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New tool for sustainable treatments: agar spray—research and practice

Ambra Giordano[1*], Maria Rita Caruso[2] and Giuseppe Lazzara[2]

Abstract

In the last decades, the research in the field of cultural heritage has shifted its attention to the development of green methods, focusing on the use of renewable and biodegradable materials. Within this scenario, Agar has been one of the most innovative materials available to the conservator. However, sometimes its physical characteristics such as rigidity and gelation temperature are not always an advantage in the treatment of artwork. The atomization of hydrocolloid, a procedure presented in 2019 under the name of *Agar spray*, has enhanced the performance of this extraordinary material. This work aims to explore the new physical and mechanical characteristics imparted to the gel by the new spray procedure, compared to agar gel that forms under normal environmental conditions. Mechanical resistance and film transparency of both soft materials have been characterized, and the speed of water release has been detected on porous material, lateral solvent flow evaluated for confined cleaning. The new residues, potentially left by the gel after the spray application, were analyzed comparing them with the residues of the gel, which gels at room temperature. The dry Agar films were studied in terms of hydrophobicity of the dry film, agar towards water and water vapor permeability. The data that emerged from the study confirm the new features imparted to the gel by the new procedure, suggesting new measures to be taken to optimize its application.

Keywords: Biopolymers, Agar, Gel, Spray, Cultural heritage, Sustainability

Introduction

In the global trend of research to increase green attitudes, the world of conservation of cultural heritage is no exception. The development of sustainable protocols for the artwork treatment is a challenging but necessary task, in particular when we deal with large surfaces. The focus is on high toxicity of substances especially when used in large quantities, the risk of leaving residues of the cleaning agents used and the disposal of special waste. The search for increasingly selective cleaning methods that are, at the same time, not harmful to operators and to the environment, but without compromising the effectiveness of the procedure, has found an important direction of development in the application of bio polymers. These have been evaluated in many case studies over the past decades, tested for controlled surface cleaning [1–4], as a coating for surface protection [5, 6] and as a consolidating agent for paint [7].

Among bio polymers Agar, which is a polysaccharide extracted from red algae since its introduction in 2003 by Wolbers [8], has proven to be one of the most innovative substances for humidification and cleaning treatments on water sensitive surfaces. The specific action and great advantage of agar gels, compared to traditional aqueous methods, dwells in its ability to capture removed soiling into the gel structure itself [9]. The use allows to obtain precise application with very strict control of the amount of water released, increased dwell time of reagent and minimal mechanical action on surface upon both, application and gel removal. It is also possible to make changes to the final structure. Thus, by altering the concentration, it is possible to manipulate viscosity, absorption, and dispersion as needed by a given treatment or application

*Correspondence: ambragiordano@yahoo.it

[1] Department of Applied Arts, Academy of Fine Arts, Via Papireto 20, 90134 Palermo, Italy
Full list of author information is available at the end of the article

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[10]. Agar, stable in both alkaline and acidic conditions, has extraordinary potential as a recyclable eco-friendly material, reusable several times converting the aqueous medium into thermo-reversible hydrogels [11, 12].

Its macro-reticulate structure based on the hydrogen bonds among the Agarose helices, allows to capture large quantities of water either bonded to the polysaccharide molecules or free [13].

The mechanism of action is strongly correlated to several specific properties of gels, such as syneresis, spontaneous release of water from the gel, its diffusion capacity into porous substrates thanks to ion concentration gradients and osmosis phenomena [10].

Differences in terms of chemical composition, gelation and melting point temperatures may vary slightly due to the natural diversity in the Agar chemical composition influenced by the Rhodophyceae species, harvest seasons, algae growing conditions, and extraction/preparation and purification technique [14].

Agar, unlike other "physical gels", due to its weak interactions, does not need a post treatment and does not leave residues on the surface. All these features, in addition to the renewability and biodegradability of the material, make it an excellent candidate for its use in conservation.

In 2007 Campani et al. were the first to test agar and agarose gel, in the rigid form, to evaluate if suitable on porous supports, in terms of water and residues released. The use of the gas chromatography technique coupled with GC–MS mass spectrometry confirmed that the gels do not leave residues. However, it is important to note that the syneresis (the release of water from the rigid gel) is slower in the agar gel compared to agarose, due to the presence of sulfate groups that reduce the pore size [12]. In this study the main disadvantage of the rigid polysaccharide gels was their inherent rigidity, which worked only applied on flat surfaces.

In 2008 to overcome this limit Anzani et al. applied the gel on three-dimensional gypsum objects, not in a solid state but in a semi-solid form, applying it during its cooling to 40 °C. For analytical validation they performed aqueous extraction of potential gel constituent materials from the fragments tested, analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography coupled with Mass Spectroscopy (GC–MS) [15].

Recently new application methods have been proposed to support different conservation problems.

In 2015 Senserrich-Espunes et al. proposed modifications to the fluid gel, incorporating air bubbles during its preparation for applications on frescoes. The white agar foam applied at 40–50 °C with a brush or spatula, increase its flexibility and allow for a gentler action during gel removal [16].

In 2021 Cremonesi introduced specific tools and the related method to restrict the application of the semi-solid agar gel. The precise application is done through a heated syringe, maintaining the gel fluid [17]. Cremonesi also presented two new ways of using rigid agar gels: preformed rigid gels as a 'cleaning stick' and as grated agar particles that can be brushed onto the surface to perform gentle surface cleaning for water sensitive painted surfaces [18]. The small size of the particles allows even more morphologically complex areas to be treated, such as the internal relief of a brushstroke. After the application, the particles are easily removed from the surface using a soft brush. Removal must be done carefully, but the presence of any residues should not cause excessive concern. The very small size of the particles causes them to dry quickly, and Agar and agarose are susceptible to mold formation when in the form of a rigid gel, i.e., in the presence of a large quantity of water. In dry form, the powders remain stable for very long periods, because they are insoluble in water at room temperature and are not hygroscopic.

In 2012 Anzani et al. proposed a similar use of the hard gel but using an electric blender to produce the tiny particles, after having it milled into a snow consistency, applying it with a spatula on Japanese paper at room temperature on vertical surfaces [9, 19]. With this application, adhesion is minimized but the release of water on the surface increases, the gel significantly decreases its transparency.

In the last year, the Agar gel has been proposed for cleaning surface dirt and soiled materials from modern water-sensitive oil [20] and acrylic paintings [21, 22]. Despite the extraordinary nature of this material and the extensive research done to improve its performance, still some application limitations prevented its use, stiffness which often causes the gel to break when handled, surface contact (not always optimal) makes soil removal poor and uneven [23, 24] also gelation temperature may be too high for many materials, and in this case the challenge becomes more difficult when the surface is three-dimensional, vertical or above us (like a ceiling).

In the 2019 Giordano et al. described a new application method of hydrocolloid for the conservative treatment of large surfaces, the procedure called Agar Spray uses a specific device *Paint applicator produced by Wagner Spa.* This method atomizes agar in the *sol* state, allowing to overcome some of the major limitations associated with the application of the gel. For the first time, it is possible to obtain a homogeneous and ultra-fine agar film, applicable in an easy way and in a short time covers large surface areas, without releasing excessive heat [25].

