Introduction to Hydrogels
in conservation cleaning

Restauratoren Nederland
CollectieCentrum Nederland

Instructor: Matt Cushman
18-22 November 2024

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WORKSHOP OVERVIEW

INTRODUCTION TO HYDROGELS IN CONSERVATION CLEANING
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Workshop Outline

Day 1: 18 November 2024

- Introductions
- Lecture Part I: Key Concepts
  - Why gels?
  - Control, developing a range of cleaning “tools”
  - Some loose definitions
  - Relating polymer structure and network structure to gel properties
  - Mass transfer in gel cleaning

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Workshop Outline

Day 1: 18 November 2024

- Lecture Part II: Practicalities of Formulation and Use
  - Mixing methods
  - Heating/cooking options
  - Casting tips
  - Application methods
  - Storage tips
  - Preservative options

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Workshop Outline

Day 1: 18 November 2024

- Lecture Part IIIa: "Rigid Gels"
  - Agar & agarose
  - Gellan gum
    - Sidebar: alginate gels

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Workshop Outline

Day 1: 18 November 2024

- Lecture Part IV: "New" Gel Materials
  - Poly(vinyl alcohol)-borax gels
  - Nanorestore Gels: Dry & Peggy
  - Xanthan-konjac/agar(ose) double-network gels
  - Curdlan
- Q&A
- End of day: 5:00

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Workshop Outline

Day 2 – Practical: 19 & 21 November 2024

- Gel preparation demonstrations
- Comparative moisture delivery experimentation
- Delivery techniques

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Workshop Outline

Day 3 – Practical: 20 & 22 November 2024

- Incorporating aqueous chemistry
- Incorporating solvents
- Experimenting & problem solving on test surfaces

- Wrap-up discussion

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Course Goals

1. Consider alternative modes of delivery for and cleaning (and humidification)
2. Develop a sense for identifying useful gel properties
3. Describe methods of formulating and manipulating hydrogels to match desired effects

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PART I: KEY CONCEPTS

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Cleaning: It's All About Control

"Control. Control. You must learn control."

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The Nature of Aqueous Solutions

Properties to tailor

- **pH**
- **Conductivity**
- **Use of chelating agents**
- **Use of surfactants**
- **Viscosity/rheological agents → gels**
- *Reactive additives: enzymes, redox reagents*

Additional factors:

- Time
- Mechanical action
- Temperature
- Addition of non-aqueous solvents

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AQUEOUS KEY CONCEPTS:

- As pH increases, acid groups become deprotonated (charged)
- If pK_a is known, we can predict the pH when the acid group becomes deprotonated (charged)
- Greater charge: increased solubility in water (generally)

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AQUEOUS KEY CONCEPTS:

- We can control the pH of solutions with the addition of a buffer
- We only need a few buffers to cover the range of our typical work
- We influence what is retained and what is removed by controlling pH

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AQUEOUS KEY CONCEPTS:

- We influence swelling on many surfaces by adjusting conductivity
- With pH, conductivity has a large influence on what is retained
- An isotonic solution will limit swelling; key for retention of original materials

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Many of our cleaning challenges can be solved by controlling pH and conductivity and by selecting an appropriate chelating agent

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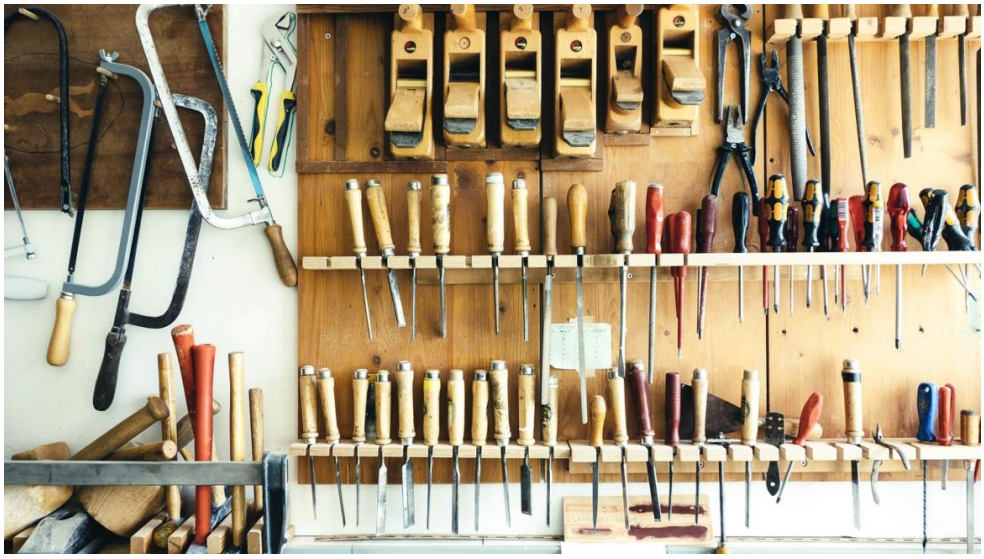
We Need a Range of Tools



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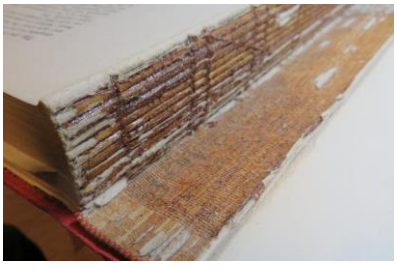
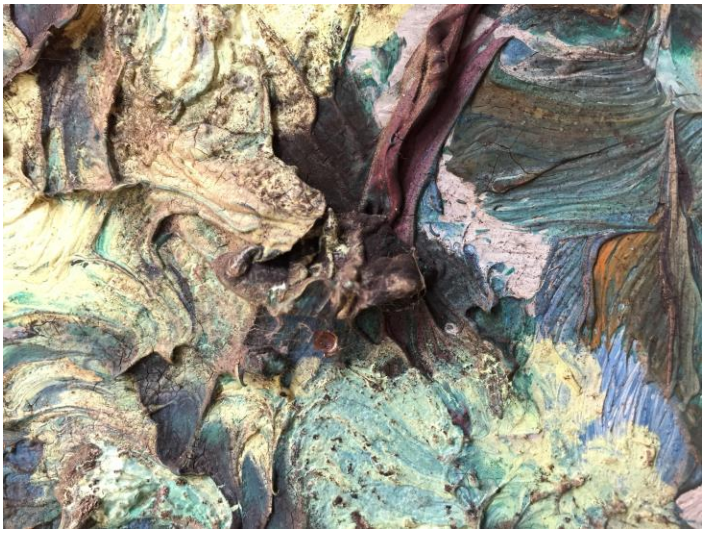
Why Gels?





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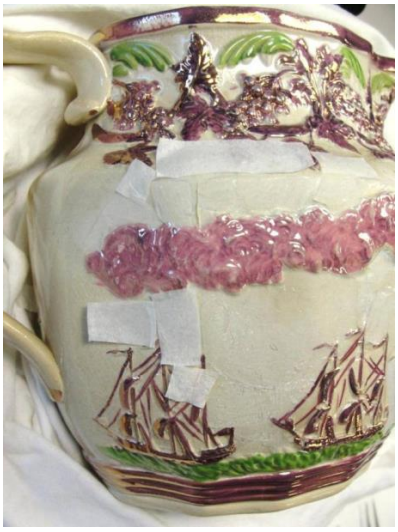
Why Gels?



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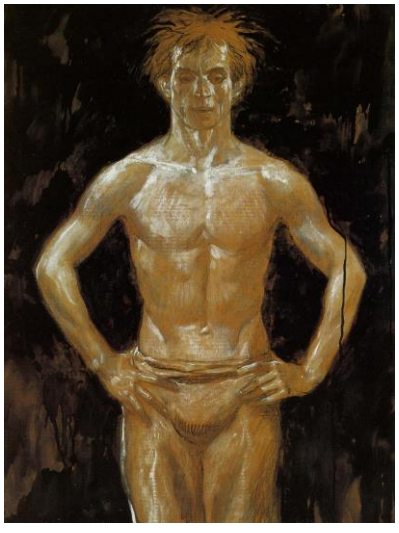
Why Gels?



Jamie Wyeth, *Nureyev*, 1977

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Why Gels?

