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Original article

An analytical study to verify the suitability of free and gelled siloxanes for the treatment of modern oil paintings

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ABSTRACT

Since its introduction, about 15 years ago, the cyclic siloxane Cyclomethicone D5 has become increasingly used in the conservation of Cultural Heritage. In free form it allows the temporary hydrophobization of sensitive surfaces that must be treated in an aqueous environment; in the commercially available gelled form it allows the formulation of water-in-oil particle emulsions for surface cleaning or removal of film-forming substances, depending on the conditions of the aqueous phase. Over time, doubts have arisen about the real inertness of this solvent towards modern oil media. In addition, European regulations have restricted its use in consideration of its environmental impact, and so the already difficult availability of the material could further complicate; this advises the search for a substitute solvent. These two arguments motivated this study, conducted on two modern oil paintings: one unvarnished on paper, the other varnished on canvas. Samples of these paintings were treated under different conditions with D5 and the potential substitute chosen: dodecamethylpentasiloxane. The GC–MS and SEM-EDS analysis of the treated samples made it possible to evaluate and compare the degree of interaction with the oil binder in terms of leaching and topographic alterations of the surface, for both the free solvents and their gelled forms. Tests conducted on specially prepared paint samples also made it possible to evaluate the degree of solvation and consequent swelling produced by the two solvents on the different binders.

Introduction

In 2009, Richard Wolbers introduced silicone solvents to the conservation community at a CAPS-Cleaning Acrylic Painted Surfaces workshop, held at the Getty Conservation Institute in Los Angeles [1,2].

The possible use of these solvents is twofold: volatile siloxanes in liquid form, such as cyclomethicones, can be applied to protect a painted surface sensitive to water before an aqueous cleaning, temporarily hydrophobizing it [3]; the same solvents in gelled form, combined with aqueous solutions, can be transformed into water-in-oil particle emulsions suitable for cleaning sensitive surfaces [4].

The solvent initially used in North America, octamethylcyclotetrasiloxane or cyclomethicone D4, had already fallen into disuse in Europe due to its potential for toxicity [5], and the cosmetics industry had replaced it with the less volatile, higher term cyclomethicone D5 [6], exempt from this toxicity classification. This is the solvent that began to spread in the European conservation community [7]. Table A1 compares the properties of these siloxanes (see supplementary, Table A1).

The choice of D5 instead of D4 is also reasonable in consideration of its better chemical stability.

An ECHA document reports this observation on D4: "*In contact with water, D4 will hydrolyse with a measured hydrolysis half-life of 69 - 144 h at pH7 and 25 °C, according to the equation below. The product of hydrolysis is dimethylsilanediol*" [8].

$$[-Si(CH_3)_2O-]_4 + 4H_2O \rightarrow 4(CH_3)_2Si(OH)_2$$

The 1000 g/l water solubility [9] of the dimethyldisilanol (or dimethyl silanediol, CAS number 1066–42–8) that is formed is responsible for the environmental impact of this type of solvents.

Abbreviations: CAPS, Cleaning Acrylic Painted Surfaces workshop held at the Getty Conservation Institute in Los Angeles; CRE, coffee ring effect; ECHA, European Chemical Agency; FTIR, Fourier Transform Infrared Spectroscopy; GC-MS, Gas Chromatography coupled to Mass Spectrometry; HMDS, Hexamethyldisilazane; REACH, European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals; SDD, Silicon Drift Detector; SED, Secondary Electron Detector; SEM-EDS, Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy; TMS, tetramethylsilane.

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The opening of the siloxane ring not necessarily implies an increase in the risk of interaction in our applications to artworks; but it can be hypothesized, for example, that this hydrolysis may gradually take place in the long-term storage of the solvent, leading to the progressive formation of a more volatile solvent mixture: the boiling point of dimethyldisilanol, in fact, is decidedly lower: 122 °C compared to 175–176 °C of D4. By comparison, D5 proves to be more stable against hydrolysis with a half-life of 66 days under the same pH and temperature conditions [10].

The very low polarity of cyclometicone, difficult to explain by the chemical structure containing as many as five Oxygen atoms, can be rationalized considering the spatial conformation of the molecule: in practice, the methyl groups completely shield the polar part, that is, the ring composed of Silicon and Oxygen. Thus, this compound is also less polar than hydrocarbons. This apolarity in fact gives cyclomethicone D5 two interesting properties that are commonly exploited in practice in various fields of application: water repellency and very low solvent power, in practice only towards other silicone compounds, or low molecular weight apolar molecules.

The stability of various paint media, lacquers and inks to cyclomethicone D5, extensively tested in conservation [2,3] made this siloxane suitable for the temporary hydrophobization of water-sensitive painted surfaces.

A proprietary gelled formulation of this solvent was commercially available: Velvesil Plus^{TM} from the American firm Momentive Inc. [11], now no longer produced and replaced by KSG-350Z^{TM} (D5 gel) from the Japanese firm Shin-Etsu Chemical Co. Ltd [12]. Table A2 compares the composition of these gels (see supplementary, Table A2).

The three structural features of the gelling polymer, apolar-hydrocarbon, apolar-silicone and polar-polyethoxylated (PEG)/polyproxylated (PPG), are equally present but differently distributed in both gelling agents; in particular, the PEG functionalities responsible for the hydrophilic character are physically located within the polymer chains of the KSG-350Z^{TM} [13–15], thus improving the emulsifying capacity of the gel, compared to Velvesil Plus^{TM}

In 2019 the European Community enforced a restriction on the use of cyclomethicone D5, due its environmental impact (see supplementary, The UE regulation on cyclomethicone D5). A great unknown remains. If production and marketing are now restricted to a few areas involving only moderate quantities, compared to the quantities previously used in the cosmetic industry and other activities such as commercial laundries, how long will the production / marketing last? Realistically, it would be important to find substitute materials, free from environmental and / or health impacts.

The matter was discussed with representatives of the parent company Shin-Etsu Chemical Co. Ltd. at a meeting in October 2019 in Tokyo, and subsequently samples of siloxanes in free and gelled form were received from the European branch Shin-Etsu Silicones Europe B.V. This applicative study was thus undertaken. In consideration of the chemical-physical properties, the choice of a possible substitute for D5 was oriented towards the KF-96L-2CS ^{TM} fluid, based on the open-chain siloxane dodecamethylpentasiloxane, also available in the gelled form of the product KSG-380Z^{TM} (Si5 gel). The characteristics of the two materials are indicated in Table A3 (see supplementary, Table A3).

The use of cyclomethicone, initially proposed to increase the safety level in the aqueous treatment of contemporary paint media, so sensitive to swelling in aqueous environment, was extended over time: treatment of other binding media [16], and even more generally different treatments, other than the cleaning of a painted surface. Typical examples are the hydrophobization of the *verso* of paintings on canvas [17,18], textiles [19], paper [20] and other objects [21] prior to aqueous treatments.

As the domain of application of D5 widened, some perplexities arose about the real absence of solving power, specifically towards the paint media of 20th century oil paintings. It must in fact be considered that the amount of cyclomethicone necessary to achieve the hydrophobization of certain surfaces can be relatively large: furthermore, the potential impact of this quantity must also be evaluated in relation to the low volatility of the siloxane which causes prolonged retention under the surface. Various conservators, for example, noted the formation of halos on certain surfaces: could this indicate the transport of the mobile phase extracted from the paint binder rather than just the surface deposit material?

Aim of this work

The purpose of this work is twofold:

- first of all, to establish whether siloxane dodecamethylpentasiloxane (Si5) could be a possible substitute for cyclomethicone D5, should the production / marketing of the latter siloxane be terminated, due to the restriction on use issued by the European Community for environmental impact.
- also, check the inertness of D5 and its possible substitute with respect to the modern oil binding media.

To achieve these objectives, an analytical study based on GC–MS was conducted to determine whether the treatment of oil-painted surfaces with siloxanes in free and gelled form modified the fatty acid profile of the oil binding media. The SEM- EDS analysis also helped to provide information on interactions with the paint. These studies were conducted on two modern oil paintings, one on canvas and the other on paper. In addition to the analytical study, practical tests were carried out to visually assess the stability of contemporary paints with the two silicone solvents.

Materials and methods

Two paintings have been the subject of this investigation: a *Mountain landscape*, 80×120 cm, varnished oil on canvas dating from the 1960s, and a *Female portrait*, 21×30 cm, unvarnished oil on paper, painted in 1980 by one of the authors.

