEM, JSM-6610LV, JEOL, JP). EDS analysis was performed by setting the acceleration voltage at 20 kV, spot size at 50, and working distance to 10 mm, after applying a gold coating to the sample.

To analyze the organic components in the paints, we performed Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo, US) with ATR (Smart orbit, Thermo, US) to investigate the characteristics of the functional groups of the paint resins and used a gas chromatography/mass spectrometer (GC: 7890B, MS: 5977A, Agilent, US) equipped with a pyrolyzer (PY-3030S, Frontier Lab, JP) to analyse the paint components.

**Table 1** Analysis methods of paints

SEM-EDS	Acceleration voltage	20 kV
	Working distance	10 mm
Raman spectroscopy	Laser	532 nm
	Grating	600 (Resolution 0.33 cm <sup>-1</sup> /2400 Grating)
	Scan range	100–2000 cm <sup>-1</sup>
ATR-FTIR	Scan range	4000–400 cm <sup>-1</sup>
	Resolution	8 cm <sup>-1</sup>
Py-GC/MS		
Pyrolyzer	Furnace	700 °C (0.2 min)
	Interface	320 °C
GC	Inlet	250 °C
	Split ratio	50:1
	Column	HP-5 ms
	Gas	He 99.999% (1 ml/min)
	Oven program	From 50 °C at 10 °C/min to 300 °C
MS	Scan range	20–500 m/z
	Source	280 °C
	Quadrupole	150 °C

## 2.2 Test for cleaning

Tests were conducted to determine the appropriate cleaning systems for the sculpture. The suitability of cleaning materials was evaluated using organic solvents, hydrogels, and non-ionic surfactants commonly used in conservation treatments. The hydrogels were developed in the NANORESTART project [14] and Peggy 5<sup>®</sup> is composed of a mixture of polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) polymers. It was known to be Peggy 6<sup>®</sup> more flexible and resilient because it was made only with PVA [15].

The tests were performed on sections on top of the artwork. The four types of organic solvents were applied with cotton swabs to evaluate their cleaning effect. The non-ionic surfactant was applied on a cotton swab to perform cleaning, after which the residual chemicals were removed by washing with deionized water. The two types of hydrogels were loaded in 20 wt.% ethyl alcohol and applied to the evaluation site for 20 min (Table 2). Appropriate cleaning materials for the artwork were selected through workability evaluations and comparison of microscopic observations (R-2000, Hirox, JP), chromaticity (CM-700d, Minolta, JP), and glossiness (Micro-tri-gloss, BYK, DE) before and after cleaning.

## 3 Result and discussion

### 3.1 Morphological characterization and elemental composition

Upon observing the cross-sections of the paint samples, we found three layers: the bottom layer is white, followed by gray, and then black/white. It is considered that the painting layers are not uniform considering that each sample has a different thickness for the same color (Fig. 2).

The analysis of the pigment of the paint layer using SEM-EDS found that calcium was the main element found in the white bottom layer. In the gray layer, titanium and silicon were detected as the main components, as well as small amounts of iron and cadmium. Among the top layers, iron and silicon were detected as the main elements in the black layer. In the white layer, a noticeably high amount of titanium was detected (Fig. 3, Table 3).

### 3.2 Pigment analysis in paint

The Raman spectra showed characteristic peaks similar to those of phthalocyanine blue at 681, 1140, 1340, 1450, and 1527  $\text{cm}^{-1}$  in the black paint layer (Fig. 4). As a result of analysis of the white paint layer, different results were found in the upper and lower layers. In the upper white

layer, peaks estimated to be rutile-structured titanium white were observed at 444 and 608  $\text{cm}^{-1}$ . However, in the lower white layer, characteristic peaks similar to calcium carbonate were observed at 280 and 1086  $\text{cm}^{-1}$  (Fig. 4) [16–18]. No distinct characteristic peak was found in the gray layer, and additional analysis was required.

### 3.3 Analysis of organic components of paint

The FT-IR analysis results of the white and black paints showed that the urethane NH stretching mode was observed at about 3300  $\text{cm}^{-1}$  and the  $\text{CH}_2$  stretching deformation mode was observed at approximately 2920 and 2850  $\text{cm}^{-1}$ . The peak observed at 1716  $\text{cm}^{-1}$  was estimated to be due to C=O stretching [19]. Bonding related to hexamethylene diisocyanate isocyanurates (HDI) was confirmed to be around 1680  $\text{cm}^{-1}$  (C=O stretching mode), and 1460  $\text{cm}^{-1}$  ( $\text{CH}_2$  bending in the backbone of the HDI monomer). At 1515  $\text{cm}^{-1}$ , –NH deformation (urethane) and C–N stretching vibration were found together, presumed to be polyurethane paint (Fig. 5, Table 4) [20, 21]. The peak that appears extensively near 1000  $\text{cm}^{-1}$  is considered to be due to the Si-based extender pigment [22, 23] or it is estimated to be due to the C–O–C bond of HDI isocyanate [20]. However, this peak appeared at a lower position than the general C–O–C bond of HDI.