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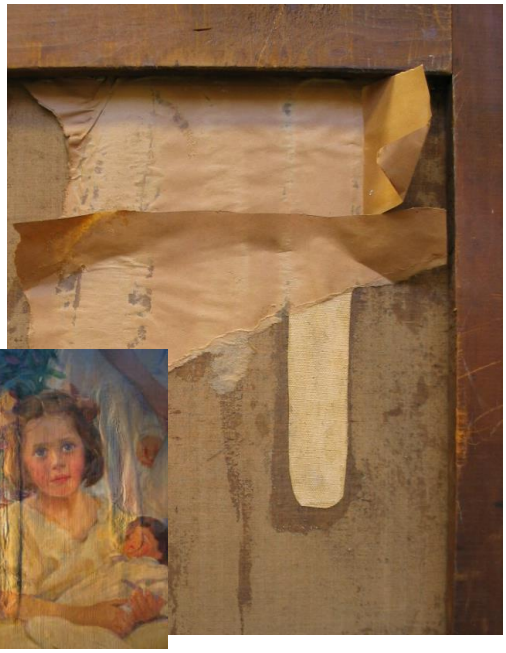
Why Gels?



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Why Gels?

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Why Gels?

Josh Sarantitis
Legacy
Philadelphia, Pennsylvania, USA
Completed 2006

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Why Gels? Practical Considerations

- Handling Properties: Control!
- Health & Environmental Safety
- Economic Considerations
- Compatibility with Other Aqueous Solution Parameters!

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Some Loose Definitions

Thickener / Thickening Agent

A hydrophilic, relatively high-molecular-weight material added to a solution to **increase viscosity** *with little influence on the structure or fluid dynamics of the solution*

Spreadable Gel

A solution with a concentration of thickening agent:
- having a **semi-solid**, weakly cohesive structure
- having **varied response to applied shear**

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Spreadable Gels: Benefits

Inexpensive; easy formulation

- Cellulose ethers, xanthan gum, Pemulen TR-2

Polymer-stabilized emulsions

- Add up to 30% (v/v) non-water-miscible solvent
- Aliphatic/aromatic:
  mineral spirits – xylenes (e.g.)
- Aliphatic/aromatic alcohols:
  butanol – benzyl alcohol

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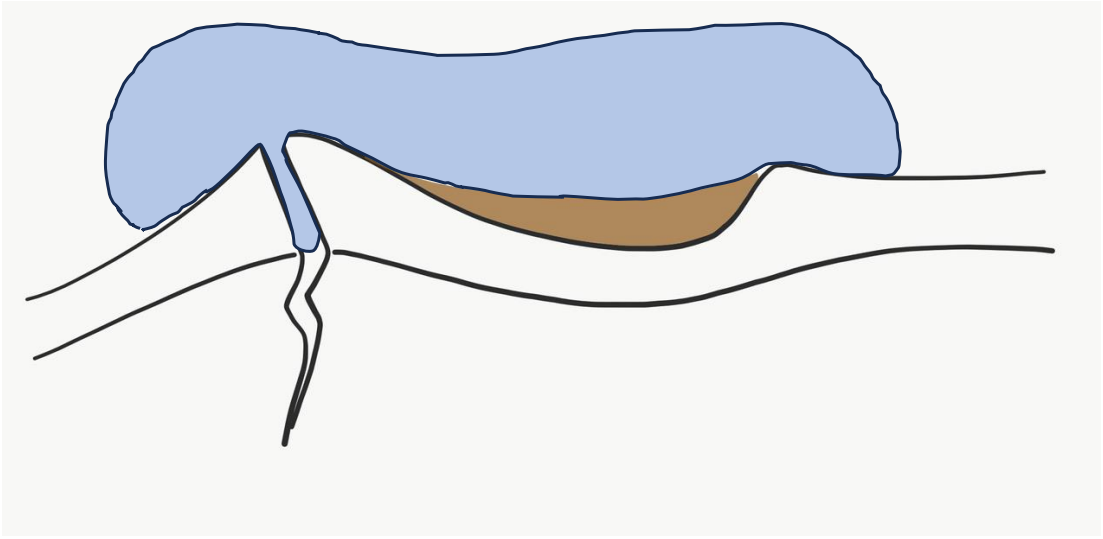
Spreadable Gels: Challenges



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Some Loose Definitions

Hydrogel

A **hydrophilic**, three-dimensional network of **entangled and/or cross-linked** polymeric material containing **>~90% water**.

Despite its high water content, the hydrogel is not soluble in water!

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Useful Properties to Exploit

- Gel cohesion
- Elasticity/Rigidity
- Water retention
- Thermo-reversibility/ Heat stability
- Solvent compatibility
- Optical properties
- Ease of formulation

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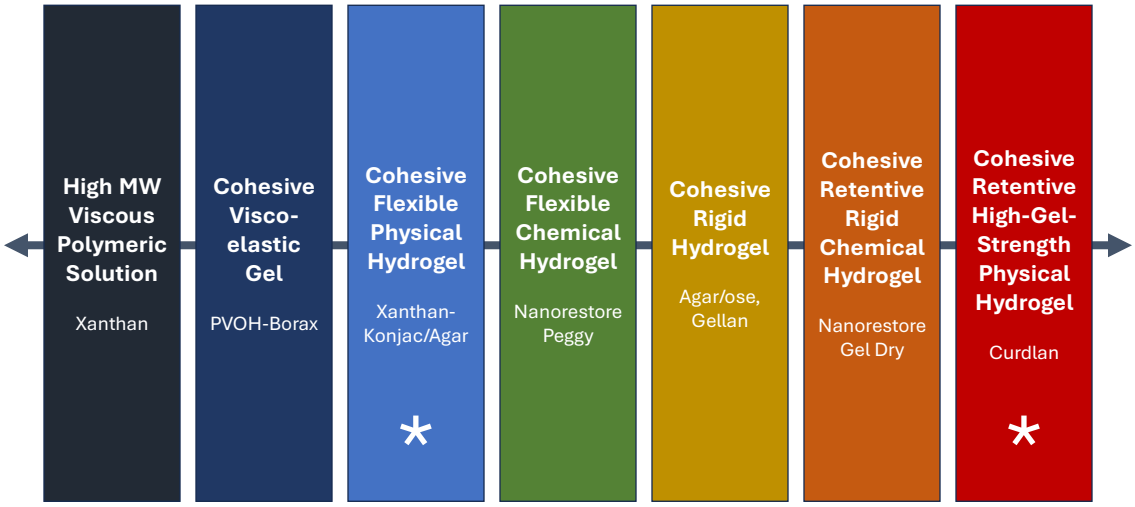
Advantages of Material Diversity



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GEL PROPERTIES

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Factors Determining Gel Properties & Rheology

- Thickener/gel **molecular weight** & **concentration**

- Polymer/oligomer structure
  - Straight vs. branched
  - Regularity/homogeneity of repeat units
  - Degree of substitution: frequency of side chains
  - Hydrophilic & hydrophobic substructures
  - If hydrophilic: Ionic? Hydrogen bonding?

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Factors Determining Gel Physical Properties

- **Type(s) of polymer chain junctions**
  - **Chain entanglement & transitory interactions (physical gels)**
  - **Covalent cross-linking (chemical gels)**

Chemical Crosslinking facilitated by:
- Crosslinking agents
- Polymer-polymer crosslinking
- Photosensitive agents
- Enzymatic crosslinking

Physical Crosslinking facilitated by:
- Hydrophobic interactions
- Ionic interactions
- Hydrogen bonding
- Chain entanglement
- Crystalline formations

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Factors Determining Gel Properties & Rheology

- Solution parameters ("solvent quality")
  - pH – gel stability; ionization state of acid groups
  - Ionic environment (conductivity, e.g.)
  - Presence of divalent metal ions (Ca^{2+}, e.g.) – ionic crosslinking
  - Co-solvents' concentration and solubility parameters
- Processing
  - Physical mixing
  - Crosslinking (chemical gels)
  - ***Temperature processing***

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Gel Polymers

- Natural polymers
  - Proteins
  - **Polysaccharides**

  Simple preparation
- Synthetic polymers
  - In theory: great variety of options
  - In practice: additional processing requirements
  - **Increased possibilities for crosslinking** (chemical gels)