The paintings chosen represent two cases with a profoundly different material issue, despite both having an oily binder.

In the painting on paper, the binder has copiously migrated from the painted image into the surrounding paper. Consequently, two diametrically opposite scenarios could be envisaged for the treatment with solvents: greater sensitivity because of the depletion of the binder, or, on the contrary, greater stability, given the migration of the more mobile, less cross-linked phase.

But another aspect is perhaps of more crucial importance. The painting is unvarnished, and a "*vulnerable medium skin*" [22] is clearly perceptible on the pictorial surface, originating from the curing and maturation of the oil paint. And this would suggest greater susceptibility to treatment with solvents. As we will discuss below, the results confirmed the latter expectations.

The material condition of the painting on canvas is different: good structural condition, with a rather uniform surface in terms of material composition, morphology and topography, and a uniform layer of varnish. The reverse of the painting was a uniformly clean canvas: no stains or halos appeared due to the migration of components of the oily binder. Potentially, therefore, the painting could be more sensitive than the oil painting on paper examined up to that point, precisely because it was not depleted of its more mobile components; on the other hand, the varnish layer could make it less sensitive to the silicone solvents.

Uniform areas in terms of color tone and thickness of the paint were sampled for the GC – MS analysis of the binder. Specifically,

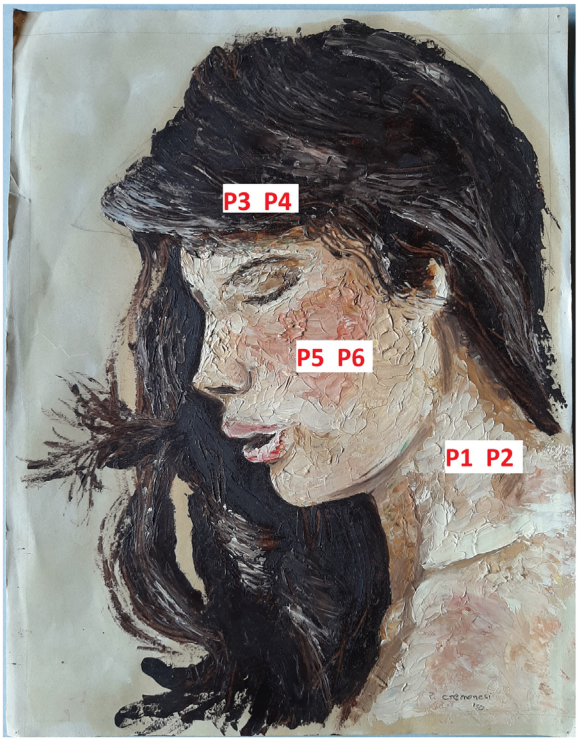

Fig. 1. Map of the areas sampled for binding medium analysis on the oil painting on paper.

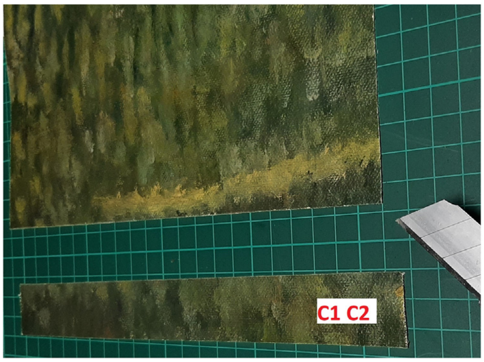

Fig. 2. Map of the areas sampled for binding medium analysis on the oil painting on canvas.

for the Portrait three color zones (Fig. 1): the complexion in the neck (samples P1 and P2) and cheek area (samples P5 and p6), and the hair (samples P3 and P4); for the Landscape (Fig. 2) only the vegetation area (samples C1 and C2).

Fragments of about 3 × 1.5 cm were cut from the same color areas chosen for the analysis of the binding media and subjected to the applications of free and gelled solvents.

For the solvent treatments, the fragments cut from the selected areas were immersed for 10 min in 2.5 ml of solvent. The solvents tested were: cyclomethicone D5 (D5), the alternative siloxane dodecamethylpentasiloxane (Si5) alone and mixed with 40% (vol) tetramethylsilane (TMS), tetramethylsilane alone, hexamethyldisiloxane (HMDS), and the proprietary ShellSol D40^{TM} (D40) hydrocarbon blend. At the end, the samples were extracted from the solvent: some were left to air dry; others were immersed for 5 min in 2.5 ml of HMDS before air drying. The samples, after drying for a few days, were subjected to GC- MS analysis.

For treatments with silicone gels, a small amount of gel, typically about 50 mg, was applied to the fragments cut out from the chosen areas, alternating laying and working with a soft brush for 10 min. The gel was then carefully removed with dry cotton swabs. The treated surface was washed three times with HMDS and left to dry in the air for a few days before samples were taken for GC–MS analysis. Table 1 summarizes the origin and the treatment for each sample.

Gas chromatography - mass spectrometry (GC–MS)

The instruments used and the analytical procedure adopted were based on those described by Casoli et al. [23] (see supplementary, Materials and Methods).

Electronic microscopy with electronic microprobe (SEM-EDS)

A detailed description of the instrument used is provided in supplementary, Materials and Methods.

Micro- Fourier transform infrared spectroscopy (FTIR)

A detailed description of the instrument used is provided in supplementary, Materials and Methods.

Microscopy

A 5-megapixel Dino-Lite. model AM7013MZT4, USB microscope was used for surface observation. 3D images were taken with a Keyence VHX-7000 ultra high-accuracy microscope 4 K (200 µm scale).

Solvent evaporation test

The substrate for experimental verification of the impact of solvent evaporation was a commercial MDF Panel (medium-density fibreboard) coated with a non-absorbent matt paint made from ultramarine blue (PB29) in a polyurethane emulsion resin (Monocomponent polyurethane varnish). Average thickness of the coating was 35 to 40 µm. This paint medium has proved to be particularly sensitive to the formation of halos, hence it was selected for these tests. Droplets of solvents were deposited on the surface, which was observed in 3Dvision under a Keyence VHX-7000 ultra high-accuracy microscope 4 K (200 µm scale) for material analysis.

'Harmlessness test'

A specific apparatus was devised for testing possible interference of the silicone solvents with different brands of commercially available paints; it was used first to apply uniform strips of paint to the paint mock-ups and then to exert a calibrated force onto the paint strips so as to evaluate the extent of mechanical abrasion.

Fig. 3d and 3e show the 3D image of an acrylic paint strip observed under the Keyence VHX-7000 ultra high-accuracy microscope 4 K (200 µm scale). Homogeneous coatings of paint were obtained in the form of thin lines, despite the great variety of chemical-physical properties, viscosity, rheology, and solvent evaporation rate of the various binders considered: in aqueous emulsion, in solvent and waxy emulsion. Examples of paint strips are shown in Fig. 4. All paint samples were aged in normal indoor environment for average eight months and were tested when perfectly dry.

The apparatus was thus modified to perform the 'harmlessness test': outfitted with a flexible microbrush (Fig. 5) calibrated to exert a selected constant pressure passing ten times back and forth over the paint strips, (a detailed description in provided in supplementary, Harmlessness test)

Table 1
Origin and treatment of samples from the oil on paper (P samples) and from the oil on canvas (C samples). D5: cyclomethicone D5; HMDS: hexamethyldisiloxane; Si5: dodecamethylpentasiloxane; D40: ShellSol D40^{TM}; D5 gel: KSG-350Z^{TM}; Si5 gel: KSG-380Z^{TM}; TMS: tetramethylsilane; Si5-TMS: 40% tetramethylsilane in dodecamethylpentasiloxane.

