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Towards a novel strategy for soot removal from water-soluble materials: the synergetic effect of hydrogels and cyclomethicone on gelatine emulsion-based photographs

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Abstract

Gels are a popular cleaning method for paper conservators and a lot of research has been done concerning gel cleaning of paper objects over the last 15 years. Despite the close interconnection between the conservation fields of paper and photographic material, research on using gels for cleaning photographs is very scarce. However, gels can provide an excellent cleaning method for photographic material. Cleaning silver gelatine prints with aqueous solvents is very complex due to the hydrophilic properties and fragility of the gelatine layer which makes mechanical cleaning difficult. The properties of gels ensure better control over the flow and evaporation of the solvent, facilitating the cleaning process. This study is the first insight into the viability of using gellan gum gel and polyvinyl acetate-borax (PVAc-borax) gel to clean contaminants from the surface of silver gelatine photographs. It is based on self-made samples that were artificially aged and contaminated with soot. Water, ethanol (EtOH), and Kodak Photo-flo were studied as solvents to remove the soot from the silver gelatine-based prints. These solvents were loaded into the aforementioned gels and applied to the samples in two different methods. These gel cleaning methods were subsequently compared with traditional cleaning methods. In addition, the usage of cyclomethicone D4 as a protective mask for the gelatine layer was studied. Measuring methods used to evaluate the cleaning were visual comparison, microscopic observation, and densitometry. ATR-FTIR measurements were also conducted to investigate potential side-effects of the cleaning methods on the prints, such as unwanted chemical transformations or the presence of gel residues after the treatments. Most of the gel cleaning methods within this study proved to be inadequate, with the exception of the gellan gum gel loaded with 30% EtOH. It was used as a granulated gel applied mechanically on a print saturated with cyclomethicone (octamethylcyclotetrasiloxane D4). Cyclomethicone proved to be a very effective protective barrier for the water-sensitive gelatine layer with minimal reduction in cleaning effectiveness.

Keywords Gel cleaning, Silver gelatine prints, Soot, Gellan gum, PVAc-borax, Cyclomethicone, Photographs

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Introduction

Silver gelatine prints are a type of black and white photographic print that was introduced in the 1880s. They quickly took over the market due to their improved light sensitivity and practicality over other photographic processes. They have been the most important type of black and white analog photographic print up until today [1, 2]. Several types of silver gelatine prints exist, but the focus of this study is the baryta-based print which was the most frequently used photographic paper up until the 1970s. This type of photographic print consists of four layers: a paper base, a coating of barium sulfate (baryta) which makes the surface of the paper more even and whiter, a gelatine layer in which the image-forming silver particles are dispersed, and a final protective gelatine coating.

Cleaning is an important and challenging part of conservation treatments. The cleaning process is an irreversible procedure that influences the appearance of the artwork and that possibly takes away matter that could be of intangible value for the material biography of the artwork. Moreover, cleaning is a delicate and complex matter especially when the surface is water-sensitive which is the case with gelatine emulsion-based photographs. Cleaning means removing unwanted dirt deposits without changing the original material or incorporating new materials. Physical damage to the surface can be caused by carbon particles, this can result in visible scratches and cracks on the surface. Chemical degradation of the gelatine emulsion can be initiated by acids, leading to discoloration, yellowing, and brittleness of the photograph. Discoloration of the photograph can be caused by organic substances such as oily material. In addition, they can act as a food source for mold and other microorganisms, which can further accelerate the degradation of the photograph [3, 4].

A cleaning treatment not only has an aesthetic purpose, removing dirt also has a conservation benefit. Dirt deposits are often harmful to the objects, according to their source, they can contain acids or other organic substances. These materials may react with the object and accelerate degradation. In addition, surface dirt, such as soot, can cause abrasion, or provide a breeding ground for insects or fungi. Mostly, soot is composed of carbon particulates combined with an oily material [5–7]. Nano-sized soot particles are difficult to remove from porous surfaces especially when they are deposited deeply in the surface [8]. Organic materials, such as gelatine of photographic prints, are very sensitive to this. In this case, the aim is to remove soot in order to enhance the stability and readability of gelatine emulsion-based photographs.

Due to the water sensitivity of these silver gelatine prints, mechanical cleaning is sometimes preferred over solvent cleaning for the removal of unsolicited deposits. However, mechanical cleaning with cotton swabs may cause abrasion which is harmful to the gelatine emulsion layer. Another problem is that, when cleaning with cotton swabs and solvent, there is no control over the solvent, therefore, it was necessary to rethink the traditional cleaning methods and seek for innovative low-risk surface cleaning methods.

Traditionally, solvent cleaning entails the application of an aqueous solvent mix with cotton swabs. However, this traditional method is not ideal due to the hydrophilic properties of the gelatine layer. When gelatine is exposed to water, swelling occurs and the surface becomes extremely sensitive to abrasion. Thus, to prevent this type of damage, solvent cleaning is only utilised when strictly necessary. Gel cleaning may provide a viable alternative as it allows for better control over the solvents. This can be achieved because gels transform solvents into a semi-solid state which helps control solvent flow. When a gelator is added to a solvent, it changes from its fluid state into a solid or solid-like state. By varying concentration, thickness or type of gelator, the cleaning process can be adapted to the specific needs of the object [9, 10].

Therefore, gel cleaning has been studied extensively for paper conservation. Especially rigid polysaccharide gels have been used with great success in the last 10–15 years for several applications: cleaning of deposits, removal of glue, as a vessel for chelators and enzymes, etc [9, 11–15]. Despite the close interconnection between paper and photography conservation, the use of gels in this last field remains limited to date. Some research on cleaning photographic prints has been done, but more systematic research on silver gelatine prints is still needed [13, 16, 17].

Both rigid and high viscosity polymeric dispersion gels (i.e. polyvinyl acetate-borax 'PVAc-borax') are used to clean delicate surfaces. The focus of this research is cleaning with gels in direct contact with the surface of silver gelatine printing. Therefore, a rigid gel and a visco-elastic gel was chosen in order to compare a cleaning method with a lower abrasive rate to an abrasive method with cotton swabs.

For the first gel-type, we selected gellan gum gel which is an anionic polysaccharide produced by the bacterium *Sphingomonas elodea*. When gellan gum is dissolved in hot water, a transparent hydrogel that can act as a sponge is formed. Gellan gum stays stable at both highly alkaline and acidic conditions while this is not the case with PVAc-borax gels. Organic solvents, enzymes or surfactants can be added to this type of gel in order to target specific types of contaminants [9, 18]. The second chosen gel-like material is the PVAc-borax system. They are known as the most advanced methods to guarantee the highest possible control of solvents during cleaning.

When borate-ions (usually in the form of a (di-) sodium tetraborate solution) are added to a partially hydrolysed polyvinyl acetate solution in water, a visco-elastic material is formed. Based on their rheological behaviour, PVAc systems cannot be considered as gels in strict sense, however, we will refer to them as gels for simplicity [19]. Moreover, it is possible to add organic solvents, chelator agents, and surfactants to these gels [20]. They can also be employed on the surface to be treated as a gum [19]. In addition, these gels are affordable and already present in most conservation labs. As shown in Table 1, in this paper we compare traditional cleaning methods with gel application techniques.

For traditional cleaning, the two most prevalent cleaning techniques were selected: washing by immersion in a water bath and cotton swab cleaning. Both methods are commonly used by conservators in spite of a number of limitations. In particular, the sensitive gelatine layer is swelled by the water when cotton swabs soaked in solvents are gently rolled over the surface of the print [21], while the applied mechanical force may cause irreparably damage. Washing of prints is considered an intrusive treatment that can only be performed when the object is in a good condition and free of water-sensitive additives such as inks, paints, glues. Both approaches are used as a benchmark for gel cleaning. More details about the cleaning methods employed in this study are explained in ("Cleaning methods") section.

In order to mitigate the aforementioned water solubility and associated swelling of the gelatine layer, the samples underwent a pre-treatment prior to cleaning. In the previous decade, silicon-based solvents have been introduced for these purposes in the conservation field [22]. In particular, octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), two volatile cyclic siloxanes, commercially known as cyclomethicones can be used as a barrier for liquids during aqueous cleaning. These slow-volatile, strong non-polar mixtures are characterized by a low surface tension. A first useful aspect is that, when gelatine is placed in cyclomethicone, it will not swell. Previous research showed that by applying cyclomehticones, cleaning can be performed without compromising the image layer [15, 23]. Furthermore, cyclomethicone applied to cotton swab as a solvent may be successful for cleaning soot on the surface of a silver gelatine print. Nevertheless, by using a cotton swab we remain with the problem of machinal cleaning and the possible damage it can cause during cleaning.