In literature the first Agar spray technique was developed by Hughes et al., the study conducted in 1968 was

supported by the Bioscience Division, Office of Space Science Application, NASA Headquarters. This report describes an improved technique for biological sampling of surfaces. The method employs spraying molten (53 °C) agar directly onto the surface to be sampled and incubating the microorganisms thereon. The agar spraying device operated with filtered air or nitrogen at 5 to 10 psi with glass reservoir to contain a molten nutrient agar [26]. However, no other references were found to the use of any type of Agar spray process.

In 2021 Giordano et al. found that the agar gel droplets produced during the nebulization process spread in the air, making the agar gel into fractions of a second impacting on the surface for the first time at a temperature compatible with numerous artefacts, around 21°. The agar spheres assemble on the surface in a uniform and ultrafine film (1–3 mm), adhering gently to large vertical and three-dimensional surfaces. Unlike thermo-reversible hydrogels that are commonly prepared by cooling down to room temperature, with the agar spray procedure the sol–gel transition processes take place in the air. The structure is formed in a system of high pressure, friction of the air and sudden cooling, all these factors modify the final structure, giving the agar new mechanical and physical properties: higher flexibility, less adhesiveness, minimal water release and ease of handling [17]. The authors assert that the use of agar spray reduces the water relying on the surface due to its ultrafine thickness and the rapid evaporation of part of the water contained in the gel during its trajectory, due to the difference between the chemical potential of water in the gel and the surrounding atmosphere. The speed of gelation depends on environmental parameters: [temperature (t) and relative humidity (rh) of the environment and artwork], and distance traveled by the gel before impact. To counterbalance the environmental parameters the right temperature of the fluid Agar should be selected to achieve 22 °C as surface temperature.

Sol–gel transition processes of algal galactans were studied by Tukivene et al. 2007 using the cryofixation method in combination with freeze–drying and scanning electron microscopy (SEM) techniques. It was established that in sol Agar/agarose a fine honeycomb structure exists, but only at temperatures much higher than those involving rheological changes related to gel formation, the honeycomb structure gradually loses during gel formation, cooling to normal room temperature conditions, creating a tighter and more homogeneous network than resulting in brittle, strong gels of high light absorbance [27].

In 2021 Giordano et al. consider the possibility that this fine honeycomb mesh, a sort of hidden precursor structure, is preserved in the spray gel due to the rapid cooling in the air, influencing mechanical and physical properties of the gel giving it greater flexibility and ease of handling less adhesiveness, and faster reintroduction of water into the gel after release [15].

The atomized agar gel network structure was observed by scanning electron microscopy (SEM), the cells are larger than the gel reticulum resulting from standard procedures and are shielded by a membrane, a sort of 'skin' that covers the surface of the gel. Numerous air bubbles were observed.

Even though agar is used in conservation practice and investigated for more than 20 years, the new structure imparted to the gel by the new procedure makes it a new material.

This study aims to characterize and verify these new features highlighted by practical experience by supporting them with scientific data. Mechanical resistance of the atomized agar was characterized by comparing it to the gel that gels under normal environmental conditions using BOSE Biodynamic testing machine, UV–VIS spectra of agar films were recorded to evaluate transparency, morphological observations of the new gel structure were made using optical microscope and Scanning electron microscope (SEM), plaster sample was used to evaluate water release on porous material. The new residues potentially left by the gel after spray application were investigated in terms of hydrophobicity of the dry film agar towards water and water vapor permeability.

The work presented also goes as far as to evaluate whether the spray application is suitable for cleaning/humidifying confined areas. The application of the gel on large surfaces eliminates the possibility of creating tide lines, because the entire surface of the work is treated in a single step (Fig. 1). The question now is if the intrinsic mechanisms of introduction and absorption of the water of the new structure also led to an improvement in water confinement performance, making it applicable also for specific treatments localized on artwork. To evaluate it, tests were carried out on cotton paper specimens and on an oil painting on cardboard from the twentieth century.

Experimental

Materials and methods

Preparation of Agar gel

Agar at 3% (w/v) was prepared heating it and then bringing it to a boiling point in a microwave oven in a covered glass beaker to minimize the evaporation of water, stirring it occasionally. The gel is cooled until it has gelled completely. The gel was dissolved again in a microwave to obtain a better performance in terms of homogeneity of the reticulum and water retention. A part of the fluid gel was cast on silicone molds to form the rigid gel. The other part of the fluid gel, at a temperature of 65 °C, was

Fig. 1 Application of the agar spray on the whole surface of a three-dimensional plaster sculpture, and its easy removal in a single step

poured into the cup connected to the lower part of the spray gun (wall sprayer model W 450 by Wagner Spa). Agar was atomized on a plate. Both samples, atomized agar and preformed mold, were prepared as a humid film and dried film at room temperature.

Paint applicator

The wall sprayer model W 450 performs using HVLP (high volume/low pressure), a pneumatic atomization technology with high volumes of low-pressure air, with an atomizing power of 110 W and a maximum flow rate of 230 ml/min (Wagner GmbH 2015). It was made to limit solvent emissions in paints, designed for the application of fluid substances.

The spray guns use hot air to maintain the paint in a fluid form without having to add extra solvent to lower its viscosity. The system uses a small but powerful turbine and emits a large flow of air at a temperature of 45 °C. A schematic cross section of the spray gun and how it works is shown in Fig. 2.

The spray gun supplied by Wagner, weighing 2 kg, is equipped with a shoulder strap. The device allows to adjust the volume of the material and has two different jet types (a vertical fan jet for horizontal surfaces and a horizontal fan jet for vertical surfaces), and switches from a wide to a narrow spray.

A Digital Microscope was used for photos having a high-resolution camera and a high-performance digitizing adapter (Dino-Lite digital microscope 30×). A Java-based image processing program, ImageJ, was used for data acquisition.

Scanning electron microscopy (SEM)

Sample surfaces were observed under Phenom Prox Scanning Electron Microscopy (SEM) with an accelerating voltage of 10 kV. used for the morphological study of lyophilized agar gel. A sample was metallized with conductive coating.

Mechanical analysis

An experimental campaign related to the mechanical characterization of the Agar Spray compared to the usual Agar in a preformed mold has been conducted on a BOSE Biodynamic testing machine at the Mechanics of Materials and Biomaterials laboratory @ ATeN-center. Five material samples of the agar spray and six of agar in a preformed mold have been prepared and cut into circular plates with a 12 cm diameter and variable thickness s, 1–2 mm as reported in the table with supporting information. The samples have been clamped into a Petri dish with a central hollow to move the actuator of the testing machine. The actuator involved a flat 1 cm diameter rigid punch connected to the fixed part of the testing machine, while the bottom of the Petri dish moves the sample against the punch. A 220 N load cell system has been used to record load data during the test and a