Oil painting on paper			Oil painting on canvas		
Sample	Origin	Treatment	Sample	Origin	Treatment
P1	Neck	None	C1	Green vegetation	None
P2	Neck	None	C2		None
P3	Hair	None	C3		D5, air
P4	Hair	None	C4		D5, HMDS, air
P5	Cheek	None	C5		Si5, air
P6	Cheek	None	C6		Si5, HMDS, air
P7	Neck	D5, air	C7		HMDS, air
P8	Neck	D5, HMDS, air	C8		D40, air
P9	Hair	D5, HMDS, air	C9		D5 gel, HMDS, air
P10	Cheek	D5, HMDS, air	C10		Si5 gel, HMDS, air
P11	Neck	Si5, air	C11		TMS, air
P12	Neck	Si5, HMDS, air	C12		Si5-TMS, air
P13	Neck	HMDS, air	C13		Si5-TMS, HMDS, air
P14	Neck	D40, air			
P15	Hair	D40, air			
P16	Neck	D5 gel, HMDS, air			
P17	Neck	Si5 gel, HMDS, air			
P18	Hair	TMS, air			
P19	Hair	Si5-TMS, air			
P20	Hair	Si5-TMS, HMDS, air			

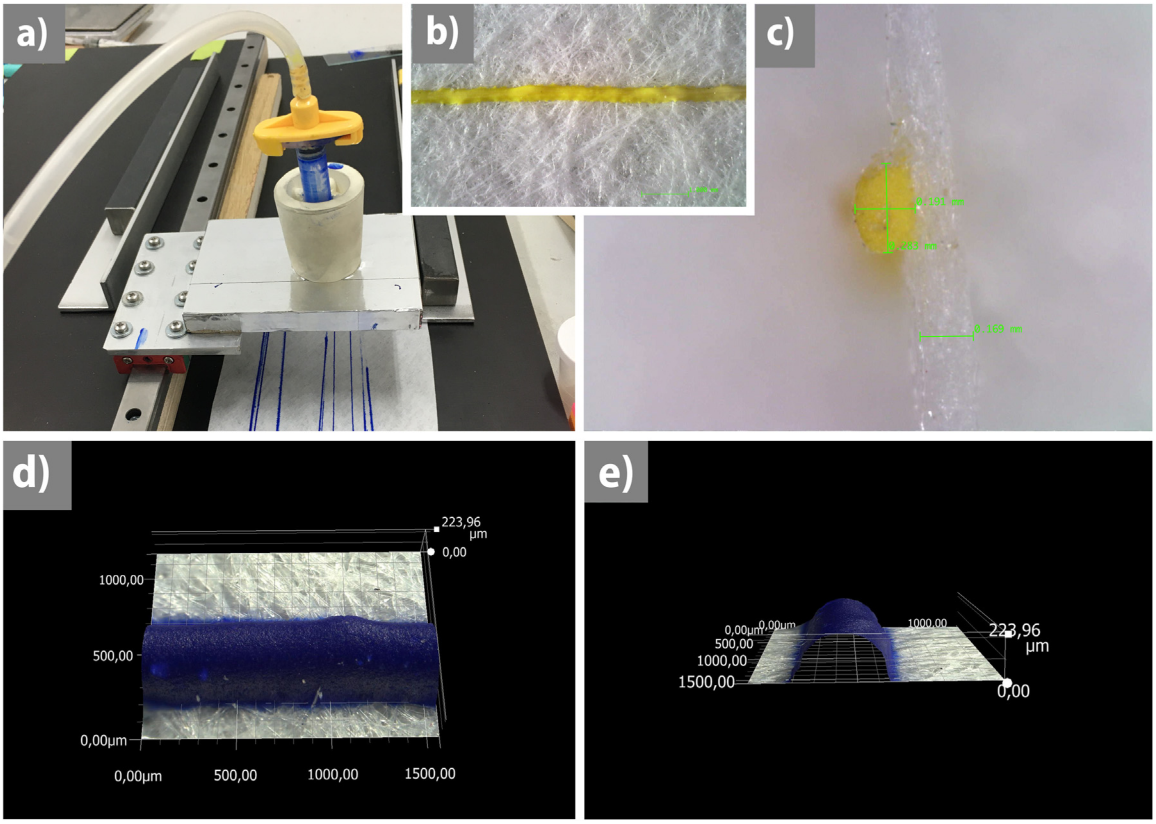

Fig. 3. a) The sliding apparatus for the application of paint strips on mock-ups; b) and c) a paint strip onto the 'Bondina' support; d) and e) 3D image of an acrylic paint strip observed under the ultra high-accuracy microscope 4 K (200X magn.).

Results and discussion

Binding medium characterization. Table A4 (supplementary material) lists the fatty acids identified in the various samples. Numbers are expressed as µg of fatty acid over 100 µg of samples from the two oil paintings, calculated in relation to the tetracosane internal standard. Accordingly, the binding media of the two paintings could be identified as oil. Specific characterization of the oil source was not possible due to the common occurrence of these fatty acids in most oils of interest. Arachidic acid (C20) and behenic acid (C22) possibly indicate the presence of safflower oil (*Carthamus tinctorius*), a commonly used oil binder for paints af-

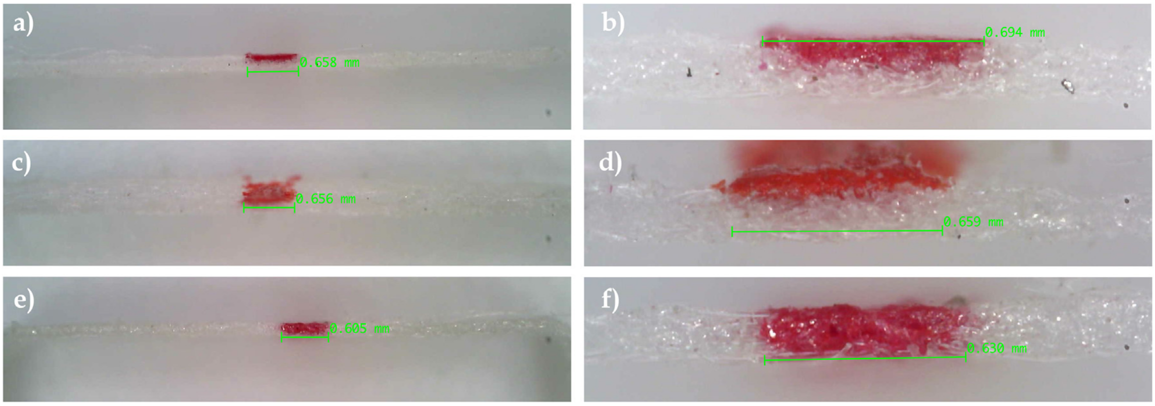

Fig. 4. Paint strips applied onto the Bondina$^{\mathrm{TM}}$ support. Abstract Sennelier Cadmium Red deep hue 606 PR 170 a) 55x magn. and b) 220x magn.; Magna Bocour Cadmium Red light Agr., c) magn. and d) 220x magn.; Lefranc & Bourgeois Flashe Vinyl color Rouge Rubis 388 PV19 Agr., e) 55x magn. and f) 220x magn.

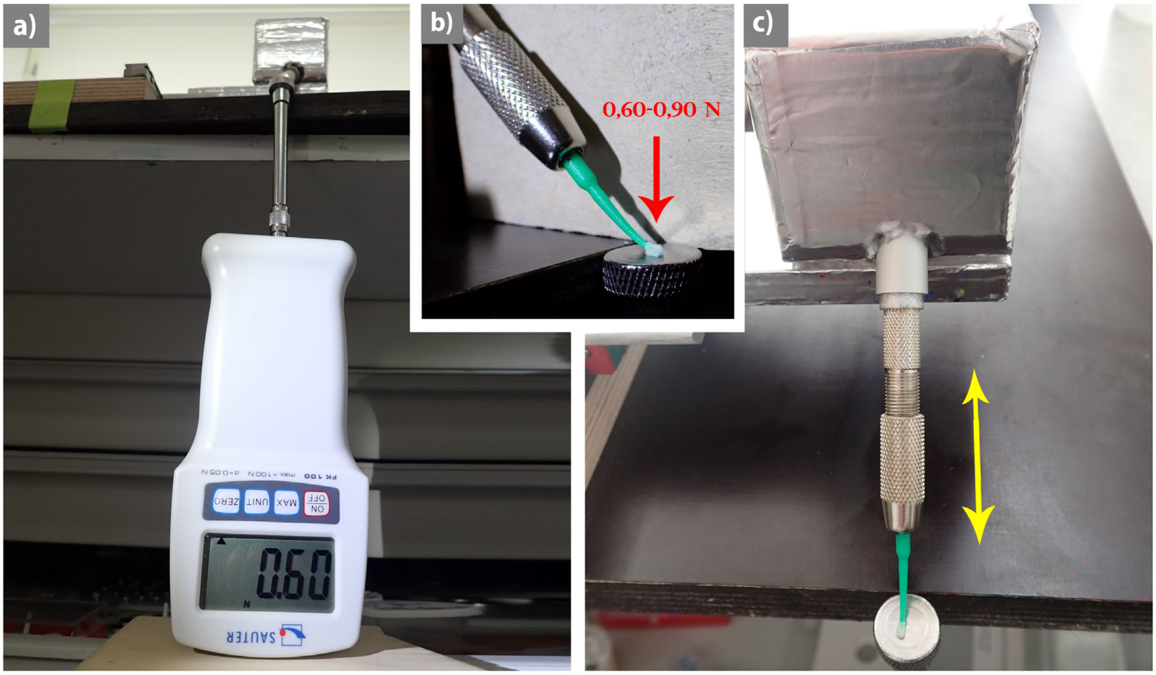

Fig. 5. Setting up the apparatus for the 'harmlessness test'. a) The Sauter force gage. b) The micro-applicator. c) The micro-applicator on the slide support base.

ter the 1960s [24]; however, the presence of historical drying oils, such as linseed and poppy seed, as minor components, cannot be excluded.