In general, the use of solvents in the cleaning of photographic material is quite limited. In silver gelatine printing, the commonly used solvents are demineralized water, ethanol (EtOH) and "wetting agents" such as Kodak™ Photo-flo. In some cases, other solvents will be used exceptionally, such as acetone, but because of the very limited and specific use of such solvents, they are not included in this study [1, 2, 21]. As illustrated in Table 1, for all solvent-based methods three solvents commonly used in the conservation of photographic material were tested: water, EtOH and Photo-flo.

The aim of this research is to find a workable and hands-on method for restorers to clean gelatine emulsion-base photographs by comparing classical cleaning methods with new ones. A key question we aim to answer with this study is: How effective are the different methods of gellan gum gel cleaning and PVAc-borax gel cleaning compared to traditional cleaning methods such as cleaning with cotton swabs with the solvents, demineralised water, ethanol, and Photo-flo, or immersing the photo in a water bath?

Table 1 overview of the traditional cleaning methods and gel cleaning methods

Traditional cleaning methods	
Cotton bud cleaning	**Water bath immersion cleaning**
100% water	
30% EtOH in water	
0.5% Photo-flo in water	
100% cyclomethicone D4	
Gel cleaning methods	
Contact gel cleaning	**Mechanical gel cleaning**
Gel 1: gellan gum (water), (1 h, 2 h, 4 h)	Gel 6: gellan gum (water)
Gel 2: gellan gum (30% EtOH), (1 h, 2 h, 4 h)	Gel 7: gellan gum (30% EtOH)
Gel 3: gellan gum (0.5% Photo-flo), (1 h, 2 h, 4 h)	Gel 8: gellan gum (0.5% Photo-flo)
Gel 4: PVAc-borax (water), (1 h, 2 h, 4 h)	Gel 9: PVAc-borax (water)
Gel 5: PVAc-borax (30% EtOH), (1 h, 2 h, 4 h)	Gel 10: PVAc-borax (30% EtOH)

Thus, water was used as a solvent in the traditional cleaning methods and an integral part of the hydrogels in the gel cleaning methods. EtOH was used as a solvent in all of the cleaning methods with a concentration of 30% while Photo-flo was also used as a solvent with a concentration of 0.5%. Every cleaning method was both carried out on silver gelatine-based print samples with and without a pre-treatment with cyclomethicone. Saturation was achieved by submerging the samples in pure cyclomethicone just before cleaning. After cleaning, all samples were air-dried. The efficiency of the cleaning treatments were assessed by visual and microscopic comparison before and after cleaning while cleaning efficiency was calculated by densitometry. In addition, Attenuated total reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) was used to investigate potential surface chemical transformations and mechanical damage induced by the treatments on the gelatine layer. Moreover, the technique was employed also to verify the possible presence of remaining gel residues after the treatment, which might promote fungal growth and thus cause damage to the prints [24].

Experimental

Sample preparation

Mock-up samples made of Ilford Multigrade FB MAT (8 × 4 cm) photographic paper were exposed and developed to an even middle grey, i.e., a tone that is, perceptually, about halfway on a lightness scale between black and white. This barite paper is considered representative for photographs from around 1900 and 1975 as most photographs from this period were printed on barite silver gelatine prints. After development, these silver gelatine prints were artificially aged through exposing them to direct UV-light for 16 h (Philips TLK 40W/05) and subsequently placing them in direct sunlight under a southern faced roof window for a period of six months (November 2018–April 2019) [25].

In a next step, the mock-ups were contaminated with soot. The goal was to simulate a photograph that has been damaged by soot from a fire and that has subsequently suffered water damage from exterminating the fire. The intention is to introduce soot into the gelatine emulsion, so that it cannot be completely removed by mechanical cleaning alone. Soot originating from a wood stove is chosen as a contaminant on the prints. A cotton swab containing stove soot is moistened with demineralized water and rubbed on the surface of the silver gelatine print. Afterwards, using a wide brush, the soot was spread evenly over the entire surface (Fig. 1B). For each sample the same amount of soot (0.05 g) was applied. Then the prints were dried under a light weight, between two layers of tissue paper, to keep the prints flat during drying. The samples were divided into three parts; the lower part (with an area of 4 × 4 cm) was completely covered with soot and subjected to cleaning. The upper part was divided into two vertical strips of 4 cm × 2 cm. The left strip represents the soot-contaminated reference strip. The same amount of soot was applied to this strip as to the part of to be cleaned. The right-hand strip is the non-contaminated reference strip where no soot was applied 'blanco strip' (Fig. 1A).

Cleaning methods

As shown on Fig. 1 and explained in the introduction, comparative traditional cleaning and gel cleaning methods were performed on samples with and without a cyclomethicone (octamethylcyclotetrasiloxane D4, Kremer pigmente) pre-treatment. When in the rest of this study reference is made to saturated samples, this means that the samples were saturated with cyclomethicone before cleaning. The saturation was done by filling a container which is slightly larger than the samples with cyclomethicone and then placing the sample in the cyclomethicone bath for ten minutes. They were then taken out and the cleaning was carried out immediately, before the evaporation of the cyclomethicone. After cleaning, the samples were dried until the cyclomethicone appeared to be evaporated. The cleaning methods used in this study were as follows (Table 1):

Traditional cleaning methods

Washing a print entailed immersion of the print in a bath with sufficient support, soaking it for a certain time, then removing the print from the bath and drying and flattening it [26].Cotton bud cleaning was performed by rolling a cotton swab over the surface soaked with either 30% EtOH, 100% demineralised water, 0.5% Photo-flo or 100% Cyclomethicone D4.

Gel cleaning methods

In this approach, the gels were applied to the contaminated surface via two methods: (a) contact gel cleaning and (b) mechanical gel cleaning. those two cleaning methods can be explained as follows:

Contact gel cleaning Gels consist of a network of intertwined polymer structures containing solvents. This structure is highly porous, and this property gives gels their cleaning effect. Two forces are relevant to the interaction between the object (and its contamination) and the gel: capillary forces and osmotic forces [27].

Due to the effect of osmosis, water will flow from the water-rich gel system towards the water-poor object. Due to the porosity of the gel system, the water that came into contact with the soot will be absorbed into

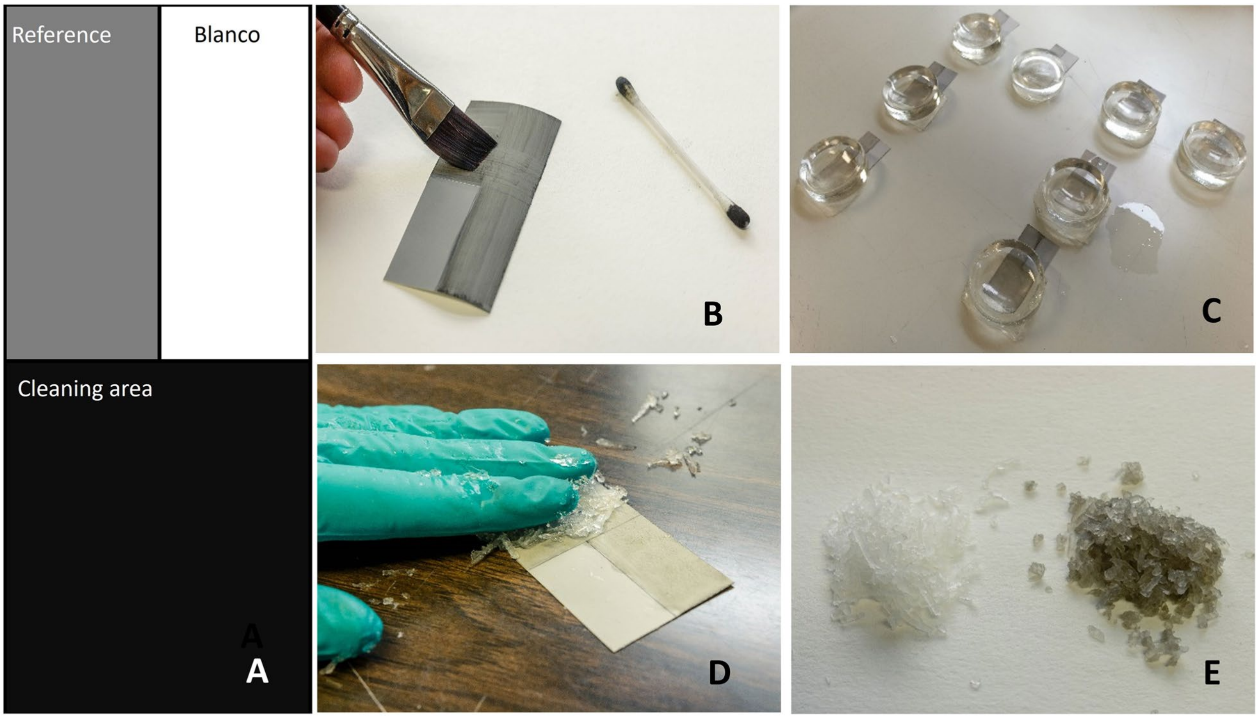

Fig. 1 **A** Scheme of the silver gelatine mock-up prints, **B** Application of soot on the silver gelatine samples, **C** Contact gel cleaning in progress, **D** Mechanical gel cleaning by rubbing granulated gellan gum over the contaminated surface, **E** Granulated gellan gum before (left) and after cleaning (right)

the pores of the gel by capillary forces. In other words, during cleaning, the soot will be loosened from the object by the water and supposably will be absorbed into the gel. Important for this operation is that there is a close contact between the gel and the object and that the gel remains in place long enough for the forces to take effect. Therefore, this cleaning is tested with a number of different time durations: 1, 2 and 4 h. In this way, it can be evaluated how long the contact should last at least for an effective cleaning. After the set amount of time, the gel was removed and the samples were dried, (Fig. 1C).

