

## Wet Treatments of Works of Art on Paper with Rigid Gellan Gels

“What cannot he express in monochrome, that is with black lines! Light, shade, splendour, the sublime, depths...”

Erasmus of Rotterdam, on the work of Albrecht Dürer

### ABSTRACT

Since 2003, the ICPAL Laboratory for the Conservation of Library Materials in Rome has been developing a conservation method to carry out cleaning interventions on works of art on paper using rigid aqueous Gellan gels, a microbial exopolysaccharide that allows a constant and controlled release of water onto the paper. The adoption of this method, which has been modified by research carried out during cleaning interventions on moveable paintings, is a result of the need to find a technique that—in comparison to traditional ones—minimizes the effects of aqueous swelling, guaranteeing the maintenance of the codicological aspects of the artefact and which takes into account that, in this type of work, paper not only plays the role of support for graphical media but is an integral part of the image itself. The mechanism of exchange that is established between the paper and the gel during treatment allows the effective removal not only of surface deposits but also of a part of the substances that are present within the paper that are responsible for its acid degradation. The effectiveness of this technique in terms of cleaning (which is attested by the variations in pH measured on treated works) can be equated to the effectiveness of the traditional system of washing with water. The technique of rigid aqueous gel has also recently been used on other types of more structural interventions, such as the removal of auxiliary supports, the removal of adhesives using enzymes and the preservation problems that are inherent to modern graphic works, generally characterised by an intrinsic fragility and chemical instability. This paper illustrates the results achieved on original works whose degree of opacity, average pH value and degree of whiteness were measured before and after treatment.

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### THE CLEANING INTERVENTION

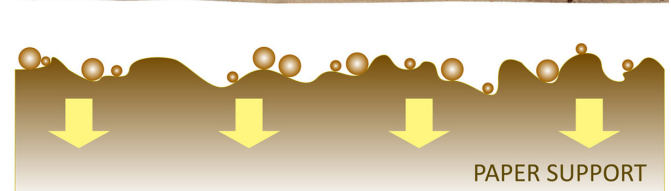
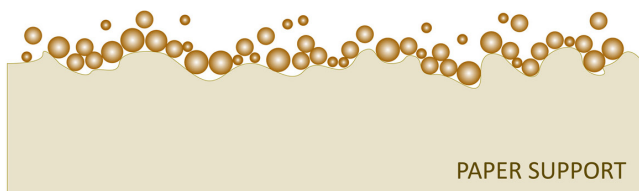
Surface cleaning of a work of art on paper is the intervention aimed at removing inorganic and organic substances which, over time, have deposited and been partly encompassed within the paper's surface. Given its completely irreversible nature, the operation must be carried out by using the difference in solubility between the substances present in the original materials and what has to be removed as a reference, and by carefully assessing the changes that can be seen on the work during the operation. While in other categories of artistic artefacts—such as movable paintings and frescoes—cleaning can be carried out selectively in line with the nature and stratification of the materials that they are made of, an intervention on a work of art on paper is much more structural as it involves the artefact in its entirety. The principal preservation issues that this type of work has for cleaning are ascribable to the high hygroscopicity of paper which, as well as being one of the most important characteristics of this material, is also responsible for the change in many of its properties. For example, the interactions that are established between the surface of the works and the airborne particulate matter (PM) that is deposited on them over time, can be caused by various factors such as the nature and dimensions of the particulate matter, the physical forces (Coulomb's law, ionic and weak secondary reactions such as hydrogen bonds and Van der Waals force) which develop to keep the PM on the surface and by several characteristics of the paper support. The most influential of these are the chemical structure of the paper support, the varying surface roughness and—above all—the degree of hygroscopicity. For example, in the presence of relatively high humidity (generally  $\geq 65\%$ ), water can condense between the airborne particulate matter and the surfaces of the artefact, acting like an adhesive between them. Generally speaking, the more permeable the material is to humidity, the more hygroscopical the surface is and the more easily water can condense on it in a way that holds the PM deposited there. Likewise, the more hydrophobic the paper, the less water will be able to act as an adhesive after

its condensation (Wolbers 2005, 13–20). Paper's propensity to absorb humidity is also at the heart of a further factor of degradation given that—over time—a consistent part of the deposits that are initially present only on the outer layer of the work, tend to penetrate into the paper support, transmitted by the molecules of water that the material absorbs in its continuous attempt to reach hygrometric stability with its atmospheric surroundings. The effects of this phenomenon, in most cases, consist of processes of chemical degradation associated with structural and chromatic alterations that profoundly modify the aesthetic aspect of the images (figs. 1–2). In addition to guaranteeing the maximum level of aesthetic legibility of the work, the cleaning intervention must in these cases also ensure the chemical stability of the paper support. Water, if used as a solvent, represents the ideal method to satisfy these preservation needs. As well as performing its intrinsic dissolving power for hydrophilic organic and

inorganic materials, water—by acting as a highly dielectric medium—is also able to partially or completely eliminate the aforementioned adhesive forces that fix the insoluble substances in the surface. However, the high level of porosity and hygroscopicity that characterise paper, together with the state of preservation and the morphological characteristics of the original material, can pose a risk factor in the use of water (or other solvents) in its free state.

#### TRADITIONAL SURFACE CLEANING TECHNIQUES

A traditional surface cleaning technique involves treating the surface of the paper support with a hydroalcoholic solution applied with swabs. Although it is reduced by the presence of alcohol, the heightened surface tension that characterises water gives the solution a limited washing power and very high sub-surface penetration, which do not allow us to check how many



Figs. 1–2. José de Ribera, *Poeta*, etching, sec. XVII. Simulation on the work of the effects caused by the penetration of the airborne particulate matter (PM) within the paper support

of the dissolved substances remain on the surface and how many—on the other hand—penetrate within the paper support. The scant opportunity to control the solvent and the high hydrophilicity of the paper can provoke excessive swelling of the cellulose fibres and thus cause tensions, deformations and tide lines that are difficult to remove. An alternative to this technique is based on the principle of the gelification of the water with adhesive substances such as ethers of cellulose, which are able to modify the surface properties of water in a way that gives the solvent an increase in its washing power whilst considerably limiting the aforementioned problems. At low concentrations in water (1–2%) and applied with a brush, these substances act as a mild surfactant that is able to generate a foam that facilitates the removal of the unwanted material (fig. 3). Particulate matter of varying origin, which has more tenaciously penetrated the fibrous surface interlacing, is trapped in the foam generated by the methylcellulose and is then removed with hydrophilic cotton swabs. The operation unavoidably results in a high level of interaction with the paper support which undergoes excessive physical-mechanical stress, caused above all by the inevitable swellings produced by the localised transfer of humidity, with the emergence of tensions between the treated areas and the surrounding dry areas. Furthermore, the use of the brush causes an inevitable mechanical stress that can not always be adequately controlled due to the development of the foam, which obstructs the operator's clear view of the support. With works in a state of preservation that is already precarious, this technique can also cause further damage such as the raising and ripping of fibres which can cause paper delamination with a substantial decrease in its original thickness and coefficient of absorbency (fig. 4). A further disadvantage is posed by the difficulty that is found, at the end of the treatment, in removing the residues of a gel based on cellulose ethers. After the evaporation of the solvent, these substances actually form an elastic and adhesive film that sticks to the outer surface of the single fibres. Thus it is necessary to systemically conduct washing, with the purpose of removing tide lines that have developed in the bordering areas between the treated and untreated areas and in order to remove the residues of the gelling agent. Traditional washing with a hydroalcoholic solution (80% water and 20% ethyl alcohol) applied with a swab does not always prove effective given that the dilution of the “adhesive-gelifying agent” can promote its further migration into the fibrous interstices of the paper. In addition to the generic contraindications in terms of preservation that we have listed so far, this method is particularly dangerous when it is used for the cleaning of graphic works of art as it permanently alters the original morphology of the support. As well as causing a lowering in the original porosity of the support, the irreversible input of adhesive substances used improperly as gelling agents is also responsible for the loss of opacity of the paper because it lowers the optical discontinuity. For example, the refractive index of CMC (carboxymethyl