Treatment with siloxanes in free form. Our investigation initially addressed the first objective of this work: the interaction of cyclomethicone D5 with the binding medium, also in comparison with its possible substitute Si5. GC–MS analysis appeared suitable for monitoring leaching phenomena, and the SEM-EDS for monitoring morphological/topographical alterations. The oil painting on paper was considered first.

The results from GC–MS analysis are listed in Table A5 (supplementary materials), where numbers are expressed as µg of fatty acid over 100 µg of treated samples from oil painting on paper

Numbers reported on Fig. 6 are calculated as percentage of fatty acids removed from the treated samples, referred to the total amount averaged from the two binding medium samples analyzed for each color area, i.e., binding medium P1 and P2 for treated samples P7, P8, P11, P12, P13, P14, P16 and P17; binding medium P3 and P4 for treated samples P9 and P15; binding medium P5 and P6 for treated sample P10.

Fig. 6 show the percentage of fatty acids removed from the treated samples.

Treatment with D5 (sample P7) on the neck area confirmed the worries that initially motivated this study: 37.4% of the original amount of fatty acids was leached out of the paint layer. The validity of the strategy commonly adopted after the hydrophobization of surfaces was also confirmed: rinsing with the volatile HMDS to speed up the drying of the surface reduced to 24% the extent of leaching in sample P8, immersed in HDMS before air drying.

To continue, it was decided to analyze the other two main color areas, the brown hair and the pinkish cheek, to verify any pigment-related difference in the extent of leaching. Treatment with D5, without subsequent washing with HMDS, caused less leaching on the cheek (27.6%, sample P10) and even less on the hair (18.8%, sample P9). Based on these findings, the neck area was thus chosen for comparative treatment with the less volatile siloxane Si5, due to its higher sensitivity to solvent action.

Si5 caused more pronounced leaching (63.8%, sample P11), well almost double that of D5. Subsequent washing with HMDS (sample P12) not only did not improve the situation but aggravated it by

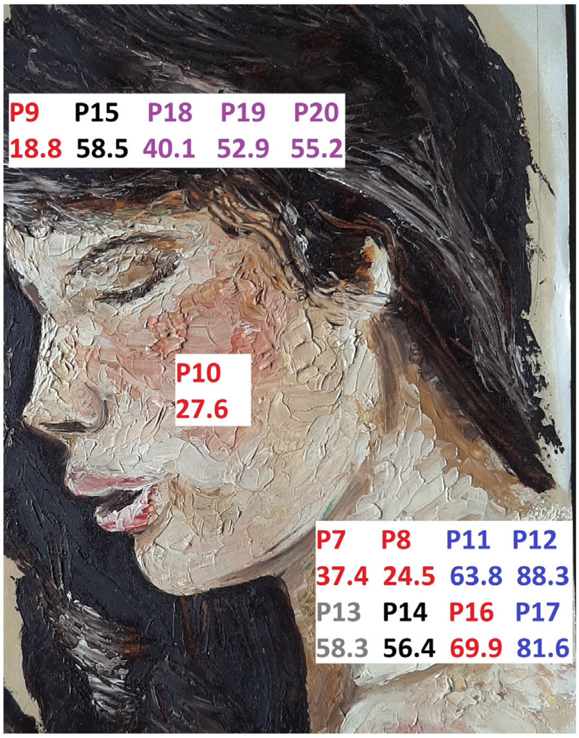

Fig. 6. Percentage of fatty acids removed from the treated samples. Samples P7, P8, P11, P12, P13, P14, P16 and P17 relate to the total amount of binding medium averaged from P1 and P2; samples P9 and P15 to P3 and P4; sample P10 to P5 and P6.

increasing to 88.3% the percentage of fatty acid removal from the treated sample.

In any case, this first set of results already led to a consideration: at this first stage of the evaluation, siloxane Si5 would not appear to be a valid alternative to D5 for the temporary hydrophobization of a young oil binder, preliminary to an aqueous treatment. However, it seemed important to compare the leaching produced by siloxanes with that produced by hydrocarbon blends, which were commonly used as 'hydrophobic barrier' before D5 entered common use. This is the reason for the treatment carried out next: D40 on the two areas of opposite sensitivity to leaching, the most sensitive of the neck (sample P14) and the least sensitive of the hair (sample P15). In both cases the percentage of fatty acid extraction was significantly higher than that produced by D5: 56.4% on the neck and 58.5% on the hair. Therefore, if the unfavorable interaction of D5 with the young oil binder is undeniable, the lesser impact compared to the traditionally used method is equally undeniable.

The subsequent development started from the observation that in the case of the less volatile siloxane Si5 the 'washing solvent' HMDS was unable to speed up the evaporation and, consequently, to mitigate the leaching action. This could be a consequence of a major dissolution in HDMS of the leached components on the surface. Apart from this analytical result, the simple visual observation of the slowness of the evaporation of Si5 from a painted surface made it considered unsuitable for practical applications of temporary hydrophobization of water-sensitive surfaces. Thus, another possibility was evaluated: formulating mixtures of Si5 with other more volatile silicone solvents, to increase the evaporation rate.

Fig. 7 shows some of the applications tested on the specially prepared polyurethane-based emulsion paints, comparing the behavior of a hydrocarbon blend (D40), D5, Si5 and a 40% TMS blend in Si5. Even when added in fairly large proportion (40% by volume) HMDS was unable to appreciably speed up evaporation of Si5 (not shown in Fig. 6), thus confirming the previous analytical findings.

Table 2
GC–MS analysis samples from the oil paintings on paper and on canvas treated with the 40% TMS in Si5 mixture.

Fatty acid	µg / 100 µg treated sample					
	from the oil painting on paper			from the oil painting on canvas		
	P18	P19	P20	C11	C12	C13
C12	0.00	0.00	0.00	0.00	0.00	0.00
C19di	0.12	0.09	0.11	0.01	0.02	0.01
C14	0.01	0.01	0.01	0.00	0.00	0.00
C15	0.00	0.00	0.00	0.01	0.00	0.00
C16	0.41	0.33	0.34	0.28	0.24	0.24
C18:1	0.18	0.14	0.10	0.02	0.00	0.01
C18	0.25	0.20	0.20	0.15	0.14	0.13
C18:2	0.00	0.00	0.00	0.00	0.00	0.00
C20	0.08	0.05	0.02	0.01	0.01	0.01
C22	0.02	0.02	0.02	0.03	0.01	0.01
Tot	**1.07**	**0.84**	**0.80**	**0.51**	**0.42**	**0.41**

In physics, a 'coffee ring effect' (CRE) is the pattern left by a puddle of particle-loaded liquid after it evaporates [25–27]. In this specific instance, droplets of solvent are deposited onto a painted surface. Because of the rugosity of the surface, the touchpoints between the droplet, air and the surface cannot move, and for this reason they are called "pinned". As the solvent starts diffusing, particles migrate outwards, carried by the solvents thus originating tide lines because of the 'coffee ring' effect. In the case of Si5 the visual impact of the 'coffee ring' is less evident, probably due to the slower migration of the liquid which concentrates less particles in a smaller area.

The choice of TMS as a component of the above solvent blend came from a series of tests of different solvents and from the consideration of the chemical-physical and toxicological properties of the solvent (see supplementary, Table A6).

It is evident from Fig. 7 that the behavior of the TMS-Si5 blend on the mock-up painted surface is very similar to that of D5. Based on this observation, it was decided to test this mixture on both oil paintings and verify whether it caused less leaching than pure Si5. On the painting on paper the test area was the hair, where D5 had produced the least interaction. The results from GC–MS analysis are listed in Table 2, expressed as µg of fatty acid over 100 µg of treated samples.