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Polysaccharides

- Monomers: monosaccharides
  - Generally: 6- or 5-membered carbohydrate rings
  - Stereochemistry contributes to polymer chain structure
  - Some monosaccharides are ionic
- Glycosidic bonds
  - Ether linkages created during condensation/dehydration reaction between two monosaccharides
  - Nomenclature: ($n_1 \rightarrow n_2$) describes the positions of the carbons on the two monosaccharides
  - α or β describe the stereochemistry on either side of the bond

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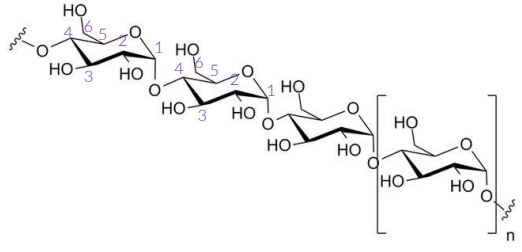
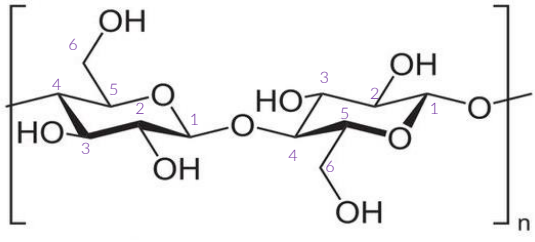
Polysaccharide Structures



Amylose: (1→4)-α-D-glucose



Cellulose: (1→4)-β-D-glucose

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Polysaccharide Chain Structures

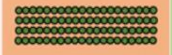
	Cellulose	Starch		Glycogen
		Amylose	Amylopectin	
Source	Plant	Plant	Plant	Animal
Monose	β-glucose	α-glucose	α-glucose	α-glucose
Glycosidic bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Diagram				
Shape				

Fig. 1.1 Examples of molecular chain structure of polysaccharides

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Polysaccharide Selection

- Rigid, brittle gels:
  - More homogenous (esp. homopolymers)
  - More crystalline in behavior (linear, rod-like structures)
  - Fewer side chains, less branching
  - Increased junction density (crosslinking, chain entanglement)
- Flexible, elastic gels:
  - Heteropolymers and branched polymers
  - Polymer networks capable of significant swelling
  - High density of strong and weak chain-chain interactions

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Biopolymer Thickeners & Gelling Agents

- **Microbial**
  - **Gellan**
  - **Xanthan**
  - Curdlan
- **Seaweed & Algae**
  - **Agar**
  - Alginate
  - Carrageenan
- **Vegetable**
  - Guar gum
  - Gum Arabic
  - Konjac
  - Locust bean gum
  - Pectins
  - Tara gum
- **Animal**
  - Chitin/chitosan
- **Proteins**
  - Caseinate
  - Gelatin
  - Soy protein
  - Whey protein

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A Note on Natural Materials

For many natural materials, the **source organism**, **geographical source** and subsequent **processing** influence the quality of the raw material:

- Optical properties
- Odor
- Gel strength (MW)

It is best to prepare a test batch of gel when switching products!

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A Note on Food-Grade Hydrocolloid Materials

CAUTION!

Some suppliers of food grade gelling agents and thickeners will include calcium or iron in their product. This increases ionic cross-linking between chains with ionic substitutions.

For lesser-absorbent structures, this is probably fine. **But such formulations are not recommended for paper supports, unprimed cotton or linen,** or other substrates that could be degraded by metal-catalyzed hydrolysis reactions.

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Effect of Processing

By adding enough energy to the system, we allow polymer chains to fully hydrate and exist as random coils in solution.

Random coils then self-arrange to concentrate hydrophobic interactions (CH_2 backbone) and hydrophilic interactions (hydrogen bonding, coordinated water, ions) to form a somewhat regular structure

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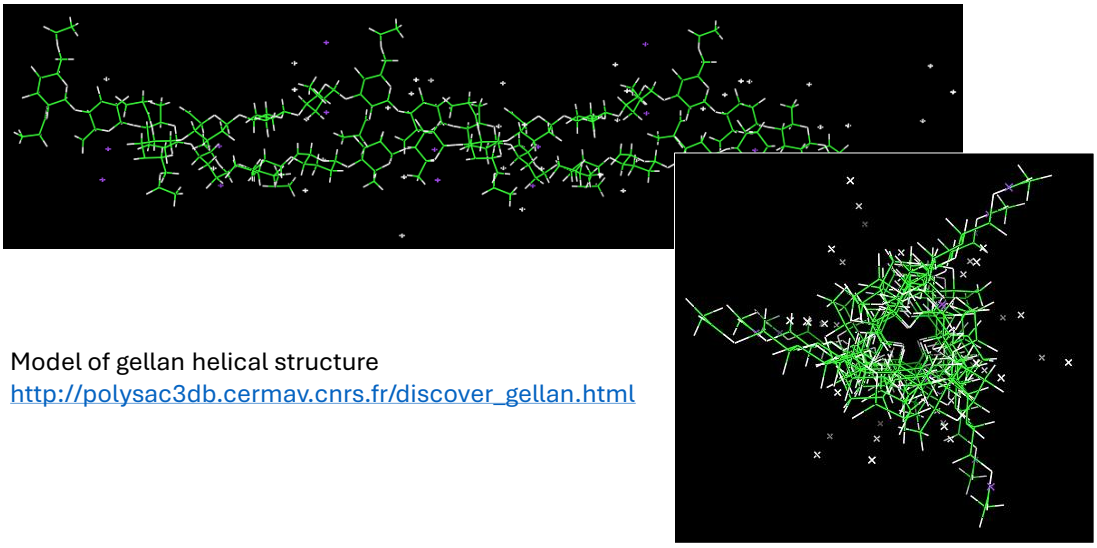
Effect of Processing



Model of gellan helical structure
http://polysac3db.cermav.cnrs.fr/discover_gellan.html

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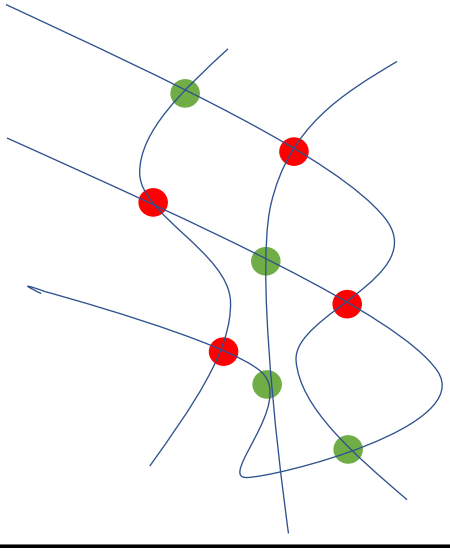
Factors Determining Gel Physical Properties



Polymer type, concentration, cross-link/entanglement density, and **solvent quality**

determines mesh size or “pore size”

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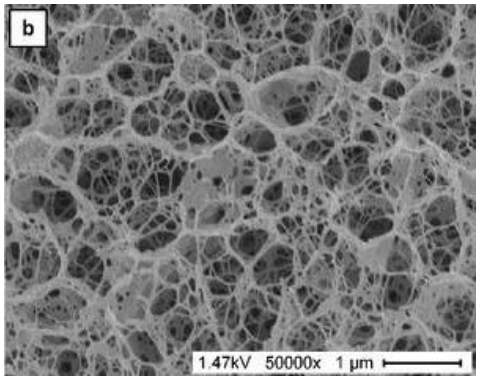
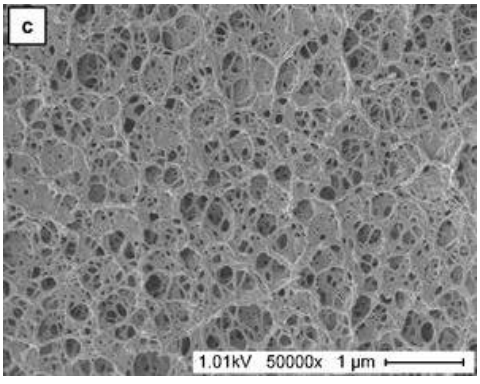
Concentration Considerations

- With increasing concentration:
  - Decreased mean pore size



2% Agarose



6% Agarose

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Ionic Crosslinking

- Electronegative groups can coordinate with divalent ions
- Method for linking between polymer chains

C. Bennacef et al. Food Hydrocolloids 118 (2021) 106782

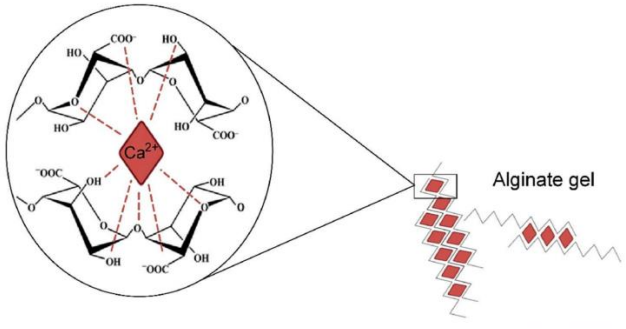

Fig. 2. Alginate gel structure in presence of calcium ions (egg-box model) (Adapted from Martău et al., 2019).