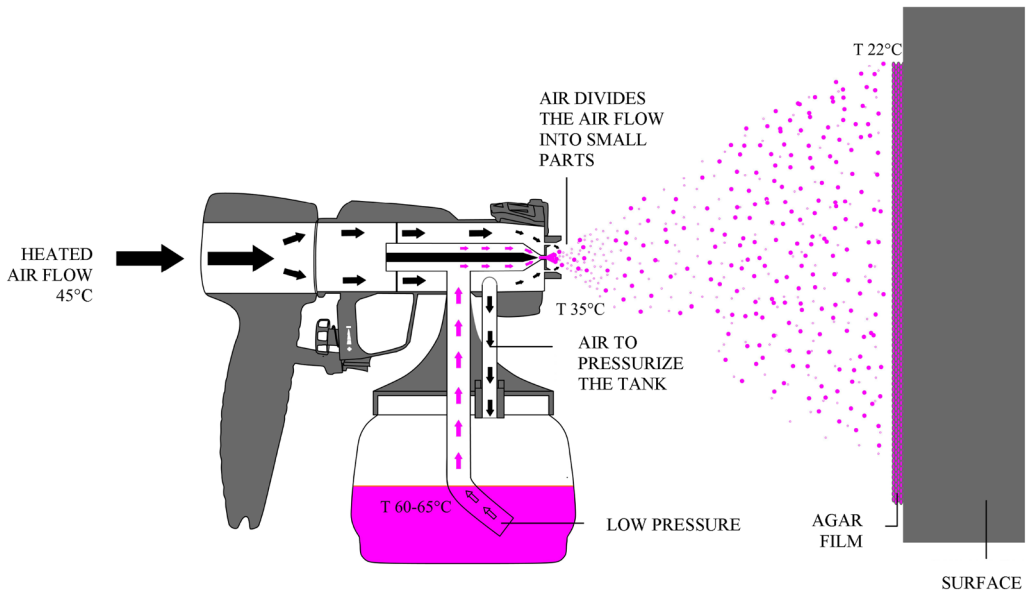

Fig. 2 Agar sprayer-schematic cross section

displacement-controlled test with speed of 0.01 mm/s was selected and the test lasted until the breakdown of the sample was reached.

Film transparency

UV–VIS spectra of agar films were recorded by a Specord S600 (Analytik, Jena, Germany) in the range between 200 and 800 nm and they were analyzed in terms of transmittance (T%).

The experiments were carried out at 25.0 ± 0.1 °C by using a Beckman spectrophotometer (model DU-640). An absorption spectrum was determined for each film. The transmission spectrum was obtained as (1):

$$T\% = 10^{(2-A)} \tag{1}$$

where A is the absorbance. The attenuation coefficient at the wavelength of 700 nm (K700/mm^{-1}) for each sample was computed as (2):

$$K_{700} = A/(2.3D) \tag{2}$$

where A is the absorbance at wavelength of 700 nm and D is the thickness of the film measured with a micrometer (± 10 − 3 mm).

Water contact angle measurements

The measurement of the contact angle allows to obtain information on the hydrophobicity of the agar film towards water. An instrument for measuring the optical contact angle OCA, Optical Contact Angle, equipped with a video system with a high resolution and high-performance CCD camera with a digitized adapter was used. The SCA 20 Software was used for data acquisition.

The contact angle was measured with the sessile drop method. The temperature of the instrument and of the syringe containing the water was equal to 25 °C and the volume of the drop of water was approximately 10.0 ± 0.5 ml. 50 images per second from drop deposition up to 30 s were collected and two measurements were made on each sample.

Water permeability analysis

The evaluation of the water vapor permeability was carried out by comparing two of the agar films, atomized and gelled in a preformed mold.

Two glass bottles were prepared with 40 ml of deionized water inside. The two dried agar films were cut into a circular shape with a diameter of two centimeters, and subsequently applied to the bottles. Plasticine made it possible to block the agar film and seal the edges of the bottle. The two bottles, perfectly identical, were weighed with an analytical scale and were subsequently placed inside a drying chamber with relative humidity and controlled temperature.

The desiccator was built in a drying vessel with a saturated solution of calcium chloride inside and a thermo-hygrometer to check the parameters. According to some studies, a saturated solution of Calcium Chloride guarantees a temperature of 28 °C and a relative humidity of 29%.

The weight of the two specimens was recorded every hour for 6 h. The data are shown in the table and a graph has been constructed that relates the D mass as a function of time.

Permeability (WVP) and water vapor transmission rate (WVTR) were calculated using the following Eqs. (3) and (4):

$$WVTR = (\Delta m/\Delta tA) \tag{3}$$

$$WVP = WVTR(L/\Delta p) \tag{4}$$

where Δm/Δt is the weight loss as a function of time (g/h), A is the surface of the film (m^2), L indicates the thickness of the film (mm), Δp is the partial pressure difference between water and saturated solution (mmHg).

Evaluation of water release

Preparation of plaster samples

Plaster samples were made of gypsum and water and cast on a silicone mold (final drying weight of about 180–190 g, 10 cm in length, 3 cm in height and 5.5 cm in length). Samples were dried at room temperature for 15 days before tests of water release control.

Water release control

Water release has been examined comparing agar spray with the traditional semi-fluid brush and rigid gel in a preformed mold. Gypsum sample, a very porous material, allowed to identify the diffusion of water after application once sectioned.

The test was performed by preparing agar gelled solution colored by organic dye, Rhodamine B241. The rhodamine allowed to control the diffusion of the water released by the agar inside the models, according to the different methods and times of application. Furthermore, rhodamine is a fluorescent dye therefore it was easier to measure water diffusion by observing samples with a Wood lamp.

Application methods, brushes, pre-formed and sprayed molds, and time length: at first 3 min, then 15 min and after dehydration, were changed to examine different scenarios.

Once the gel was applied and removed, according to the pre-established times, the samples were sectioned longitudinally by an electric blade after 24 h.

Water spreading evaluation

Cotton-based paper was used for tests. The sheets of paper were cut with scissors into 15 × 15 cm samples.

The tests were performed with paper: Arches ∞ France watercolor paper, made from 100% cotton pulp through a semi-mechanical process that is relatively similar to that of handmade paper, rough texture, base weight (mass of 1 sheet of paper per square meter) of 185 g. The paper was stained with rhodamine B dye, the dye was first dissolved in water and brushed on the paper surface and dried in the stove at 30° for 5 h.

A mask obtained from a plastic sheet with three windows of 4 × 4 cm was cut from it, fixed to the paper sample with neodymium magnets. The Agar gel at 3% was placed on the surface of the paper sample stained with rhodamine B dye in three different ways: in a preformed mold blotting the gels before application with non-cellulosic, non-woven Evolon tissue; brushed in a semi-solid state at 40 °C and sprayed, with an application time of 3 min. The presence of water solubility dye Rhodamine B facilitates the formation of tidal lines. The surface was observed after treatment with the optical microscope (Dino-Lite digital microscope).