The comparison between the treatment with only TMS (sample P18) and with the 40% TMS mixture in Si5, without (sample P19) and with subsequent washing with HMDS (sample P20) showed an increasing leaching in this order: TMS (40.1%), 40% TMS in Si5 (52.9%), 40% TMS in Si5 then HMDS (55.2%). Also, in this case the percentage was much higher than that produced by D5, and the 'washing solvent' HMDS was unable to mitigate the extraction of mobile components from the binder, as previously demonstrated.

At this point, the other artwork was also taken into consideration: the varnished painting on canvas, A sample collected from this varnish, analyzed by FTIR spectroscopy, was characterized as natural terpenoid resin (Fig. 8).

The results from GC–MS analysis of the solvent-treated samples are listed in Table A7 (supplementary materials), expressed as µg of fatty acid over 100 µg of treated samples from oil painting on canvas.

Numbers reported on Fig. 9 are calculated as percentage of fatty acids removed from the treated samples (referred to the total amount averaged from the two binding medium samples C1 and C2 from the green vegetation).

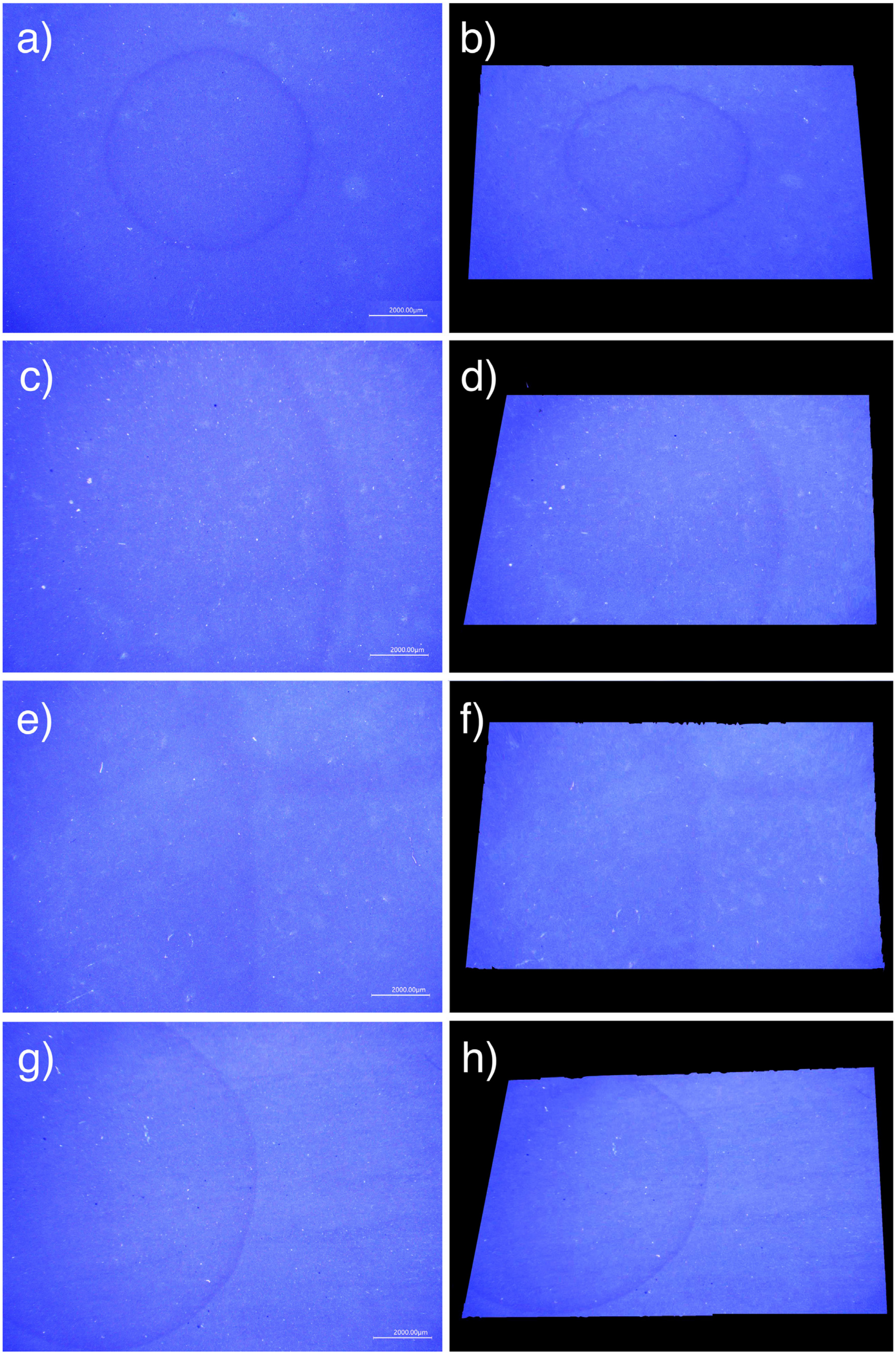

Fig. 7. 3D Vision of painted mock-ups treated with droplets of various solvents after complete drying. a and b, D40 (Naphtha petroleum, hydrotreated heavy N °CAS 64,742–48–9); c and d, D5; e and f, Si5; g and h, 40% TMS in Si5.

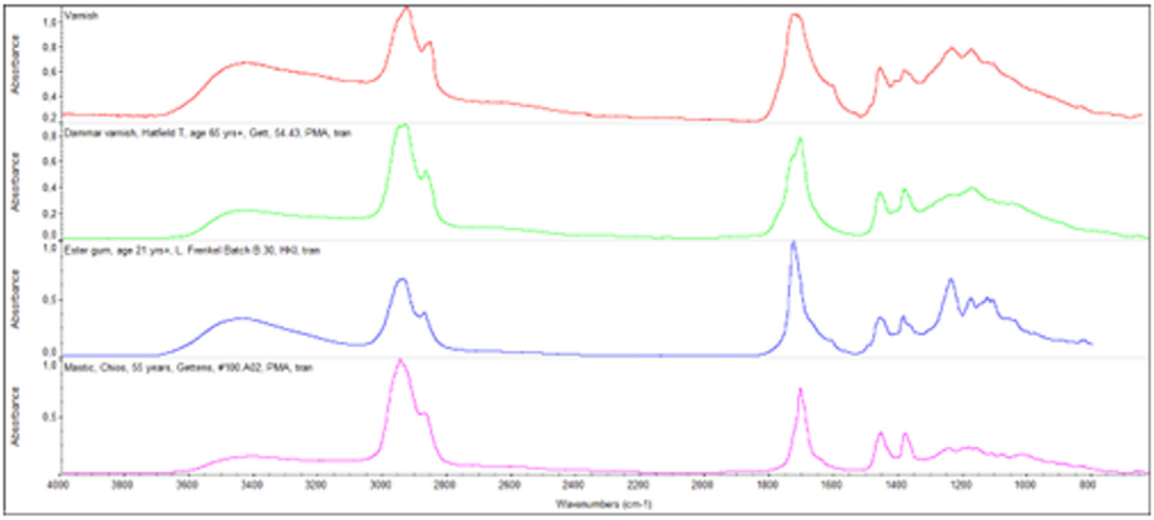

Fig. 8. FTIR spectra of (top to bottom): varnish sample from the oil painting on canvas; Dammar varnish 65 yrs; Ester gum, 21 yrs; Mastic Chios, 55 yrs.

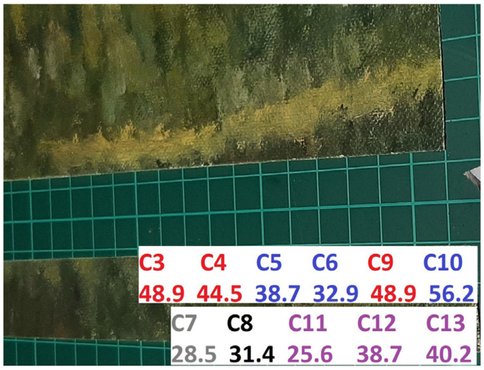

Fig. 9. Percentage of fatty acids removed from the treated samples from the oil painting on canvas.

The very first tests, comparing the D5 and the potential Si5 substitute, air dried with and without preliminary 'washing solvent', showed an opposite behavior compared to the painting on paper. In the treatments with Si5 and air drying (sample C5) and preliminary treatment with the 'washing solvent 'HMDS (sample C6) the extraction of mobile components from the oil binder, respectively 38.7% and 32.9%, was appreciably lower compared to the corresponding treatments with D5 without HMDS (sample C3) and with HMDS (sample C4), respectively 48.9% and 44.5%. In addition, washing with the volatile HMDS now produced the expected result of the faster evaporation of Si5: less leaching.