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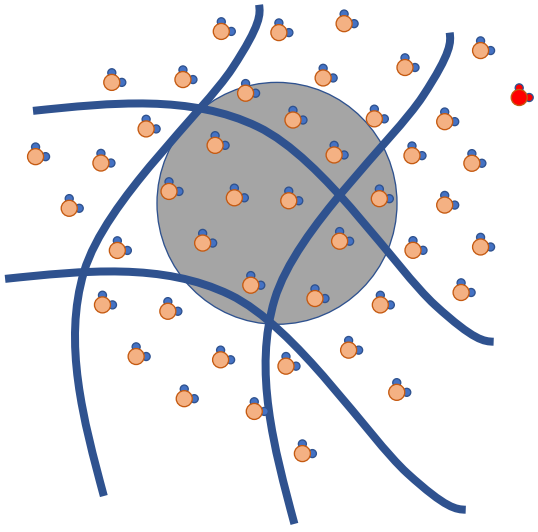
Diffusion in Hydrogels



- **Solutes will diffuse through hydrogels if:**
  - It would normally diffuse freely in a solution of the same composition
  - The solute is smaller than the mesh/pore size of the hydrogel
- **Diffusion will be inhibited if:**
  - The solute encounters an energetically favorable location
  - The average mesh size ≤ solute size

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Capillary Action in Hydrogels

- In simplistic terms:
  - Capillary action is driven by **surface forces** between the gel material and the liquid phase
  - Capillary action is **spontaneous** and occurs without the application of external pressure
  - A simple model of capillary action in hydrogels: a bundle of tubes with a uniform radius

In a hydrophilic, porous medium, it is expected that capillary forces will imbibe water into the structure.

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Syneresis

- With applied stress, and relaxation of stress, the microstructure of the gel can be altered:
  - Helical structures can tighten
  - Physical bonds can break and reform
  - The gel structure can become more dense
- and water can be expelled spontaneously: syneresis!

- Syneresis can be caused by slight temperature changes, gel "maturation", introduction of differing solvent quality

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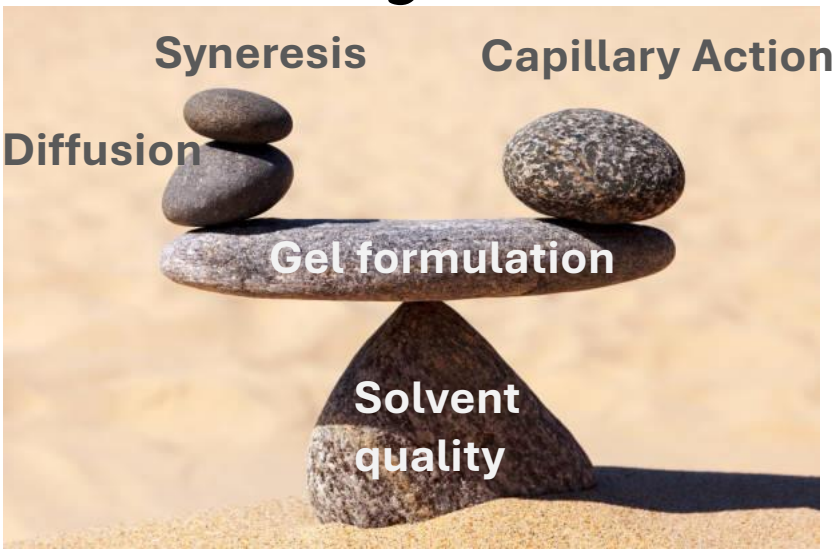
Moisture Delivery and Retention



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GEL RHEOLOGY & MOISTURE RETENTION

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General Trends: Rheology and Moisture Retention

With decreasing pore size:

- ***Decreased rates of diffusion***
- ***Increased capillary action***

Increased polymer concentration and junction density will increase moisture retention

With increasing brittleness:

- ***Increased syneresis***

Flexible, elastic gels will exhibit decreased syneresis

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General Concepts: Hydrogels

- Think of hydrogels as a "vessel" for delivering water/moisture
- Lower polymer concentration: more open structure; vessel empties faster
- Better surface contact: more efficient diffusion and capillary action
- Smaller mesh/pore size: increased capillary action, but slower delivery. *Testing will help you to find the balance!*

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Intentional Formulations

Intentional polymer selection, concentration, appropriate thermal processing, solution formulation

will result in gels that:

- ***are brittle, tough, elastic, stiff, loose, cohesive, fluid***
- ***control delivery of aqueous chemistry***
- ***provide beneficial working properties for the conservator***

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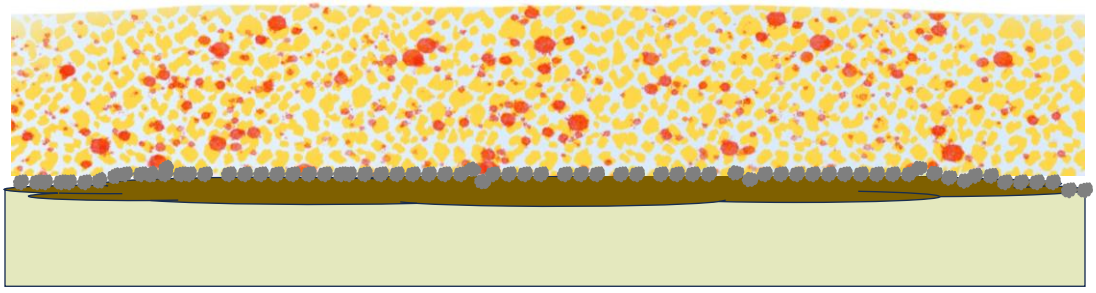
Mass Transfer in Gel Cleaning

Gel matrix Free Water Solutes



Can we formulate and load a gel to control how material moves into and away from the surface?

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Mass Transfer: Practicalities

- **Predicting mass transfer can be difficult:**
  - Heterogeneous gel pore/mesh size
  - Gel surfaces often have small flaws
  - Surface contact can be incomplete
  - Unpredictable interactions between solutes & gel matrix
  - Unpredictable influence of object porosity, condition, treatment history etc. etc. etc.

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Mass Transfer: Practicalities

- **Questions to ask:**
  - *Are we able to control the delivery of moisture?*
  - *Is the solution achieving the desired result?*
  - *Is the time scale appropriate?*
  - *Are solubilized/affected materials sorbed into/onto the gel, or do they remain at the surface of the object?*
  - *Once cleaning is complete, are there signs of residues from the gel matrix and/or the delivered solution?*

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PART II: HYDROGEL PREPARATION FOR CONSERVATORS

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Useful Equipment

- **Scale**
  - Ideally: accuracy better than 0.05g (kitchen scales < USD 20.00)
- **Mixers**
  - **Magnetic stir plates** (some compact units < USD 40.00)
  - Battery-powered milk frothers/mixers (USD 6.00–20.00)
  - Stir rods, spatulas

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Mixing Tips

- **Overnight hydration**
  - Good idea for high-viscosity solutions
- **“Pre-Hy”**
  - Use an immersion/stick blender to quickly disperse polymer and eliminate “fisheyes”
  - Creates SO MANY BUBBLES
    - Vibration stage
    - Vacuum pump
    - Generally not going to be a problem with vigorous heating

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Useful Equipment

- **Hot plate**
  - For water baths (search for home brewery equipment)
- **Immersion circulator**
  - For precision temperature contrc (some models USD 60.00)
- **Microwave**

