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Review

Biologically Derived Gels for the Cleaning of Historical and Artistic Metal Heritage

Arianna Passaretti [1,2], Luana Cuvillier [1,2], Giorgia Sciutto [3], Elodie Guilminot [4] and Edith Joseph [1,2,*]

[1] Haute Ecole Arc Conservation-Restauration, HES-SO, Espace de l'Europe 11, 2000 Neuchatel, Switzerland; arianna.passaretti@he-arc.ch (A.P.); luana.cuvillier@he-arc.ch (L.C.)
[2] Laboratory of Technologies for Heritage Materials, Institute of Chemistry, University of Neuchâtel, Av. Bellevaux 51, 2000 Neuchatel, Switzerland
[3] Department of Chemistry, University of Bologna, Ravenna Campus, via Guaccimanni, 48120 Ravenna, Italy; giorgia.sciutto@unibo.it
[4] Arc'Antique conservation and research laboratory, 26 Rue de la Haute Forêt, 44300 Nantes, France; Elodie.GUILMINOT@loire-atlantique.fr
* Correspondence: edith.joseph@unine.ch or edith.joseph@he-arc.ch

Abstract: In the general global rise of attention and research to seek greener attitudes, the field of cultural heritage (CH) makes no exception. In the last decades, an increasing number of sustainable and biologically based solutions have been proposed for the protection and care of artworks. Additionally, the safety of the target artwork and the operator must be kept as core goals. Within this scenario, new products and treatments should be explored and implemented in the common conservation praxes. Therefore, this review addressing metal heritage is aimed to report biologically derived gel formulations already proposed for this specific area as reliable tools for cleaning. Promising bio-gel-based protocols, still to be implemented in metal conservation, are also presented to promote their investigation by stakeholders in metal conservation. After an opening overview on the common practices for cleaning metallic surfaces in CH, the focus will be moved onto the potentialities of gel-alternatives and in particular of ones with a biological origin. In more detail, we displayed water-gels (i.e., hydrogels) and solvent-gels (i.e., organogels) together with particular attention to bio-solvents. The discussion is closed in light of the state-of-the-art and future perspectives.

Keywords: metal; conservation; cleaning; hydrogels; organogels; bio-solvents; cultural heritage

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1. Metal Care in Cultural Heritage: An Overview

In the motley world of cultural heritage, metals are among the main actors since the emergence of metalworking of gold, silver, and copper [1]. Due to their inherent chemo-physical properties and aesthetic potential, metals have had a broad spectrum of applications in art through the ages: sculptures, musical instruments, jewelry, utensils, scientific instruments, decorative arts, and so forth [2–7]. Such a massive presence in cultural heritage has inevitably yielded a plethora of studies on metal preservation to safeguard this inheritance through generations.

The core problem for the preservation of metals is the spontaneous process of corrosion towards which they naturally tend [8]. Indeed, corrosion is a thermodynamically favored phenomenon, which alters metals' original features and represents a tremendous economic loss in whichever sector, as well as a conservation issue in the heritage field [9]. Different aspects can influence corrosion processes: along with the basic dual presence of water and oxygen, the characteristics of the surrounding environment rule and meddle the phenomenon. Factors such as burial soil, marine location, microbiological activity, atmospheric pollutants, and, in general, alloys' complexity and exposure conditions play an important role in this detrimental process [10–12].

From a preventive perspective, despite the utopic willingness to artificially control the micro-environment, not all the active agents in corrosion can be avoided or adjusted, especially if we consider outdoor artifacts. Therefore, in metal care, the first phase consists of tackling the corrosion layer present. This usually means either stabilizing or removing the corrosion compounds, depending on the substrate nature and the type of alteration exhibited, in addition to an evaluation according to restoration principles (e.g., noble or unstable patina, corrosion as proof of authenticity or anesthetic degradation) [13]. Both issues can be addressed from different angles. For stabilization, the current techniques go from electrolytic reduction, dichlorination, and immersion in an alkaline sulfide solution for archaeological iron artifacts, to the use of chemical chelating agents or corrosion inhibitors such as benzotriazole (BTA) for copper-based relics [14–17]. On the other side, for corrosion removal, we can cite potentially invasive mechanical methods such as wet or dry abrasion (sanding paper or cloth, sandblasting, scalpel, laser, or cryogenics), as well as chemical approaches, exploiting electrochemical reduction or synthetic complexing agents such as ethylenediaminetetraacetic acid disodium salt dihydrate (Na_2EDTA), tetraethylenepentamine (TEPA) and triammonium citrate (TAC) [18].

In the following step, a solid solution is to prevent the interaction between the metal surface and the external detrimental factors. The use of organic coatings is thus a favored method, being able to achieve a film with the required physical, mechanical, and aesthetical characteristics [19]. The typical products employed are both from natural or synthetic origin—e.g., beeswax, epoxy resin, acrylic-based varnish [20]—however, the latter has acquired more relevance since they are designed with the desired features and fine-tuned to be the most environmental-proof as possible [21]. These compounds are also sensitive to detrimental factors through time, even if to a lesser degree or merely not like metals. Therefore, there might be the necessity of removing—and replacing—them once their preservative purpose is compromised (e.g., film cracking and detachment, harmful reaction with the underlying substrate itself, visual appearance no more acceptable according to conservation standards) [22,23].