Results and discussion

Optical analysis of agar gel: structure observation

Morphological observation

Agar was sprayed on a microscope slide, micro-photographed at 240× magnification using Dino-lite digital microscope under normal light, showed that the agar beads have an area ranging from 0.013 to 0.308 mm^2 (Fig. 3). Inside the spheres there are various air bubbles where you can see the junction points of the spheres, these are connected to each other forming a network (Fig. 4). The distribution of the spheres through the device allows to obtain ultra-thin and perfectly homogeneous films (Fig. 5). The image shows the small agar spheres assembled, impacting each other they deform and create common sides with the adjacent spheres. This assembly creates hexagonal shapes with common sides forming a strong and firm structure, on a mechanical

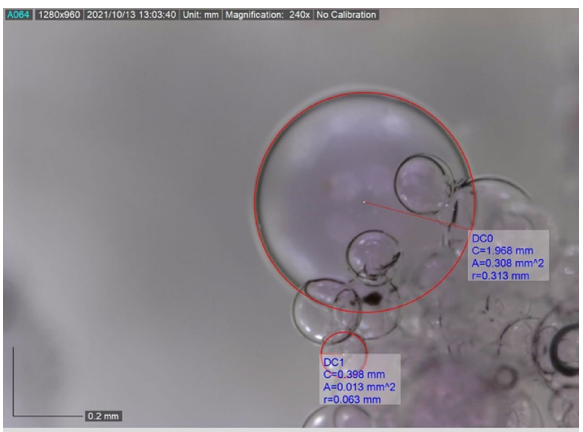

Fig. 3 Agar spray under light microscope with magnification ×250, with corresponding gel sphere measurements

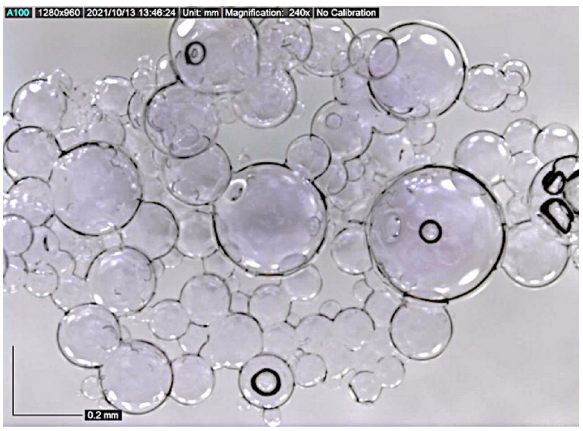

Fig. 4 Agar spray under light microscope with magnification ×250, with corresponding gel sphere measurements

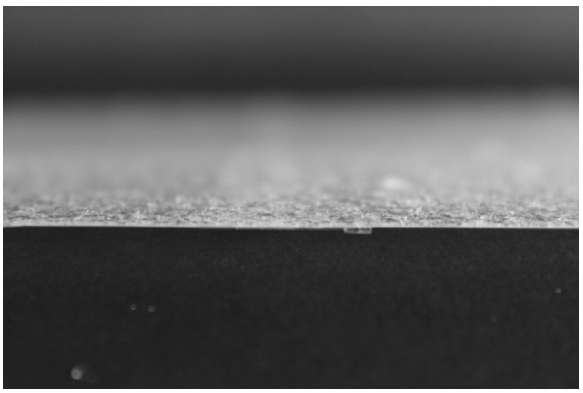

Fig. 5 The homogeneous and thin film of agar spray obtained after atomization

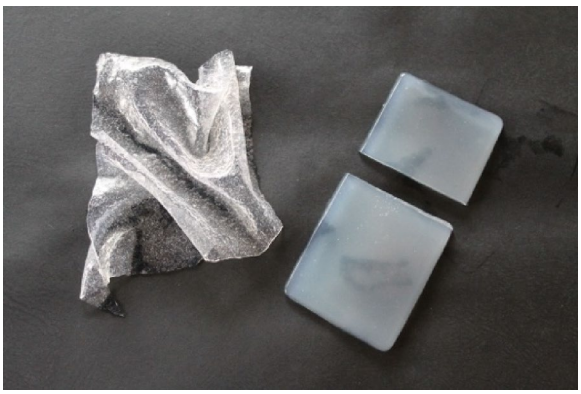

Fig. 6 Comparative image of the manipulable agar spray compared to the rigid agar obtained with traditional procedures

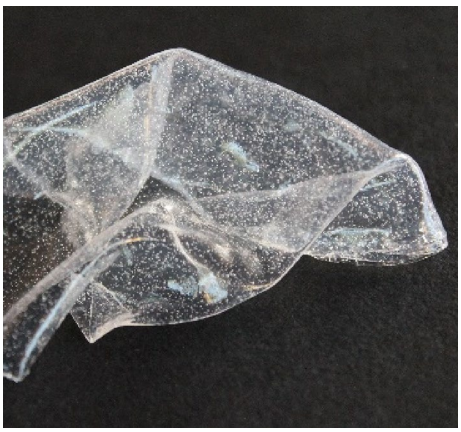

Fig. 7 Air bubbles incorporated in the thin gel layer

level a structure of this type looks like a very solid construction and is maintained over time without collapsing on itself or easily breaking (Fig. 6). Macroscopically, a distinction must be made between the internal face of the film in direct contact with the surface, and the external one where the last spheres of the gel are deposited. The interior takes the shape of the object that it comes into contact with due to the impact of the gel spheres which, under the thrust of acceleration, mold themselves to the surface, adapting to the shape of the object. If in traditional agar the external face always appears smooth as the gel slowly gels under the action of gravity, in the spray application the minuscule agar drops impact the solid state while retaining the spherical shape resulting from its atomization. For this reason, the external skin of the gel is covered by a multitude of regular spherical protuberances similar to a *bubble wrap*, due to the passage of the hot air it is forced to pass through the fluid gel at high speed and numerous air bubbles are incorporated in the gel spheres, they are visible as small voids interrupting its volume (Fig. 7).

Scanning electron microscope

Scanning electron microscopy (SEM) was used for the morphological characterization of lyophilized agar gels. A sample had been frozen by immersion in liquid nitrogen, then fractured subsequently lyophilized using a Labconco Lyophilized model Triad. The lyophilizate has been deposited on aluminum stubs coated with conductive carbon adhesive and metallized up to 8 nm of gold thickness and observed. Different accelerating voltage and magnification were used to observe the internal and external morphology of the gel.

Morphological observation of external spray agar gel shows a three-dimensional structure consisting of the assembly of agar sphere networks, the entire surface of the gel appears shielded by a very thin membrane, a sort of 'skin' that covers the spheres (Fig. 8). The cells

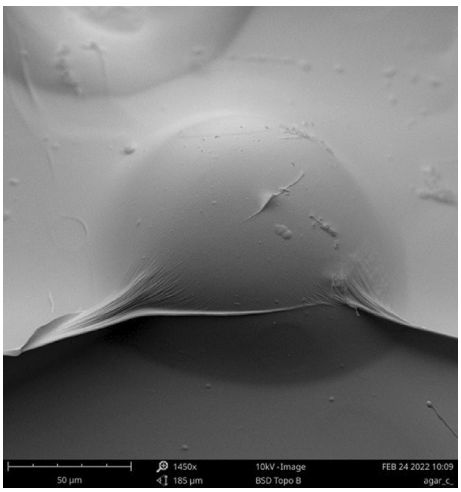

Fig. 8 SEM topographic image of external surface of freeze-dried CTS spray agar at 3% w/v

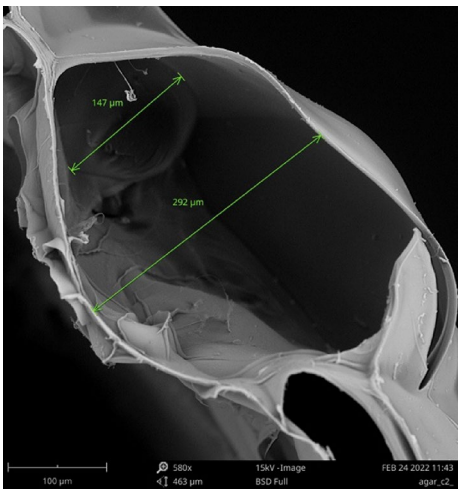

Fig. 10 SEM image of freeze-dried CTS spray agar at 3% w/v, with corresponding spheres measurements