Polyurethane is a polymer compound composed of a urethane bond (–NHCOO–), and in general, it is made by bonding an isocyanate and a polyol containing alcohol groups. Isocyanates commonly used in polyurethane manufacturing include TDI (2,4-Toluene diisocyanate), 4,4'–diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI) [24]. The paint used on the artwork showed characteristic peaks that were very similar to those of HDI isocyanurate.

As a result of the Py-GC/MS analysis, crotonaldehyde, benzaldehyde, benzonitrile and phthalic anhydride were found in the white paint; in particular, significant amounts of hexamethylene diisocyanate (HDI) and benzoic acid were detected. In contrast, crotonaldehyde, phenol, o-cresol, benzoic acid, phthalic anhydride, and HDI were detected in the black paint. Bisphenol A was also found at approximately R.T. 19.935 (Fig. 6, Table 5).

As the HDI was confirmed in the Py-GC/MS analysis results, it is estimated that the paints used in the artwork is polyurethane based [22]. Benzaldehyde is known to be used as an additive for polyurethane paints [25], and o-cresol are components used as blocking agents for polyurethane paints [26]. Phthalic acid and benzoic acid were also detected in the analysis of polyurethane paints [26, 27], and bisphenol A is known to improve the durability of polyurethane coatings through cross-bonding

**Table 2** List of cleaning solutions with preparation, application, assessment

Cleaning system	Detailed options	Preparation	Application	Assessment
Organic solvents	Ethyl alcohol 99,9%	Not required	Rubbed with cotton swabs up to 10 times to cover an area of approximately 4 cm <sup>2</sup>	After the cleaning test, the surface changes on the specimens were evaluated (microscopic observation, chromaticity and gloss)
Mineral spirit	Ethyl alcohol 50% w/w in deionized water	Ethyl alcohol was diluted in deionized water, and used	As above	As above
	Isopropyl alcohol 50% w/w in deionized water	Isopropyl alcohol was diluted in deionized water, and used	As above	As above
	GAMSOL <sup>®</sup>	Not required	As above	As above
Non-ionic surfactant	JW-1 OOX <sup>®</sup> 1% w/w in deionized water	Non-ionic surfactant was diluted in deionized water, and used	Rubbed with cotton swabs up to 10 times to cover an area of approximately 4cm <sup>2</sup> Residues on the surface were removed by rubbing them up to 3 times with deionized water	As above As above
Hydrogels	Peggy 5 <sup>®</sup>	Gels were cut into regular sizes (2 cm <sup>2</sup> ) and used. Soak in deionized water and rinse before using	Gel pieces were placed on surface for 20 min. There was no significant change after removing the gel, and after removing the applied gel, the surface residue was wiped with a cotton swab	As above
	Peggy 6 <sup>®</sup>	Gels were preloaded with a cleaning solution (ethyl alcohol 20% w/w in deionized water) by immersion for 24 h		As above

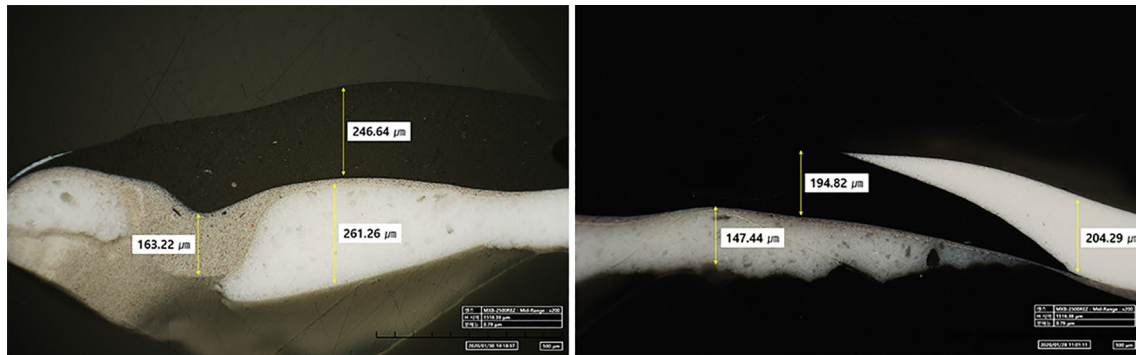


Fig. 2 Microscopic image showing a cross-section of the sample of the artwork (×200)

