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Gels: Effective instruments for cleaning of graphical works

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***Abstract**: Article discusses the application of hydrogels for cleaning the works as effective and important tool for restoration and conservation of cultural heritage artworks on paper. The basis from not every work during restoration can be cleaned with water and solvents, because it can damage the work. For example, the work can be too damaged or can have can have water based paint coating, the use of gels in these cases is relatively new method, although it has good potential because it is effective, harmless and neutral to artworks, and also it does not posethe health hazards for the restorers.*
This work analyses the research and publications about the peculiarities and advantages of the use of different kinds of gels considering their effectiveness for different applications. The article highlights also the experience of use of gellan and agargels by the author in the process of cleaning the works with purpose of practical testing of the gels effectiveness.

***Key words:** restauration, paper basis, hydrogels.*

I. Introduction

Restoration is an important set of measures needed to preserve monuments. Restoration objects, for the most part, are unique and important, they require an individual approach in the development and implementation of methods for proper preservation. Active research and implementation of new technologies expand the tools for conservation and restoration, sometimes speeding up and simplifying the work of restorers, while reducing the risks to their health.
Innovative technologies in conservation of graphics are the result of international scientific research and is the basis for preservation of material cultural heritage for current and future generations. Conservation of graphics encompasses preventive and remedial conservation as well as restoration in order to extend the useful life of the artefact (Committee for Conservation of International Council of Museums, 2015).
Wet cleaning is an important part of remedial conservation (Figure 1) and one of deciding steps for conservation of artworks on paper basis (Mazzuca et al., [1]).Gels are increasingly popular method of wet cleaning with growing potential for versatile applications (Micheli et al., [2];Mazzuca et al., [3] Isca et al., [4]; Möller, [5]).

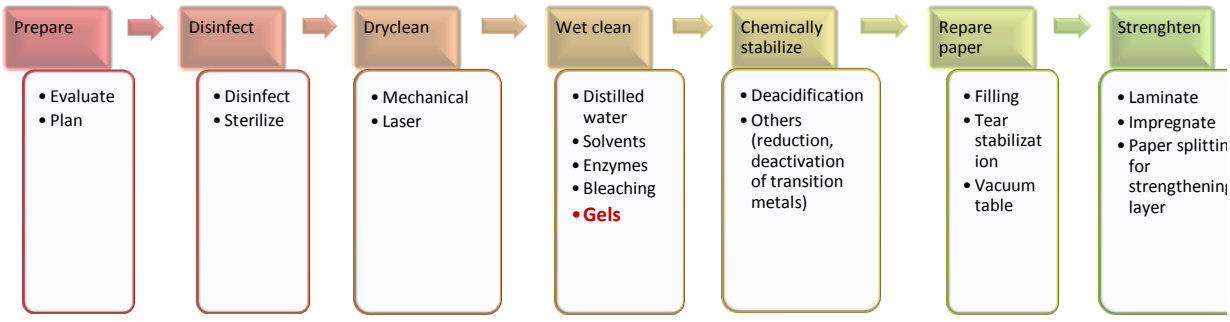


Figure 1Measures for corrective conservation and restauration of graphics with examples based on work by Zervos and Alexopoulou ([6]). Gels are used for wet cleaning of graphics.

II. Advantages of innovative gels

Cleaning of graphics be it from contamination(Mazzuca et al., [1])or prior restoration interventions is challenging because its physical and mechanical properties deteriorate with aging (Baglioni et al., [7]). Cleaning process must be controlled, as well as non-toxic and selective therefore, direct use of solvents is not appropriate method (Baglioni et al., [8]). Currently, innovative gels are preferred over mechanical/solvents for cleaning of graphics (as well as other materials as stone and paintings on different surfaces (including water sensitive watercolour paintings (Domingues et al., [9]; Möller, [10]) water sensitive inks and pigments(Mazzuca et al., [1]), glasses, metals) because of their significant advantages over mechanicalor solvent cleaning (Baglioni et al., [11]; Baglioni et al., [12]; Carretti et al., [13]; Domingues et al., [9]; Möller, [10]), which include:

1) Fit even for water sensitive works (e.g. watercolour paintings, inks) due to adjustedproperties (hydrophilicity, water retention, mechanical strength);
2) Easily adjustable solvent penetration in the work eliminate paper swelling.
3) Non-toxicity and evaporation control of solvent in the gel;
4) Easily defined treatment zone and gel viscosity.
5) Easy removal without residuesdue to elastic, viscous structure of innovative gels which is easily peeled frompaper surfacewithout the use of additional chemicals, with minimum mechanical action and no need for removing solvents unlike for traditional gels;
6) Innovative additions (e.g. magnetic nanoparticles, organic solvents, micro-emulsions, enzymes and chelates in aqueous solutions) allow gels to respond to external stimuli (e.g. pH, temperature, magnetic field) and to be applied as versatile highly-selective cleaning tools.