Fig. 3. Surface cleaning with aqueous gel of hydroxyethyl methyl cellulose

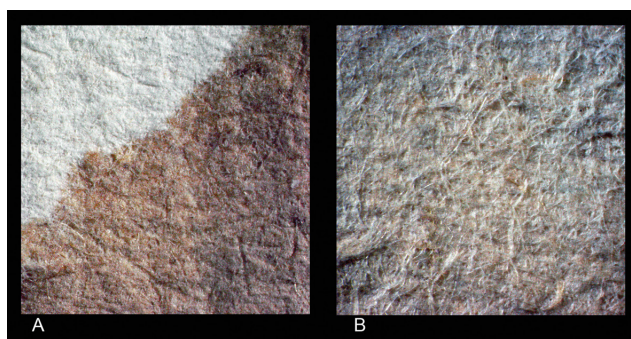


Fig. 4. The texture of a handmade sheet of paper pre-1635 (felt side) before (A) and after (B) surface cleaning with hydroxyethyl methyl cellulose at 2% in water followed by removal with a hydroalcoholic solution. Stereo microscope photograph (40x)

SUBSTANCE	REFRACTIVE INDEX
Cellulose	1,55
CMC Film	1,51
Loads (CaCo <sub>3</sub> )	1,5/1,6

Fig. 5. Comparative table of refraction indices of cellulose, calcium carbonate and dry carboxymethyl cellulose

cellulose) when dry in fact results as very similar to that of the cellulose: when the ether spreads into the inter-fibre spaces it gives it greater homogeneity because it seals the empty zones previously occupied by air, creating ‘continuity’ between one fibre and another (fig. 5). This phenomenon makes the paper more compact and uniform from an optical point of view, making it more transparent to light, to the detriment of the legibility of the image.

### THE AESTHETIC ROLE OF PAPER IN THE CONTEXT OF GRAPHICAL WORKS

The irreversible changes that paper undergoes using the aforementioned interventions jeopardise two of the fundamental functions that this material has for graphical works: the role of support of the work—including its historical value represented by a series of codicological elements contained within it—and its role as the material that is essential, together with graphical media, for bringing images to life. As can be seen in the precepts of ancient painting manuals, artists' choice of materials to be used in their works was made in relation to the graphic result that they wanted to achieve. The choice of paper destined to support their graphical work, for example, did not occur by chance but on the basis of very precise technical characteristics such as the degree of whiteness, brightness, compactness and uniformity of the surface—all particularly accentuated on the *felt* side of the sheets compared to the *wire* side, which is instead characterised by a high surface macro-roughness (fig. 6). Generally speaking, very thick paper was used for drawings with inks or pigments in solution, and thus the paper was very opaque and was characterised by a consistent surface sizing. The more homogenous side (the *felt* side) was used, as it allowed a better distribution of the colours applied with the pen or with the brush. If, on the other hand, the artist chose to use solid colouring substances for his composition, the drawing was done on the *wire* side of the paper as the roughness present on this side facilitated the adhesion of the pigments to the paper support (Armenini 1988 [1586], 60) (fig. 7). With the advent of printing between the 15th and 16th centuries, *original* engraving—both xylographic and chalcographic—took hold in the search for the autonomous expressive qualities of every individual technique, as engraving had now been released from its traditional duties of text interpretation and the reproduction of pictorial works. The spread of this new artistic means of expression caused further technical diversifications in the field of the process of papermaking. As concerns engraving, artists—for example—needed paper that had the best ability to exalt the intrinsic singularities of the chosen techniques and the chromatic performance of their compositions. In one of the first “technical manuals” on the art of printing (Zonca 1607, 77–78), thin paper is recommended for etchings, whilst for burin engravings—characterised by very deep cuts—very thick supports were recommended. For example, Albrecht Dürer used paper with different characteristics for his works. According to studies carried out by Joseph Meder (Meder 1971), the German artist used paper with the watermark of the Bull's Head or the High Crown for his works commissioned by the most prestigious of patricians (fig. 8), whilst in etchings by Rembrandt, paper with the *Giullare* (jester) watermark is recurring (Ash-Fletcher 1998) and present in many variations. The first essential characteristic was the brightness

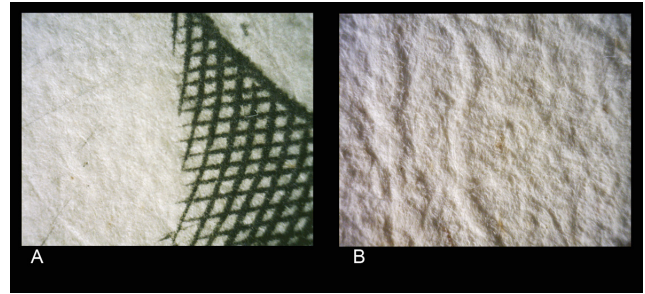


Fig. 6. (A) Felt side of paper support; (B) Wire side of paper support. Digital video microscope (50x)



Fig. 7. Anonymous work from the early 16th-century, Testa di donna. Natural pietra rossa on white paper

and degree of whiteness that only paper made from raw materials of excellent quality and rich in loading substances had. Thus the paper had to be obtained from a sufficiently refined pulp that made it more uniform and compact, and which was therefore better able to reflect the light in order to exalt the luminosity of the lighter tones achieved exclusively by exploiting the whiteness of the support. A good level of refining of the raw material was also essential in order for the paper to have a degree of plasticity that was sufficient to

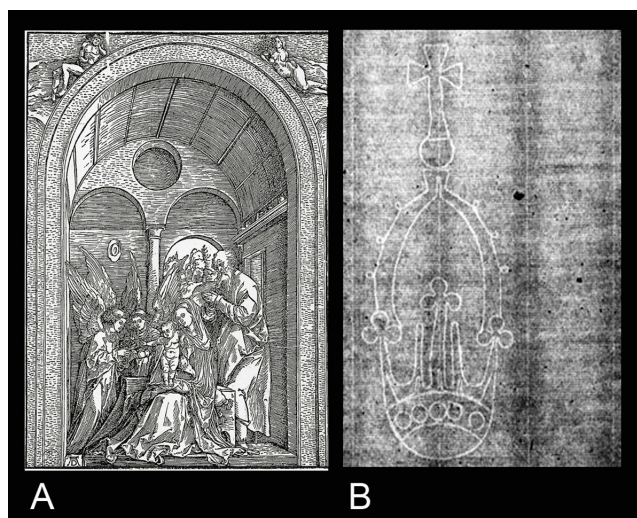


Fig. 8. (A) Albrecht Dürer, *The Holy Family with two angels in a vaulted hall* (1503–1504), burin engraving; (B) High crown watermark, Meder 20

receive the printing marks: the permanent structural modification caused by the pressing of the matrices on the paper which gives the final image an unmistakable material aspect. The paper was thus dampened before proceeding with the printing in order to increase its ductility and also to promote the absorption of the ink. This guaranteed the distinctness and the legibility of the individual graphic signs which, transferred onto the support, took on typical and clearly identifiable conformations, according to the technique adopted by the artist (Griselini 1770, 22). In the case of chalcographical engravings, thin surface rises were obtained in line with the grooves of the metallic matrix in which the paper penetrated; the surface layers of the paper therefore absorbed a more or less significant quantity of the ink that was deposited on it, creating the so-called ‘chalcographic relief’, identifiable on the *recto* of the work and, in the case of more significant stretches, even visible on the *verso*. In the case of xylographic