To achieve this purpose of removal, the most employed approach is the dissolution of the no more-desired coating present [24–27]. Solubility follows the basic principle of like dissolves like: "chemically similar" substances—i.e., mainly in terms of intermolecular forces — are soluble in each other. Despite its simplicity, the rule allows to navigate when choosing solvents; also, conservators often rely on helpful solubility diagrams, such as the Teas Chart [28], for the selection of appropriate solvents according to the case treated.

However, solvents can turn to be unsafe for users due to their flammability or by prolonged inhalation for instance. This scenario, unfortunately, fits with the role of conservators, who often employ in a confined workplace solvents such as xylene, toluene, isopropanol, ethanol, acetone, white spirit, turpentine [29]. Nevertheless, their dangerous repercussions are also visible on a vast scale in nature pollution and consequently global human health [30], thereby addressing the world of conservation to responsible greener solutions [31,32].

Furthermore, in art conservation, one of the leading priorities is the safety of the artwork itself. This entails the importance not only of suitable products but also of an appropriate application methodology [33,34]. In the case of metal heritage, the presence of a corrosion layer turns the substrate into highly porous and drastically more water/solvent-sensitive. Moreover, solvents can be potentially corrosive if not properly handled and retained [35,36]. Furthermore, it might happen that the coating, once solubilized, is not taken away and gets re-deposited on the surface.

To minimize such potential inherent drawbacks of solvents and comply with the need for a proper application procedure, delivery systems are a valid alternative for art conservation, to assure a controlled release of treating loaded solutions.

2. Gels: A Reliable Delivery System

Nowadays, various methodologies are at the disposition of conservators to obviate the use of neat solvents or unrestrained treating solutions [37–41]; however, the most reliable, tailorable, and performing are certainly gels [42].

Gels can be defined as biphasic systems made of at least two components: a polymer and a fluid phase. The polymer, acting as a thickening agent, forms a three-dimensional network in the liquid medium [43]. This cross-linked system can trap the liquid, limiting simultaneously evaporation and release. The liquid is retained in the network using interactions between the polymer chains. Due to their chemical nature, these interactions can be reversible thanks to weak bonds—i.e., hydrogen bonds, van der Waals—or irreversible in presence of covalent bonding. The different bonding leads to the formation of physical and chemical gels [42], respectively, with different chemical features [42]. In particular, the inherent forces within chemical gels are stronger than the adhesive forces between gel and substrate to be treated. This implies an easier removal of such formulation, thereby avoiding extra steps to get rid of potential residues [44].

Finally, gel systems can be classified according to the fluid contained inside the polymer matrix: in presence of water, they are called "hydrogels", while non-aqueous formulations, hence loaded with organic solvents, are defined as "organogels" or "solvent-gels" [42].

Cleaning Gels in Cultural Heritage

At the beginning of the nineties, Richard Wolbers introduced gels to the world of art conservation [45]. His work focused on the treatment of paintings [46], which are water- and solvent-sensitive targets; thus, gel formulations seemed optimal for higher-controlled and less invasive interventions. Considering the promising evidences, this technique became rapidly captivating in several fields, including wall paintings and stone care [47–49]. Moreover, the employment of gels turned to be essential when dealing with paper or wood substrates, for which the conventional procedure by immersion into water solution was not ideal [50,51].

Nowadays gel-based cleaning protocols are recognized as well-grounded and effective methodologies, thanks to their high retention and interesting rheological properties that allow a precise and selective treatment confined to the upmost layer [52,53]. In addition, such systems can adsorb the undesired substances to be removed (i.e., corrosion products and degraded protective materials) in the polymeric matrix. Finally, they drastically limit solvent fumes released in the air, thereby creating a less hazardous work environment for operators.

Nevertheless, the use of gels is still anecdotic on metal artworks, even though there is the need for localized treatments, considering how heterogenous they can be: composite artifacts, gilded artworks, painted metals, etc.

In a comparative study on gel and swab cleaning on brass, AFM (Atomic force microscopy) pictures proved the existence of scratches after the swab action due to particles originally present on the metal. On the contrary, the gel performance, although slightly less efficient, was smoother and non-invasive, leaving no physical changes on the surface [54]. These observations led to the setting-up of a project named "Gels-Métaux", initiated in France and expanding to a larger-scale, calling forth an international appeal. The project tackles various tricky topics: gel preparation protocols, compatibility between formulations and active agents (i.e., chelators), and introducing gels into new branches of metal conservation like archaeological findings [55].

Notably, some studies regarding the use of synthetic gels have been published for metal conservation. In 2014, a set of indoor bronze sculptures were successfully treated via Carbopol-gel applications to remove layer-by-layer dirt, protective waxes, and corrosion phases [56]. While water-based formulations made of the synthetic polymer poly (vinyl alcohol) (PVA) were designed by Baglioni et al. as part of the NANORESTART project and assessed on copper alloys [16,57]. Despite the captivating potentialities, high attention must be addressed to their waste management and the correlated ecological impact. For instance, PVA is readily water-soluble; however, inadequate disposal can cause pollution of groundwaters. Its biodegradation is performed by very peculiar bacteria, barely represented in nature [58,59]. Another critical point is the sustainability of gelling agents' production. Although bio-derived from cellulose, often the synthesis of cellulose-based polymers cannot be considered green, since it may require reagents hazardous for the aquatic environment (e.g., chloroacetic acid used for the synthesis of carboxymethyl cellulose) [60].