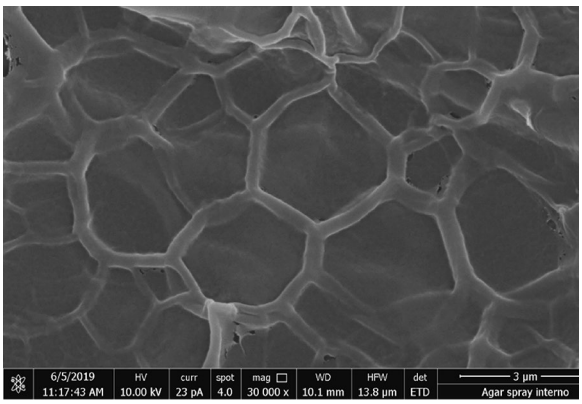

Fig. 9 SEM image of freeze-dried CTS spray agar at 3% w/v, the hexagonal mesh protected by a thin skin/membrane

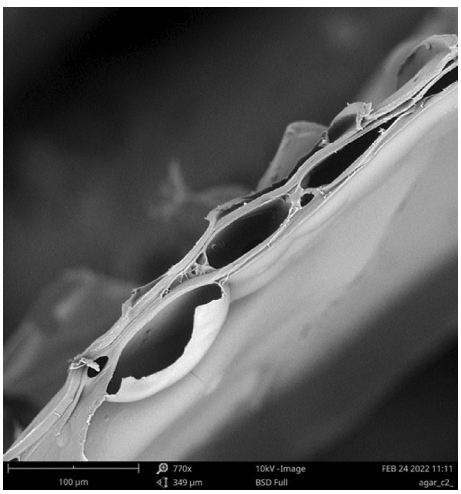

Fig. 11 SEM image of freeze-dried CTS spray agar at 3% w/v, polymeric foam structure

underline the membrane, appear barely sketched and not always visible, they are larger than the gel reticulum resulting from standard procedures, the corresponding cell measurements are around 2500 µm (Fig. 9).

Inside the gel there are air chambers created by the assembly of the gel spheres. The spheres are hollow and sometimes have other smaller spheres of gel inside (Fig. 10). This structure, visible in the images, is like a foam structure. This kind of polymeric foam is created by the instrument that generates the dispersion of the gas (air) in Agar in sol state. Closed cell foams have a cellular structure in which contiguous air bubbles are entrapped within a continuous macromolecular phase as shown in Fig. 11 [28].

The ability of polysaccharide gels, to form well-ordered spatial structures during cooling of their hot polymeric solution is a complex process that depends on several factors such as temperature, polymer concentration, polysaccharide structure, also on the presence of co and counter-ions [29, 30]. Gelation of agar in water solution involves transformation from a fluctuating disordered coil conformation in solution to a rigid ordered structure (co-axial double helix), forming the junction zones of the gel network [31]. In atomized agar gel the changes made to the 3D final structure are the result of a sol–gel transition process that takes place in a high-pressure system, and by rapid air-cooling, we can only hypothesize that

the air blown into the gel, compression to which the Agar spheres are subjected due to air resistance, and a cooling which occurs in fractions of a second modifies the structure. The external membrane that covers the gel can be the result of the high speed with which the agar drops come out of the instrument and the consequent friction with the air, which causes the collapse of the labile structures that are forming. The widest hexagonal mesh is the result of external pressure, exerted on the sphere by air friction, causing the structures to occupy as little space as possible, through the shape of the hexagon. The larger dimensions and the barely sketched appearance of the mesh are due to the impossibility of creating a narrow and articulated structure, requiring slower cooling times. It is hypothesized that the wider mesh allows the passage to larger molecules. Advantages of Polymeric Foams in Comparison to Solid Polymers are weight, variable density, high strength per unit weight, ease of molding, impact strength [32].

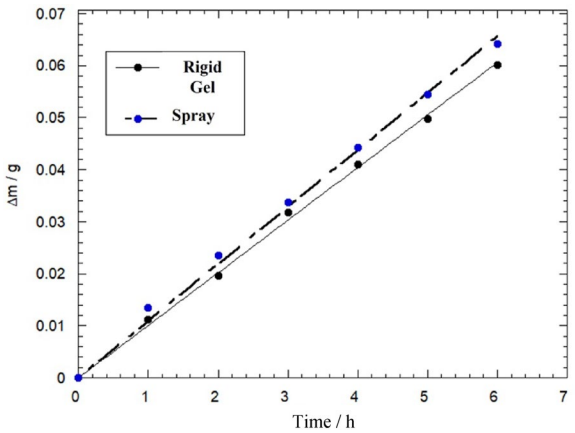

Fig. 12 The graph shows the behavior of two samples through the variation of mass as a function of time, and the different slope of two lines representing the samples

Surface properties of biofilms

Water permeability analysis

Water vapor transfer between the demineralized water and the environment with a saturated solution at T 28 °C and RH 29%, occurs through agar film: permeability value of the water vapor is proportional to the speed of vapor transmission water, therefore increasing the WVTR of agar film increases the permeability value (Table 1).

Results allowed a comparison between two systems, highlighting that permeability of atomized agar film is greater than permeability of agar film in a preformed mold. Water vapor moves through the atomized film faster than film obtained in a preformed mold, water diffusion inside atomized film is facilitated by the empty spaces of air that is incorporated during application (Fig. 12).

Two films were observed with the Dino-Lite digital microscope (30×), and it was possible to identify the compressed air bubbles that form spaces even after drying (Figs. 13, 14). On the other hand, film obtained in the preformed mold is very homogeneous. Water permeability can also be influenced by the chemical structure of the agar, SEM images showed that the atomized gel has a chemical structure formed by hexagons with a larger diameter than the shapes of the open pentagons that are in the agar obtained in a preformed mold. Hexagons, with a larger diameter, and the air bubbles that create empty spaces favor vapor diffusion inside the film.