works, the paper underwent heavy pressure of the ‘full’ zones of the wooden matrices, thus giving it a structural deformation in the opposite direction to that of chalcographic works and visible both on the *recto* and on the *verso* (fig. 9). The level of refining however had to not be so forced as to totally uniform the dimensions of the fibres dispersed in water. This phenomenon would have increased the transparency of the support, compromising another important optical characteristic required by the artists: the ability to sufficiently contrast the graphical media on the *recto*, preventing the unwanted phenomenon of visibility on the *verso*. An excessively refined pulp would also have caused an increase in the points of optical contact between the cellulose fibres, which would result in a material that was structurally more compact and homogeneous but at the same time more transparent to light. Similarly to what already occurred for drawings, paper used for *original* engraving also fully took part in defining the *chiaroscuro* of the image in terms of light or maximum luminosity (de Denaro 1994, 104–112). In order to demonstrate this, we can refer to a small but symptomatic variant introduced by artists in works produced after the 16th century, relating to the placing of the artist’s signature on the work. On drawings, this is no longer present on the surface of the paper involved by the image but is placed in very marginal areas of the sheets (just as happened on paintings) or removed. In engravings, monograms or dates, which were abbreviated according to the circumstances, appeared within the engraved image in rocks or hanging from trees like *ex-voti*. In line with what was stated by Erwin Panofsky about Albrecht Dürer’s work, there is thus the conjecture that “the artist urged the spectator to interpret the paper not only as the material sheet on which the characters could be printed as if they were printed on the pages of a book, but as an imaginary plane of projection through which the pictorial space and its contents are seen” (Panofsky 1979, 111). During the 16th century, the stylistic evolution of engraving techniques, increasingly prone to emulating the effects of contemporary painting, radically transformed the traditional link between the image and the paper support, giving the latter

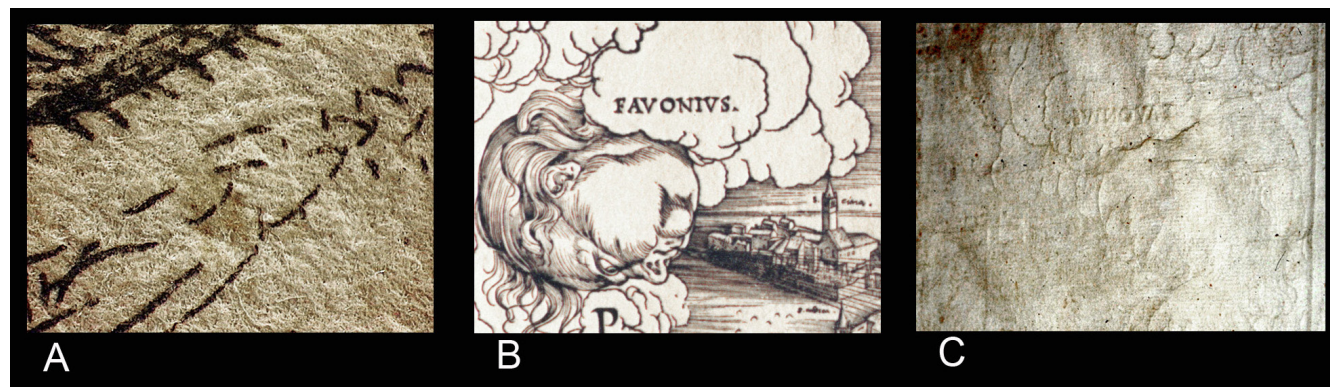


Fig. 9. (A) Salvator Rosa, *Soldato*, etching (sec. XVII), close-up of the chalcographic cut with a microscope (15x); Jacopo de’ Barbari, *Venetie M.D.*, woodcut printed on six sheets (1500). Close-up of the printing ink marks on the *recto* (B) and on the *verso* of the woodcut (C)



Fig. 10. Ugo da Carpi, Diogenes, a woodcut after Parmigianino (1526–27), chiaroscuro woodcut on paper



Fig. 11. Raffaello Sanzio. Madonna, Bambino, Santa Elisabetta e san Giovannino (1507). Pen, watercolour inks and highlighting with white lead

the further function of 'colour'. With the *cameïeu* and xylographical *chiaroscuro*, together with the varied range of grey tones induced by the *peintre-graveur* in their chalcographic engravings, the graphical developments covered almost all of the surface of the supports with the intention of using paper exclusively as a colour, using its white colour for the definition of highlighting (Ficacci 2006, 45–49) which, in drawings, was however produced with the positioning of pigmented layers on top of each other (figs. 10–11). Before carrying out surface cleaning, it is therefore necessary to carefully assess the level of interaction that traditional techniques currently used can cause on this type of work, even when they are carried out professionally. The uncontrolled introduction of sources of humidity or additional substances that is seen in current methods can in fact alter the original characteristics we have mentioned, relating both to the surface aspect and to the structural conformation of the paper. These are aspects that, for the aforementioned reasons, represent an undeniable priority. Although it is not possible to prevent the material from coming into contact with sources of humidity (above all when it undergoes a conservation intervention), it is nevertheless necessary to optimise the use of water, minimising its impact on the paper. Thus experimentation was begun on techniques that are alternatives to the ones described in this paper so far, aimed at the use of rigid aqueous gels, which have been successfully tested in other conservation sectors (Anzani et alii 2007).

#### RIGID AQUEOUS GELS

Rigid aqueous gels or hydrogels, widely used and tested in the cleaning of paintings following the work of Richard Wolbers, are formed of long polymeric chains dispersed in water. Given the hydrophilic nature and the particular type of interaction with water, these are commonly defined as hydrocolloids or substances that—in certain conditions—take on specific structures capable of holding and trapping the molecules of free water that they are put into. In other words, they are able to gelify, forming networks that hold water, reducing its spread and stabilising its presence. Generally speaking, the sol-gel transition of rigid gels follows the *coil to helix* model when hot solutions are cooled at room temperature. Hydrogels can be formed from various natural composites, such as Agar agar (Campani et alii 2007) and Gellan, a linear, anionic heteropolysaccharide produced by a microorganism (*Sphingomonas elodea*). Its structure is based on a tetrasaccharide repeating unit composed of (1-3)- $\beta$ -D-glucose, (1-4)- $\beta$ -D-glucuronic acid, (1-4)- $\beta$ -D-glucose, and (1-4)- $\alpha$ -L-rhamnose as the backbone. Gellan gel in native form is esterified with L-glycerate and with acetate at C-2 and C-6 (approx. 50%) positions of the (1-3)-linked D-glucose, respectively. Gellan gel forms different types of gels depending on acyl contents (Bajaj et alii 2007, 341–345) (fig. 12). The gelation process is generally considered to involve two

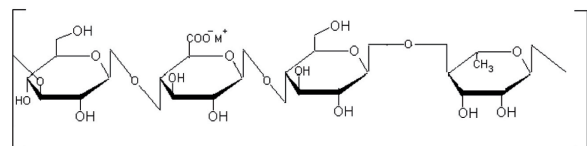


Fig. 12. Primary structure of deacetylated Gellan gel

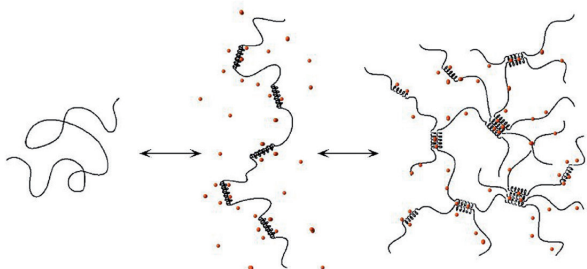


Fig. 13. Gellan gel coil-helix transition scheme. The stabilisation of the gel is caused by the presence of  $\text{Ca}^{++}$  ions. Image taken from M. Caggioni, P. T. Spicer, D. L. Blair, Rheology and microrheology of a microstructured fluid: The gellan gum case, in: "Journal of Rheology", 51-5 (2007) pp. 851-865