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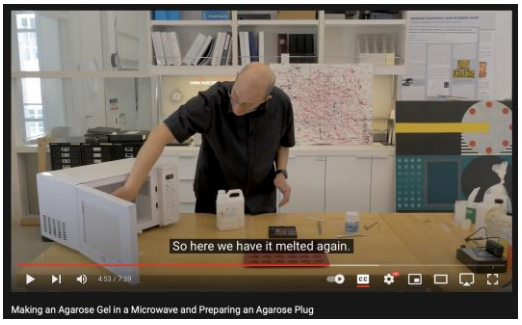
Microwave Method

- Disperse polymer in distilled water in a microwave-safe container. Cover loosely!
- Microwave on half power for 20-30s at a time
- Remove from microwave and swirl after each heating
- Avoid allowing the solution to boil over!
- As solution cools, but before gelation, pour into mold



https://www.youtube.com/watch?v=V490KuFsU4k

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Immersion Circulator Method

- Set bath temperature above the hydration/melting temperature
- Disperse polymer in distilled water (or other solution) in a well-sealed container or bag
- Submerge container in bath; remove periodically to mix contents
- Allow the contents to reach the bath temperature; remove from bath
- As solution cools, but before gelation, pour into mold

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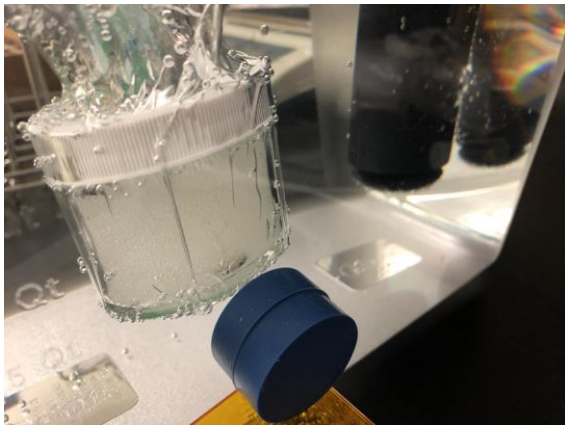
Immersion Circulator Method



Tip: Rare earth magnets can be used to keep enclosed solutions submerged.

Pictured:
silicone-coated magnets for sous-vide cooking outside the bath and a small rare earth magnet inside the jar.

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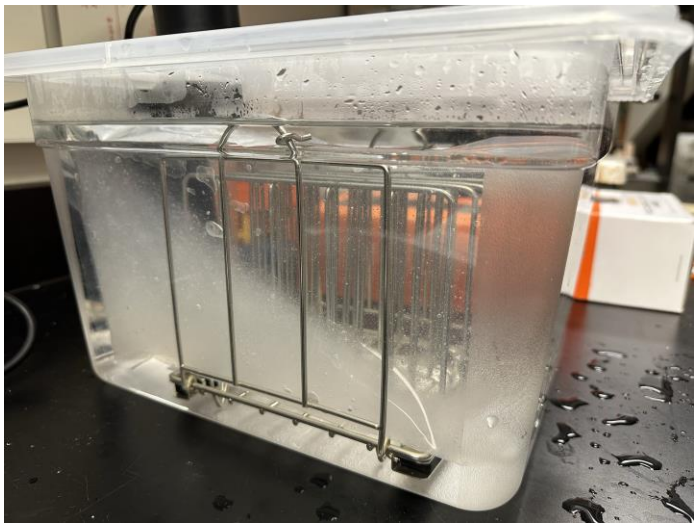
Immersion Circulator Method



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Caution!

Take extra caution when handling hot solutions!

Hot, viscous gel solutions will stick to your skin, making burns worse!

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Useful Equipment – Molds

- Silicone molds – food prep, baking, candy making
- Glass containers – Petri dishes, watchglasses, ashtrays
- Pyrex dishes
- Mylar/ Melinex trays

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Useful Equipment – Molds

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Large-scale Casting



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Useful Equipment – Molds

- **Tip: Silicone splicing tape!**
  - Adheres to silicone molds -- labeling
  - High temperature tolerance
  - Easily removable
  - Can be reused: securing small rolls of Mylar scraps

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Measuring pH of Gels

- **Use enclosed, all-in-one electrodes**
- **Spear probe meant for soft foods; flat surface probes**
- **pH indicator papers or test strips**

We can measure gel conductivity using a flat conductivity meter like the Horiba Laquatwin EC meter!

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STORAGE OPTIONS

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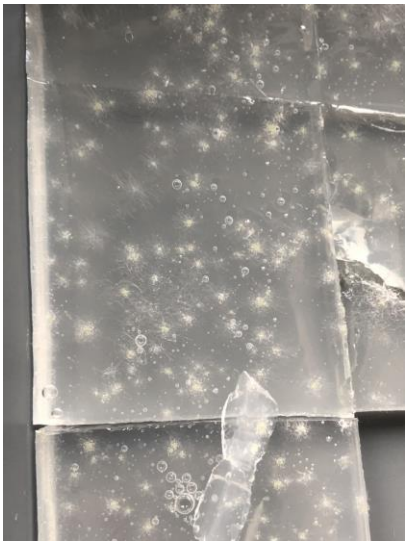
Storage: Limiting Handling and Oxygen Exposure

- High moisture content and polymer composition present favorable environments for biological activity
- Use clean glassware and molds; sterilize tools
- Wear gloves when handling
- Store between Mylar/Melinex films in the refrigerator



Star-like growths in a gellan hydrogel

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Storage: Limiting Handling and Oxygen Exposure

- Storage in aqueous solution
- Storage in hydro-alcoholic solutions
- Vacuum sealing
  - Silica gels
  - Oxygen scavengers

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Potentially Useful Equipment: Vacuum Sealers

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Considering Preservatives

- Preservatives can prolong the usable life of a hydrogel preparation
- However:
  - Health and safety concerns (esp. parabens)
  - Preservatives may contribute unwanted solubility parameters
  - Some preservatives are fatty acid salts – could contribute to metal soap formation

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Selected Preservatives

- Parabens (Germaben II) – Not recommended!
- Phenoxyethanol – 0.5%; Permissible ≤1% w/v
  Can decarboxylate with heat: benzene…
- Potassium sorbate – 0.025%; requires acidic pH
- Sodium benzoate – 0.05%; requires acidic pH

Preservatives might be best used for test kits meant to be kept at room temperature – not for full treatments.

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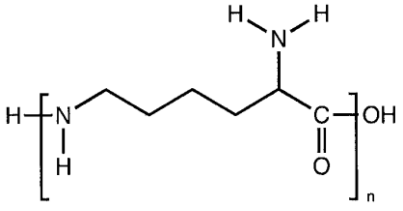
Preservative for Nonionic Gels: ε-Poly-l-lysine (ε-PL)



- GRAS; biodegradable
- High solubility in water
- Stable in a wide pH range, 2-9.5
- Effective against a broad range of pathogens
- High MW (unlikely to migrate into surfaces)
- Effective at 0.025% w/w
- **May contribute turbidity with anionic biopolymers**

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TYPICAL APPLICATIONS & DELIVERY METHODS

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Cold Methods

- **Use of cast gels:**
  - Surface testing
  - Controlled moisture delivery
  - Stain reduction/poulticing
  - Surface cleaning

Warm Methods

- **Use of warm solutions:**
  - In-situ casting
  - Syringe, brush application
  - Embedded fabric supports
  - Sprayed application

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PART III: "RIGID" GELS

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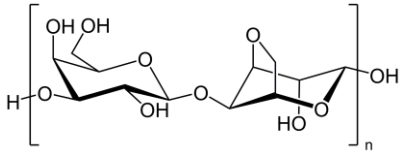
Agar – Industrial Production

- **Agar** is a biopolymer contained within cell walls of red algae
  - Major component: **agarose**



  - Fraction inhibiting gelling: **agaropectin(s),** a complex mixture of carbohydrates and <u>sulfates</u> thereof

- Cold waters → thicker cell walls (**more to extract**)

Geographical location, environmental factors contribute to product quality

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Usable Agar Products

- Food-grade agar - *~10-30 USD/100g*
- Technical agars (bacteriological) - *~30 USD/100g*

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A Note on Food-Grade Hydrocolloid Materials

CAUTION!

Some suppliers of food grade gelling agents and thickeners will include calcium or iron in their product. This increases ionic cross-linking between chains with ionic substitutions.

For lesser-absorbent structures, this is probably fine. **But such formulations are not recommended for paper supports, unprimed cotton or linen,** or other substrates that could be degraded by metal-catalyzed hydrolysis reactions.