In contrast, scarcer is the literature on green or bio-based alternatives. Therefore, an overview of both hydro- and solvent-gels is proposed here, highlighting their suitability for metal heritage.

3. Bio-Based Hydrogels for Metal Preservation

A wide variety of hydrogels based on natural polymers have been exploited, especially in the biomedical field, including polysaccharides and proteins (collagen and gelatine) [61]. However, in art conservation, mainly polysaccharides have been employed, namely agar, gellan gum, xanthan gum, and chitosan (Figure 1). The resulting formulations all belong to the class of physical gels. Indeed, the water is physically retained within the gel network by hydrogen bonding of the polar groups of the bio-polymers [62]. Although the literature mentioning their application on metals is quite unusual, bio-based systems appear as perfectly fitting it.

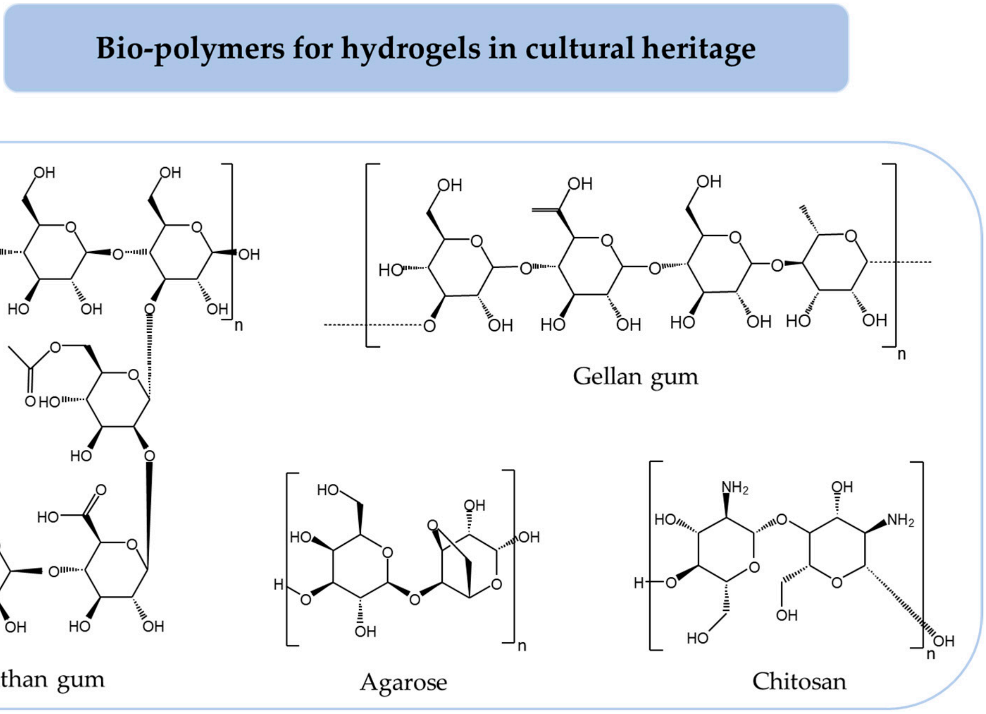

Figure 1. Bio-polymers used for hydrogel formulations in cultural heritage: structural formula of xanthan gum, gellan gum, agarose and chitosan.

3.1. *Physical Hydrogels*

3.1.1. Agar

Rigid gels are valid delivery systems due to their capability to retain solvents that allow to focus the cleaning on the uppermost layer, thereby limiting negative actions on eventual sensitive underlying materials. Moreover, their compact consistency makes them appreciated for the easy removability or even peelability [63]. However, their main advantage is also their main weakness. Being rigid, it is difficult to achieve good performances on rough substrates where the contact gel-surface is difficult to maintain. In art conservation, the leading thickening agent in this category is uncontestably agar. Agar is a gelling powder, extracted from red seaweed membranes, in particular *Gelidium* sp., *Pterocladia* sp. and *Gracilaria* sp. [64], which forms a rigid hydrogel after being heated above 90 °C and cooled down [63]. Agar is usually prepared in concentration from 2 to 6% *w*/*v*.

Agar is broadly available, with various purity and composition according to different assigned purposes in the food industry, biomedicine, or art conservation [65,66]. The primary compound is agarose, which is more often used impurified together with agaropectin, being less expensive [63].

The heating process can be a turn-off for conservators, especially when they are required to work out of their lab, with no heating devices. In addition, an agar gel cannot be formed with acidic or basic solutions, which, however, can be absorbed by immersion once the gel is created. Finally, it gives particularly satisfying results when directly applied hot on the target, as in a liquid state, it still has the chance to conform to the artifact surface [55].

A gel called Nevek® has been recently developed and is mentioned as particularly suitable for the cleaning of metallic surfaces [55]. It is a ready-to-use 5% double gellified agar with the addition of 5% ethanol to avoid microbial growth during storage.