separate thermo-reversible steps. Molecules of Gellan gel are in a disordered coil (single chain) upon heating in aqueous solutions. The molecules transform into an ordered double helical conformation upon subsequent cooling, followed by associations between the helices through weak interactions, such as hydrogen bonds and Van der Waals forces (fig. 13). The deacetylated type forms hard and brittle gels in the presence of cations (especially  $\text{Ca}^{++}$ ) that are able to promote and stabilise the ordered "crystalline-like" structure of the gel at the end of the transition process. The compactness of the molecular structure, obtainable by hydrating low acyl Gellan gel in aqueous solutions containing  $\text{Ca}^{++}$  ions thus produces a gel with a molecular weight equal to  $2\text{-}3 \times 10^5$  Daltons. The rheological properties highlight a structure that has a very high degree of visco-elasticity, and is filmogenic, homogenous, transparent, and very stable both at high temperatures and at pH variations (Sworn 2009, 204-227 and Shah-Jani 2009, 48-58). The gelling agent, tested in terms of effectiveness and biocompatibility (Pszczola 1993, 94-96), has a very widespread use in different production areas such as the food industry, as well as the biomedical and pharmaceutical industries and in the field of biological and microbiological research. For the purpose of selecting the product that best responded to the requirements of a conservation intervention on paper, a series of tests were carried out on samples of ancient paper, comparing Agar agar and Gellan, prepared at different concentrations, and applied to the surface to carry out contact cleaning. As well as being more transparent than Agar agar (fig. 14), the rigid gel obtained from Gellan was more effective in terms of water retention, above all at low concentrations of 1-2% (fig. 15). Given that one of the fundamental requirements for



Fig. 14. José de Ribera, Poeta, etching (sec. XVII). Top, a close-up of the work before treatment. Bottom, a sample of surface cleaning of the work with Gellan at 3% on the left and Agar agar at 3% on the right

W/Agar	10 minutes	18 hours
W/ H <sub>2</sub> O	242%	270%
W/Agar 1%	177%	206%
W/Agar 2%	150%	193%
W/Agar 3%	126%	175%
W/Agar 4%	125%	163%

W/Gellan	10 minutes	18 hours
W/ H <sub>2</sub> O	242%	270%
W/Gellan 1%	155%	182%
W/Gellan 2%	132%	174%
W/Gellan 3%	125%	149%
W/Gellan 4%	92%	122%

Fig. 15. Comparison of percentages of increase in weight in samples of Whatman paper (cat. no. 1001090) immersed in 200 ml of water and placed in contact with Gellan and Agar agar at increasing concentrations, for 10 minute and 18 hours respectively. Readings carried out with Wunder scales at 26°C and RH equal to 55%

the application of this technique is the necessity to be able to modulate the level of water transferred to the paper and to be able to monitor both the work and the process of extraction of the substances to be removed, the subsequent tests were carried out with rigid Gellan gels. Between 2003 and 2008, cleaning interventions were carried out with Phytigel Gellan prepared at different concentrations (Iannuccelli-Sotgiu 2004,

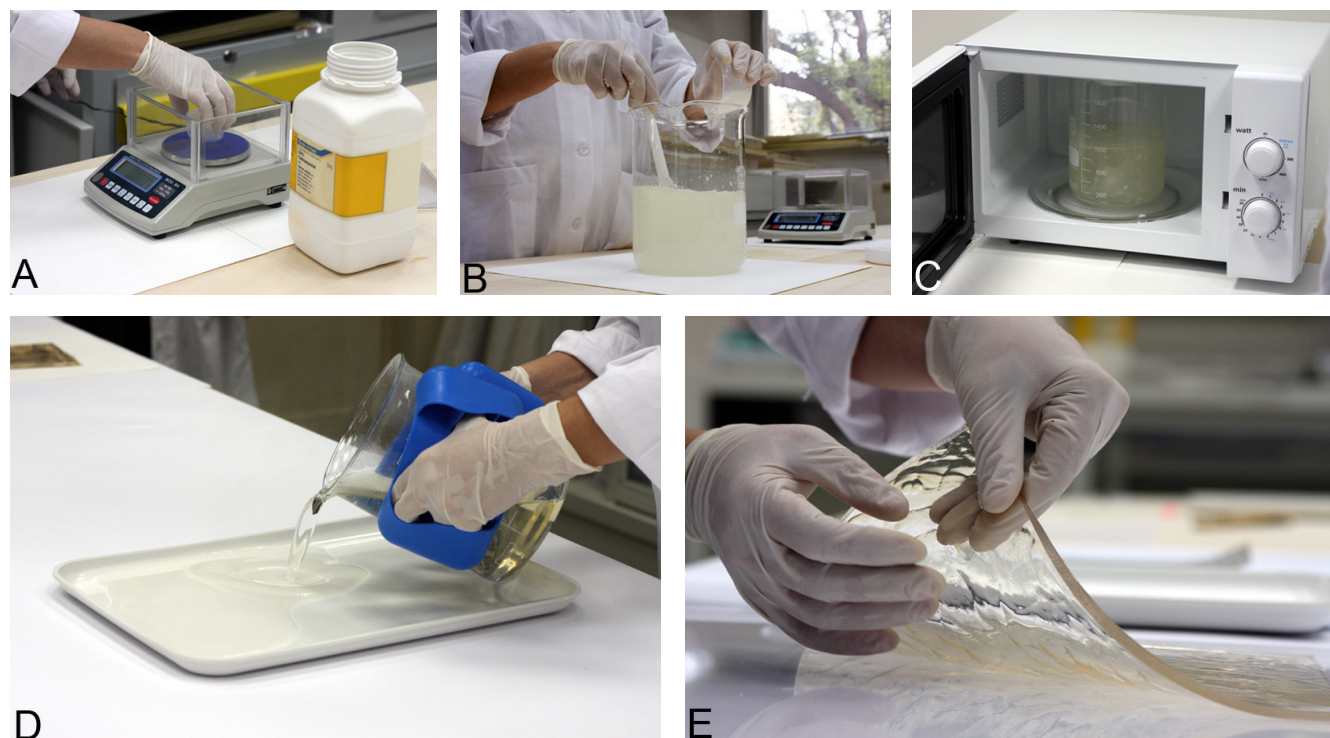


Fig. 16. (A) a saline solution of calcium acetate at low concentrations in deionised water (0.4g/l); (B) addition of Gellan powder to the saline solution; (C) the complete hydration of the colloidal dispersion is obtained by heating the compound to boiling point; (D) pouring of the solution in a basin (E) a gel obtained upon cooling of the hot solution

15–24). Subsequently two other brands of Gellan available on the market were tested: Gelrite and Gelzan CM, in addition to Phytigel. The aim was to widen the range of Gellans that can be used. Out of these three, Gelzan CM was chosen as it offers greater transparency and better stability at equal concentrations, as well as the capacity of gelifying deacidifying aqueous solutions based on calcium propionate (Iannuccelli-Sotgiu 2010, 73–94). A valid alternative however is Kelcogel GC-LA, which is equally effective and is much more economical and produced by the same company (CP Kelco Inc. (<http://www.cpkelco.com/products-gellan-gum.html>)).

#### RIGID GELLAN GEL PREPARATION METHOD

As the mechanism of gelation, in addition to being directly influenced by temperature, is correlated to the presence of bivalent cations in water, it is necessary to gelify a saline solution based on calcium acetate,  $\text{Ca}(\text{CH}_3\text{COO})_2$  (0.4g/l) which provides the  $\text{Ca}^{++}$  ions needed to stabilise the structure taken on by the polymer in the gel phase. The quantity of Gellan powder, which is calculated according to the concentration that is desired, is then added to the saline solution. At low concentrations in water (1–4 %), Gellan gel forms a thermoreversible gel in which temperature plays a fundamental role. The three-dimensional network that characterises Gellan

gum is so compact that, if the polymer is placed in water at room temperature, there is no homogenous colloidal dispersion. It is in fact necessary to heat the compound to boiling point to allow the complete hydration of its structure. While it is still liquid and runny, it is poured into a specially chosen basin and allowed to cool. The gelification of the dispersion happens rapidly once it cools to a temperature of between 40 and 30 °C (fig. 16). Gel made in this way can be kept in the fridge for 1–2 weeks if it is sealed with waterproof cling film used for food conservation.