Mechanical gel cleaning Gellan gum gel and PVAc-borax gel were used in two different approaches. The gellan gum was grated so that the granules can be rubbed with fingertips over the surface. On the other hand, the PVAc-borax was rolled in small pieces, as small gums, with the fingertips over the surface. The action of the gel in this cleaning is mainly similar to that of the contact cleaning. However, the difference in this cleaning process is the added mechanical force by using gentle rolling over the surface. This cleaning is an improved version of dry cleaning with erasers [19]. It will mainly be the mechanical action that cleans here, but this is supplemented by the osmotic and capillary forces (Fig. 1D and E).

Gel preparation

Gellan gum (Kelcogel® CG-LA) gels were prepared and loaded with three different solvents as indicated in (Table 1). For the (2 wt%) gellan gum gels loaded with only water, the gel was made by measuring 0.6 g of gellan gum in a measuring cup, after which the cup was filled with the 29.4 ml of demineralised water (Table 2). This solution was stirred on a magnetic stirrer with hot plate which was set to 110 °C. When the gellan gum was fully dissolved, the hot plate was turned off to cool the solution down to temperature ca. 50 °C and stirring was continued. In case of loading the gel with other solvents (i.e., 30% EtOH or 0.5% Photo-flo), the desired amount of the solvent was added to the solution. Continuous stirring was used until a homogeneous solution was obtained, after which the solution was poured into a mould with a flat bottom. The solution was left to cool down to room temperature to form the crosslinked gel.

The preparation of the PVAc-borax gel followed the procedure explained in [28, 29]. Briefly explained, two stock solutions of 10% PVAc (Kuraray Poval 48–80) and 6% of borax (di-sodium tetraborate decahydrate, 99 -103% AnalaR NORMAPUR® Reag. Ph. Eur. analytical reagent) were prepared (Table 2). The PVAc solution was dissolved in water at 30 °C while the borax was dissolved in cold water. The final concentration of PVAc in

Table 2 Formulations of gellan gum gel and PVAc-borax

Gellan gum gels (total weight = 30 g)	Gellan gum	Water	Other solvents	
Gel 1/Gel 6 (water)	0.6 g	29.4 g	–––	
Gel 2/Gel 7 (30% EtOH)	0.6 g	20.4 g	9 g EtOH	
Gel 3/Gel 8 (0.5% Photo-flo)	0.6 g	29.25 g	0.15 g Photo-flo	
PVAc-borax gels (total weight = 50 g)	**10% PVAc stock solution**	**6% borax stock solution**	**Water**	**EtOH**
Gel 4/Gel 9 (water)	15 g	8.33 g	26.67 g	–––––
Gel 5/Gel 10 (30% EtOH)	15 g	8.33 g	11.67 g	15 g

the gels was 3 wt% and 1 wt% for the borax. The borax was added last to crosslink with the gel. For the formulations containing solvents, the solvents were added prior the addition of the borax. It is worth mentioning that when the borax was added to the formulation including Photo-flo, no gel formed due to the pH of the Photo-flo solution which is below 7.5, lower than the pH value (ca. 8–9) that allows the cross-linking of the PVAc [19]. This means that Photo-flo was only used in the gellan gum gel.

The following parts were combined in a measuring cup: 15 g of 10% PVAc solution (final concentration: 3%) and the desired EtOH volume (see* MERGEFORMAT Table 2). Demineralized water was then added. These liquids were mixed, after which 8.33 g of 6% borax solution (final concentration: 1%) was added. The addition of the borax solution led to an immediate gelation of the liquid.

Evaluation methods

The effect of the cleaning treatments were evaluated and documented using visual photography, optical microscopy (OM) and densitometry. The homogenous removal of soot particles and possible abrasion of the surface was evaluated by means of visual photography and Dino-Lite Edge 3.0 Digital Microscope. In particular, micrographs were collected at 200X magnification of each sample before and after the cleaning process. In order to quantify the cleaning efficiency, we implemented densitometry (Heiland B&W Densitometer TD-Series for photographic applications) in reflection mode to calculate cleaning percentages based on the change in darkness, before and after cleaning of the sample or object. More details on the technique can be found elsewhere [30].

For this study, the density in reflection was measured. Calibration was obtained by measuring a completely white area (zero value) from a blank area of photographic paper as the samples. The density of the non-contaminated area and the contaminated part was recorded at three locations from which average values were calculated. These locations were taken on the basis of a plastic sleeve with three holes that serves as a template to ensure a constant measuring location. After cleaning, the density of the contaminated area was measured again at the same location. The cleaning percentage for each sample was then calculated using the formula: (B–C)/(B–A) × 100.

A: average density of the non-contaminated part.

B: average density of the contaminated area before cleaning.

C: average density of the contaminated area after cleaning.

The FTIR measurements were conducted in ATR mode using an Agilent 4300 Handheld FTIR spectrometer. The spectra were collected at a resolution of 8 cm^{-1} with 128 scans in the range of 4000–650 cm^{-1}. To avoid any kind of distortion, no smoothing, baseline correction or any other adjustment were applied to the spectra. All the results shown in the manuscript are based on the average of three different point measurements. Analysis were conducted on all areas of the samples (blanco, reference and cleaned with different cleaning methods) as well as on the dried gels used for the cleaning (as reference for the detection of residues).

Results and discussions

Traditional cleaning methods

Visually, the cotton bud cleaning methods with 100% water and solutions of 30% EtOH and 0.5% Photo-flo in water yielded relatively similar cleaning results. The relative homogenous removal of soot on the mock-ups by means of cotton bud cleaning is exemplified by Fig. 2 and is expected to significantly improve the legibility of a historical photograph.

From the visual comparison of the samples taken before and after cleaning using traditional cleaning techniques, it can be observed that much of the soot has been removed. The cleaning is quite even, no spots or stripes are visible. Due to the mechanical force performed in this cleaning, the edges of some samples were damaged. Using water causes swelling to the gelatin and, in this process, it becomes susceptible to damage especially at the edges, this hereby results in material loss. In Fig. 2,