III. How do innovative gels work?

Gels can be polymer-basedwith co-solvents, detergents, enzymes to improve cleaningquality (Baglioni et al., [12]).Innovative gels usually containadditivesand are prepared bythe inclusion of nanoparticles and micro-emulsions into the gel matrix (Figure 2).

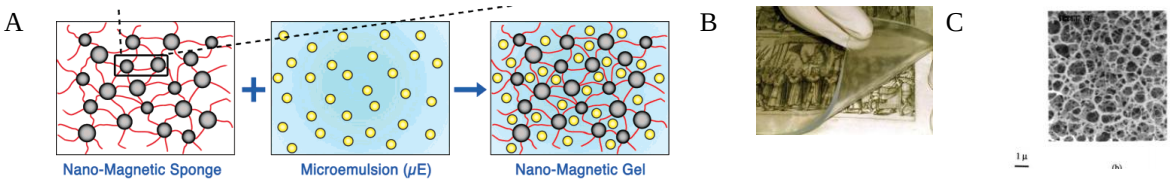


Figure 2A) Preparation scheme of nano-magnetic gel: ferrite magnetic nanoparticles areembedded in a polyacrylamidematrix withchemically attached nanoparticlesand loadedmicro-emulsion. Black spheres = magnetic nanoparticles; Red line = polymer network, yellow circle = micro-emulsion droplet, blue background = water, white - air(Baglioni et al., [8]); B) Application/ removal of gel from graphical art (Micheli et al., 2014); C) SEM micrograph example of Gellan gel 1% (Mao et al., [14]).

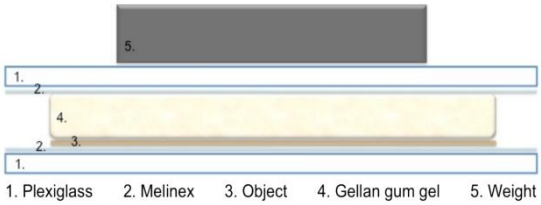
Promising gels response to external stimuli (light, chemicals, temperature) to change their physical (viscosity) or chemical (redox state) properties (Baglioni et al., [12]).The characteristics of gels are actively researched to broaden the palette of restauration instruments.

Gels could be divided into: 1)**Rheoreversible** gels, which reversibly change viscosity from gel to liquid by reacting to applied gases (CO2 and N2 or dilute acids for liquid state)(or to gently mechanical action (brushing) for reduced viscosity(Mazzuca et al., [15]) to slow down the diffusion during cleaning and to easily remove gel (fluid) with tissue (without reuse)(Carretti et al., [13]).

2) **Magnetic**Gels (Figure 2 A), behave as sponges with aqueous micellar solutions (oil and water) micro-emulsions which can be dried and rehydrated to approx. 10 oftheir driedweight, while still maintaining high viscosity for easy precise handling and application and tuned release or uptake of the confined material. These gels are moved with an external magnet(Carretti et al., [13]).

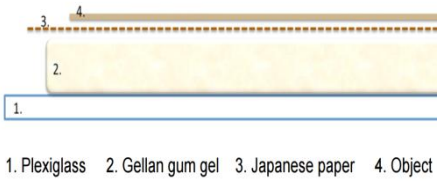
3) "**Peelable**" Gels are highly elastic can be peeled from a surface in one piece withoutintroducing a strong lateral force or adding other chemicals.Hydrogels that can be very stiff or quite malleable depending on their structure (averagemolecular weight, component concentrations) and physico-chemical properties of aqueous part (temperature, pH) (Carretti et al., [13]).Depending on the sensitivity of the object under restoration the application of gels differs (
Figure 3).

A



Melinex or plastic sheet; glass or Plexiglas plate; weight optional

B



Japanese paper (for isolation, easy handling)

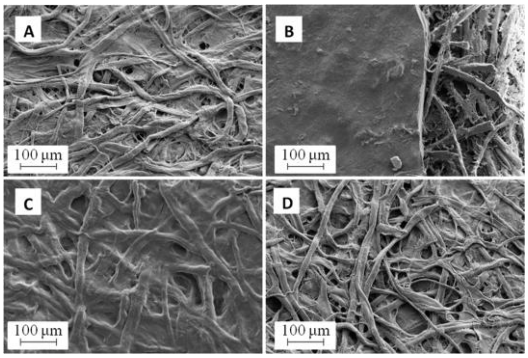
Figure 3 Gel application procedure after paper prehumidification for:A) regular (graphic prints, paper) and B) sensitive (drawings, fragments of objects and very thin or degraded papers)graphical works. Gel yellows with absorbing degradation production and dirt from treated paper (Möller, [10]).