Table 1 WVTR and WVP value of two samples

T: 28 °C, UR: 29%	Agar in a preformed mold	Agar spray
WVTR ($g/h*m^2$)	32.2	34.8
Err. WVTR ($g/h*m^2$)	0.3	0.5
WVP ($g*mm/(h*m^2*mmHg)$)	0.0414	0.0449
Err. WVTR ($g*mm/(h*m^2*mmHg)$)	0.0004	0.0006

Film transparency

An important optical property for materials is transparency that is influenced by morphology of the film and the filler concentration. The efficiency of light scattering for transparency analysis is important to calculate the linear attenuation coefficient. This coefficient is the ability of a material to attenuate the beam of radiation that passes through it due to its density. Therefore, morphology and the tendency to form aggregates is

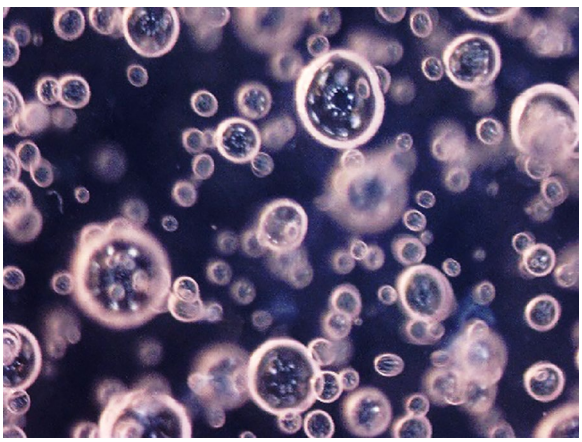

Fig. 13 Agar spray bubbles observed at Dino-Lite Microscope before dry

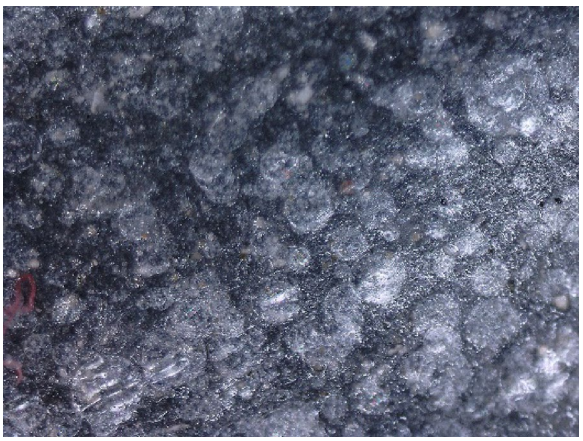

Fig. 14 Agar spray bubbles observed at Dino-Lite Microscope after dry

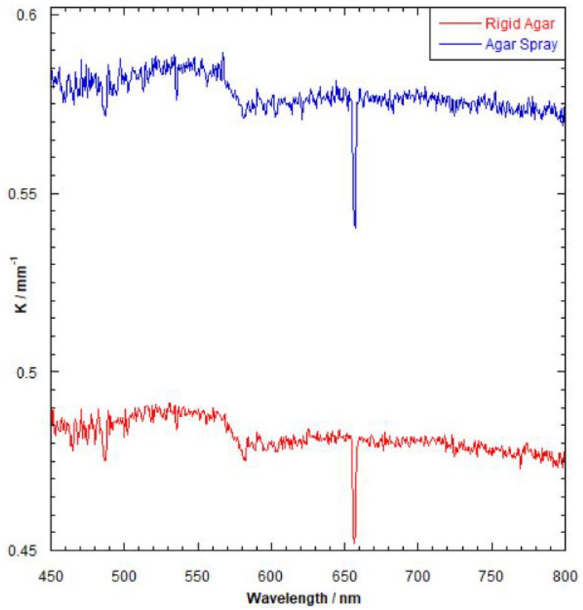

Fig. 15 The graph shows the linear attenuation coefficient representing the samples for transparency analysis, agar spray and rigid agar

affected. The trend in Fig. 15 confirms that Agar Spray doesn't change his transparency. Moreover, the attenuation coefficient for both agar, spray and rigid, are on range between $0.49 < K < 0.59$.

This result is particularly interesting, in particular when compared to the results obtained with polymeric foams in general, in the foam, bubbles are extremely small and numerous and have much more reflective surface than the liquid from which they are formed.

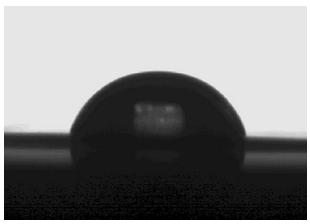

Fig. 16 Rigid gel

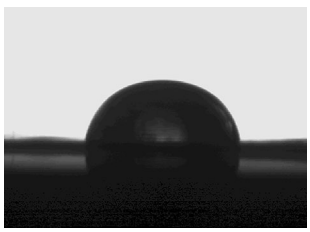

Fig. 17 Agar spray

Since all wavelengths of light are reflected, the resulting color is white and makes the gels not transparent.

Despite the high number of air bubbles created in the gel, the spray procedure does not alter the transparency. This is a great advantage, as the surface can continue to be observed through the gel during treatment.

Contact angle analysis

Contact angle analysis of atomized agar film was compared with agar film, prepared in a preformed mold. Images (Figs. 16 and 17) show different behavior of agar films; in fact, atomized agar film has more hydrophobic performance than agar film obtained in a preformed mold (Table 2).

The two processes that are active during the measurement of the contact angle are absorption and spreading of water on the film, which are closely linked to each other. The data obtained were modeled and graphed, using the following Eq. (5):

$$q = q_{in} \exp\left(-K_q t_n\right) \tag{5}$$

Table 2 Contact angle parameters of agar spray and agar in a preformed mold

	Agar in a preformed mold	Agar spray
Contact angle	73	80
K, constant decay of the contact angle	0.13	0.23
Err. K	0.0051	0.0081
n (1/0)	0.35	0.28

where q_{in} is the initial contact angle at time t = 0, n is the value due to the spreading or absorption contribution, in fact if n = 0 there is pure absorption, instead if n = 1 there is pure spreading.

It's possible to analyze the kinetics of the drop, namely the speed at which the contact angle changes, through the graph that shows contact angle as a function of time and the equation described above. The contact angle constant decay is greater for the atomized agar film; therefore, the contact angle changes faster.

The value of n indicates which two processes, absorption or spreading, has most influenced the constant decay of contact angle:

- n = 0.35, the contribution given by the absorption process is greater for the agar film of gel in a preformed mold.
- n = 0.28, in this case, on the atomized agar film, the major contribution is given by the absorption process.

In accordance with the measurement on permeability, water diffusion inside atomized agar film, i.e. moisture, is faster than water diffusion in the agar film obtained in a preformed mold, due to the morphology of the film that is affected from different applications (Fig. 18). Therefore, water diffusion inside the atomized agar gel is facilitated.

Mechanical analysis

The results of the test showing the values of the stiffness and the load strength is reported in Table 2 for both samples.

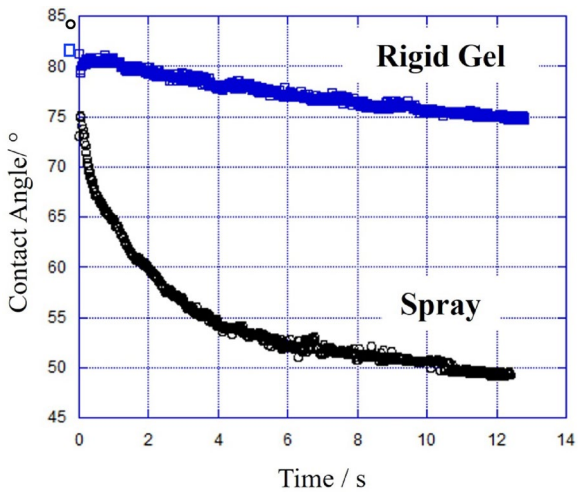

Fig. 18 Kinetic of contact angle

The average value of the elastic moduli of the material obtained by ratio among the stiffness G_0 and the momentum of inertia proportional to s^3 of the sample as well as the standard deviations are reported in Table 3.

It is clear that agar in a preformed mold is stiffer than the agar spray of a percentage of about 65% and the standard deviations are in general higher for the traditional agar. The conclusion of this preliminary investigation campaign is that the use of spray agar results into a more flexible film with higher strength of about 45% compared to a traditional deposited material and can result into a more useful method for cultural heritage restorations.