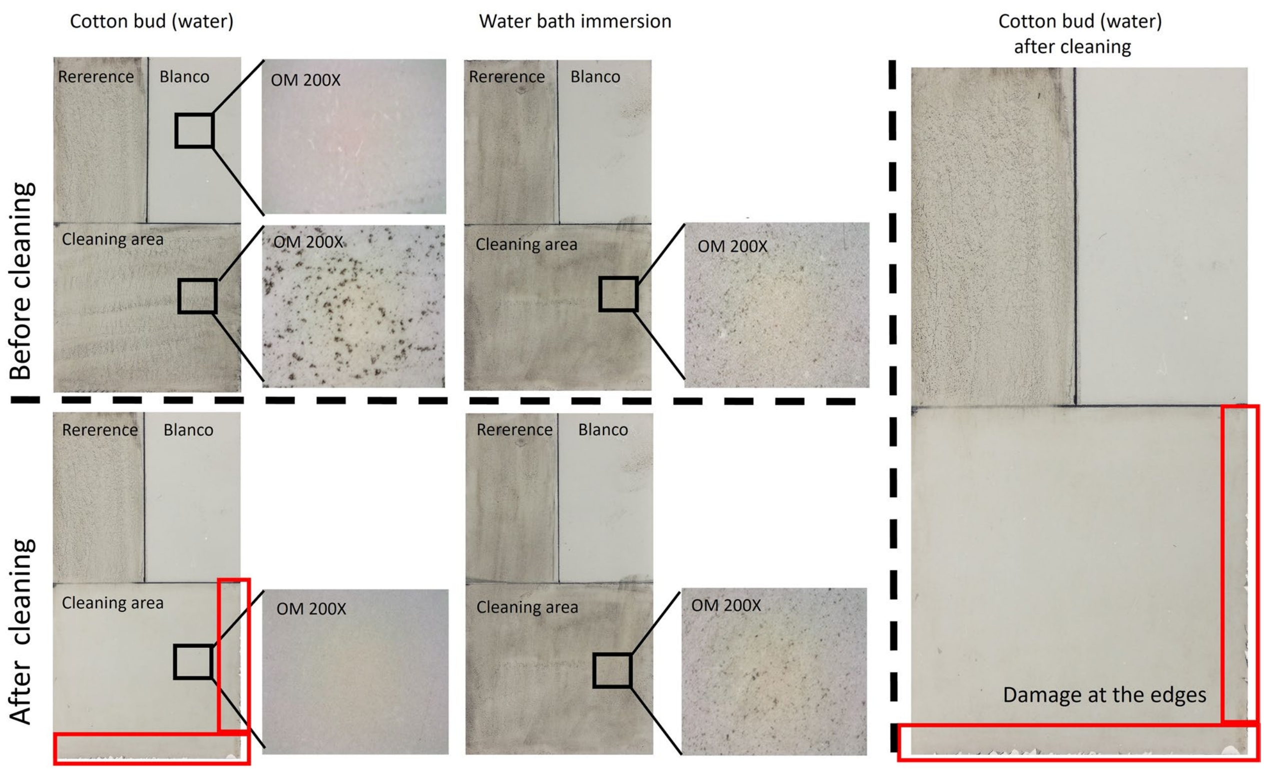

Fig. 2 Comparison between the two most prevalent cleaning techniques, cleaning with a cotton swab versus washing by immersion in a water bath. Damage at the edges after cleaning with cotton swab can be seen

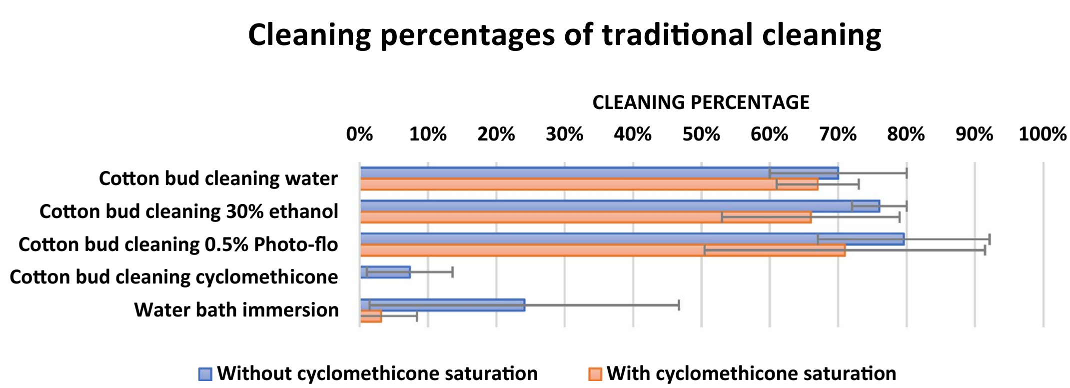

Fig. 3 Cleaning percentages of traditional cleaning methods (cotton bud cleaning and water bath immersion)

it can be observed that the soot is largely removed on the sample cleaned with cotton bud. However, there is still a minor difference between the cleaned surface and the uncontaminated reference strip, which shows that not all of the soot has been removed yet. At the edge at the bottom of Fig. 2 on the sample cleaned with cotton bud it can be observed that some flakes came off during cleaning. The samples treated with swabs loaded with 30% EtOH, water and 0.5% Photo-flo were similar to this sample. On the microscopic image, it can be observed that the small carbon specks that were present before cleaning are no longer visible. The surface is now uniformly gray. Furthermore, no residues from the cleanings can be observed either, such as cotton fibers.

Densitometry confirms the observed cleaning efficiency. In particular, Fig. 3 reveals how a cotton bud soaked in water removes about 70% of the soot, while the mere immersion in a water bath eliminated only ca. 25% of the soot, suggesting that the mechanical contact plays a vital role. Next to the quantification, the effect of the immersion in a water bath is also visually hard to observe, as illustrated by Fig. 2. When the mock-ups were pre-treated by means of a cyclomethicone D4 saturation to mitigate the swelling of the water sensitive gelatine, the overall efficiency of the cotton bud cleaning seems to drop with 5–10%. Figure 3 demonstrates how the cotton bud soaked in 100% water approach is least affected (minus 5%), while the removal of soot by immersion in a water bath is almost entirely prevented by the pre-treatment with cyclomethicone. Visually, this drop in cleaning is hardly perceivable the surface is now evenly grey, but more importantly under the OM no damage is visible.

Densitometry demonstrates how adding 'wetting agents' such as EtOH and Photo-flo to the water boosts the cleaning rates of the cotton bud cleaning with a few percentages, however this difference is not visible under OM. The 0.5% Photo-flo solution stands out as the most effectual approach with a cleaning rate of almost 80%. In contrast, cleaning with a cotton bud soaked in 100% cyclomethicone appears ineffective, with merely 7% of the soot taken away. The soot on the surface was removed, however, the soot trapped inside the gelatine and could not be removed. This means that there is soot residue left resulting in a negative cleaning result. The mock-up looks the same before and after cleaning under OM.

Gel cleaning

Contact gel cleaning

Unfortunately, none of the contact gel approaches yielded a cleaning result that is visually perceivable. An example is shown in Fig. 4. on the mock-up cleaned with PVAc-borax (30% EtOH). In the microscopic images in Fig. 4, a lot of soot can still be observed after cleaning; however, no residues of gel were observed. From the general visual representation, it can be concluded that this cleaning does not improve the readability of the object.

This is confirmed by the limited cleaning efficiency quantified by densitometry. As shown in Fig. 5, the best results were obtained by gellan gum with Photo-flo and PVAc-borax with EtOH and water yielding cleaning rates close to that of traditional water baths (ca 25% soot removal). What is striking here is that no cleaning percentage exceeds 24%. The cleaning percentages vary between 2 and 24%. Moreover, the duration of the gel cleaning has little influence on the cleaning percentage; in most cases, the cleaning percentage with the same gel at 1, 2 and 4 h is approximately the same.

With the investigated gels, the difference in cleaning percentage fluctuates between the samples that are saturated with cyclomethicone and those that are not saturated. There is also no clear indication that any type of solvent or type of gel has any advantages over the other types. The differences and fluctuations are quite inconsistent and are presumably due to other parameters that are not under control, such as differences in thickness of the soot layer. This would also be the case in reality and is peculiar with cleaning objects.

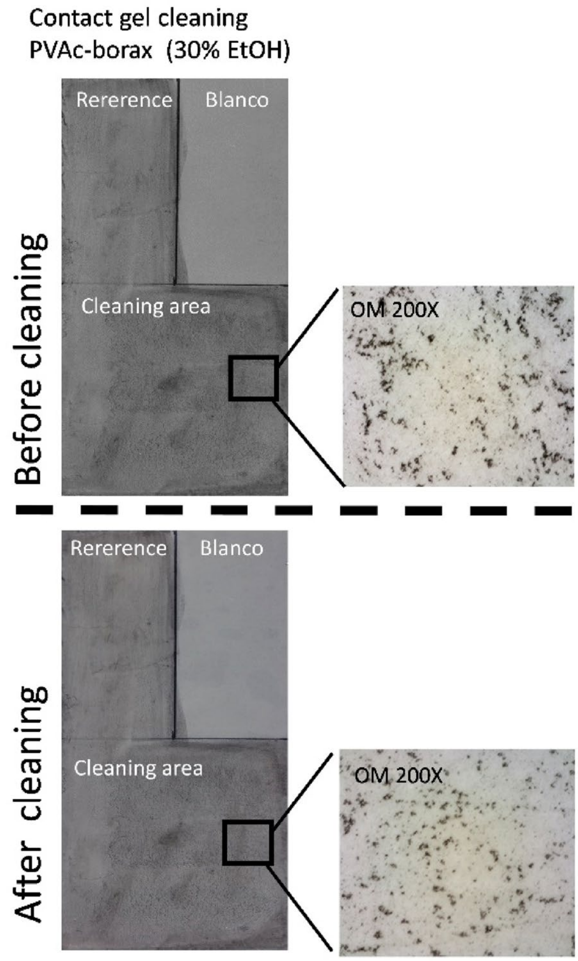

Fig. 4 Contact gel cleaning with PVAc-borax (30%EtOH)

Mechanical gel cleaning

Overall, the mechanical gel cleaning yields cleaning rates that are far more effective than contact gel cleaning and even superior to the traditional methods. A first visual comparison of the sample in which the highest cleaning percentage was measured (gellan gum gel with 30% EtOH without saturation of cyclomethicone) is shown below in Fig. 6. It can be seen that the soot has largely been removed and that the cleaning is fairly uniform. No gel residue can be observed, however at the edges there is a very small material loss. A slightly less effective, but still very good, cleaning can be observed when the gellan gum