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Agarose Purification

- Agaropectin(s) removed from high quality agar:
  - Various processes: precipitation, extraction, absorption

Processing methods contribute to product quality!

- Additional processing adds to expense: >100 USD/100g

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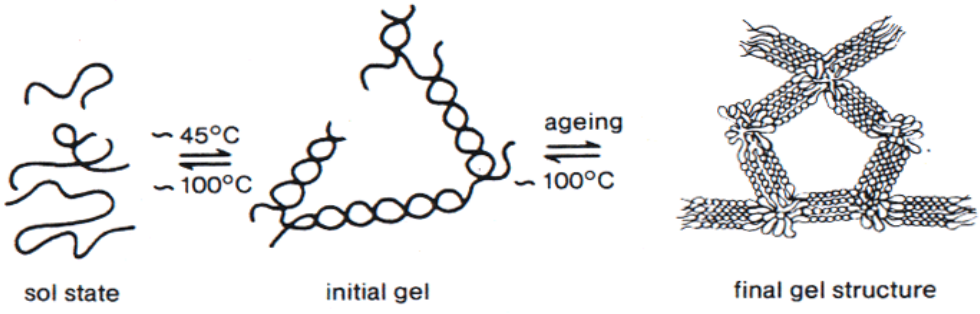
Agar & Agarose Properties to Consider: Gelation Hysteresis



- Reversible process: sol – incipient gel – elastic gel* – turbid rigid gel – expression of water (**syneresis!**)

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Agar & Agarose Properties to Consider

- Optical properties: color, transparency
- Melting temperature
- Gelling temperature

Gelation hysteresis!

- Gel strength
- Sulfate %
- EEO (electroendosmosis)

Homogeneity/purity/ionic quality

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Agar & Agarose Properties

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Agar or Agarose? Which Type?

- **What is the goal of the treatment step?**
  - Simple hydration/humidification: **Agar ($)**
  - Increased gel flexibility: **Agar**
  - Large surface areas: **Agar ($)**
  - Controlled hydration/humidification: **Agarose**
  - Controlled delivery of aqueous cleaning solutions: **Agarose**
  - Aqueous cleaning on water-sensitive surfaces: **Agarose**
  - Controlled delivery of temperature-sensitive reagents: **Low-gelation-temperature agarose (Very expensive!)**

Preferred agarose: Agarose LE (low electroendosmosis).

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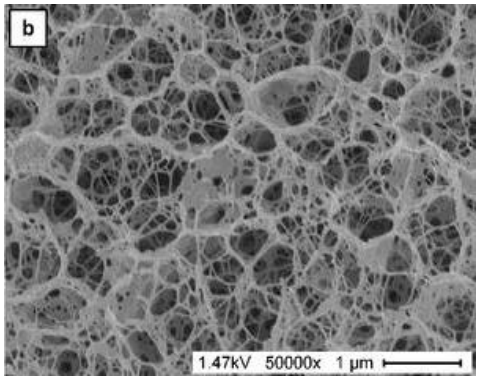
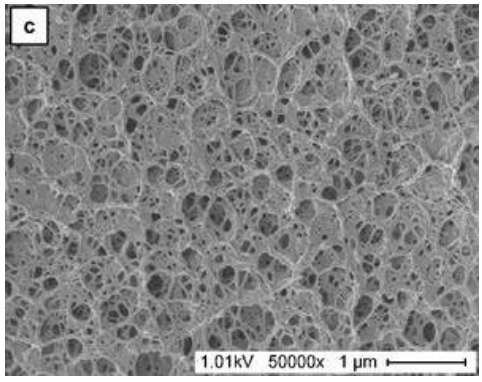
Concentration Considerations

- **With increasing agar/ose concentration:**
  - **Decreased mean pore size**



2% Agarose



6% Agarose

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Concentration Considerations

- Typical concentrations range from ~1% - 10+% (w/v)
- With increasing agar/ose concentration:
  - Increased water retention
  - Increased gelation temperature (lesser gelation hysteresis)

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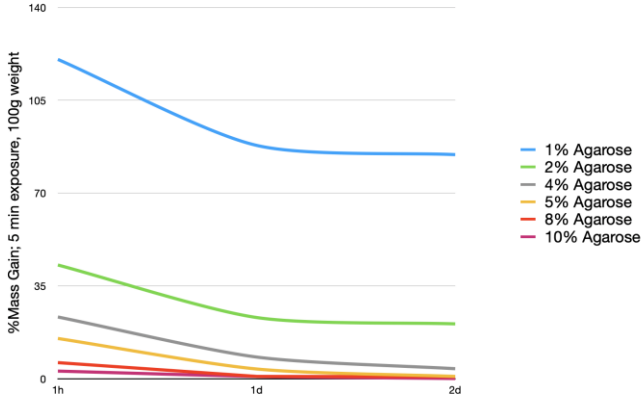
Agarose Moisture Delivery/Retention

- Greater gel concentration :: greater retention
- 'Fresh' gels :: lesser retention



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A Thought Experiment

- Agarose gel of lower concentration
- Relatively flat, thin object with stains
- Agarose gel of higher concentration

In what direction should the water and stains move?

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Adding Aqueous Cleaning "Tools"

- Agarose most stable in pH ranges 5-9
- Two options for tailoring aqueous parameters:
  - Add to agarose solution before heating
  - Allow cast gel block to equilibrate in aqueous solution
- Components to avoid heating: enzymes, surfactants

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AGAR & AGAROSE IN CONSERVATION: *Applications*

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Agar & Agarose – Cold Methods

- **Use of cast agarose:**
  - Surface testing
  - Controlled moisture delivery
  - Stain reduction/poulticing
  - Surface cleaning

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Estimating Surface pH and Conductivity

Erica Rota, Claudio Bozzi, Paolo Cremonesi & Anna Lucchini (2021) Study of the Best Methodology for Measuring Surface pH of Linen Canvas, *Studies in Conservation*, 66:6, 313-320, DOI: 10.1080/00393630.2020.1838711

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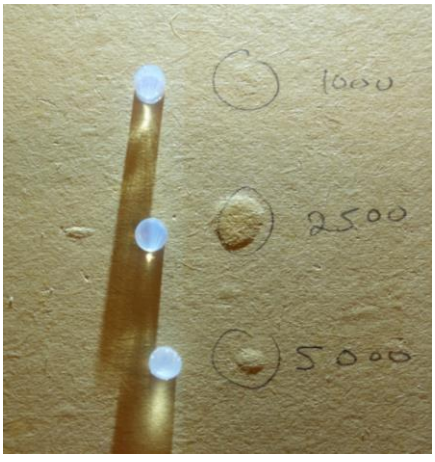
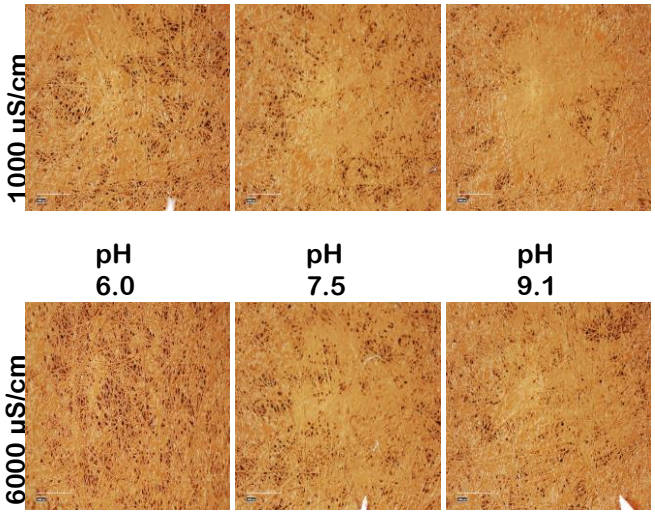
Testing Surface Swelling





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Large-Scale Stain Reduction

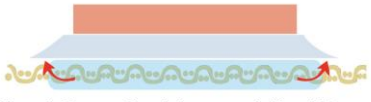

Figure 4 Diagram of beveled agarose gel with weight.