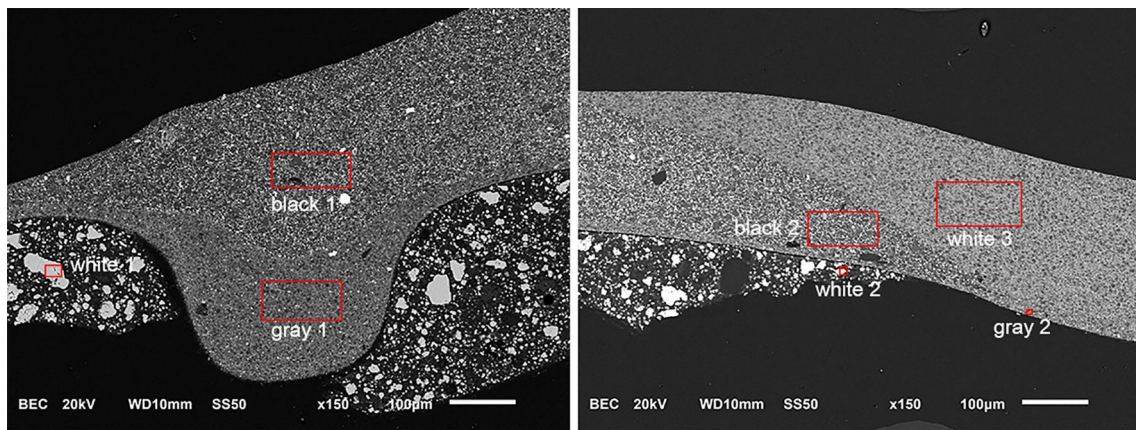


Fig. 3 Scanning electron microscope images with indication of the analyzed area (×150)

Table 3 Results of EDS

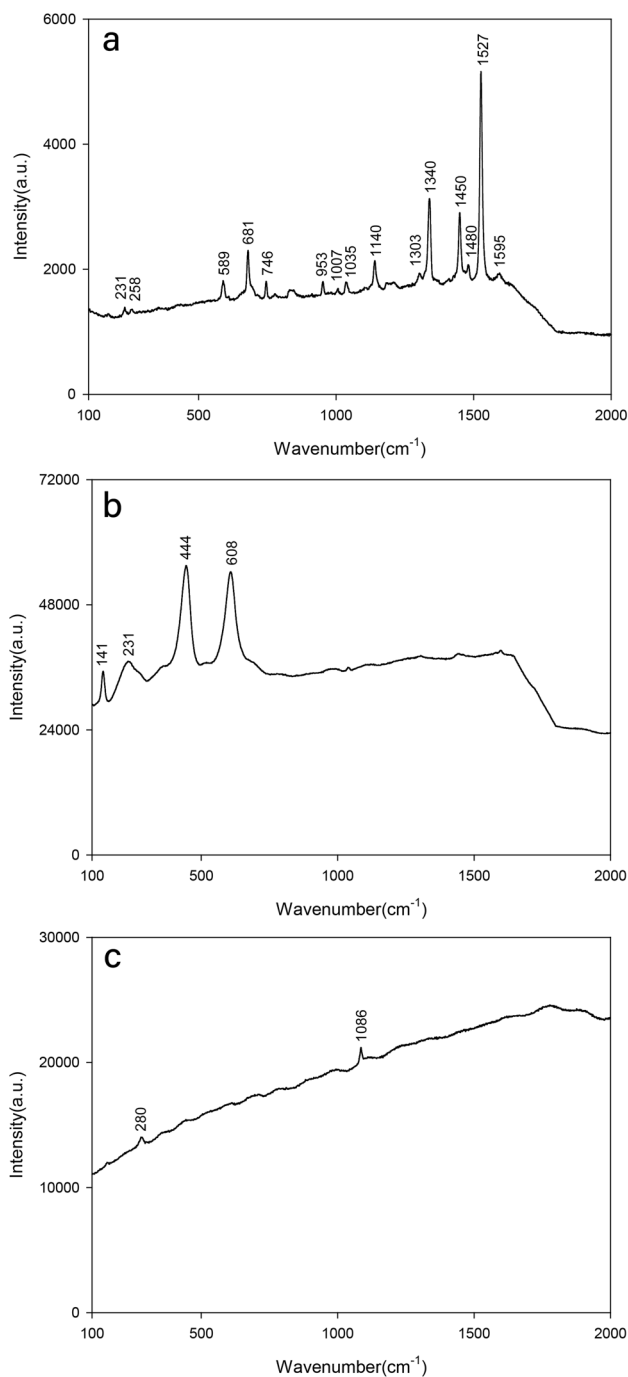
	Color	Element (wt%)									
		C	O	Mg	Al	Si	Cl	Ca	Ti	Fe	Cd
Putty	White 1	19.30	52.2	0.16	–	0.07	–	28.02	0.15	0.10	–
	White 2	22.69	50.13	0.15	–	0.11	–	26.62	0.10	0.19	–
Primer	Gray 1	44.85	38.58	–	0.14	6.06	–	–	8.44	0.79	0.76
	Gray 2	45.93	38.66	–	0.15	5.58	–	–	8.17	0.71	0.81
Base coat	Black 1	46.26	33.94	–	–	4.98	0.08	–	–	8.81	–
	Black 2	51.84	34.95	–	–	5.37	–	0.02	0.09	7.72	–
	White 3	42.51	39.89	–	0.24	5.57	–	0.08	11.71	–	–

with polyisocyanate [27]. In the case of crotonaldehyde, there is a case of detection in off-gases of polyurethane [28].