#### SURFACE CLEANING WITH RIGID GELLAN GELS

Once the physical-mechanical stability of the inks has been tested, the application method for printed graphic works consists of directly placing the Gellan film on the *recto* of the work, which is lying on a polyester sheet. In order to ensure complete uniformity of contact between the two surfaces, we suggest exerting light manual pressure using another polyester sheet placed on top of the gel. To contain the evaporation of the water held in the Gellan film and keep the level of humidification constant over the entire surface of the work, the ‘sandwich’ is placed under moderate pressure using a sheet of crystal which—thanks to its transparency—allows us to constantly monitor the treatment (fig. 17). Whilst the



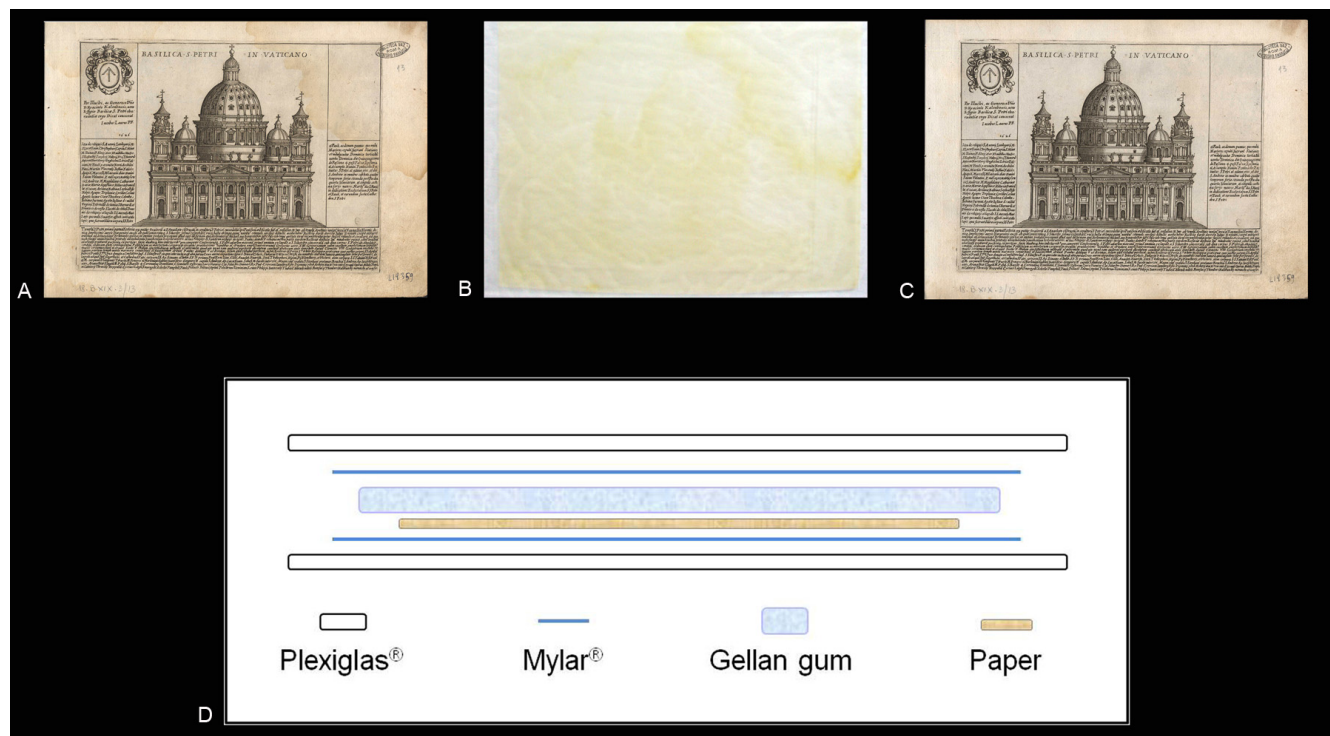


Fig. 17. Giacomo Lauro, Basilica S. Petri in Vaticano (1626), burin engraving. (A) before cleaning and (C) after treatment; (B) the clearly yellowed gel after treatment; (D) scheme of the application of the gel on a burin engraving

gel gradually releases water molecules onto the underlying paper, the most common degradation elements present on it are picked up by the Gellan film which, following application, visibly yellows (fig. 18). One of the possible causes of this chromatic alteration is due to the migration of products of the acid degradation of the paper and thus of water-soluble organic acids ( $R-COOH$ ) that are transferred into the gel from the paper support, the final pH value of which is always higher after contact with the film. The pH values of Gellan prepared at different concentrations (2, 3 and 4%) were measured before and after application on paper supports that were heavily oxidised or acid. The average difference of the pH values of the gel were equal to one point, whilst the pH value of the paper was raised by around one and a half points. The physical phenomenon that takes place during treatment in fact consists of a process of exchange between the paper and the gel. In the initial phase, the water tends to spread spontaneously in the paper, solubilising acid degradation by-products of cellulose. Subsequently, the concentrated solution of these products, present in the inter-fibre spaces of the paper support spreads according to the gradient of concentration from the paper to the gel (Lienardy-van Damme 1990, 23–30). Thus the treatment is not only limited to the removal of PM, but most likely it is able to carry out a cleaning action that is similar to actual washing with water. Measurements conducted by

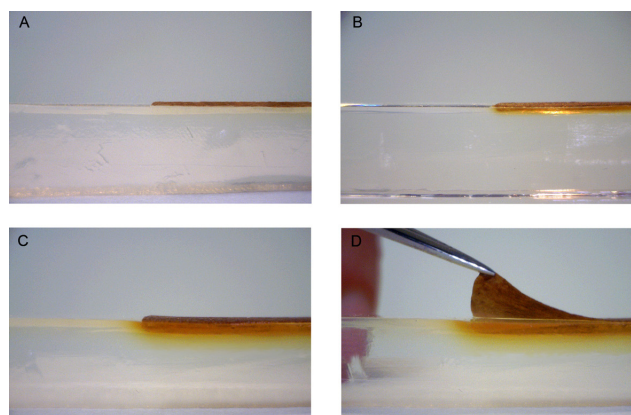


Fig. 18. The process of exchange between a very acidic and oxidised paper and a Gellan gel at 2%; (A) start of treatment; (B) after 5 minutes; (C) after 15 minutes; (D) after 25 minutes. Macro-photographs taken with a video microscope (15x)

the ICPAL Physics Laboratory on works that have undergone a simple cleaning treatment with the gel have highlighted that the intervention caused no significant variations to the original opacity of the supports that were treated, whilst there was a moderate improvement in the level of brightness and a reduction in the yellowing measured according to the colour coordinate system of CIE Lab (fig. 19). The method described

herein does not bring about structural or surface modifications to the paper supports as the cleaning intervention occurs spontaneously following the mere contact of the gel with the paper, which in fact simply undergoes controlled humidification. The safeguarding of morphological characteristics is further guaranteed by the visco-elasticity of Gellan gel. This

POINT	$\Delta E$	$\Delta L$	$\Delta a$	$\Delta b$
1	3.82	+ 1.63	- 0.80	- 3.37
2	1.78	+ 1.10	+ 0.03	- 1.41
3	6.07	+ 2.41	- 0.69	- 5.53
4	3.02	+ 1.55	- 0.30	- 2.58
5	5.61	+ 3.38	- 1.05	- 4.36
6	3.57	+ 2.59	- 0.49	- 2.42

Fig. 19. CIELab color variations measured with tri-stimulus Minolta CR200 chromo-meter on a burin engraving on paper by Giacomo Lauro, Basilica S. Petri in Vaticano (1626)