Samantha Skelton, Corina Rogge & Zahira Véliz Bomford (2016) Testing the limits: The theoretical development and practical reality of a large-scale agarose gel treatment for a discolored Morris Louis, *Studies in Conservation*, 61:sup2, 214-218, DOI: 10.1080/00393630.2016.1181865

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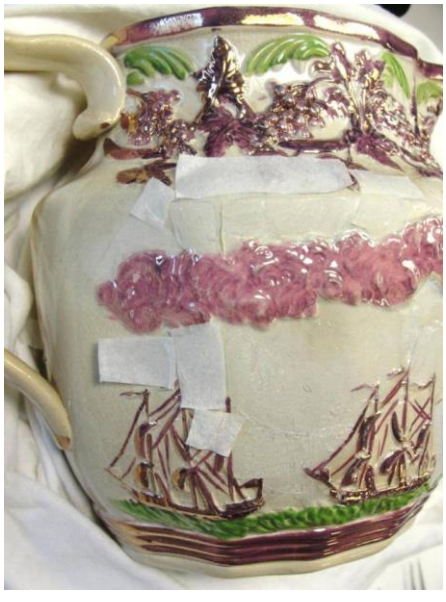
Poulticing

Images: Lauren Fair



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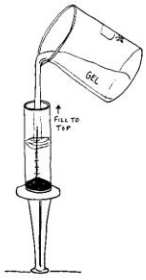
"Stain Stick"



4. CAST THE GEL
While the gel is still hot and liquid, pour it carefully into the cut open end of the syringe. Standing the syringe on the end of the plunger is usually stable – if it is not, have a partner hold it for you. Pour excess gel into other prepared syringes or into a flat, heat-proof container for use as a cast gel. The syringes take longer to set than cast gels because they retain heat longer in their cylindrical shape! Leave the gel for at least thirty minutes to ensure it is fully set. The agarose will appear slightly hazy and blue when set.

5. USE THE GEL
Push the plunger down slightly to expose the gel. With a clean blade, cut the gel flush with the plastic syringe to trim off the meniscus of the gel. The "Stain Stick" is now ready to use! Lightly pounce on your object where necessary; longer dwell time or more pressure will release more water. Try cutting the tip of the gel into a chisel or point for detailed work! Avoid vigorous rubbing across the object's surface, which can cause crumbling of the gel and abrasion of the object's surface. As the end of the gel becomes stained with imbibed discoloration products, trim it off with a clean blade. Store the gel in a plastic bag and in the refrigerator for up to two or three weeks.

SYRINGE-CAST AGAROSE HANDOUT, M. BROCKMAN, ED. 2020 | 2

Image: Madison Brockman, AIC BPG

103

Surface Cleaning: Grated Crumbs

Paolo Cremonesi (2016) Surface cleaning? Yes, freshly grated Agar gel, please, Studies in Conservation, 61:6, 362-367, DOI: 10.1179/2047058415Y.0000000026

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Surface Cleaning: Grated Crumbs

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Fragmented Gels

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Warm Application/In-situ Casting

Concerns:

- **Temperature stability of original surface**
- **Ingress of fluid solution into cracks and pores**
- **Personal safety: Hot gel and exposed skin are a bad mix!**

But consider:

- If the gel temperature is sufficiently low, you can wait to apply the warm solution to the surface just before gelation
- If the gel concentration is high, you can expect faster gelation, limiting ingress
- Temporary hydrophobization may protect cracks and pores

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Warm Application/In-situ Casting

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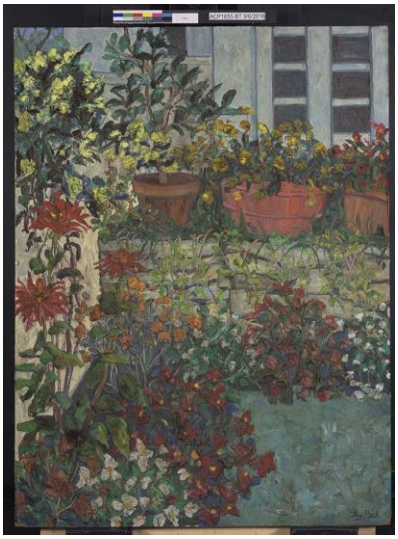
Agarose – Warm Brush/ Poured Application



Diana Hartman, Laura Eva Hartman & Caroline Hoover (2019) Experimenting with Agarose: New Methods for Cleaning Sensitive Modern and Contemporary Surfaces, AIC Paintings Specialty Group Postprints 32, 157-172.

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Agarose – Warm Brush/ Poured Application

Diana Hartman, Laura Eva Hartman & Caroline Hoover (2019) Experimenting with Agarose: New Methods for Cleaning Sensitive Modern and Contemporary Surfaces, AIC Paintings Specialty Group Postprints 32, 157-172.

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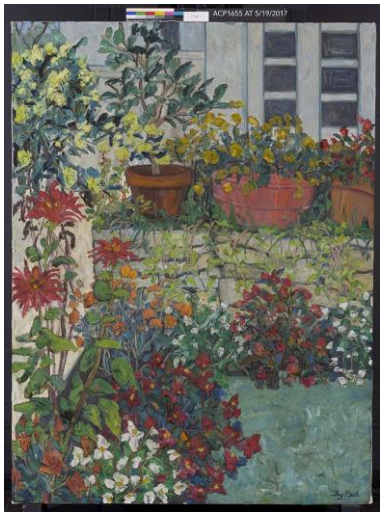
Agarose – Warm Brush/ Poured Application



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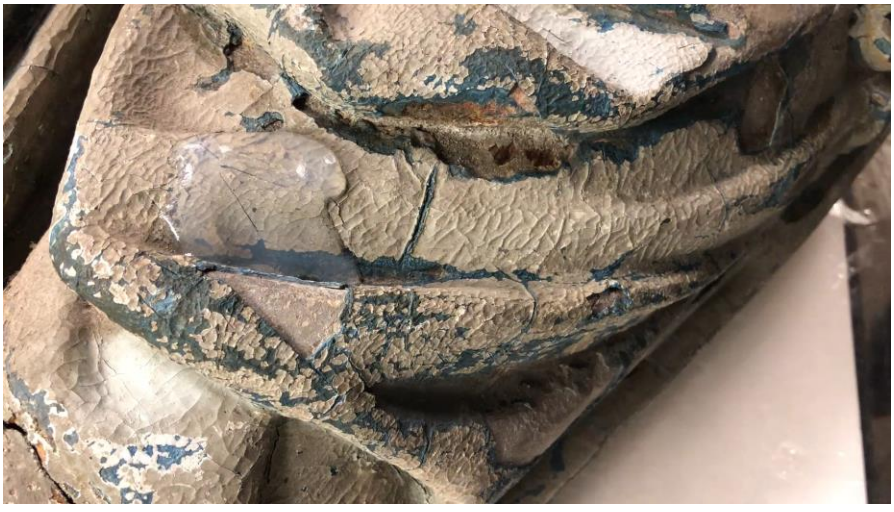
Agarose – Warm Application



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Agar – Sprayed Application

Ambra Giordano & Paolo Cremonesi (2021) New Methods of Applying Rigid Agar Gels: From Tiny to Large-scale Surface Areas, Studies in Conservation, 66:8, 437-448, DOI: 10.1080/00393630.2020.1848272

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Surface Conformation

Ambra Giordano & Paolo Cremonesi (2021) New Methods of Applying Rigid Agar Gels: From Tiny to Large-scale Surface Areas, Studies in Conservation, 66:8, 437-448, DOI: 10.1080/00393630.2020.1848272

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GELLAN GUM

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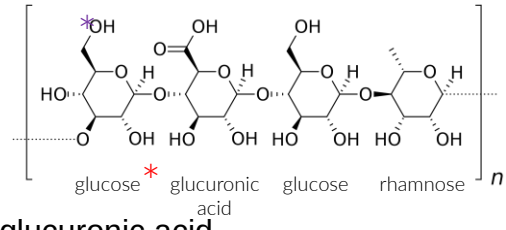
Gellan Gum



Bacterial branched anionic gum

- Backbone of glucose, rhamnose, glucuronic acid
- Occasional acetyl (<50% of tetrasaccharides) and glycerol (>50% of tetrasaccharides) substitutions

Practical Considerations

- **Fairly expensive (USD 40.00/100g)**
- **Hydrates in cold water**
- Typical concentrations: **0.75–2.0%; can be greater**
- **Creates very viscous solutions**
- **Heated solutions are very clear, less viscous**

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Gellan Gum – Acyl Substitutions

Natural form: High-acyl gellan gum

- High numbers of acyl groups: flexibility, opacity

Low-acyl gellan gum

- Chemically treated to remove most acyl groups
- Fewer substitutions: more rigid structure
- Optically less cloudy than agar gels

Both structures require calcium ions to stabilize the gel: 0.4g Calcium acetate added per 1L

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Gellan Gum Preparation

Material selection decisions

- High-acyl: less common in conservation applications
- Low-acyl: more common; used similarly to agar/ose
- Two main suppliers: CP Kelco, Royal DSM
- Polymer concentration

General procedure

- **Dissolve calcium acetate in water**
- **Add gellan gradually, with mixing**
- **Heat to clarity (near boiling)**
- **Cast into prepared mold/form**

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Gellan Hydrogels: Notes

Gellan mixtures can form clumps. If time allows, allow the mixture to sit overnight to promote hydration.