In previous literature, several methodologies based on agar were tested on metals. In the case of archaeological silver horns, an agar gel was prepared and impregnated with the active compound before application [67]. Meanwhile, on Islamic inlays copper-alloys, agar powder was mixed to a complexing solution, buffered at pH 7, and then warmed up to gel [68]. In 2013, an agarose rigid gel was successfully exploited on Japanese lacquer objects, to face the complex combination of metals present, namely tin, lead, and iron. The use of a hydrogel system addressed the electrolytic reduction treatment exclusively on the corroded areas, without affecting and altering the surrounding water-sensitive lacquers [69]. Recently agar formulations resulted to be efficient carriers for the electrochemical cleaning of silver threads and silver leaves [70,71]. However, they were not performing at the best on non-flat objects due to their rigidity and thus their tendency to crack [71].

Still, attention should be drawn to the recent shortage of agar supplies, because of its increasing exploitation in numerous fields and the unpredictability of its production due to the dependence on marine conditions (i.e., warmth, infesters). Although the usage of agar and agarose is moderate in art conservation compared to other sectors, it is important to be aware of these issues and try to act accordingly, by choosing other gels whenever possible [64].

3.1.2. Gellan Gum

Gellan gum is a polysaccharide produced by the bacterium *Sphingomonas elodea* [66]. Similar to agar, it forms a rigid gel, compatible with impregnation of acidic and basic solutions once prepared and best-performing if applied warm [55]. Though some references mention the incompatibility of gellan gum with complexing agents [68].

A commercial derivative-form, the Phytagel®, which can be prepared cold, has been used on copper artifacts [72]. It was selected thanks to its adherence on vertical surfaces, ease of removal, and compatibility with the chosen active agents (i.e., microorganisms). In addition to the transparency considered an asset as it allowed to observe and monitor the treatment, its gelling properties are displayed even with low concentration (0.5 to 5 g/L) and are stable in a wide pH range [72].

3.1.3. Xanthan Gum

Xanthan gum is a thickening agent biosynthesized by the bacterium *Xanthomonas Campestris* through the fermentation of sucrose or glucose [61]. It is compatible with aqueous solutions in a wide range of pH, although appears to be less effective in gelling basic solutions [55]. The inherent high viscosity makes its removal complicated from metallic substrates [55,68], requiring the use of water afterward for a perfect elimination, which would annul the primary goal of the use of gels.

Although never tried out on metallic substrates, the removal of Paraloid® B72, the most common coating for metals in CH [20], was achieved on a painting thanks to Vanzan® N-FC, a commercially available xanthan gum, with only 5% of solvent in the liquid aqueous matrix. This is an encouraging step towards the removal of acrylic coatings on metals with the use of aqueous natural gels that have the advantage of being safer, both for the environment and conservators [73].

3.1.4. Chitosan

Chitosan is the N-deacetylated form of chitin, which is, in turn, the most abundant animal polysaccharide present in the exoskeleton of crustaceans and the cell wall of fungi [61]. Currently, chitosan is exploited mostly for drug delivery [61]. In general, it can gel in presence of both alkaline and acidic solutions [74].

In art conservation, it is rather uncommon, but it was used to develop chitosan-based coatings for corrosion mitigation, of copper alloys [25]. The research aimed to design a non-toxic, sustainable, easily-applicable, and, whenever necessary, removable matrix to incorporate corrosion inhibitors for copper—mercaptobenzothiazole (MBT) and BTA [25]. Remarkably, the chitosan polymer allowed the presence of a reduced quantity of toxic inhibitors and diminished their leaching in the environment. The transparent and colorless appearance of the chitosan-based lacquer meets the aesthetic standards in metal care. In addition, it showed a great adhesion on metals [25]. Furthermore, the development of chitosan-based active protective coatings has been carried out for aluminum alloys as well, by doping the matrix with either Ce^{3+} ions or MBT [75,76]. In CH, this could be of particular interest for aeronautical heritage, considering for instance relics from World War II [77].

Finally, chitosan-hydrogels have been investigated for their capacity to be loaded, and thereafter release BTA on metallic surfaces [78].

3.2. Chemical Hydrogels

Lai et al. achieved chemical cross-linking of a bio-based polymer containing chitosan, L-cysteine, and itaconic anhydride. Interestingly, the end-product presents metallic ions uptake properties. The synthesis is described as simple: after mortar-grounding the three components, the mixture is placed into a mold and left in immersion in an acetic acid solution for twenty-four hours [79].

Chemical hydrogels can be easily realized using the so-called Michael addition reaction [61,79]. The covalent bonding between the different polymer chains is hence obtained thanks to amino groups [79]. As opposed to the chemical hydrogels formulated by Baglioni et al. [39,44,57], these natural chemical hydrogels come from renewable sources and are biodegradable [80]. These qualities combined with the inherently favorable consistency of chemical gels, make them promising actors for the treatment of metal surfaces in cultural heritage.

4. Organogels for Organic Coatings Removal

Nowadays organogels as cleaning systems have been explored mostly on paintings and graphic documents, being multi-component artifacts and strongly sensitive to solvents [81–83]. On the contrary, in the literature rare is evidence of their application in the branch of metal conservation [84,85]. The main critical aspect of such implementation appears to be the rigidity of such systems. Most of the time, indeed, it implicates a non-even contact and adhesion on the surface, which, for metals, can be complex in terms of shape (e.g., curves, vertical position) and morphology (e.g., due to corrosion). However, the high modularity of gels eases the feasibility of satisfactory results on metals alike on other substrates.