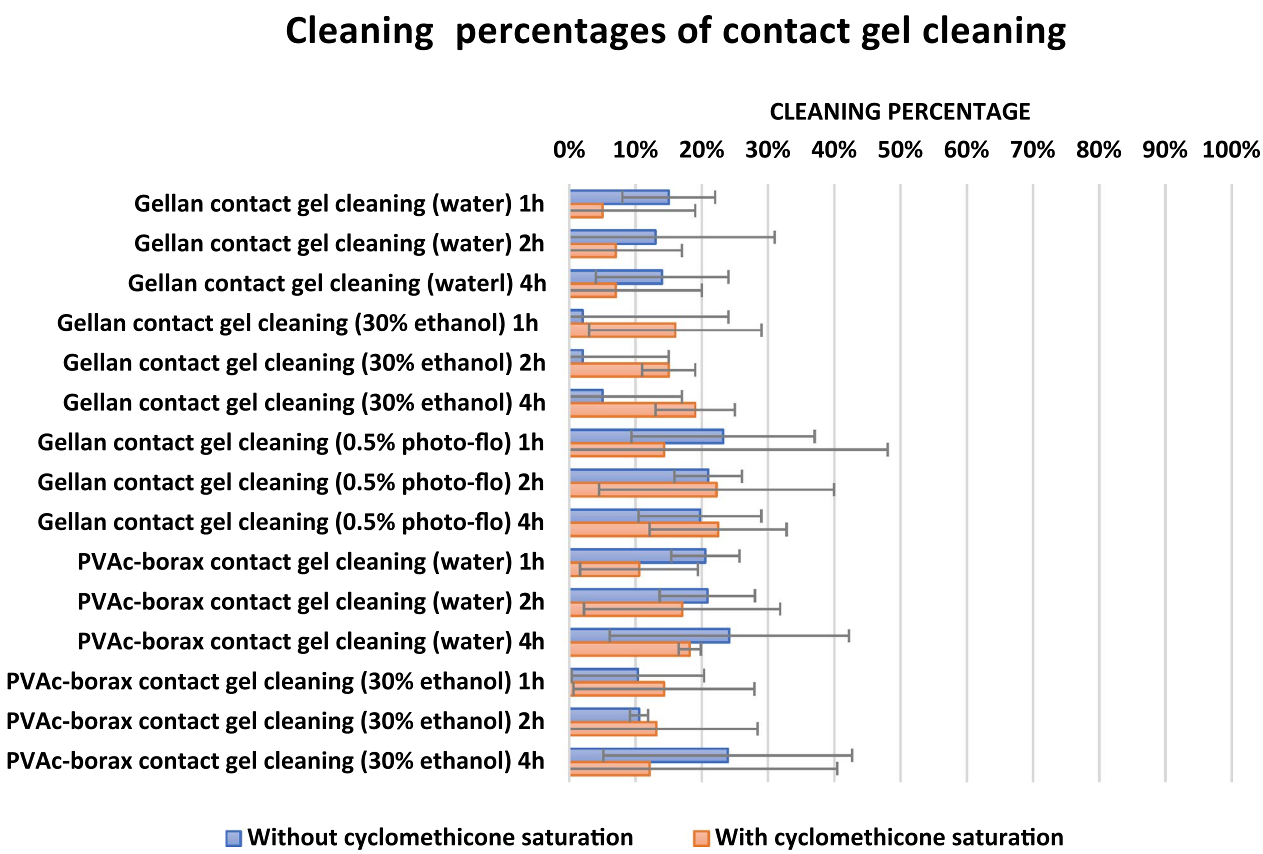

Fig. 5 Cleaning percentages of contact gel cleaning (gellan gum gel and PVAc-borax gel)

gel with 30% EtOH as a granulated particles is used with a cyclomethicone-saturated sample (see Fig. 6). The microscopic images of the saturated samples show that most of the large soot particles have been removed. Similarly, no gel residues can be observed and there is no loss of material. The cleaning methods performed with the gellan gum gel with water and 0.5% Photo-flo are quite similar to those of the gellan gum gel with 30% EtOH. However, there is gel residue left after cleaning (see Fig. 6). Overall, the cleaning results of the gellan gum mechanical gel cleaning are more or less the same. The samples that were not saturated show an effective and fairly smooth cleaning with a slight loss of material at the edges, and the samples that were saturated show a slightly less effective but smooth cleaning without loss of material.

The least effective cleaning methods of this range are those of the PVAc-borax gels. There are noticeable differences between the non-saturated and saturated samples. Here, the non-saturated samples have a fairly good cleaning effectiveness, with the most effective cleaning being the PVAc-borax gel with water. The problem that occurs here, however, is strong material loss (Fig. 7). In places where the gelatine layer is damaged (e.g. small cracks), or at the edges of the sample, the gelatine delaminates during cleaning. The damage is considerably greater than that during cleaning with the gellan gum gels. Furthermore, the cleaning is not smooth, especially at the edges it can be noticed that a large part of the soot is still present in a spot-like pattern. The example shown on Fig. 7 of the PVAc-borax gel with water is also representative of the PVAc-borax gel with 30% EtOH, whereby the gel with EtOH cleans slightly less effectively and is less damaged. In the microscopic images it can be seen that the cleaning is very wave-like, where a number of places were cleaned of soot, but other places are darker due to the presence of soot. This could indicate that the soot particles have been rubbed out over the surface and were not sufficiently absorbed by the PVAc-borax gel. The same method performed on the samples saturated with cyclomethicone does not result in damage and material loss. The PVAc-borax gel with only water removes a large proportion of the soot but does not clean evenly. No residue from the gel can be observed with these methods, as can be seen in (Fig. 7).

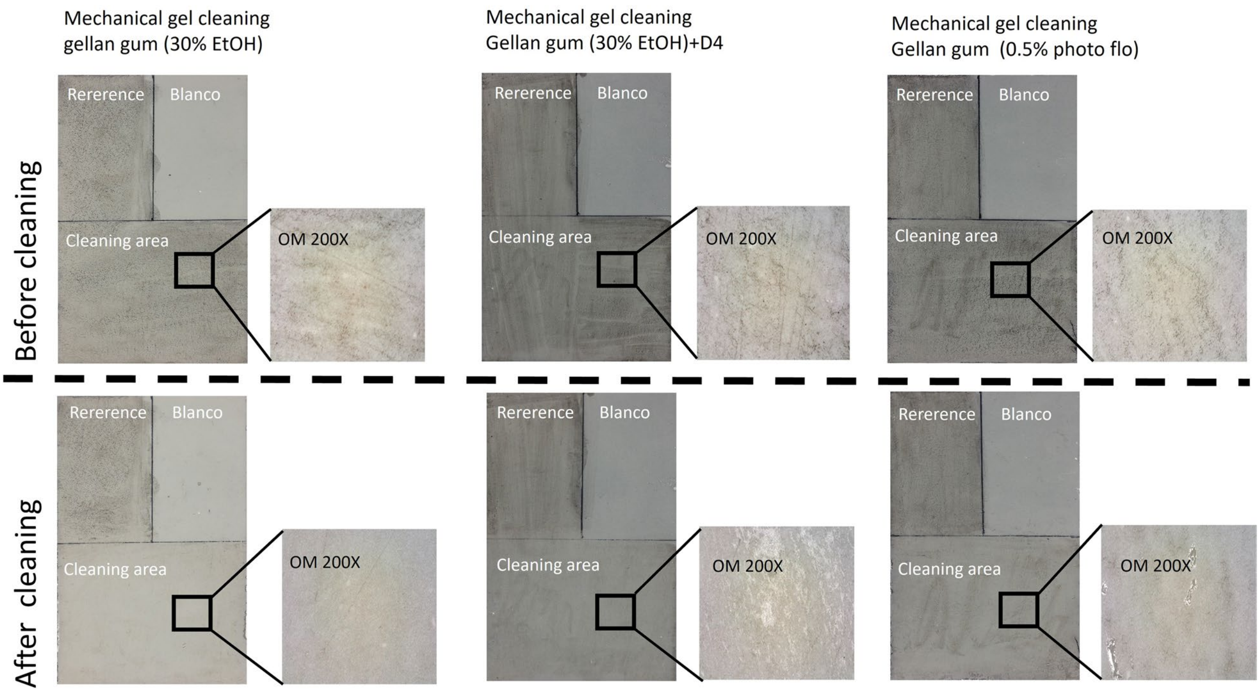

Fig. 6 Mechanical gel cleaning of some samples treated with gellan gum gel. Gel residues can be seen in the OM image of the sample treated with Photo-flo