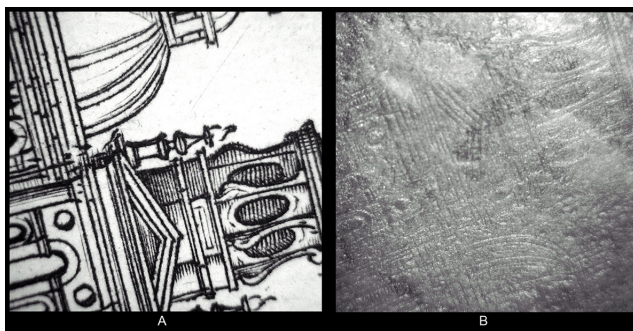


Fig. 20. (A) Giacomo Lauro, Basilica S. Petri in Vaticano (1626), burin engraving on paper. Close-up of chalcographic engraving; (B) Close-up of the gel at 2% which—following contact with the work—shows the mirror image of the chalcographic engraving

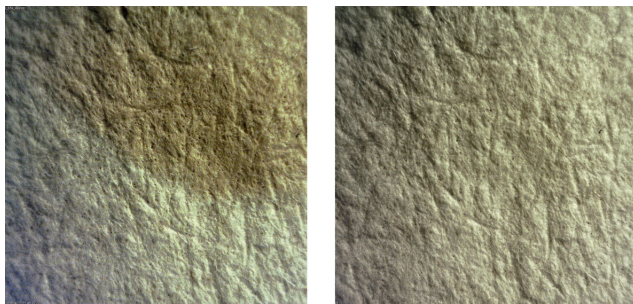


Fig. 21. A same piece of paper from 1635 before (left) and after treatment (right) with Gellan gel at 2% applied for 30 minutes. Images taken with Dinolite video microscope (65x)

allows the gel to mould itself to the three-dimensional relief of graphic print marks and to the surface texture of the paper (figs. 20–21). Neither of these suffer alterations following contact with the gel, on which we can observe the impression of the codicological elements and printing marks. And finally, after cleaning has taken place, the removal of a compact, non-adhesive film does not cause substantial presence of residues of gel on the support as is the case with cellulose ethers. Once it has been used, the gel can be disposed of as biodegradable organic waste. Gellan gel, which is in fact stable when it is in dry powder form, is on the other hand easily biodegradable in its gelified form, due to its high content of water and due to the fact that it is essentially impossible to work in sterile conditions when working on handmade artefacts in normal working conditions.

SELECTING THE ‘IDEAL’ CONCENTRATION

The water uptake of the support is inversely proportional to the concentration of the gel: the greater the quantity of powdered Gellan gel used—and thus the more tightly reticular structure of the gel—the smaller the quantity of water transferred into the paper in the same time interval. From results shown in the graph (fig. 22), it can be seen that the percentage of increase in weight ( $P_2 - P_1 / P_1 \times 100$ ) of samples treated increases substantially with the decrease of the concentration of the biopolymer. Even after an extended contact period of 18 hours, the quantity of water transferred into the samples nevertheless results as less than what is absorbed by a sample immersed in water for ten minutes. In any case, the ‘ideal’ concentration of Gellan gel depends on the degree of wettability of any single paper to be treated. The degree of surface porosity of the paper and its level of wettability in fact depend on the type of fibre that make up the pulp, on the

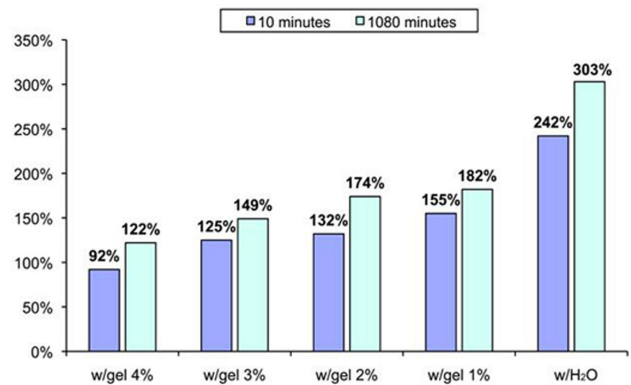


Fig. 22. Comparison of percentages of increase in weight in samples of Whatman paper (no.001090) after contact with Gellan gel at different concentrations (w/gel x%) and after immersion in free water for 10 minutes and for 18 hours. Readings taken with Wunder BH-150 scales (Max 150 g; d: 0,005 g) at 26°C and RH equal to 55%

extent and type of sizing present, as well as the level of refining of the cellulose fibres and the state of preservation of the materials present. Thus it is useful to carry out a simple test of the degree of wettability before choosing the best concentration of Gellan to be used and, if necessary, a humidification treatment in an ultrasonic humidifier chamber can be carried out if the paper is particularly hydrophobic.

#### THE CLEANING TREATMENT ON DRAWINGS

Conversely to the application method developed for printed works, the cleaning treatment for drawings is carried out by placing the gel on the *verso* of the work after verifying the stability of graphical media to water (fig. 23). As a further safety precaution, it is necessary to place a piece of Japanese paper between the gel and the work as an interleaving tissue. The latter does not interfere in the exchange process that takes place during the treatment, thanks to its excellent permeability, but, at the end of the treatment, it will assist the removal of the item from the gel surface. The technique also prevents the temporary fixing of any fragments with adhesives that could cause a substantial change to the support's absorbency of water. Generally speaking, when using an interleaving tissue, a low concentrated gel (about 1%) will work more effectively to overcome the presence of an additional support. In any case, the gel concentration has to be selected according to paper wettability, which can vary even in a similar paper. In an attempt to counteract the unavoidable stresses caused by different hygroscopic behaviour during the wetting procedure on a series of drawings that showed problems of this sort, we used two gels at different concentrations to ensure the uniformity in the imbibition phase, preventing the appearance of risky physical-mechanical tensions between areas showing different hydrophilic levels (fig. 24). The contact times depend on the characteristics of the works and the quantities of residues to be removed, taking into account that, if necessary, applications using clean gel can be carried out until no more yellowing of the film can be seen.

#### THE REMOVAL OF AUXILIARY SUPPORTS WITH RIGID GELLAN GELS

During conservation treatments of graphic works, it is not uncommon to come across auxiliary supports applied with amylaceous or protein adhesives. In these cases, their presence brings about chromatic alternations associated with structural modifications that—with the varying of thermo-hygrometric parameters of the conservation area—become the cause of deformations, tensions, as well as surface darkening of works to such a point that their use is compromised. Whenever the conservation intervention should require the removal of these and the subsequent removal of the adhesives, rigid gels offer an effective technique for the

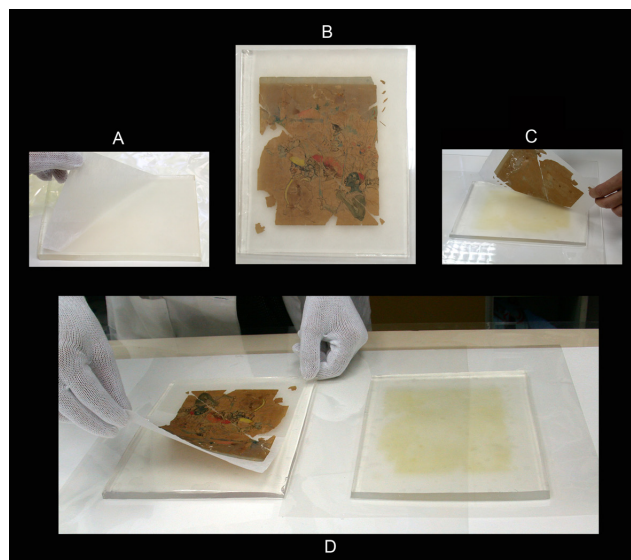


Fig. 23. Japanese paper placed on top of the Gellan gel (1%) placed on a polyester sheet (A); placement of the work on the Japanese tissue (B); removal of the work with the aid of Japanese tissue (C); placement of the work on a second gel with the aid of Japanese tissue (D)