Through the artist’s other works and art brochures, it is known that Jean Dubuffet used matte polyurethane paints to create artworks [13, 29, 30]; this was confirmed by the analysis. Polyurethane paints seemed to have been used in the arts as the polyurethane industry expanded in the 1960s. In fact, it has been reported that polyurethane

paints have been used in many outdoor artworks in the late twentieth century [1, 20].

As a result of SEM–EDS analysis of the paint used in the artwork, it was classified into three layers. The lower white layer had relatively large and irregular particles compared to the upper white layer, and calcium was detected as a main component. This was confirmed by the Raman analysis result as calcium carbonate, and this layer is thought to be the putty (or first primer) used to smooth the surface of



**Fig. 4** Raman spectrum of paints (a: black basecoat, b: white basecoat, c: white putty)

the work [31]. The gray layer is considered to be a primer surfacer to maximize the appearance and performance of the basecoat and to even out the surface, as it is located under the top coat layer [32]. Ti was identified as the main component in the gray layer, and it is assumed that titanium white was used. Also, Fe and Cd were detected, indicating that a small amount of iron oxide and cadmium

pigment were mixed together. The detection of Si can appear to be due to the use of silicone as an extender for paints in general [10, 33]. The white and black layers of the uppermost layer represent the color of the artwork as a basecoat. The upper white layer containing Ti as a main component was confirmed to be titanium dioxide (rutile) as a result of Raman analysis. In the black layer, the detection of Fe is presumed to be associated with iron oxide and Prussian blue [34]. As a result of Raman analysis, a peak of phthalocyanine blue was detected, but iron oxide and Prussian blue were not confirmed. It is considered that there is a limit to the peak detection of the pigment due to the various components mixed in the paint. However, it is presumed that these pigments were used because black can be produced when the warm color of iron oxide and the blue color of phthalocyanine blue and Prussian blue are mixed together.