Organogels in CH are frequently designed with non-green polymers and/or solvents [82,83,85,86]. Indeed, little is the attention addressed to the development of sustainable solvent-gel formulations, which can be achieved by the selection of specific green solvents (Sections 4.1 and 4.2) and thickening agents (Section 4.3.1). Despite the clear principle of assembling two components to form a gel, these components must be compatible to create well-polymerized gels that are satisfactory in terms of stability and performance [39].

The acceptance of green organogels should be addressed to the sustainability of all the components employed (i.e., polymer matrix, solvents, and additional constituents). Utmost care should be paid in the choice of the materials, considering features ranging from the original derivation of the sources to their recyclability and degradability [87–89].

4.1. Solvent Greenness

Solvents are indispensable chemical tools in art conservation, as much as in a broad spectrum of sectors: pharmaceutics, fuel, food industry, household products, cosmetics, paints, etc. In other words, solvents are part of everyday life. Therefore, it appears obvious to put these substances under review, not only for possible consequences on direct users but also for the potential impact on a wider scale in the environment, and consequently, on global health. The topic is crucial and reached the attention of renowned institutions such as the World Health Organization [90] that pointed out problems derived from certain substances and drew up localized restrictions on their use, to mitigate the derived hazard.

Besides the spheres of human and nature health, in the field of cultural heritage, the evaluation of the potential harm on the pieces of art themselves is crucial, even overriding compared to the abovementioned factors.

From this perspective, it is legitimate that there is growing concern around turning the page from several commonly used solvents towards the so-called "green" solvents. This term gathers a wide range of greener alternatives that can be selected and recognized using twelve factors listed in the journal *Green Chemistry* [91]. They face aspects such as renewable origin, recyclability, relative energy consumption and biodegradability; toxicity and flammability; availability on a large scale, and affordability; but most importantly, they should display properties and performances analogous to traditional solvents.

Hence, water could be ascribed among the greenest solvents, being fully human and environmentally harmless, readily supplied, and not expensive. Nonetheless, several reactions cannot be faced with water alone due to solubility factors. In addition, for metals, it is important to remind that water is a key player in the spontaneous natural process of corrosion, implying the willingness of substituting it with more substrate-friendly organic alternatives.

Besides water, an organic solvent satisfying even a few of the Green Chemistry principles can be rated as "green" weighed against its conventional counterparts. Thus, a proper comparative assessment should be carried out, considering the three macro-subjects of health, safety, and nature, according to one of the numerous scoring-guides proposed in the literature [90,92].

4.2. Bio-Based Solvents

Solvents obtained from biomass are named "bio-solvents". They are produced from readily renewable feedstocks, by fermentation or chemical transformation of biomass derivatives [90]. This implies the valorization of sources otherwise considered as wastes, increasing the greenness score of this class of chemicals.

Due to the strong lack of previous literature regarding bio-solvents in the field of metal heritage, the present review proposes a reasoned selection of bio-solvents.

4.2.1. Bioethanol and Derivatives

Ethanol is a ubiquitous solvent in several fields, in cultural heritage it can be used to work with natural resins and varnishes.

While the petrochemical industry produces ethanol by ethylene hydration, the bio-based version is naturally obtained from yeast's metabolic activity from agricultural wastes rich in sugars and lignocellulosic materials [90]. Its production via fermentation allows benefiting from sources judged as discards conversely, hence accomplishing the green principle of sustainable origin. Therefore, bioethanol is a perfect example of a drop-in eco-friendly replacement of possible large spread in any area of application since it is a well-known solvent with a green origin. Because of its evident identical features to ethanol, bioethanol is one of the most popular bio-based solvents and alcohols.

Furthermore, bioethanol can be employed as raw material for the synthesis of other organic solvents such as acetone and ethyl acetate [90]. The bio-derived acetone is free from some non-renewable contaminants, such as benzene, phthalates, and other phenols, possibly coming from petroleum [93]. On the other side, ethyl acetate has begun to be selected as a favored choice to replace several polar solvents [94], including acetone itself. In art conservation, in general, ethyl acetate is used normally to dissolve synthetic lacquers (e.g., acrylic- and nitrocellulose-based), guaranteeing low vapor pressure, toxicity and cost, in addition to a pleasant odor which is leading it to a massive use in the cosmetic industry [95].

4.2.2. n-Butyl Alcohol and Derivatives

n-Butyl alcohol (or n-butanol) is a colorless solvent, which, apart from a petrochemical origin, can be bio-sourced therefore acquiring the title of "bio-butanol". It can be produced by bacterial fermentation of renewable feedstocks sugar- or lignocellulose-storing and, remarkably nowadays, this green process is economically equal to the non-sustainable counterpart [90].