Water release analysis

The samples were observed in visible light and with a Wood lamp to compare the fluorescence of the organic dye, which marked the diffusion of the water inside the plaster specimens. The table shows the data obtained measuring water diffusion by micrometer.

By comparing the results, it is possible to note a reduction of water diffusion inside the samples where agar spray has been applied, about 1 mm, varying the times between 3 and 15 min (Fig. 19). When the drops of atomized agar impact on the surface they are already gelled, temperature of 20-22 °C, so water release is more controlled than traditional methods. Agar gel applied by brush is greater than the agar gel obtained in a preformed mold, because in this case the water is already completely incorporated inside of the cross-linking structure of the agar and there isn't free water in semi-fluid agar. In the atomized agar, agar drops colliding with the air instantly and gelled, therefore water is incorporated inside the helices formed by the rigid polysaccharide tubes, before reaching the surface. The air plays a very important role in the gelation process, the cooling of the agar in the air occurs when the thermo-hygrometric conditions are such as to reduce the temperature of the gel.

Water spreading evaluation

After the test the treatment with Agar in preformed mold results in an uneven cleaning, due to little contact with the rough surface of the paper and tidelines, no residues

Table 3 Mechanical parameters for agar spray and agar in a preformed mold

Material	Average elastic modulus [N/mm^2]	Average strength [N]
Agar in a preformed mold	0.665	3.35
Agar spray	0.402	4.85

Reproducibility is within 5% for both parameters

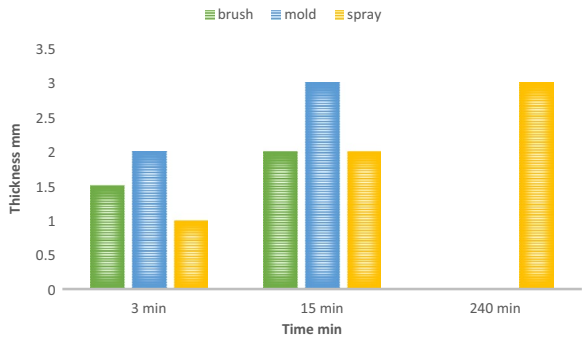

Fig. 19 Water release analysis comparing different methods

were found on the surface after treatment. Agar in semi solid state, brushed, passed under the mask, not allowing precise application, visible formation of a tideline and the presence of numerous perimeter residues, the paper is deformed due to the excess water released on the surface. The treatment with the agar spray cleaned evenly, there are no tide lines and residues. Application results are shown in Fig. 20. Additionally, ATR -FTIR experiment on the surface after the application of the agar spray did not show the characteristic signal of the agar which, instead, is present after the treatment with semi-solid agar. The strong similarity of the reported spectra of the paper samples before and after the agar spray treatment indicates that the spray agar has been completely removed (see Additional file 1: Fig. S1).

Oil paint on cardboard from the second half of the twentieth century unvarnished, with a widespread craquelure was used to verify the control of the procedure on a limited area.

A mask was made by cutting some sections of the surface of a plastic sheet to confine the atomization to a limited area fixed with neodymium magnets. After the test, 3% Agar with a water solution with 0.5% w/v citric acid/NaOH at pH 6.5 prepared as already described, was sprayed on the mask, followed by a clearance step with the Agar with adjusted water at the same pH Agar at 3% (w/v). After application time of 2 min the film was removed in two different ways by rolling the film on itself and lifting it, the observation with an optical microscope shows that the cleaning appears equally uniform, on the border line of the clean area a very precise application without tide lines is visible (Figs. 21, 22). SEM images showed the agar spheres are assembled on the three-dimensional nature of the brush strokes of the paint, in a homogeneous film, also cleaning the interstices and the craquelure (Fig. 23, 24). SEM images in Figs. 25 and 26 show that the procedure does not damage the paint film, and the cleaning action is very delicate and moderate. It's important to emphasize that the surface where the agar spray film has been raised to remove and where the gel thickness was less than one millimeter, some residues were found. No residue was present where the film has been rolled onto the surface and the thickness was more than one millimeter. These residues, due to incorrect procedure, were left on the surface for 3 months, the mechanical action with dry methods on the dry residues was not effective, given the hydrophilicity of the dry film of the agar spray confirmed by the analysis, we decided to treat these residues with a nebulizer to swell the residues and remove them with a delicate mechanical action with soft silicone brushes, the residues were easily removed without damaging the surface.

Conclusions

This quite unique morphology obtained by the spray procedure, affects the mechanical and physical properties of the gel. The experimentation has shown that the agar spray has an extraordinary ductility, guaranteeing less adhesion and more control over diffusion of the aqueous solution.

The procedure allows to obtain precise applications with greater water control than traditional applications, in addition to the treatment of large surfaces. Agar spray cleaning action is made faster and more effective by the impact/compression of the small gel spheres on the surface. In fact, in traditional applications water is slowly released into the substrate surface depending on dwell time; thanks to syneresis soiling is dissolved by the water and subsequently absorbed into the gel through capillarity action within the cavities of molecular gel structure and with the help of osmosis [15]. In the spray application, the process is accelerated by the elastic response. Water sweeping out from agar gel spheres full of air, after impact, is released into the surface and Syneresis is enhanced under external deformation that the gel undergoes. The gel as "molecular sponges," in an elastic response to compression, quickly draws back the water inside and fixing the dirt to the skin of the gel. This rapid exchange also allows great control of the water confinement for the rapid recapture of the liquid by the gel, preventing tidelines.

The micro spheres of agar can coat complex surfaces ensuring a homogeneous cleaning, but the thickness and the method of removing the film from the surface is a factor of fundamental importance to avoid residues. An incorrect removal of the gel on complex or very absorbent surfaces or too thin films, less than one millimeter, can cause some spheres to disengage during the removal phase or the film to break.