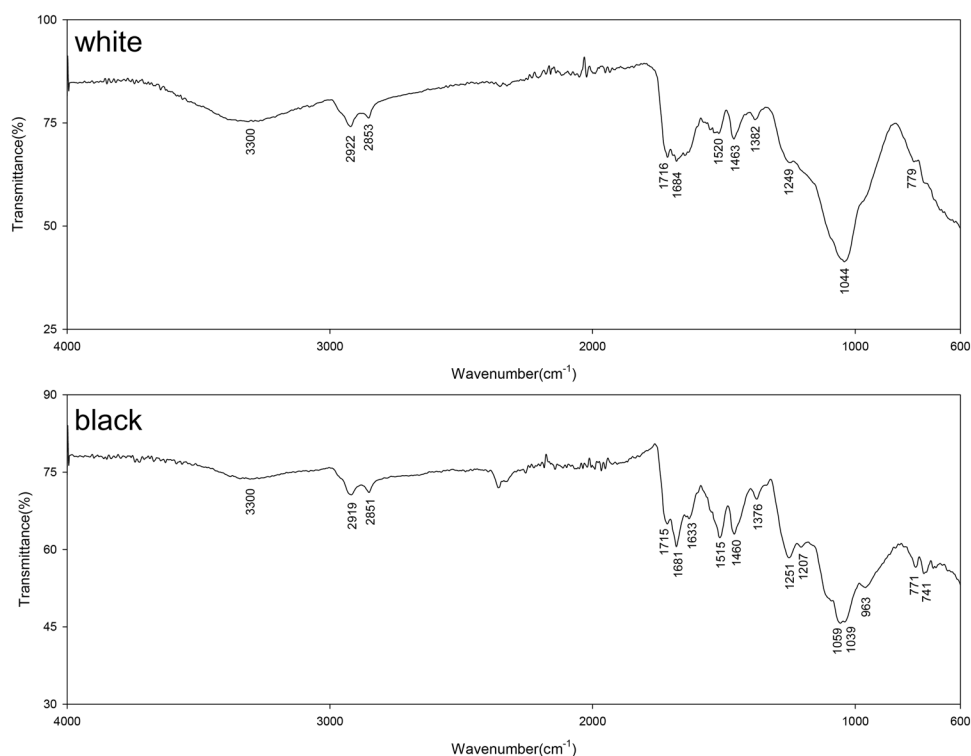
### 3.4 Test for cleaning

The results of microscopic observations before and after cleaning showed superiority of cleaning effects in the following order: hydrogels 1 and 2 < mineral spirit < 99.5% ethyl alcohol < 50 wt% ethyl alcohol < 50 wt% isopropyl alcohol  $\approx$  1 wt.% non-ionic surfactant. The 50 wt.% isopropyl alcohol and 1 wt.% non-ionic surfactant solutions easily removed the pollutants, and compared to these, the 99.5% ethyl alcohol and mineral spirit did not completely remove the pollutants. Regarding the hydrogels, the pollutants were not absorbed by the gels, showing almost no cleaning effect, and the pollutants could be removed only when they were wiped with a cotton swab after removing the coated gels (Table 6).

The color difference comparison results showed that when isopropyl alcohol and a non-ionic surfactant were used, the color difference (Lab\*) was 6 or higher, showing definite changes. In the case of the 99.5% ethyl alcohol solution, the color difference was less than 3. After using the hydrogels, the color difference was between 4 and 6; however, it was not the effect of the gels themselves, as the effect was obtained by wiping with a cotton swab after removing the hydrogels (Fig. 7a).

The glossiness measurement results showed a glossiness of less than 10 GU (Gloss unit), confirming that the surface was matte. Similar to the results of the color difference analysis, 50 wt% isopropyl alcohol and 1 wt% non-ionic surfactant showed significant glossiness changes among the solvents, except for the two types of hydrogels. However, as the change in glossiness was less than 3 GU overall, the change in glossiness before and after cleaning was insignificant (Fig. 7b).

The pollutant removal results and workability varied depending on the solvent type; the types were compared

**Fig. 5** IR spectrum of white and black paint**Table 4** IR band position of paint samples and their assignment

Wave number (cm <sup>-1</sup> )		Assignment
White	Black	
3300	3300	Secondary urethane N=H stretch/NH bonded/N-H stretching vibration band
2922	2919	va CH <sub>2</sub>
2853	2851	vs CH <sub>2</sub>
1716	1715	H bond C=O stretch
1684	1681	H bond C=O stretch/tertiary urethane C=O/C=O bonded
-	1633	Carbonyl groups in urea bonds (C=O)
1520	1515	δ-NH and va C-N
1463	1460	δ-CH <sub>2</sub>
1382	1376	δ-C (CH <sub>3</sub> )
1249	1251	(O=) C-O-C stretch/urethane C-O stretch
1044	1059-1039	Si-O-Si
779	771	C-N skeletal stretch

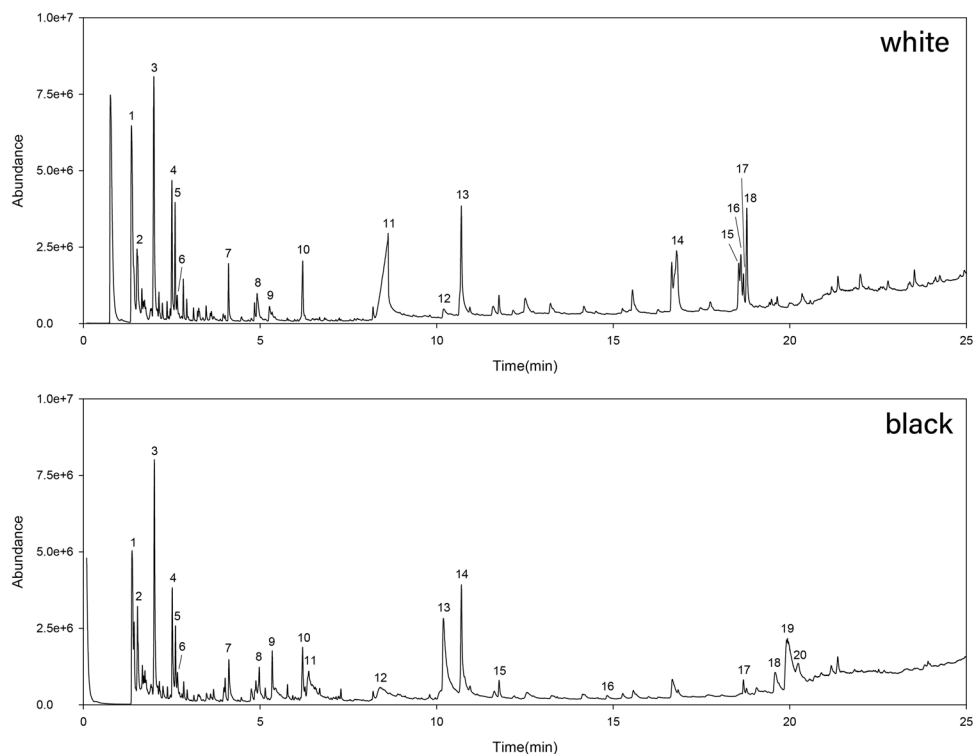
and evaluated numerically. Considering ethyl alcohol, no significant change was observed overall when removing pollutants and they could be removed only by applying more force, compared with the case of isopropyl alcohol. The 50 wt% ethyl alcohol solution had relatively lower volatility, and a change was observed when it was washed and then wiped with a dry cloth. In the case of 50 wt% isopropyl alcohol, it was easy to remove the pollutants and it took relatively less time to process, because the volatility of the solvent was high. The mineral spirit showed a lower