The inherent low acute toxicity makes n-butyl alcohol accepted in the food and personal care industry, as well as in the field of art conservation [90,96]. Indeed, its efficacy as a lacquer solvent is well-known for example on hard copal and shellac. However, its fumes can have a toxic effect by lengthened inhalation; thus, despite the bio-origin, this solvent is harmful under the irrevocable criterion of human health. Nevertheless, its employment is not only limited as a solvating agent but also in the manner of raw material to produce other widely used substances, including n-butyl acrylate and n-butyl acetate.

n-Butyl acrylate is widely used as a precursor to several synthetic binders and adhesives, used in contemporary art and conservation praxis [97,98]. On the other hand, n-butyl acetate is well-recognized as a strong solvent for cellulose nitrate-based and other synthetic resins, and most interestingly its vapors are considered not toxic [96]. As confirmation, it is an active compound in personal care goods and household cleaners, as well as an artificial flavoring in the food industry [90].

The employment of n-butyl acetate for the formulation of cleaning organogels is noteworthy. A series of methyl methacrylate-based (MMA) gels has been loaded with various organic solvents and performances compared for precise removal of unwanted adhesives and varnishes from easel paintings [82].

4.2.3. Ethyl Lactate

Lactates are progressively becoming protagonists in numerous industrial sectors as environmentally-benign solvents [99]. They derive from lactic acid, which can be manufactured by renewable technologies engaging biomass as a primary source. Depending on the microorganisms involved, it can be obtained either as pure (R)- or (S)- enantiomer or as a racemate through fermentation of hexoses and other carbohydrates [100].

Because of the chemical properties and the natural derivation, the lactates family is gaining attention to substitute more hazardous and toxic substances like toluene, xylene, or methyl ethyl ketone (MEK) [101,102]. Besides the clear green impact on the formulations and syntheses, for which these solvents were normally necessary, the replacement with lactates ensures a dually safer workplace and final goods for the health of operators and end-users [103].

Among the most employed lactates, besides propyl and butyl, ethyl lactate (ethyl 2-hydroxypropanoate) stands out. It accomplishes many green principles [99]: it is produced by esterification of bio-lactic acid, hence its origin is sustainable and renewable; it has low production cost, low toxicity, and readily biodegradability into water and carbon dioxide [103,104].

As a solvent, ethyl lactate appears a reliable alternative due to its low vapor pressure, high boiling point, and ability to dissolve both polar and non-polar species [102,104]. Thus, its features make it apt for the formulation of industrial dyes, paints, and varnishes [90,102].

Appealed by these assets, several research and articles have been published on the potential insertion of ethyl lactate in the broad field of art conservation.

Compared to other solvents for the preparation of acrylic resins—i.e., Paraloid® B72 and B44 –, ethyl lactate is not sufficiently volatile for this purpose [105]. The fact that it remains partially trapped inside the adhesive itself has posed concerns on the potential consequences on the mechanical properties of the film and the treated artifact.

On the other side, quite a few studies have been carried out on its cleaning efficacy. Its value is proved and recognized in the removal of graffiti inks from underlying original supports [106]. Notably, ethyl lactate demonstrated not only a good solvent strength on graffiti but also a satisfactory selectivity towards specific binders without impacting the subjacent original paint. As a confirmation of its well-noted efficacy, it is reported that ethyl lactate is bulkily sold to companies for the cleaning of graffiti, composites, and analogs [90].

Similarly, ethyl lactate led to satisfactory removal of natural terpenic varnishes from oil paintings [107]. Remarkably, in this study, the solvent was retained into a bio-derived gel system to face the low volatility of ethyl lactate and mitigate the quantity of possible residues on the treated surface.

4.2.4. Gamma-Valerolactone

γ-valerolactone (GVL) is one of the most common lactones. It is a natural polar chemical that can be obtained from levulinic acid, eco-friendly derived from lignocellulosic and carbohydrates biomass [90,108]. Besides being bio-sourced, the spectrum of its green features also includes biodegradability and low toxicity. This latter quality brought GVL to become a valid candidate to replace dipolar aprotic solvents nowadays outlawed because of their toxicity [108]. In the industrial world, γ-valerolactone is experimented as a green fossil-fuel additive and it is notable for its use in food and cosmetic goods because of its safety and pleasant scent [99].

In the perspective of metal conservation, GVL's polarity makes it a suitable solvent to treat equally polar media. In parallel, the very low volatility and the non-toxicity shows compelling advantages for restorers and conservators, yielding a safer workplace with scarce volatile organic compounds (VOC) emissions.

Thanks to these characteristics, a few years ago, γ-valerolactone was exploited for the first time in the field of cultural heritage. The research involved the cleaning of paintings through the removal of natural (i.e., dammar) and synthetic (i.e., Paraloid®) varnishes from the surface [81]. Due to its low vapor pressure and potential harmfulness on such sensitive works of art [107], γ-valerolactone was applied in a gelled formulation, to better control its activity and release. The encouraging results have recently driven research to further investigate the potentiality of this solvent in art conservation with the use of a cutting-edge delivery material [109].

4.2.5. Biodiesel and Derivatives

To obviate the traditional reliance on fossil-fuels, biodiesel has been developed as an innovative green option. Nowadays it can be extracted from vegetable oils or algae, labeling it as renewable, bio-sourced, and biodegradable [90,99].

From the chemical point of view, biodiesel is a blend of alkyl esters and long-chain fatty acids [84]: this makes it an appropriate solvent for non-polar substances.