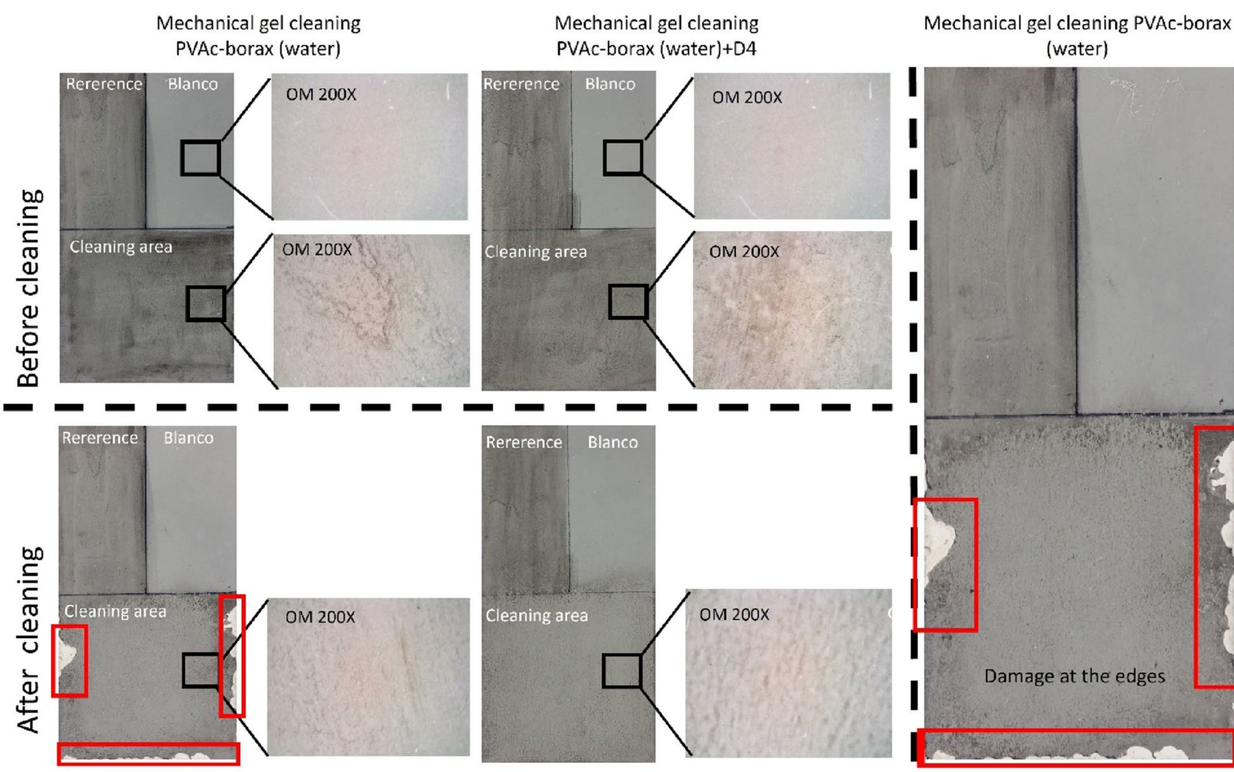

Fig. 7 PVAc-borax mechanical gel cleaning methods of some samples with saturation and without saturation of cyclomethicone D4

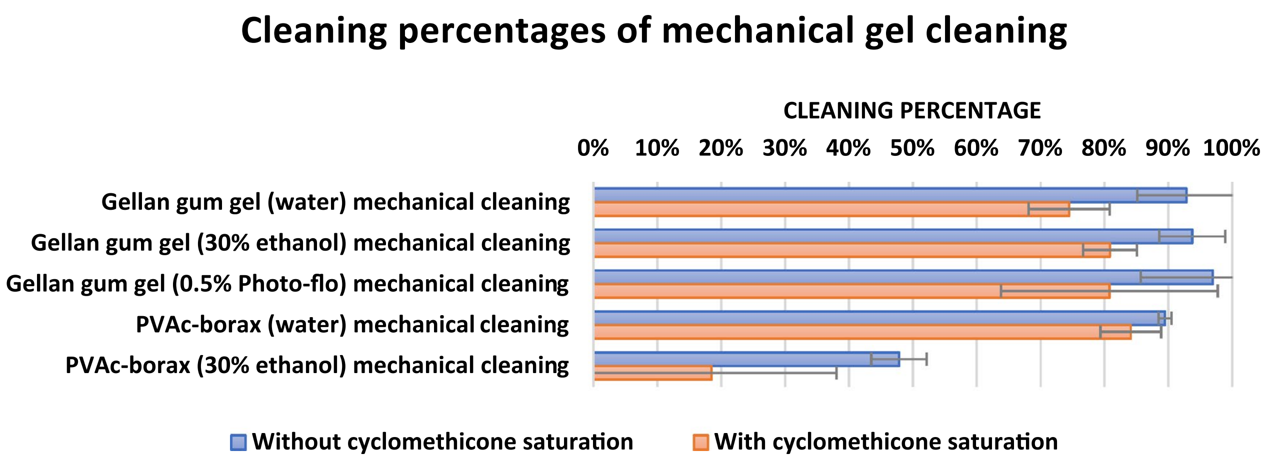

Fig. 8 Cleaning percentages of mechanical gel cleaning

Figure 8 shows the densitometry results of the mechanical gel cleaning methods. Of all the samples tested in this study, these methods gave the best results. The differences are very small and may also be due to the difference in pressure during mechanical cleaning. The most effective cleanings of this series are those with the gellan gum gel in the non-saturated samples, with rates higher than 90%. The least effective methods of this series are the PVAc-borax gels. The PVAc-borax gel with 30% EtOH cleans 48% of the soot in the samples that were not saturated with cyclomethicone and only 18% in the samples that were saturated. The PVAc-borax gel with only water cleans considerably better, with cleaning percentages of 89% (not saturated) and 84% (saturated).

ATR-FTIR results

The ATR-FTIR analysis mostly showed no significant differences between the spectra of the treated samples and that of the reference non-contaminated areas (blanco), as shown in Fig. 9. This confirms that the gels and the solvents caused no detectable chemical changes to the outermost gelatine layer. The only changes can be clearly seen in the spectra of the samples suffering from damage of the gelatine layer, for instance, the non-saturated samples that was cleaned with PVAc-borax loaded with only water. These samples showed some clear changes in the 1200–900 cm^{-1} region of the spectrum (Fig. 10). These changes can be linked to the mechanical damage of the surface gelatine layer caused by the cleaning method. The two bands appearing at 1178 cm^{-1} and 980 cm^{-1} can be in fact assigned to the stretching vibrations of the SO_4^{2-} group of barium sulfate [31–33]. This clearly shows how the protecting gelatine-top-layer was completely removed during the cleaning, exposing the underlying baryta layer.

The spectra presented in Fig. 9 also clearly show how the majority of gel treatments left no detectable residues after the cleaning. The only exception is the sample mechanically cleaned with granulated gellan gum gel loaded with Photo-flo, in agreement with the results of the OM examinations. The spectra of this sample show in fact a relative increase of the intensities of the C-H stretching peaks at ~ 2922 cm^{-1} and 2855 cm^{-1}, together with changes in the 1200–850 cm^{-1} region (in particular C-O stretching at 1148 cm^{-1} and 1024 cm^{-1}, and C-H bending at 893 cm^{-1}) [34], in good agreement with the reference spectrum of the gellan gum (see Fig. 11). These peaks are not present in the non-contaminated areas, which confirms that the spectral changes observed are caused by gellan gum residues remaining on the surface of the prints after the treatment.

Final observations

When using the solvents, there is no clear pattern that shows one solvent has a better effect on cleaning soot than any other. The cleaning result is entirely dependent on a combination of method, solvent, type of gel and saturation. The cyclomethicone saturation reduces the effectiveness with these cleaning methods but with most cleaning methods this loss is quite low, with an average loss in effectiveness of 14.6%. In addition, cyclomethicone reduces the risks of damaging the sensitive gelatine layer. Thus, taking into account the cleaning rate, the gel residues and the surface damage we can conclude that mechanical cleaning with gellan gum (30% EtOH) combined with cyclomethicone D4 saturation gives the best results.