The treatment time lasts minimum 30 minutes and no rinsing is needed, as no traces are left (Casoli et al., [16]). Treatment depends on paper wettability, thickness and degradation state and can be stopped at any time (Möller, [10]).

IV. Study of the effectivenessof gels

Gellan gel (peelable type) is effective for cleaning of hydrophilic contaminants without paper damage and without activating anomalous long-term degradation(Micheli et al., [17]). Enzymes and surfactants can be added for removal of hydrophobicmoleculesof dustor glue(Micheli et al., [17]; Micheli et al., [18]). For example, gellan gelwith hydrolytic enzymes is effective to remove starch paste (old glue) from paper (Figure 4 A), with other advantages being: easy, relatively cheap, fast and safe method (Mazzuca et al., [15]).
Combining a peelable or rheoreversible gel with a selective electrochemical biosensor (to measure fungi-produced glucose) is an innovative approach to effectively clean the paper while monitoring the process of removal of both contaminants and degradation products (Figure 4B)(Micheli et al., [18]).

A



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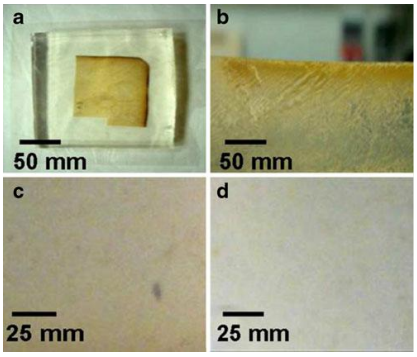

Figure 4 A); SEM images of (A) uncoated paper sample, (B) paper sample partially coated with starch paste, (C) paper coated with starch paste after cleaning with Gellan gel, and (D) paper coated with starch paste after cleaning with Enzymatic Gellan gel (Mazzuca et al., [19]);

B) a) Appliedtransparent Gellan gel to paper sample; b) Cross section of Gellan gel 1 hour after application on paper. Adsorbed paperdegradation products and pollutants are clearly visible; c) and d) Comparison of paper sample before (c) and after (d) treatment withgel, Effect of cleaning is evident from significant lightening of paper colour (Micheli et al., [18]).

Study by Micheli et al., ([18]) showed that one-hour treatment is enough to remove about 80% of the glucose produced by fungal attack.

Gellan gel was also effective in study by Mazzuca et al. [1] who applied it for papers of different age (16-19 centuries) and, therefore, of different properties. Comparing to conventional washing procedure (immersion in deionized water) Gellan gel proved to be more effective in removing pollutionand degradation products from paper while maintaining paper morphology (Figure 5 A).

Research by Mazzuca et al., [15] tested two innovative synthetic rheoreversiblegels for paper cleaning from new and old oil contamination. More hydrophobic gel proved to be more effective and almost totally removed the oil (Figure 5 B). Authors list the following additional advantages of these gels: easy to prepare "on-site", no paper damage, do not activate anomalous long-term degradation, versatile (as their efficiency is little sensitive to pH), relatively cheap and non-toxic, less susceptible to microbial degradationdue synthetic nature, significantly more effective compared to immersion in water method(Mazzuca et al., [15]; Mazzuca et al., [3]). Rheoreversible gels can be used to remove contaminants in wide hydrophobicity range as their properties are easily tuned by selectingappropriate polymer for their preparation (Mazzuca et al., [15]).