In the field of metal conservation, biodiesel evidenced the capability of acting as a cleaning agent for the removal of wax from a bronze sculpture [84]. Regrettably, besides the solvent efficiency on non-polar coatings, the research pointed out the non-volatility of biodiesel, which appears as the main drawback of such application. Even if englobed in a gel system, the solvent tends towards leaving residues on the artifact. Given the fact that biodiesel could be a potential carbon source for microorganisms, eventual biodegrading bacteria and fungi present could induce a biodeterioration of organic materials such as canvas, textile, or wood. Therefore, despite its satisfactory application in this specific case, this protocol gives the impression of being unadvisable for the more sensitive substrates mentioned above, no less than metals in a negative state of conservation (e.g., highly-porous corroded).

Derived as a by-product of biodiesel, glycerol arises as a promising green solvent: renewable, biodegradable, non-volatile, non-toxic, and affordable [90,99]. It is classified as an intermediately polar solvent [108]; however, its use in industrial activities and reactions have been often limited due to its high viscosity [99]. Even in combination with choline chloride, creating a Deep Eutectic Solvent (DES) [90], the derived chemical is still too viscous for certain applications [99], in addition to the inherent non-volatility of DES systems.

In art conservation, it used to be employed chiefly in paintings as a moistening and plasticizing medium [96]. However, for the same reasons narrowing down its application in industry, glycerol does not seem an appealing solvent in this field. Indeed, the non-volatility, one of its main green advantages, turns into a weakness in conservation practices, being unable to evaporate from the dissolved substance or the targeted surface.

4.3. Bio-Based Organogels for Cleaning

4.3.1. Biopolymers

Biopolymers are naturally occurring polymers (e.g., polyhydroxyalkanoates—PHAs) or derived from bio-based monomers (e.g., polylactide—PLA) [110]. Their most evident green quality is that starting resources are not petroleum-based. Biodegradability is not implicit, indeed only those biologically synthesized are inherently biodegradable. That is the reason for the increasing number of publications on life cycle analysis (LCA) of polymers [87].

Biopolymers appear as valid candidates to replace petrochemical counterparts; however, the generally high cost of production draws some boundaries for wider diffusion. They are broadly employed for biomedical applications (e.g., suture threads [111], drug carriers [112]) because of their natural deterioration and human-compatibility, without any side effects. However, they have also spread in fields ranging from food industry to waste management, passing through cosmetics and household products [113–117].

To develop reliable bio-organogels for metal conservation, a deep investigation on these innovative polymers should be carried out to assess their suitability as thickening agents and the fulfillment of conservation ethics criteria. Regrettably, limited research was carried out in this field and to the best of the authors' knowledge, only one biopolymer has been explored so far: polyhydroxybutyrate (PHB).

PHB belongs to the family of polyhydroxyalkanoates (PHAs), and therefore, to the esters class. PHAs can be produced by more than 300 bacteria and archaea species, in both oxic or anoxic environments. The synthesis occurs either during the growth phase or under stress conditions (e.g., depletion of vital nutrients) while in excess of carbon [118]. PHA is hoarded as intracellular granules in the cytoplasm and kept as energy storage.

PHAs generate high appeal in many industrial sectors thanks to their inherent chemo-physical features, like well-known and spread petrochemical polymers such as polypropylene (PP) and polystyrene (PS). Notably, PHAs' natural degradation into carbon dioxide, water, and biomass requires about two months [119]. Nonetheless, as reported in up-to-date research, the current cost of PHAs is nearly six times higher compared to fossil-sourced plastics, clearly restricting these biopolymers to a wider use [118].

PHB is a semi-crystalline polymer synthesized by many microorganisms (e.g., *Alcaligenes* spp., *Bacillus* spp., *Azotobacter* spp., *Pseudomonas* spp.) from renewable feedstocks rich in sugars [120,121]. From a green perspective, its core advantages are bio-origin, biodegradability, and biocompatibility. From a hands-on point of view, it owns thermoplastic processability and solubility in polar solvents but not in water [122]. In the sporadic applications in art conservation, the form poly-3-hydroxybutyrate (P3HB) has been chosen [84,107,123,124] (Figure 2).