pollutant removal effectiveness, compared with other materials, and did not show significant overall changes. Meanwhile, 1 wt% non-ionic surfactant easily removed the pollutants, but washing with distilled water was required after using the solvent. The hydrogels were not suitable for the artwork because they showed virtually no cleaning effect (Fig. 7c).

Gel systems are usually applied to flat artworks, such as oil paintings and paper canvas, because their stability and workability for artworks are superior and their toxicity



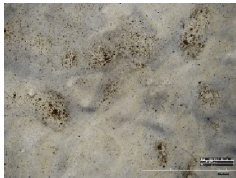
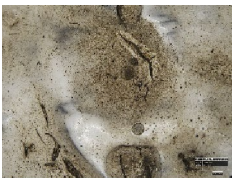


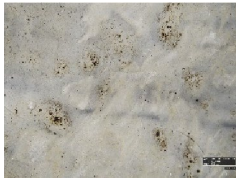
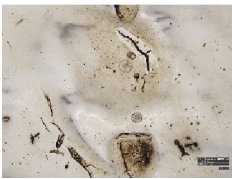



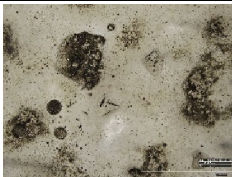

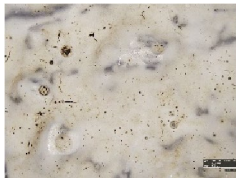
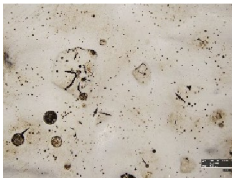

**Fig. 6** Pyrograms of white (**a**: benzoic acid, **b**: hexamethylene diisocyanate) and black paint (**a**: phthalic anhydride, **b**: hexamethylene diisocyanate, **c**: bisphenol A)



**Table 5** Compounds identified in white paint(left) and black paint(right)

R.T (min)	Compounds	Main ions(m/z)	R.T (min)	Compounds	Main ions(m/z)
1	2-Methyl-1-butene	55, 70, 39	1	2-Methyl-1-butene	55, 70, 39
2	Crotonaldehyde	70, 41, 39	2	Crotonaldehyde	70, 41, 39
3	2-Methyl-2-butenal	84, 55, 39, 78	3	2-Methyl-2-butenal	84, 55, 78, 39
4	Octenol	57, 71, 29, 41	4	Octenol	57, 29, 41, 71
5	1-Undecene	41, 83, 69, 98	5	1-Pentadecene	41, 83, 69, 39
6	Toluene	91, 92	6	Toluene	91, 92
7	Hydroxyacetone	43, 72, 59, 31	7	Hydroxyacetone	43, 72, 59
8	Benzaldehyde	105, 106, 77, 51	8	Isopropylbenzene	105, 120, 106, 77
9	Benzonitrile	103, 76, 50	9	Isopropylbenzene	105, 120, 106, 77
10	Octenol	57, 71, 29, 86, 41	10	Octenol	57, 71, 29, 86
11	Benzoic acid	105, 122, 77, 51	11	o-Cresol	108, 107, 79, 77
12	Phthalic anhydride	104, 76, 50, 148	12	Benzoic acid	105, 77
13	Hexamethylene diisocyanate	56, 41, 85, 99, 98	13	Phthalic anhydride	104, 76, 50, 148
14	2-Heptadecanone	58, 43, 59, 71	14	Hexamethylene diisocyanate	56, 41, 85, 99, 98
15	Octadecanal	43, 71, 55, 96, 82	15	Benzoic acid	105, 77
16	Octadecanal	43, 71, 55, 96, 97	16	Diethyl phthalate	149, 105, 133
17	Diisononyl phthalate	149, 69, 41	17	Diisononyl phthalate	149, 69, 41
18	2-Nonadecanone	58, 59, 43, 71	18	Diisononyl phthalate	149, 86, 150
			19	Bisphenol A	213, 228, 119, 214
			20	Bisphenol A	213, 228, 119, 214

**Table 6** Microscopic observations before and after cleaning tests

	Ethyl alcohol	Ethyl alcohol 50 wt%	Isopropyl alcohol 50 wt%	Mineral spirit
before				
after				
	Non-ionic surfactant 1 wt%	Hydrogel 1	Hydrogel 2	
				
				

\* The images of the hydrogels are after applying the gel and wiping it off with a cotton swab.

is lower, compared with conventional cleaning methods [35–37]. And research on the applicability of objects and three-dimensional parts of artworks has been conducted [38, 39].