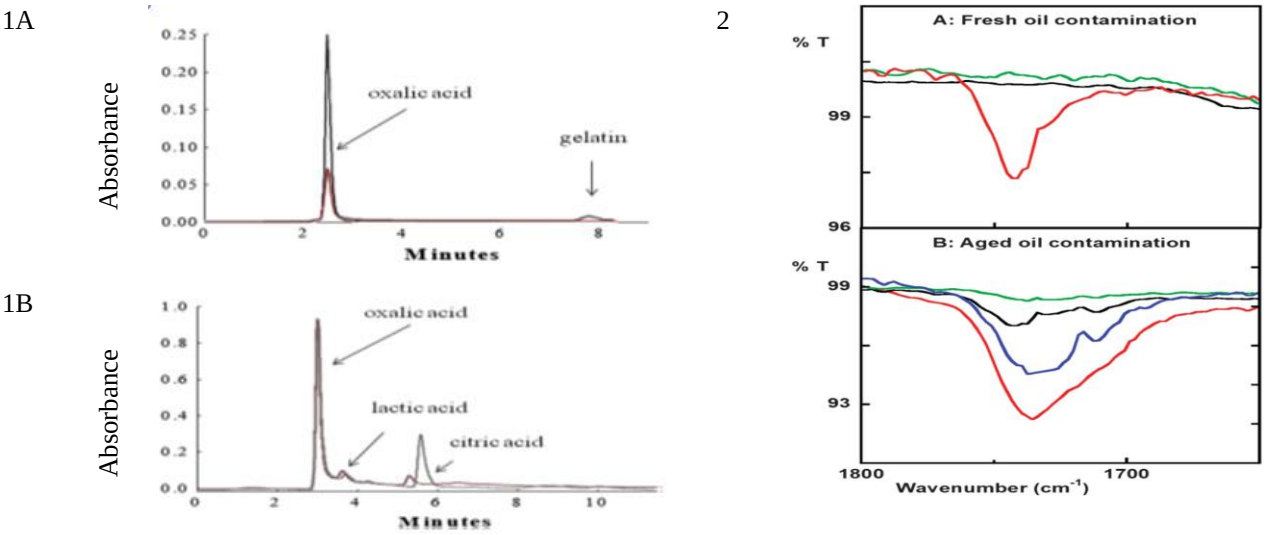

Figure 51)HighPerformanceLiquidChromatography measurements on water extracts of paper samples belonging to XVI (1) and XIX (2) centuries before (black line) and after (red lines) Gellan gel treatment (Mazzuca et al., [1]);
B)Infrared attenuated total reflectancespectroscopy of paper samples (T – transmittance). Paper after contamination (red line), samples contaminated and afterwards treated with more hydrophilicgel (black line), more hydrophobic, and more effective, gel(green line) and water (blue line). The graphs report data obtained on samples contaminated with fresh linseed oil (A) and aged linseed oil (B)(Mazzuca et al., [15]).

V. Preservation of paper qualities and practical application of hydrogels in restoration

Peelable rigid gels (Agar and Gellan) preserve cellulose fibres in paper better than medium viscosity gel (Klucel G) applied by brush, which and unlike wishab sponge (dry cleaning) did not cause release of residuals(Casoli et al., [16]). Cleaning with peelable gels (Agar and Gellan gum 1-3%)moderately improvestrength and elasticityof

the of paper unlike immersion indeionisedwater which caused significant paper deformation and weakening, which is important ability for paper assembling which can be compromised due to dimensional change of fragments (Isca et al., [4]). Additionally, authors state these peelable gelsdo not accelerate paper degradation in the long term.

Another valuable property of Gellan gel is preservation of gelatine in the hand-made paper (as shown on 16th, 17th and 18th centuries) which is important for its physical–mechanical properties, unliketraditional cleaning by immersion in distilled water (Casoli et al., [16]).

The author of this article used two types of hydrogels in restoration practice, both of which belonged to the type of peelablegels, namely Gellan gel and Agar gel. Previously, there was an internship in the restoration department of the National Gallery in Prague, where the training involved working with hydrogels, studying methods of their preparation, application on samples of works on paper basis. In parallel, the study of hydrogels effectiveness with the use of methods of visual inspection, systematization, comparison and generalization, as well as with the use of optical devices.

Later, both types of gels, Gellan-gel and Agar-gel, were used for the restoration of architectural graphics on paper, created in the 30-50s of the twentieth century by Ukrainian architects. The works were made in mixed technique, were restored from an emergency condition, had significant damage to the base, stainsand pollution of various kinds. In the process of developing restoration methods, given the emergency state of the projects and mixed techniques, it was decided to use hydrogels to implement the processes of their purification.

Practical application of gels has shown certain advantages of their use during restoration, in particular: efficiency of surface cleaning for works sensitive to water; the relatively low cost of using such materials for restoration, which is important for countries with low funding of the restoration activities.

To predict and improve the gel efficiency, the cleaning processes should be understood to the nanoscale (Baglionietal., [8]). Currently, active research is underway to improve the process of purification using gels, which indicates the significant potential for their effective and universal application in the field of cultural heritage.

VI. Conclusion

The use of hydrogels in the restoration of graphic works on a paper basis is an important and promising research direction. It allows to solve the problem of cleaning of water-sensitive artworks with a damaged base, unstable inclusions in the base or paint layer.

A diverse palette of gels and the ability to use them with the addition of enzymes, surfactants, nanoparticles, used in combination with a selective electrochemical biosensor, to measure glucose from fungi activity, etc., increases their efficiency and expands the impact on pollution of various kinds. Also the ability to change the structure of certain types of gels is important, for example, during the transition from liquid to gel state and vice versa, which enhances their penetration effect and allows to easily remove gels from the base after the restoration process.

The neutrality of gels and their ability to preserve the original structure of the paper, compared to the procedures of washing the artworks with distilled water, is an important indicator in choosing this method in the restoration. These characteristics emphasize the need to develop the research on the gels application in the restoration process.

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