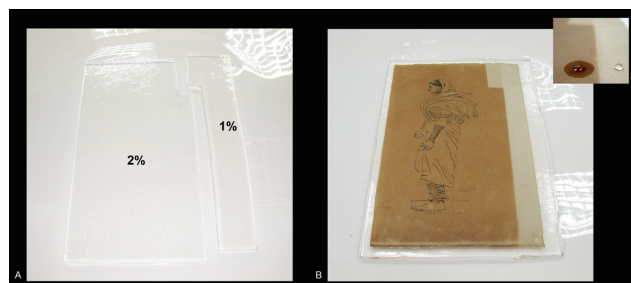


Fig. 24. Close-up of the 'contact angle' test performed with two droplets of water on a 19th-century drawing (C); two Gellan gels prepared at different concentrations (A); both gels placed underneath the work (B)

humidification of the paper support. Traditionally, the intervention is conducted via localised humidification with steam, produced by an ultrasonic generator, or with packs of gelified water. Both removal techniques inevitably result in a high level of interaction with the work that is subjected to a substantial physical-mechanical stress, as all the materials present in it—original paper support, adhesive, strengthening material or integral lining—tend to swell in their interaction with the water solvent and subsequently shrink in a different way. The variations in size that are found in successive cycles of *swelling-shrinkage* bring about structural deformations that are irreversible. The extent of these deformations depend on the degree of interconnection of the abovementioned constituent materials, on the force applied during the operation of the separation of the various paper layers and on the pressure used during the mechanical removal of the adhesive, as well

as on the inhomogeneous quantities of water transferred onto the areas that are individually treated. The aim of the use of rigid aqueous gels for the removal of additional material, is to keep the level of the humidification of the entire surface of the work uniform and constant throughout, avoiding the risk of over- or under-dosage of water and the aforementioned consequences. Conversely to the function it has during the intervention of surface cleaning, the rigid gel in this case is used exclusively as a reservoir for the constant and controlled release of molecules of water for the purpose of making all the materials present in the work sufficiently hydrated throughout the intervention. As a rule, the removal of additional supports is carried out immediately after the surface cleaning intervention is completed, repeating the application of Gellan film prepared at a concentration that is suitable for the nature and quantity of materials that are to be removed. The coefficient of the diffusion of the water solvent within the work will in fact be substantially influenced by the percentage of water present in the gel, on the degree of porosity and wettability of the paper, on the presence of additional elements (original sizing) and on the quantity and state of preservation of the adhesive present. In order to minimise mechanical tractions that—even if they are mild—could be caused on the original surface, the Gellan film is in this case also applied to the *recto* of the work—placing a sheet of Japanese paper between the paper and the gel which will then serve to lift up the work once the operation is completed (fig. 25). The intervention is however conducted on the *verso*, once the ‘sandwich’ has been turned over using two sheets of Plexiglas and after having

carried out a test aimed at assessing the extent of the force required to separate the two or more paper supports to be separated. Subsequently, the mechanical removal of the adhesive is carried out: the constant and uniform inflow of water molecules from the gel under the work and the subsequent decrease in the viscosity of the adhesive, allow the operation to be carried out quickly without tide lines or mechanical tractions, thus preventing irreversible distortions and any losses of cellulose fibres from the original support. However, although this technique allows a raised hydration of the adhesive layer, the permanence in the layer of internal friction—which is somewhat high—prevents its complete removal.

#### ENZYMATIC GELLAN GELS

The operation of removing support material and the subsequent removal of the adhesive can be assisted by the application of enzymes (hydrolases) that—as is well known—act as catalysts for hydrolysis reaction of specific substrates. The enzymatic gels prepared over recent years and the gelified enzymatic solutions with gelling agents of different types have several limits. Ready-to-use enzymatic packs (Schwarz et alii 2003, 98–108) only act on amylaceous adhesives, and other different types of gelling agents, like cellulose ethers, polyacrylic acid neutralised with sodium hydroxide and natural polysaccharide gums require a subsequent phase of mechanical removal from the paper surface. The need to remove residues of gelling agents can be eliminated by using a rigid gel used as a carrier for enzymatic solutions (Campani et alii *cit*, 16). The preparation of the enzymatic Gellan gel is carried out only once gelification has taken place as the preliminary phase of the hydration of the polymer takes place around 90–100°C, a temperature that would denature the protein molecules of the enzymes. The milligrams or the grams of enzyme (Cremonesi 1999, pp. 46–48), calculated in line with the total quantity of saline buffer solution (0.4g/l calcium acetate and Trizma base or other buffers) which is transformed into gel, are hydrated in a few millilitres of the same solution. In this way, we obtain a concentrated enzymatic solution in a homogenous medium (water) which is then deposited with a micropipette and distributed uniformly over the surface of the gel using a synthetic brush. As a rough guide, for a Gellan film at 3% made starting with 800g of pH 7 aqueous buffer solution and the surface of which is 20 x 30 cm, 5–6 ml of concentrated enzymatic solution are sufficient.

The intervention can be carried out only when the solution has been completely absorbed by the rigid gel. Initially distributed only on the surface, the enzyme molecules tend to spread throughout the microporous structure that characterises Gellan film via capillary action in the space of just a few minutes (fig. 26). The gel is placed directly in contact with the adhesive layer to be removed for a period of time that varies according to the thickness of the deposit, its nature and its



Fig. 25. Positioning of Japanese paper and of the gel on the *recto* of a print (A); removal of the auxiliary support and of any previous conservation interventions, working on the *verso* and using the gel as a humidifying support (B); mechanical removal of the adhesive (C)