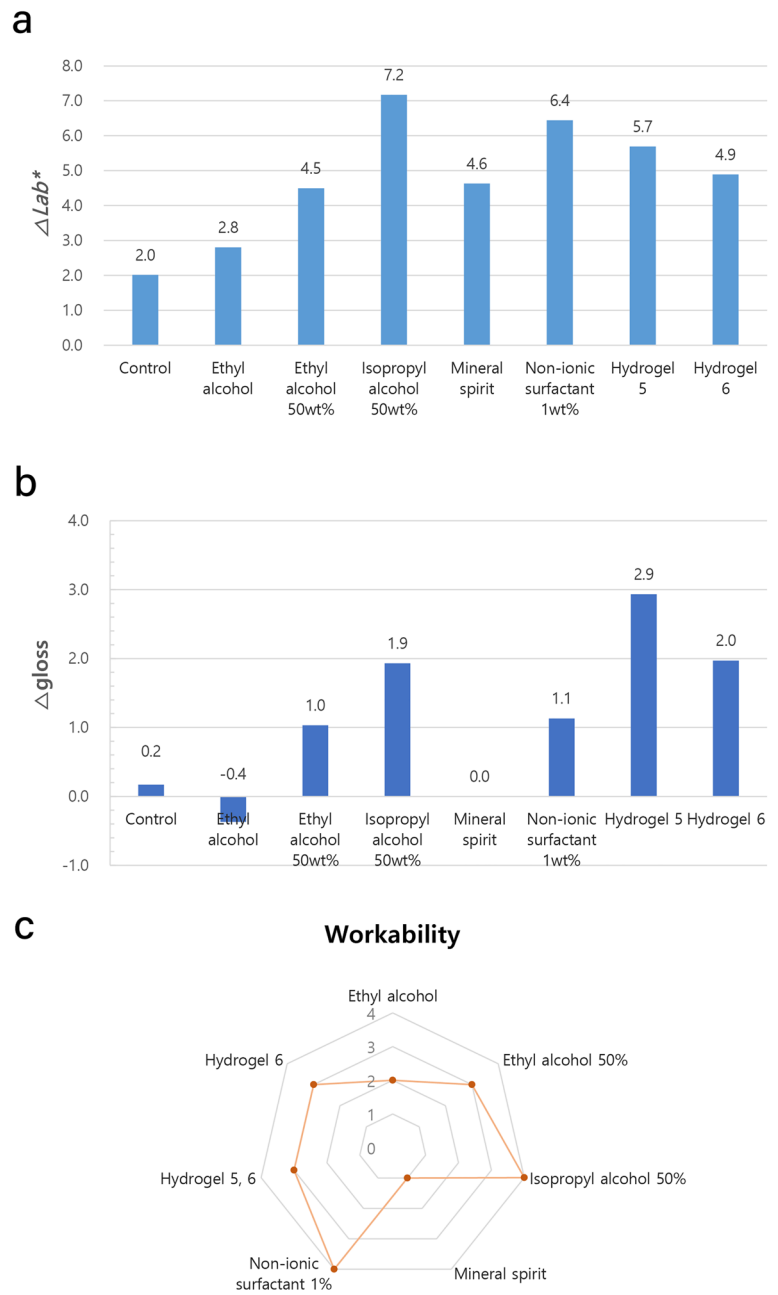
However, no cleaning effect could be seen on this artwork. It is thought that the surface was not smooth and had many irregularities, and that the gels were not attached to the three-dimensional artwork, so the cleaning effect was not significant. The effect of the gels has different characteristics such as flexibility and strength depending on the type of gel, and it seems to be affected by the correlation between the material and the gel used in the artwork [40]. Therefore, it is considered that the method of using the gel applied in this test was not suitable for the artwork, and it is judged that it is necessary to study the type and method of the gel that can be applied to synthetic paints in the future.