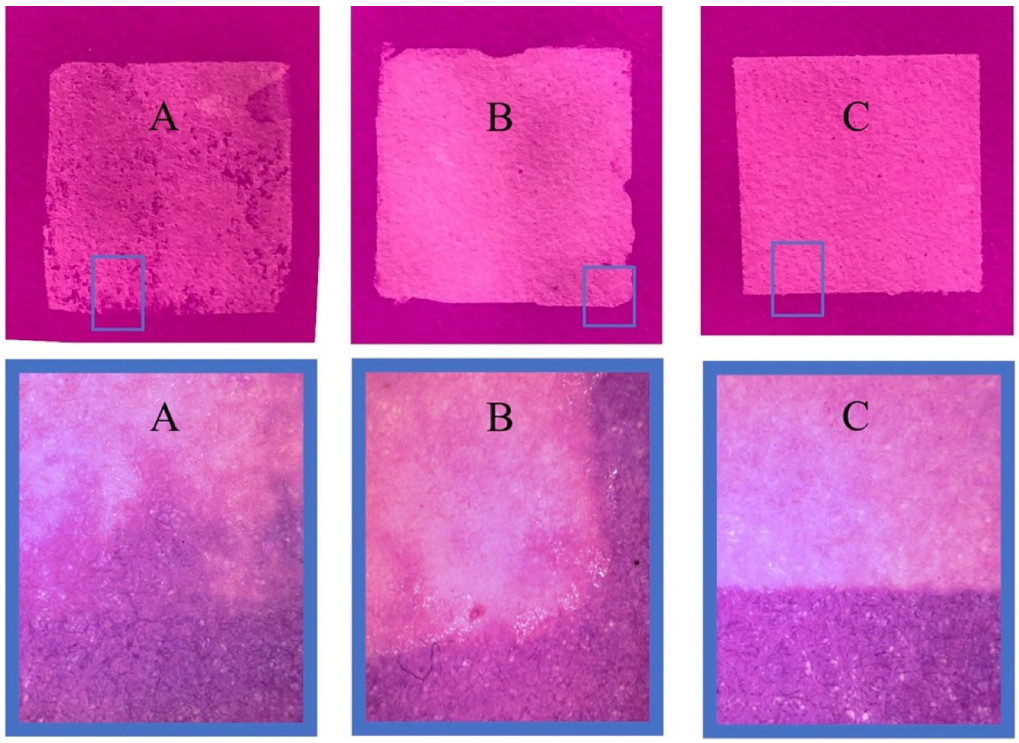

Fig. 20 Image of the surface of the paper specimens stained with rhodamine, after the application with Agar in preformed mold (**A**), Agar in semi solid state (**B**), Spray Agar (**C**), with the corresponding detail of the surface observed under an optical microscope ×50

Fig. 21 Image of the oil painting on cardboard and clean area at the top

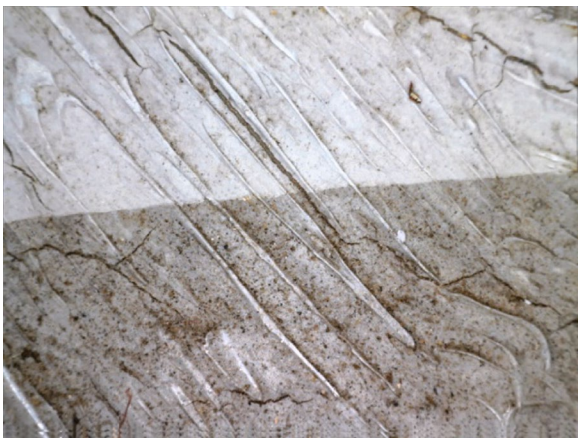

Fig. 22 Detail of the border area after cleaning

Due to their small size, agar spheres (area ranging from 0.013 to 0.308 mm^2), dry rapidly.

The experiment has shown that the residues left on the surface, once dry, are difficult to remove, due to the impact it makes them adhere effectively to the surface. The water permeability analysis of the dry agar spray confirms a greater/more significant water permeability, the

Fig. 23 Oil paint surface observed under optical microscope at ×50 before cleaning

Fig. 24 Oil paint surface observed under optical microscope at ×50 after cleaning with spray agar

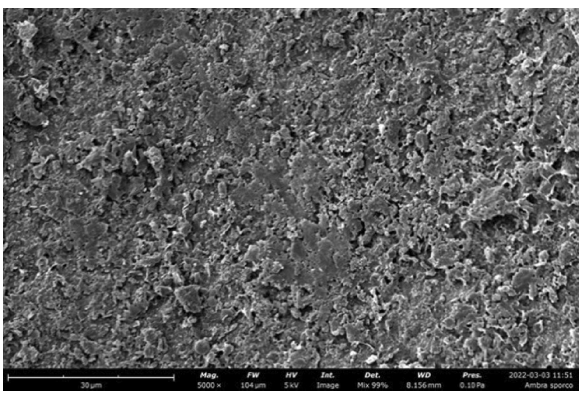

Fig. 25 SEM image of paint surface before cleaning

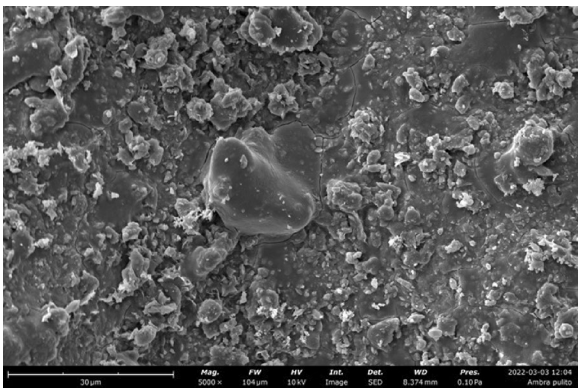

Fig. 26 SEM image of paint surface after cleaning with spray agar, the surface still has traces of dirt

experiment has shown that using a vaporizer is useful to reactivate the residue and remove it with the use of soft silicone brushes, easily and safely.

This data contradicts the literature data, defining agar as a perfectly stable material, non-hygroscopic when dry [12, 15]. Future studies will need to be conducted to evaluate biodeterioration of dry spray residues in very humid environments and for the optimization of the procedure based on environmental parameters. An addition investigation to be investigate regards poor mechanical cohesion/adhesion surfaces that might be damaged by spray application.

Materials

Agar is a polysaccharide extracted from algae of the family Rodoficee (Gelidium and Gracilaria species) capable of giving stiff thermo-reversible gels (Gelling temperature: 38–42 °C, melting point: 85–90 °C, pH of a 1.5% solution: 6.0–7.5) and it was purchased from CTS Europe, AGA RART.

Deionized water (18.2 Ω cm resistivity at 25 °C) was used in the experiment. Calcium chloride dihydrate, $CaCl_2$, ($\geq$ 99%) was from Panreac and a saturated solution of $CaCl_2$ was prepared to control temperature and humidity on the desiccator. Rhodamine B241, a fuchsia-colored organic dye, is a Sigma-Aldrich product, that was used for water release control. Gypsum, $CaSO_4{\cdot}2(H_2O)$, was purchased from ZECCHI.

Abbreviations

A: Absorbance; CCD: Charged-coupled device; D: Mass; FTIR: Fourier Transform Infrared Spectroscopy; GC–MS: Gas Chromatography coupled with Mass Spectroscopy; G0: Stiffness; HVLP: High volume low pressure; IR: Infrared; L: Thickness; NaOH: Sodium hydroxide; OCA: Optical Contact Angle; q: Contact angle; qin: Initial contact angle; s: Thickness; SEM: Scanning electron microscopy; UV–VIS: Ultraviolet–visible; WVP: Water vapor permeability; WVTR: Water vapor transmission rate; Δm/Δt: Weight loss as a function of time; Δp: Partial pressure.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00756-9.

Additional file 1: Figure S1. ATR-FTIR spectra of paper specimens. Paper non treated (**a**), paper after Agar Spray (**b**), paper after Agar in semi solid state (**c**) and Agar (**d**) itself.

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Author contributions
AG conceived and designed the research, she planned and carried out the experiments and part of the analyzes, she carried out the drafting of the manuscript. MRC performed the measurements, processed the experimental data. GL aided in interpreting the results and helped supervise the project. All authors provided critical feedback and helped shape the research, analysis and reviewed the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

Author details
[1]Department of Applied Arts, Academy of Fine Arts, Via Papireto 20, 90134 Palermo, Italy. [2]Department of Physic and Chemistry, University of Palermo, Viale delle Scienze, Ed. 17, 90128 Palermo, Italy.

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