The composition of the oil binders in the two works, precisely in the chromatic areas where Si5 was applied (the green in the oil painting on canvas and the neck in the oil painting on paper) highlights a great difference. By averaging the values of samples P1 and P2 for the oil painting on paper and samples C1 and C2 for the oil painting on canvas, C16 (palmitic acid) and C18 (stearic acid) represent 89.78% of the total fatty acids in the painting on canvas, but only 54.91% in the painting on paper. Another significant difference is in the amount of azelaic acid (C9di): 6.57% in the oil painting on canvas and more than double, 14.72%, in the oil painting on paper. Answering this question would require further study, and only hypotheses can be formulated at this level; however, experimental data seems to support the idea that perhaps the 'structural affinity' between the molecules of siloxane and those of fatty acids plays an important role in determining the leaching capacity of the solvent; perhaps even more important than the volatility factor. The results obtained seem to indicate that the consideration of the solvent volatility alone is not sufficient for a correct interpretation. Precisely, the mixtures of TMS and Si5 have not shown ability to reduce the amount of leaching in the treatment of the oil painting on canvas (Table A6, supplementary materials, and Fig. 4): the TMS alone caused limited leaching (sample C11, 25.6%) while the mixture 40% TMS in Si5 caused the same leaching (sample C12, 38.7%) as pure Si5, and washing with HMDS (sample C13) produced a comparable leaching (40.2%). Thus, the higher volatility of the solvent mixture TMS-Si5 does not seem to be a relevant factor in the interaction of the silicon solvents with the binding medium of the painting on paper.

The treated surfaces from both paintings were then examined by SEM. The analysis had a dual purpose: to highlight any alterations in the topography of the surfaces treated with silicone solvents, particularly those in gelled form, and to monitor the pres-

Fig. 10. Areas of the painting on paper before (left) and after (right) treatment with the Si5 gel and macro visible image (center) of the area before treatment.

Table 3
Chemical-elemental composition of the areas on the painting on paper treated with siloxanes D5 and Si5. Averaged semi-quantitative data.

Element			D5 Treatment		Si5 Treatment	
Number	Symbol	Name	Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.
6	C	Carbon	80.4	75.2	80.7	75.8
8	O	Oxygen	19.5	24.3	19.3	24.2
30	Zn	Zinc	0.1	0.5	–	–

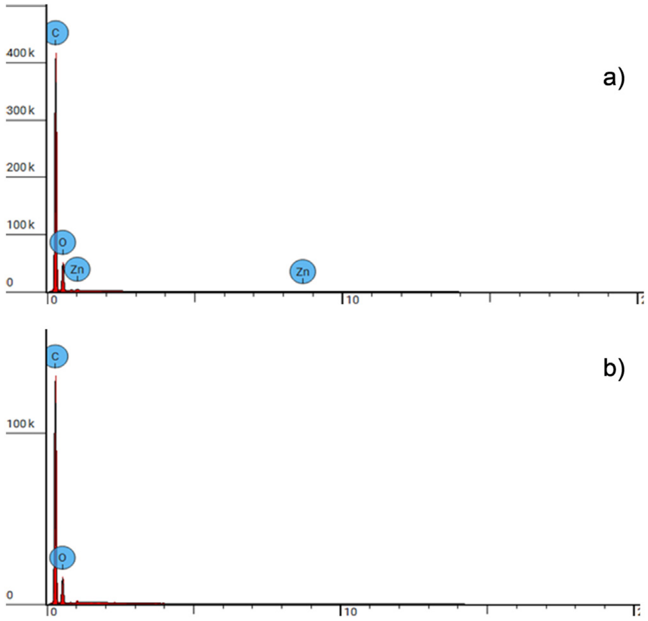

Fig. 11. EDS spectra of the area treated with a) D5 and b) Si5.

ence of any silicone residues, also in this case especially for gelled forms.

The analysis of the painting on paper, however, was able to address only the first purpose: the mapping of Silicon, in fact, showed the presence of this element already on the original surface, not subjected to treatment. At the time of purchase in a second-hand market, the painting was correctly hung on a wall, but it can be assumed that it was previously preserved in other conditions, probably leaning with the painted surface against a wall to have suffered contamination from the sandy material of the plaster.

The areas treated with D5 and Si5 (both pure and in mixture with TMS) both air dried and rinsed with HMDS, were analyzed one week after the treatments. The high-resolution images obtained did not show any signs of abrasion of the surface. This finding confirms the conclusions from the simple visual observation under the stereomicroscope both in visible and UV light of the treated areas: no interruption in the continuity of the surface varnish and no discontinuity of its yellow-greenish fluorescence.

On the painting on paper, conversely, it was possible to conduct the analysis to answer both questions: alterations of the surface topography and the presence of silicone residues. Samples were analyzed one week after the solvent treatments. The elemental maps did not show the presence of Silicon in any of the areas treated with D5 or Si5.

The last part of the analytical investigation took into consideration the gelled forms of the two siloxanes, D5 and Si5: respectively, the proprietary formulations D5 gel and Si5 gel.

This is an aspect of great practical significance. The siloxanes D5 and Si5 in free form, in fact, in practical applications play only a 'passive' role: to protect the sensitive surface during an aqueous treatment. Conversely, their gelled forms have a much more important 'active' role: they constitute the gelled dispersing phase of water-in-oil particle emulsions that can be specifically formulated and used for surface cleaning or for the removal of film-forming substances depending on the characteristics. of their aqueous dispersed phase (concentration, pH, conductivity, additives such as chelators). Thus, in the economy of the restoration intervention, these gelled forms are used much more frequently than the respective free solvents.

The treatment of the oil painting on paper (Fig. 6) on the chromatic area of the neck, produced extensive leaching: less with the D5 gel (sample P16, 69.9%) and more with that of Si5 (sample P17, 81.6%). The corresponding treatment on the oil painting on canvas (Fig. 9) produced significantly less leaching than in the previous case, and confirmed the order seen previously: less with the D5 gel (sample C9, 48.9%) and more with that of Si5 (sample C10, 56.2%).

In both cases, therefore, siloxane Si5 in the gelled form of KSG-380Z^{TM} does not appear suitable as a potential substitute for D5 in gelled form. Moreover, D5 itself in the gelled form of KSG-350Z^{TM} already shows high interference with the oil paint. It would be expected that the high viscosity of the gelled formulations, and the emulsifying capacity of the gelling polymer could ensure less subsurface diffusion of the solvent, thus decreasing the leaching action. But the result of the practical applications contradicted these expectations: evidently the low volatility of the two solvents, combined with the emulsifying action of the gelling agent, works in the opposite direction to theoretical expectations, promoting an important extractive action on the mobile components of the oily binder.

Also in this case, the treated surfaces were then examined by SEM, to monitor whether the gelled forms would cause topographical alterations, unlike the corresponding free solvents D5 and Si5. Analysis was carried out on both paintings, but here we only show the results from the treatment with Sì5, potentially more aggressive than D5, on the painting on paper which, being unvarnished, had the potentially most sensitive surface. Topographical SEM images of areas before (on the left) and after (on the right) the treatment with the Si5 gel are shown in Fig. 10. In the figure, also a visible macro image of the area before gel treatment is shown (in the middle). But in this regard no negative action has been highlighted: it can be clearly seen that the gels did not produce any morphological / topographical alteration of the treated surface.

The chemical-elemental composition of the gel-treated areas is listed in Table 3, and the corresponding EDS spectra are shown in Fig. 11a) and b).