### 3.5 Conservation treatment

Based on the results of the cleaning solvent tests, cleaning was performed. A non-ionic surfactant was used for

first-phase cleaning; this removed pollutants from the entire surface. Isopropyl alcohol was used for second-phase cleaning to remove the yellowish parts, severely polluted parts, and parts with scribbling and foreign substances that remained after the first cleaning phase. It was washed twice or thrice with deionized water to minimize residue. This had to be performed delicately because the surface was uneven and the paint layer had been weakened by degradation. Due to the physical size of the sculpture, the cleaning process took about five months. After cleaning, a one-component urethane coating was injected into the partially cracked and lifted parts of the paint layer to reinforce the paint layer of the artwork. Through color and glossiness comparisons before and after the conservation treatment, we confirmed that the treatment was performed stably. In particular, it was confirmed that the color difference in the yellowed parts before and after cleaning was 14 or higher, and the aesthetic value could be recovered through cleaning (Figs. 8, 9, 10; Table 7). Also, fifty years have passed since the work was created, but information on the color used in the work could not be confirmed.

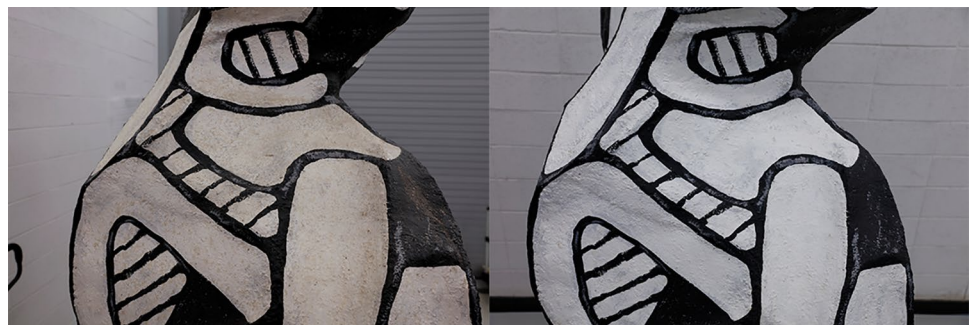
**Fig. 7** Result of the cleaning test (**a**: color difference, **b**: gloss, **c**: workability [0–5 points given, depending on the cleaning effect])





**Fig. 8** a A conservator cleans *Guard Dog II*, b before and after cleaning, c reinforcement treatment of cracks

**Fig. 9** Detail of *Guard Dog II* (left: before treatment, right: after treatment)





**Fig. 10** Condition of *Guard Dog II* after treatment

**Table 7** Color comparison before and after treatment

	White	Black	Gray	Yellowing
Before				
<i>L</i>	90.43	24.86	50.48	77.16
<i>a</i>	-0.93	0.39	-0.09	0.62
<i>b</i>	6.30	-0.68	0.11	14.50
After				
<i>L</i>	91.49	24.31	49.28	87.78
<i>a</i>	-0.88	0.40	-1.46	-0.78
<i>b</i>	3.34	-0.75	-2.43	5.12
Color difference				
Lab*	3.14	0.56	3.12	14.24

Through this process, it was meaningful to be able to understand the color of the work.

## 4 Conclusion

The aim of this study was to analyze the paints used in Jean Dubuffet's *'Guard Dog II'* and to suggest materials and methods for stable cleaning in the artwork. As result of the multiple analyses, FT-IR and Py-GC/MS analysis confirmed the type of paint used in the work, and the pigments used in each paint could be estimated through SEM-EDS and Raman analysis.

Considering the characteristics of the artwork, an efficient conservation treatment method was required because it was large (more than 3 m high) and the surface was not smooth. Accordingly, a cleaning test was performed by applying organic solvents commonly used in conservation treatment and hydrogels that have recently been used as cleaning materials. The results showed that 50 wt% isopropyl alcohol and 1 wt% non-ionic surfactants were the most effective. Hydrogels were expected to be effective because of their currently known characteristics; however, they were found to be unsuitable for artworks with uneven surfaces, such as *Guard Dog II*. Research on hydrogels continues to develop, and studies on the applicability of gels to modern oil paints and modern synthetic paints are in progress [15, 40]. However, as hydrogels have various types and characteristics depending on the manufacturing method, it is thought that research on the relationship between each artwork and material is necessary.

Conservation treatment was carried out based on the results of the cleaning test, and the artwork was stably conserved through cleaning and strengthening treatment of the surface of the work. Most previous research on cleaning methods has focused on paintings. However, this study will provide effective information on the conservation of three-dimensional objects by suggesting a suitable cleaning method for synthetic painted sculptures.

**Acknowledgements** The research was made possible by the National Museum of Contemporary Art in Korea(MMCA). We are grateful for MMCA's support.

**Authors' contribution** YB and HH provided support and guidance for this study. YB performed all the experiments and conservation treatment and wrote the first draft of the manuscript. NR performed the analysis of paints and interpreted the data. YM and JA supported the basic investigation and cleaning of the artwork. SM contributed to the conservation treatment. HH reviewed the manuscript. All authors have read and approved the final manuscript.

**Funding** Not applicable.

**Availability of data and materials** All data are available from the corresponding author upon reasonable request.

**Code availability** Not applicable.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interests.

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

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