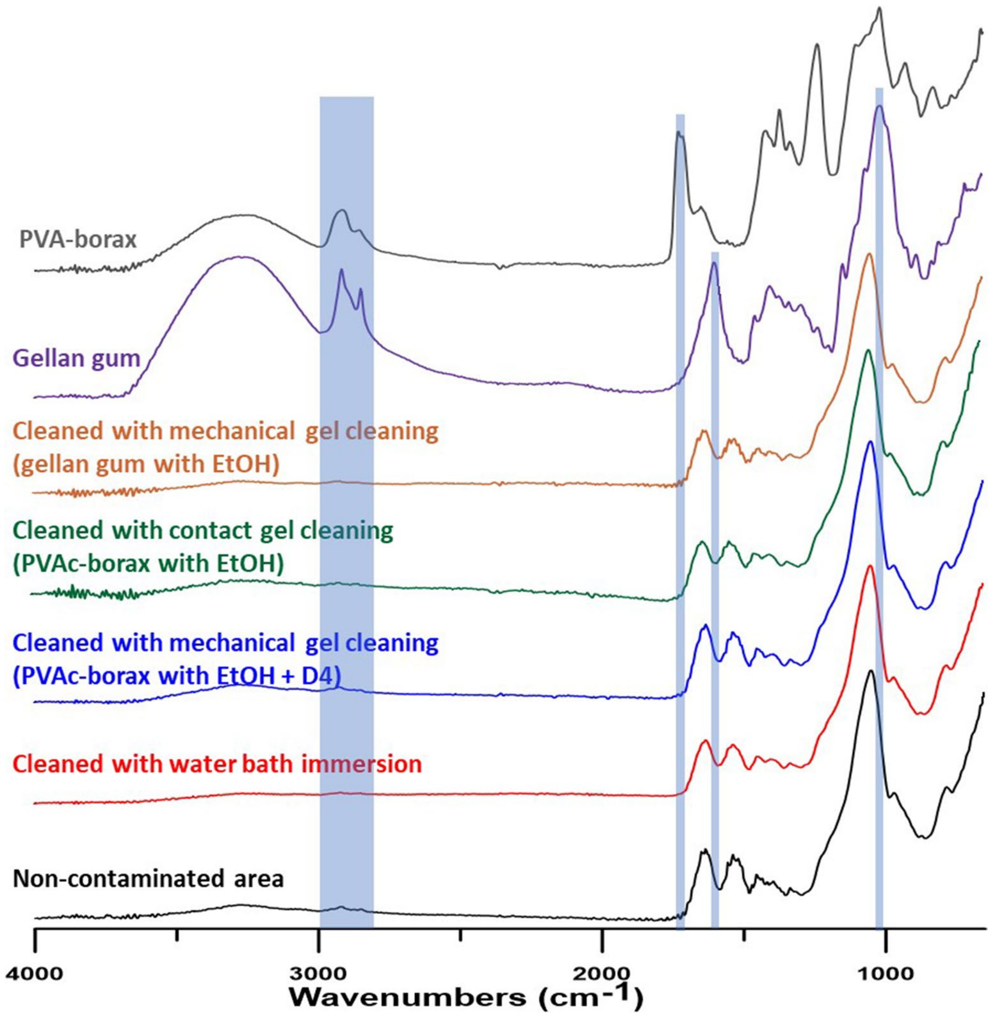

Fig. 9 ATR-FTIR spectrum of a non-contaminated area (blanco) compared with spectra of areas cleaned with different cleaning methods. These spectra show no changes in the characteristic peaks and, in addition, they do not exhibit the characteristic peaks of the gels, indicating that no gel residues remain after the cleaning

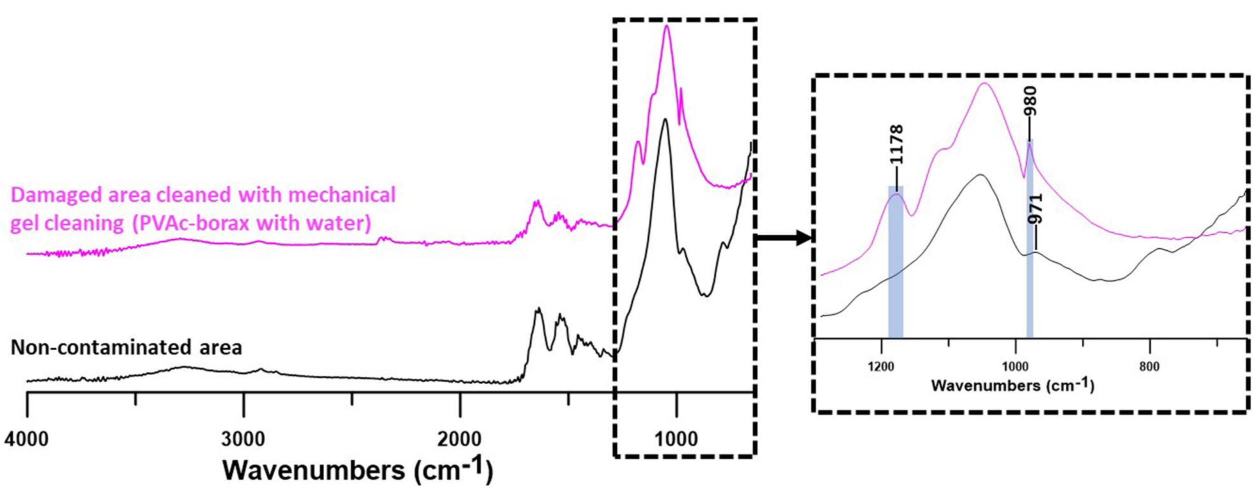

Fig. 10 ATR-FTIR spectra of an area damaged during mechanical cleaning with PVA-borax loaded with only water and a non-contaminated one

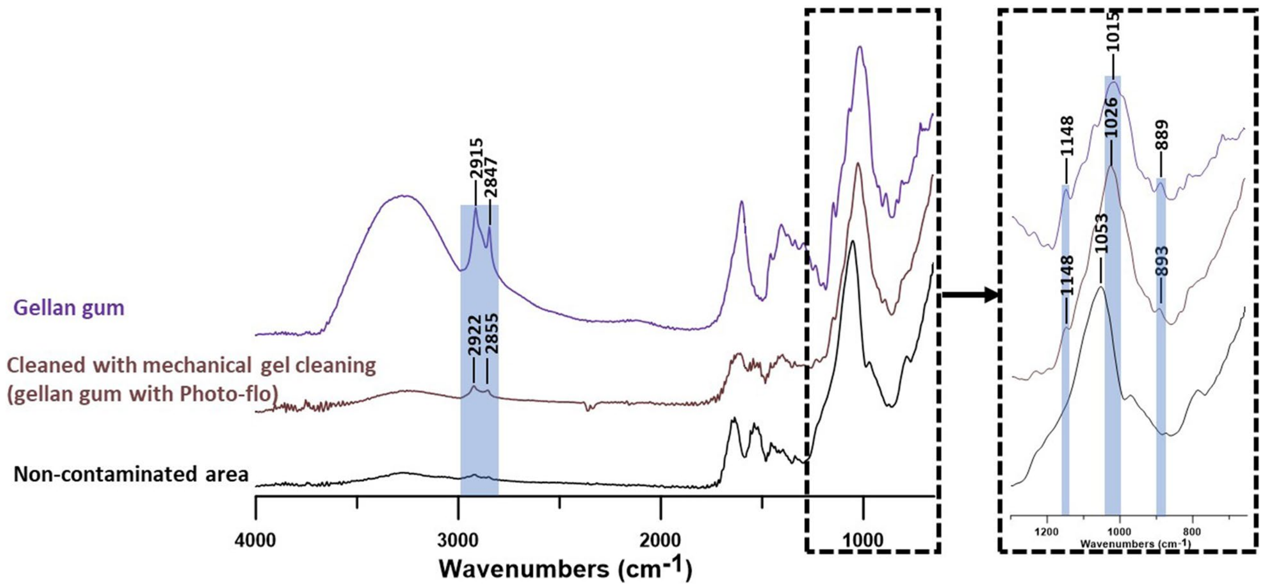

Fig. 11 ATR-FTIR spectra showing the presence of gel residues on the non-saturated samples treated with granulated gellan gum loaded with 0.5% Photo-flo

Case-study on a historical photographic print

The most successful gel cleaning method found in this study is the granulated gellan gum with 30% EtOH on a print that is saturated with cyclomethicone. All other methods have been shown to have flaws: mechanical damage, gel residue or uneven cleaning. To further test this successful gel cleaning method, a practical test was set up by artificially contaminating a historical baryta-based silver gelatine print with soot. The print has no heritage value, but is estimated to be made in the first half of the twentieth century. The contamination process was the same as the one used for the samples. Results were measured in the same way as before. The gel used for this cleaning method was prepared the same as before. Before cleaning, the historical print was saturated with cyclomethicone by submerging it in a bath of 100% cyclomethicone D4 for 10 min.

Cleaning was performed by grating the gel and using the flakes as a granulated gellan gum, as can be seen in (Fig. 12A). Gel flakes were replaced with a fresh batch when they were darkened. The cleaning process was finished when the gel flakes stay clear during the cleaning. After cleaning, the print was air-dried.