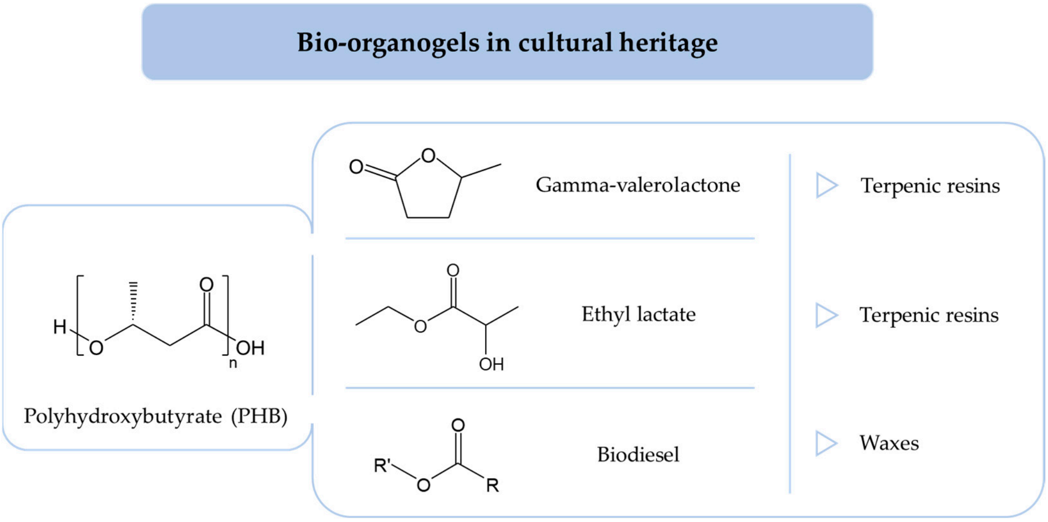

Figure 2. Bio-organogels (i.e., bio-polymer and bio-solvents) employed in cultural heritage and the respective organic coatings targeted. The structural formula of polyhydroxybutyrate, γ-valerolactone, ethyl lactate, and biodiesel.

4.3.2. Bio-Organogels in Art Conservation

In the first case study here reported, PHB was employed together with alginic acid to create a functionalized organogel for the treatment of archaeological wooden findings [123]. The core idea was the addition of iron chelators to the gel, to examine its potentialities to develop innovative in situ applications. Regrettably, to enhance polyhydroxybutyrate solubility, chloroform was employed to obtain lower molar mass polymer chains. This intermediate step would represent a critical drawback for large-scale use in conservation, due to the severe health danger associated with chloroform [125]. Its use and the unclear outcomes highlighted the need of improving the preparation protocol and exploring different chelating agents.

The first fully bio-based organogel in CH was made from polyhydroxybutyrate (PHB) as a thickening agent and γ-valerolactone (GVL) as an organic solvent, with or without the addition of triethyl citrate (TEC) as a plasticizer to test the different mechanical properties of the prepared gels [124]. The resulting PHB-GVL and PHB-GVL-TEC systems led to the removal of terpenic resin from oil paintings, leaving only little residues of GVL that did not appear concerning in terms of retention into underlying layers. Finally, no improvements were observed with the addition of the TEC plasticizer, making feasible and reliable the formulation with only PHB and GVL components [81].

However, the unwanted deposition of solvent on the object is a weakness, especially when referring to rigid gels. It is a crucial point that attracted the attention of supplementary studies [126]. An additional implementation of the PHB-GVL formulation has recently been published and involves the use of cutting-edge electrospun material, interposed between gel and painting, able to further minimize the residues of γ-valerolactone (GVL) on the target [109].

Another PHB-organogel was designed exploiting ethyl lactate (EL) as solvent. Indeed, the bio-based solvent was able to dissolve the polyhydroxybutyrate, thereby creating the so-called PHB-EL gelled system [107]. The obtained formulation performed satisfactorily to remove dammar from the surface of oil paintings [107]. Notably, its action was comparable both to traditionally applied free solvents and to the PHB-gel carrying dimethyl carbonate (DMC) as a green—but not bio-based—alternative solvent. The drop in mechanical stress is remarkable relating to ethyl lactate englobed in the gel or used neat for the same purpose of cleaning. Still impressive is the little amount of EL residues after treatment despite its inherent low vapor pressure, ascertained by solid-phase microextraction (SPME) analysis [107].

Finally, the last fully bio-derived polyhydroxybutyrate-gel involves biodiesel (BD) as a key solvent [84]. As biodiesel itself is not able to create a gel out of PHB, the formulation included also dimethyl carbonate (DMC) to dissolve the PHB polymer. Interestingly, the PHB-DMC/BD system was the only one applied on bronze objects coated with waxes. Previous tests demonstrated that dimethyl carbonate alone does not affect non-polar materials (i.e., wax); therefore, the sole action of biodiesel for the removal of such coating was proved. However, the research points out also the well-known non-volatility of biodiesel, which appears as the main drawback of such a procedure. Indeed, even if retained in a gelled system, biodiesel tends towards leaving residues on the treated surface, implicating an additional cleaning with free DMC to remove these undesired remains.

5. Future Perspectives

In 2020, the authors of this review conducted a survey, spread through numerous worldwide networks to ask conservators about their normal practices in metal heritage preservation. Remarkably, despite the global trend into more sustainable products, no feedback reported the use of green or bio-solvents, as well as the exploitation of gels for the treatment of neither the metallic substrates themselves nor the protective organic coatings present. Numerous were the factors deducible to explain the rare use for the bio-conservation of metals, including the relatively high price, the unawareness of either risk related to traditional methods or existence of reliable alternatives, and the effort required to change long-established habits in favor of unprecedented methodologies.

Therefore, for the extensive practice of bio-based gels in metal conservation, the first crucial point appears the close cooperation between scientists and stakeholders, to formulate and present ground-breaking safe alternatives that conservators will be prone to rely upon. Furthermore, the proposed bio-gels should have a non-prohibitive cost and be easily set up by conservators in their workplaces or supplied by research labs.

In light of the current state of research on biologically derived solutions for art conservation, it is not far-fetched to say that completely eco-friendly, user-harmless, and metal-safe gel formulations might be available soon for cultural heritage professionals.

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