No residual Silicon from either gel is detectable on treated surfaces. These two images highlight an interesting detail: the zinc signal is barely present in one area and completely absent in the other. Yet the zinc white pigment is abundantly present in these chromatic areas of the painting. The only detectable signals relate to C and O, that is the organic material of the 'skin' formed by the exudate of the oily binder. The presence of this organic material is so strong that it hides that of the underlying pigment

A 'harmlessness test'

The results from the GC–MS analysis have provided information on the interaction that could be defined an 'invisible damage': the

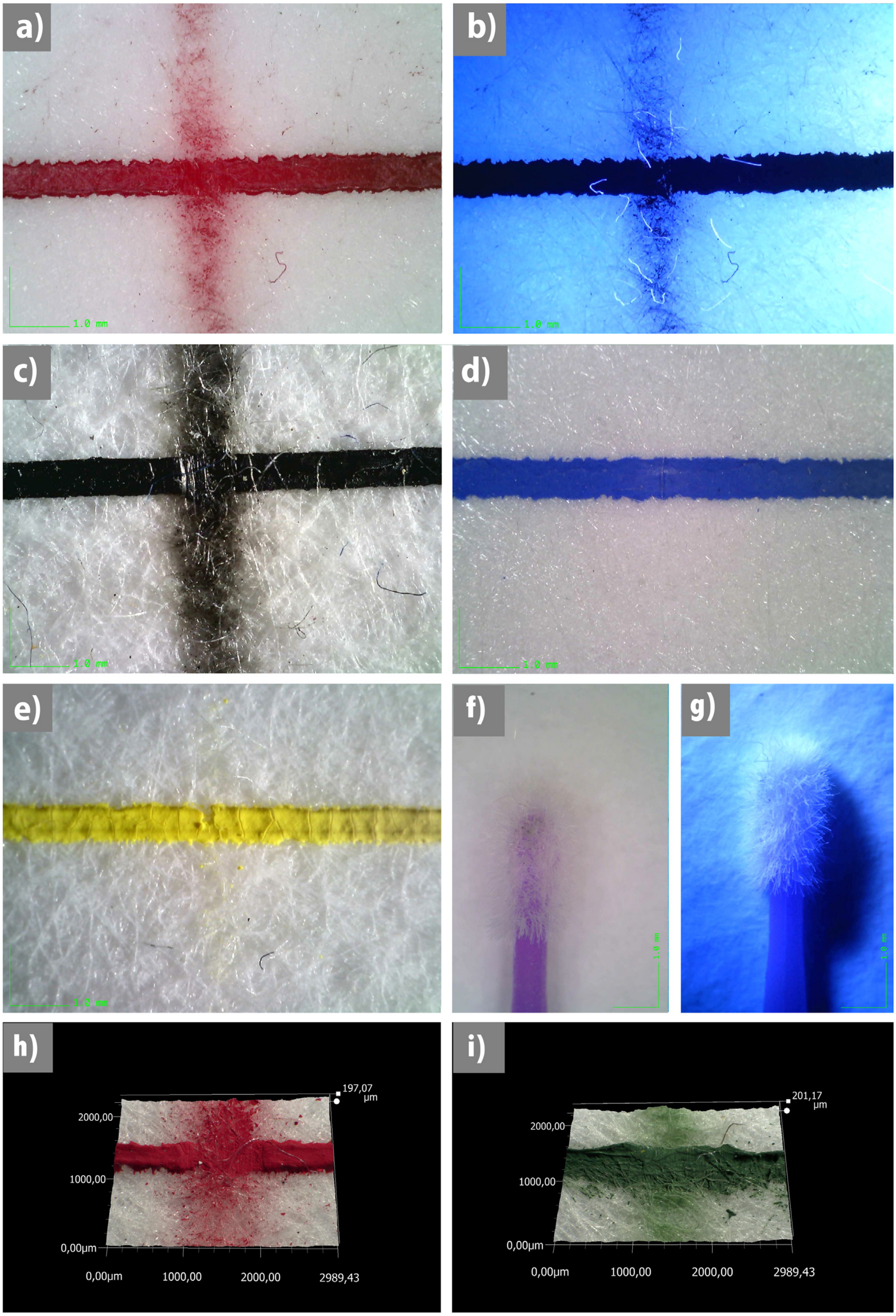

Fig. 12. Some results of the 'harmlessness test' on painted strips. Microscope images, 55x magnification, strong solvation (a) in visible and (b) UV incident light and (c) in raking visible light; (d) polishing; (e) abrasion. 3D images from the ultra high-accuracy microscope 4 K (100X magn., representing examples of strong solvation: (h) D40 on a layer of Rembrandt Casein Tempera Rouge de cadmium, ca. 1950; (i) D5 on a layer of Rembrandt Casein Tempera Oxyde de chrome, ca. 1950. The head of the micro-applicator in visible (f) and UV (g) light.

Table 4
Solvent testing of sixty previously and currently available paint samples with D5, Si5, both pure and mixed with 40% TMS in Si5, ShellSol D40^{TM}. Evaluation of the interaction: * no visible solvation; ** poor solvation; *** solvation; **** strong solvation.

PAINT MATERIAL	D40	D5	Si5	Si5 +TMS
Magna BOCOUR Yvory black (solvent-borne acrylic paint)	****	**/*	*	*
Magna BOCOUR Ultra blue (PB29) (solvent-borne acrylic paint)	****	*	*	*
Magna BOCOUR Cadmium red light (solvent-borne acrylic paint)	****	**	**	**
Magna BOCOUR Cadmium yellow med (solvent-borne acrylic paint)	****	****/***	**	**/*
Magna BOCOUR Yvory black w/Magna Varnish	***	**	**/*	**
Magna BOCOUR Ultra blue (PB29) w/Magna Varnish	***	**	**/*	**
Magna BOCOUR Cadmium red light w/Magna Varnish	****	***/**	**	**/*
Magna BOCOUR Cadmium yellow med w/Magna Varnish	****	**	**	**
Liquitex Mars Black in tube, circa 1970 (acrylic emulsion paint)	**/*	*	*	*
Aquatec Bocour Cobalt blue DP tin tube, circa 1970 (acrylic emulsion paint)	*	*	*	*
Rembrant Talens Cadmium red deep aluminum tube, ca 1980 (acrylic emulsion paint)	***	*	*	*
Aquatec Bocour Cadmuim yellow DP tin tube, ca 1970 (acrylic emulsion paint)	**/*	*	*	*
Abstract Sennelier Mars Black 759 PBk 11, 2021 (acrylic emulsion paint)	***	*	*	*
Abstract Sennelier Ultramarine Blue 314 PB 29, 2021 (acrylic emulsion paint)	***/**	*	*	*
Abstract Sennelier Cadmium Red Deep Hue 606 PR 170, 2021 (acrylic emulsion paint)	***/**	*	*	*
Abstract Sennelier Primary Yellow 574 PY74, 2021 (acrylic emulsion paint)	***	*	*	*
Polyflashe Lefranc&Bourgeois Bleu Hoggar 036, ca 1980 (vinyl-acrylic emulsion paint)	***	***	*	**/*
Polyflashe Lefranc&Bourgeois Rouge Breughek 359, ca 1980 (vinyl-acrylic emulsion paint)	***	*	*	*
Polyflashe Lefranc&Bourgeois Jaune citron 169, ca 1980 (vinyl-acrylic emulsion paint)	***	*	**/*	*
Rowney pva colours Burnt sienna, ca 1960 (vinyl emulsion paint)	*	*	*	*
Rowney pva colours Ultramarin, ca 1960 (vinyl emulsion paint)	*	*	*	*
Rowney pva colours Vermillon Hue, ca 1960 (vinyl emulsion paint)	*	*	*	*
Rowney pva colours Lemon yellow, ca 1960 (vinyl emulsion paint)	*	*	*	*
Ocavin P.V.A Ocaldo Calder Colours Viridian, ca 1990 (vinyl emulsion paint)	*	*	*	*
Ocavin P.V.A Ocaldo Calder Colours Cerise, ca 1990 (vinyl emulsion paint)	*	*	*	*
Ocavin P.V.A Ocaldo Calder Colours Vermillon 3830, ca 1980 (vinyl emulsion paint)	*	*	*	*
Ocavin P.V.A Ocaldo Calder Colours Lemon 3830, ca 1990 (vinyl emulsion paint)	*	*	*	*
Flashe vinyl color Lefranc&Bourgeois Noir 265 PBk11-PBk7, 2021 (vinyl emulsion paint)	****	**	**	*
Flashe vinyl color Lefranc&Bourgeois Bleu outremer 043, 2021 (vinyl emulsion paint)	*	*	*	*
Flashe vinyl color Lefranc&Bourgeois Rouge Rubis 388 PV19, 2021 (vinyl emulsion paint)	***	**	**/+	**/*
Flashe vinyl color Lefranc&Bourgeois Jaune Japonais clair 183 PB74, 2021 (vinyl emulsion paint)	**	*	*	*
Sennelier Egg Tempera Yvory Black 755 PNk11-PNk1, 2020	*	*	*	*
Sennelier Egg Tempera Ultramarine Blue 357 PB 29, 2020	***	*	*	*
Sennelier Egg Tempera Cadmium Red Deep Genuine 606 PR, 2020	****	****	***	***
Sennelier Egg Tempera Cadmium Yellow Light Genuine 529 PY, 2020	*	*	*	*
Casein Tempera Rembrant Noir d'ivoire, ca 1950	****	***/**	***/**	**
Casein Tempera Rembrant Oxyde de chrome ca 1950	****	***	***/**	**
Casein Tempera Rembrant Rouge de cadmium ca 1950	****	****	****	****
Casein Tempera Rembrant Jaune de cadmium, ca1950	***	*	*	*
Richeson Casein The Shiva Series Ivory black PBk9, 2021	**/*	*	*	*
Richeson Casein The Shiva Series Ultramarine blue deep PB29, 2021	**	*	*	*
Richeson Casein The Shiva Series Cadmium red Extra deep PR108, 2021	**	*	*	*
Richeson Casein The Shiva Series Cadmium yellow medium PY35, 2021	**	*	*	*
W&N Cerola (wax) Waterproof poster colours Chrome green light, ca 1950	***	***	**	**
W&N Cerola (wax) Waterproof poster colours Chrome lemon, ca 1950	***	***	**	**/*
Pure Beeswax Crayons STOCKMAR black, ca 1970	****	****	****	****
Pure Beeswax Crayons STOCKMAR blue, ca 1970	****	****	****	****/***
Pure Beeswax Crayons STOCKMAR red, ca 1970	****	****	****	****
Pure Beeswax Crayons STOCKMAR yellow, ca 1970	****	****	****	****
Omnigouache J.M. PAILLARD Bleu 336, ca 1950 (Gouache)	*	*	*	*
Omnigouache J.M. PAILLARD Rouge 253, ca 1950 (Gouache)	*	*	*	*
Omnigouache J.M. PAILLARD Jaune de chrome 01, ca 1950 (Gouache)	*	*	*	*
LINEL Gouache extra fine Lefranc&Bourgeois Ivory Black 269, 2021	*	*	*	*
LINEL Gouache extra fine Lefranc&Bourgeois Deep Ultramarine 086, 2021	*	*	*	*
LINEL Gouache extra fine Lefranc&Bourgeois Cadmium Red scarlet, 2021	*	*	*	*
LINEL Gouache extra fine Lefranc&Bourgeois Cadmium yellowlight 158, 2021	*	*	*	*
Bréhat Aquarelle extra fine DALBE Noir d'ivoire 535, 2021	**/*	**/*	*	*
Bréhat Aquarelle extra fine DALBE Bleu Outremer foncé 392, 2021	*	*	*	*
Bréhat Aquarelle extra fine DALBE Rouge de cadmium clair véritable, 2021	*	*	*	*
Bréhat Aquarelle extra fine DALBE Jaune de cadmium clair véritable 081, 2021	*	*	*	*