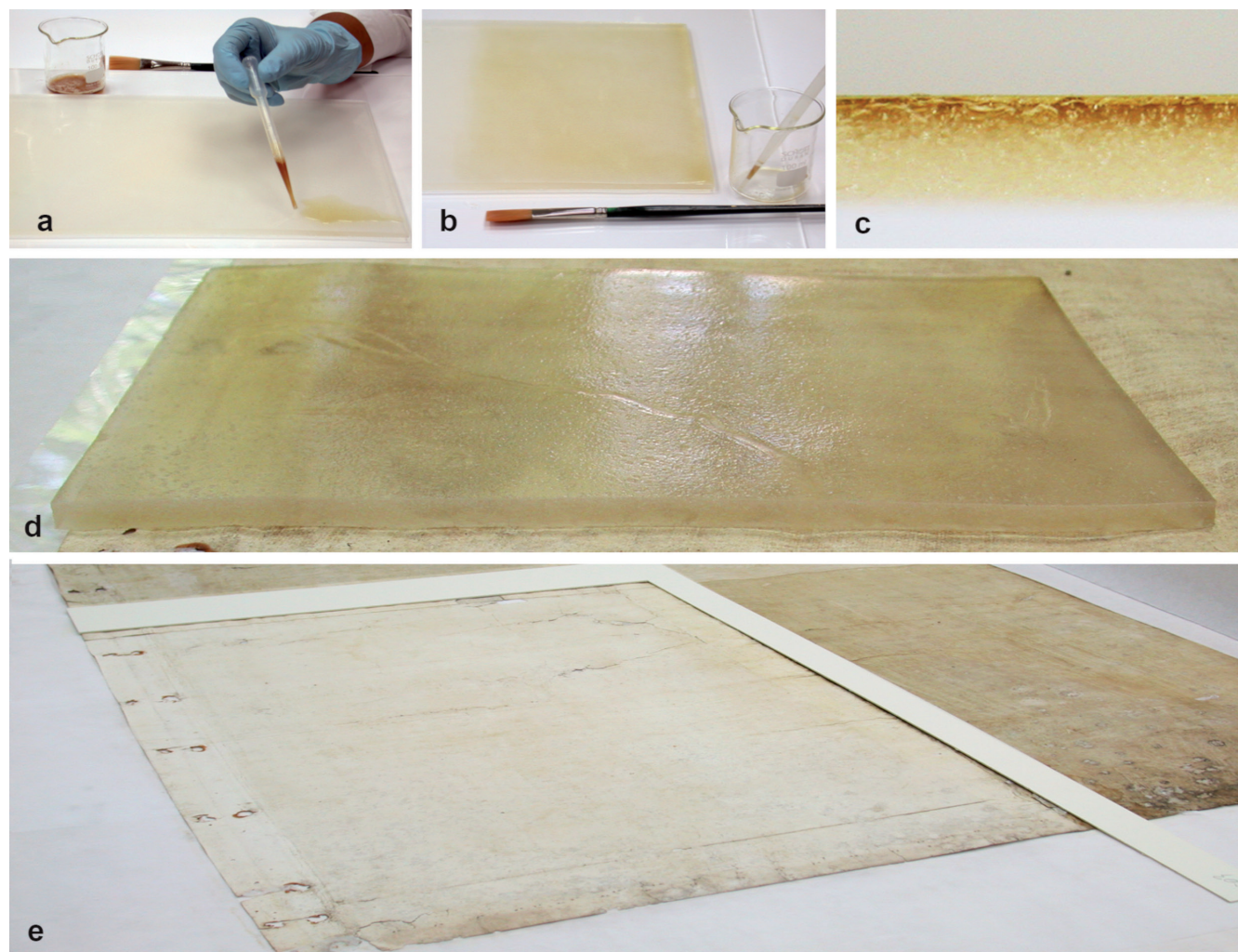


Fig. 26. Distribution of the enzymatic solution and absorption by the gel (A-B-C); application of the gel (D) and the result of cleaning on the reverse of a large-scale work (E)

state of preservation. At the end of the treatment, the by now depolymerised adhesive can be easily removed using swabs without any sort of mechanical traction. The residues of the substances present on the support of the work—enzymes and traces of depolymerised adhesive—can be easily removed by applying another aqueous gel, or, if the state of preservation and the graphical media allow it, by washing on a sloping surface (Kirchner 2004, 124–135).

#### CHEMICAL STABILISATION OF PAPER SUPPORTS WITH GELLAN

Sometimes the precarious state of preservation of work necessitates an intervention for chemical stabilisation which, as a rule, involves the carrying out of a deacidification and reduction-oxidation treatment. The products studied and used at ICPAL are calcium propionate as a deacidifying agent

and tert butyl aminoborane as a reducing agent. The latter can be used only if the graphical media that are present do not contain copper compounds. Again in this case, the wide range of stability of the pH of Gellan allows the use of deacidifying aqueous solutions and reduction-oxidation agents in gel phase, which can be used separately, at the same time or in subsequent interventions. The reduction-oxidation gel is prepared starting with the calcium acetate solution (0.4g/l) to which the necessary Gellan powder is added, using however the forethought of inserting the tert butyl aminoborane (7g/l) immediately after the dispersion has ended the heating cycle in a microwave, an operation that requires the use of personal protective equipment and which is always conducted under a fume hood (fig. 27). The tert butyl aminoborane dissolves immediately and so it is possible to pour the compound into a basin—as is common practice—and wait for the sol-gel transition to take place once it has cooled. Even in

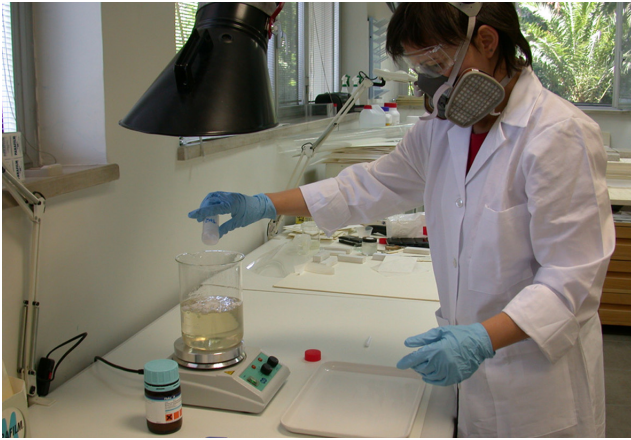


Fig. 27. The tert butyl aminoborane (7g/l) is added under the fume hood, when the hydration process of the Gellan is complete, using personal protective equipment

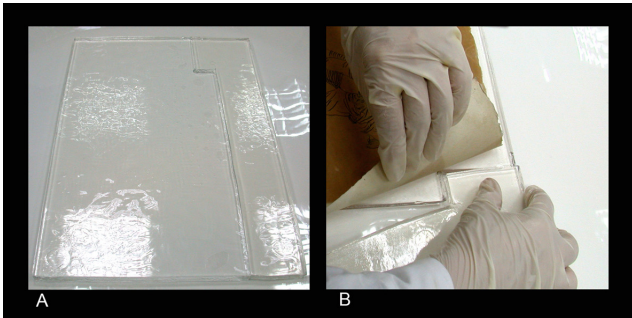


Fig. 28. An example of localised oxidation-reducing treatment: (A) a rigid oxidation-reducing gel and a simple rigid aqueous gel made according to a template; (B) positioning of the two gels under the drawing at the same time



Fig. 29. The deacidifying gel positioned under the two drawings, using a sheet of Japanese paper as an interleaving tissue

the presence of tert butyl aminoborane, the gel maintains its visco-elastic properties and its transparency. Application takes place by contact, using methods that vary according to the graphic techniques present, as described previously for the cleaning intervention. The possibility to gelify deacidifying and/or reduction-oxidation solutions allows the carrying out of interventions also during chemical stabilisation, as in the

case of a group of drawings from the end of the 19th century treated by positioning different gels at the same time (fig. 28). At the end of the intervention, the duration of which was generally two hours, a rinsing treatment with a simple aqueous gel was carried out in order to remove any residues of tert butyl aminoborane. Due to the presence of tert butyl aminoborane, the reduction-oxidation gel must be disposed of as hazardous waste. When it is necessary to carry out a deacidification treatment, a rigid deacidifying gel is prepared, starting—as always—with a saline solution based on calcium acetate (0.4g/l) to which calcium propionate (3.5-5g/l) is added, followed by the necessary Gellan, and the total compound is then heated up in the microwave. The deacidifying gel is slightly opaque but maintains its filmogenic and elastic quality (fig. 29). The treatment takes around two hours. The ICPAL Physics Laboratory has tested the effectiveness of the gelified aqueous solutions of calcium propionate and tert butyl aminoborane by conducting, amongst other things, measurements of pH and alkaline reserve on different paper samples from the 17th century, the 19th century and on samples of Whatman and Fabria paper. The results of these studies are in the publication phase.

#### CONCLUSIONS

The aim of the studies on Gellan gel use conducted between 2003–2004 by ICPAL was to develop an alternative technique that could remove substances that cause degradation on works of art on paper without causing morphological changes to the support. The gradual and controlled release of water molecules from the gel to the paper, its capacity to absorb hydrosoluble substances of degradation, the ease of application and removal, and its visco-elasticity make it particularly suitable for use in this field, ensuring the maintenance of the overall function—both structural and aesthetic—of this type of artefact. In experiments carried out in recent years, the versatility of this material in other phases of conservation has emerged, including the removal of auxiliary supports, its use as a carrier for enzymatic solutions and for deacidification and reduction-oxidation solutions. The results achieved in terms of the variations of optical properties, as well as in terms of the pH and alkaline reserve, are extremely encouraging. Future developments of the research are being directed at identifying the substances that the gel is able to remove from paper supports using *Size-Exclusion Chromatography (SEC)* and the verification of the effects that it can produce on different types of paper through *mechanical testing*. *These studies are currently in progress on treated paper samples, as well as on untreated samples, as part of the research project 'Gel rigidi polisaccaridici per il trattamento di pulitura di materiale cartaceo'* ([http://www.icpal.beniculturali.it/progetti\\_ricerca.html](http://www.icpal.beniculturali.it/progetti_ricerca.html)). Partners involved in the project include the ICPAL Physics Laboratory and the ICPAL Laboratory for the conservation of library materials (Istituto

centrale per il restauro e la conservazione del patrimonio archivistico e librario), the OPD (Opificio delle pietre dure—Florence), Cesmar7 (Padua) and the University of Parma.

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