The appearance of the silver gelatine prints before contamination, after contamination and after cleaning, is shown in Fig. 12C, D and E. Here, it can be seen that after the cleaning, the legibility of the photo has improved. The most visible soot spots have been removed but not all of them. After cleaning, the photo was still noticeably darker than the photo before contamination. No damage was detected that would have been caused by the cleaning. In Fig. 12 D1 and E1, a microscopic image is shown from the same location before and after cleaning. This image shows that a large part of the soot contamination is removed, but some soot is still present. In addition, no gel residue is visible.

Below, a graph is shown with measured densities on six locations with a different darkness (see Fig. 9B). Densities were measured before and after contamination as well as after cleaning. The cleaning percentages were calculated using the aforementioned formula in "Evaluation methods" Section (Fig. 13). The cleaning performed on this photo was less effective than that performed on the samples. The average cleaning percentage is 30% which is 51% less effective than the cleaning percentage of 81% that was measured with the sample. This difference presumably lies in the different composition and manufacturing treatment of the photo compared to the modern samples. Furthermore, a longer aging process (and thus cross-linking of the gelatine) of the historical photo can have an influence.

However, the cleaning can be called successful. The microscopic and general comparison of the silver gelatine print shows that a great deal of soot particles are removed and the legibility is greatly improved. Furthermore, no residues can be observed and the photo is not damaged. It can therefore be said that the 2% granulated gellan gum gel with 30% EtOH used on a silver gelatine

Fig. 12 **A** Gellan gum gel (2%) flakes with 30% EtOH on the silver gelatine print before cleaning, **B** Location of densitometry measurements **C** Silver gelatine print before contamination, **D** Silver gelatine print after contamination, D1 Microscopic enlargement (200x) before cleaning, **E** Silver gelatine print after gel cleaning, E1) Microscopic enlargement (200x) after cleaning

print saturated with cyclomethicone is a possible cleaning technique that is suitable for works of art.

Conclusion

This research provides a first insight into the use of gellan gum gels and PVAc-borax gels for cleaning silver gelatine baryta-based prints. In this study, an attempt is made to remove soot from the gelatine layer of such prints using these two types of gels. Gellan gum gels were prepared in three ways: only water, loaded with 30% EtOH and loaded with 0.5% Photo-flo. On the other hand, PVAc-borax gel was prepared in two ways: with only water and with 30% EtOH. These gels were applied to aged gelatine print samples in two different methods: (a) contact gel cleaning by placing the gels on the surface and (b) mechanical gel cleaning by rubbing the gel on the surface. These gel cleaning methods were compared with traditional cleaning methods. Additionally, the effect of cyclomethicone saturation of the silver gelatine print on the cleaning result was investigated.

The effectiveness of the different cleaning methods on the silver gelatine prints was investigated by visual comparison, microscopic observation and densitometry. This research shows that the use of both gellan

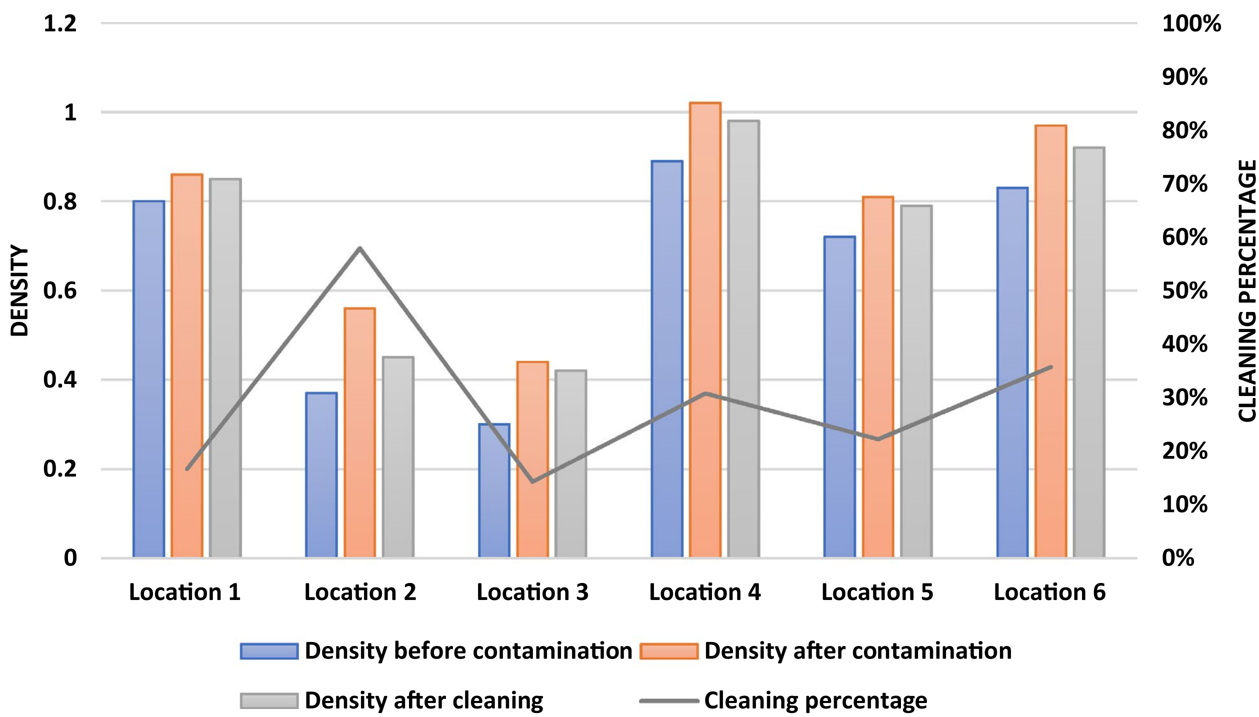

Fig. 13 Density before and after contamination and after cleaning the silver gelatine print

gum gel and PVAc-borax gel as contact cleaning in this case was barely effective. Furthermore, it appears that the mechanical gel cleaning methods were very effective in cleaning soot from these prints, equally effective as the traditional cleaning methods. However, most of these methods have side-effects: the samples that were not saturated with cyclomethicone produce mechanical damage, most mechanical gel cleaning methods left gel residues which was proved by both OM and ATR-FTIR. The PVAc-borax gel with only water produced, despite a very high cleaning percentage, an uneven cleaning effect. There was only one gel cleaning method that was effective in cleaning soot from the gelatine print that had no side-effects, i.e. granulated gellan gum gel with 30% EtOH, which was applied on a gelatine print saturated with cyclomethicone.

The saturation of the samples with cyclomethicone before the treatment provided a very effective mask to prevent damage to the gelatine emulsion during aqueous cleaning. This study shows that cyclomethicone produces cleaning less effective but this remains fairly limited with most cleaning methods. Cyclomethicone was also investigated as a solvent applied by a cotton swab cleaning. Unfortunately, the results showed that this solvent was not very effective as a cleaning tool.

The general conclusions of the research on the mock-up samples, is that most gel cleaning methods either cleaned very little, damaged the gelatine layer or left residues. Only one method achieved a positive and safer results which is the granulated gellan gum loaded with 30% EtOH. These results were confirmed by visual and OM examinations, densitometry and ATR-FTIR measurements. This mechanical gel cleaning method was performed on a silver gelatine print dates back to the first half of the twentieth century. From this it is concluded that, despite a less effective cleaning than the ones measured on the mock-up samples, this cleaning method is suitable for use on works of art.

Further research on the effects of cyclomethicone for use on historical material is needed. The effect of this solvent on the emulsion of silver gelatine prints in the long term is as yet unknown. Neither has this study focused on the possible promotion of fungal growth that could occur due to possible gel residues that were not visible microscopically or within the detection limits of the ATR-FTIR. These parameters would therefore still have to be investigated before this cleaning technique is applied in practice. Furthermore, this study also does not conduct research into changes in gloss due to these cleaning methods. This study is the start of a further elaboration and investigation of a cleaning method with granulated gellan gum gel and cyclomethicone on water-sensitive photographs.

Abbreviations

ATR-FTIR	Attenuated total reflection-Fourier Transform Infrared
EtOH	Ethanol
D4	Octamethylcyclotetrasiloxane
OM	Optical microscopy
PVAc-borax	Polyvinyl acetate-borax

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Author contributions
NO and RA wrote the main manuscript text. RA carried out the experimental work. NO and RA performed the densitometry measurements and OM examinations and interpreted the data. EA contributed to the strategy of the research and revising the manuscript. AM conducted the ATR-FTIR measurements and contributed to their interpretation with EA. Also, GV, KJ, and SC revised the manuscript. All the authors read and approved the final manuscript.

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Declarations

Competing interests
The authors declare no conflict of interest.

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