leaching of mobile components of the oil binding medium. Invisible, but no less serious than any visible damage: this interaction, in fact, causes an impoverishment of the binder, making the paint more fragile, more porous, more sensitive.

Not necessarily leaching is associated with a preliminary high swelling of the paint layer, as has been well described by Baij et al. [28]. Even swelling can be difficult to perceive by simple visual observation unless it manifests itself as blanching following alterations in the surface topography. The SEM-EDS analysis, adequate to provide information about surface alterations, has clarified this aspect as well as providing additional information which is also of fundamental importance: the possible permanence of superficial and /or sub-surface silicone residues.

But we felt the need for this study to also give information more directly linked to practical experience, to the conservator's judgment based on direct observation, to his ability to reconnect the theoretical information acquired to the sensory data. This is the motivation that gave rise to the subsequent study, to complement the analytical study: the experimental verification of the interaction of silicone solvents with paint layers, using the specially prepared strips painted on the Bondina support, and conducted in the most reproducible conditions possible. After solvent treatment through the micro-applicator, the painted strips were examined and documented with digital microscope observation under incident and raking visible light and UV light, to establish the degree of interaction to be correlated with the solvation efficiency of the solvents used. Fig. 12 shows, with 55x magnification, different aspects of the interaction: strong solvation (a) in visible and (b) UV incident light and (c) in raking visible light; (d) polishing effect; (e) abrasion. 3D images from the ultra high-accuracy microscope 4 K (magnification scale: 200 µm) representing examples of strong solvation are also shown: (h) D40 on a layer of Rembrandt Casein Tempera Rouge de cadmium, ca. 1950; (i) D5 on a layer of Rembrandt Casein Tempera Oxyde de chrome, ca. 1950. Also shown is the head of the micro-applicator in visible (f) and UV (g) light.

Sixty commercially available formulations of paints with different binders from the Atelier Héritier collection (Table 4), covering a time interval of about seven decades, were tested with these solvents: D5, Si5 both pure and mixed with 40% TMS, in comparison with the hydrocarbon blend D40. The assigned evaluation is classified as follows: * no visible solvation; ** poor solvation; *** solvation; **** strong solvation.

Some unexpected results surprised us, and once again demonstrate how varied and difficult to generalize is the universe of commercially available colors, even if nominally based on the same binding medium. The unexpected sensitivity of egg tempera and casein colors, for example, could be associated with the presence of cholesterol in the former, but in the latter it is certainly not attributable to components of the binder itself but rather to the presence of additives. However, this interference is strongly dependent on the color brand. On the other hand, there were no unexpected interactions of the solvents with the hydrophilic binders of the watercolors and the gouaches.

As expected, acrylic paints both from emulsions and solvent-born have proved to be sensitive to the hydrocarbon solvent and, in some Magna colors, also to silicone solvents. Vinyl or acrylic-vinyl colors have shown greater stability in general, albeit with exceptions. Even old Bocour colors have shown great stability.

Conclusions

This investigation considered the applications of two siloxanes, in free and gelled form, to two modern oil paintings to assess the degree of interaction with the paint binder. D5 is commonly used as a ‘hydrophobic barrier’ in aqueous treatments, and Si5 would be a potential replacement.

Both siloxanes tested showed an interaction with the oil-based paint layers in terms of depletion of the binder. Leaching was more pronounced with Si5, and further studies would be interesting to establish a possible correlation between the open-chain structure of this siloxane and those of the leached fatty acids.

Furthermore, the interactions had opposite trend: more marked for the open-chain Si5 on the oil painting on paper, even when mixed with the more volatile TMS, and on the contrary more marked for the cyclic siloxane D5 on the oil painting on canvas. Opposite tendency also been demonstrated for the action of the volatile washing solvent HMDS, used to speed up the evaporation of the siloxanes: effective in reducing the interaction of D5 but not that of Si5. We can only hypothesize that the higher solvent power of HMDS combined with the lower volatility of Si5 could explain these differences, but even in this case further investigation would be needed.

This would lead to the conclusion that neither of the two siloxanes is suitable for the hydrophobic treatment of young oil paints. But it is only necessary to consider these preliminary findings in a broader context. First, only two oil paintings cannot be representative of a whole category, and can only provide preliminary indications that hopefully motivate further study.

Secondly, these results should be evaluated in a wider perspective: traditionally the temporary hydrophobization treatment of water-sensitive surfaces would be performed with hydrocarbon mixtures, which in the present study demonstrated greater leaching action than siloxanes. Furthermore, the hydrocarbon considered here was a fully de-aromatized blend; in traditional use, on the other hand, white spirit was often used which, due to its aromatics content, normally 17–20%, would exert an even stronger extractive action.

The gelled forms of the two siloxanes D5 and Si5 also showed interference in terms of leaching with the oil binder on both paintings, more on the unvarnished painting on paper and less on the varnished painting on canvas. In both cases, the gel from less volatile Si5 caused more extensive leaching. The SEM analysis showed that in no case did the siloxanes in free or gelled form produce interference with the surface of the two paintings, causing morphological / topographical alterations. This would lead to the conclusion that the extraction capacity of these solvents is not accompanied by appreciable swelling action, probably due to their very low polarity. The latter phenomenon, in fact, would have repercussions on the surface integrity, easily highlighted by SEM analysis.

A ’harmlessness test’ was also conducted, to complement the analytical study and evaluate and compare the possible disrupting action on the surface: solvent application, through a micro-applicator with constant controlled pressure, on strips of colors specially prepared from sixty commercial products with different binders. The force exerted by the micro-applicator was calibrated in such a way as to produce damage only in case of sufficient solvation of the binder by the applied solvent. This verification constitutes an important database useful to the conservator as a reference for practical applications.

Authors’ contributions

All four authors contributed to experimental design, data collection and processing, to writing and editing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All research data obtained during this study are included in this article. Raw data are available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.06.006.

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