Gellan mixtures are often used as replacements for agarose (lesser cost!) but they do not exhibit the same syneresis

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Gellan Hydrogels: Notes

Tip: Use an immersion blender to rapidly mix and hydrate gellan (low-acyl or high-acyl)!

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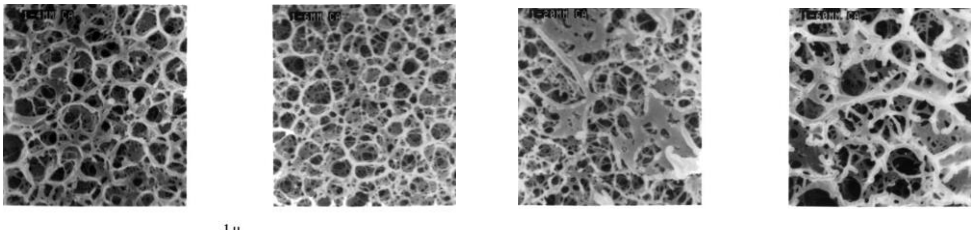
Gellan Gum – Effect of Ca^{2+}

R. Mao et al. / Carbohydrate Polymers 46 (2001) 365-371

0.4g Calcium acetate/1000mL solution: ~2.5 mM

- Molarity: $[(158.166\ g/mol)(1L/0.4g)]^{-1}$



4 mM 6 mM 20 mM 60 mM

We might be able to influence capillary action by adjusting Ca^{2+} concentration

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Gellan Gum – Effect of Ca^{2+}

Table 1
Water holding capacity W/W_0 (%) of 1% gellan gels after 125 days storage at 4°C

Ca^{++} (mM)	Average	Standard deviation
2	98.72	0.30
4	98.94	0.02
6	99.10	0.35
8	98.73	0.37
14	99.20	0.05
20	98.91	0.12
30	99.20	0.15
40	99.23	0.13
50	98.34	0.34
60	98.95	0.11
70	99.15	0.06
80	98.95	0.37

R. Mao et al. / Carbohydrate Polymers 46 (2001) 365-371

Water holding capacity appears to be independent of Ca^{2+} concentration

Syneresis is a minimal factor in low-acyl gellan gum moisture delivery

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Gellan Hydrogels: Typical Applications

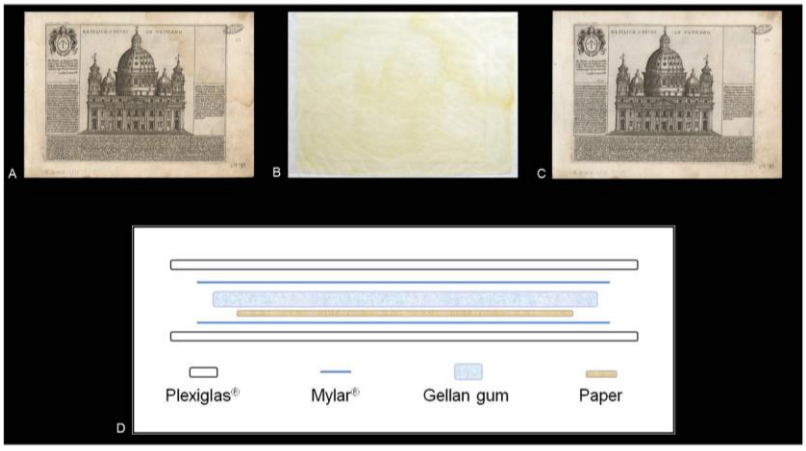

Fig. 17. Giacomo Lauro, Basilica S. Petri in Vaticano (1626), burin engraving. (A) before cleaning and (C) after treatment; (B) the clearly yellowed gel after treatment; (D) scheme of the application of the gel on a burin engraving

Iannuccelli and Sotgiu *Wet Treatments of Works of Art on Paper with Rigid Gellan Gels* The Book and Paper Group Annual 29 (2010)

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Gellan Hydrogels: Typical Applications

Fig. 14. Henry John White (Printer), The Holy Bible, (King James Version), 1832 or 1833, 28.0 x 22.0 x 6.0 cm, Library and Archives Canada, AMICUS 23024642.

Maheux *Cross-Disciplinary Uses for Gellan Gum in Conservation* The Book and Paper Group Annual 34 (2015)

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Combinging low-acyl and high-acyl gellan: Increased Flexibility

- **Prepared in the same methods as agar/ose, creating a gel with interesting elasticity and efficient moisture delivery:**

  2% 9:1 low-acyl gellan gum:high-acyl gellan gum

  Microwave method works well.

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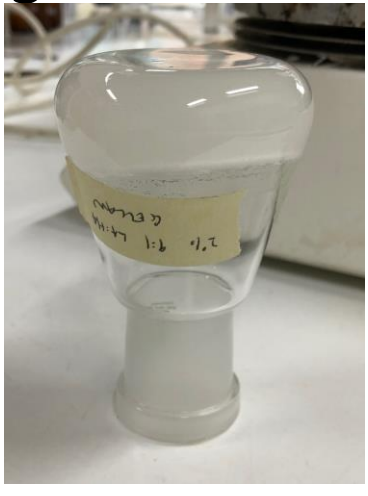
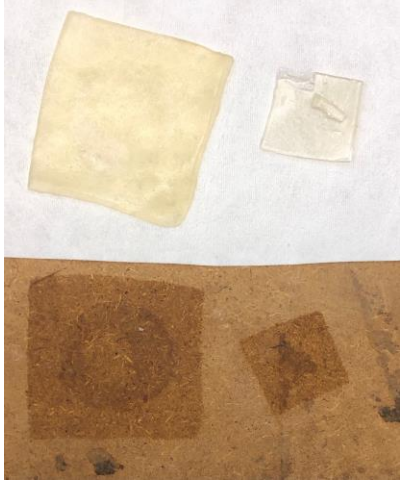
Combining low-acyl and high-acyl gellan: Increased flexibility





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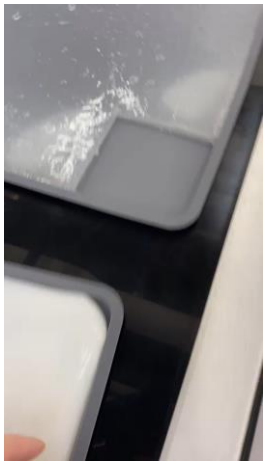
Comparing low-acyl, high-acyl, and blended gellan gum



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Re-using Thermoreversible Gels

- **Collect like scraps and "clean" waste to re-melt**
- Add water, fragment, re-heat, re-cast
- Concentration will be uncertain
- Perfect for non-presentation surfaces and "dirty" work
- Consider the addition of a preservative

Particularly useful for expensive hydrogels like agarose.

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PART IV: "NEW" HYDROGELS

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PVOH-Borax Gels

Viscoelastic chemical gels

- Weakly coordinated bonds
- Highly viscous behavior
  - Ductile
  - Cohesive
  - Self-healing behavior
- Good solvent compatibility
- Literature: minimal residues
- Poor pH stability (must be near neutral!)
- Properties can be tailored with component concentrations

Image: A. del Bianco

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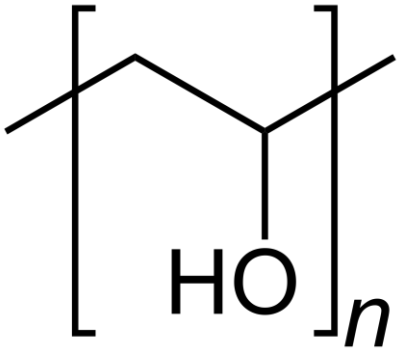
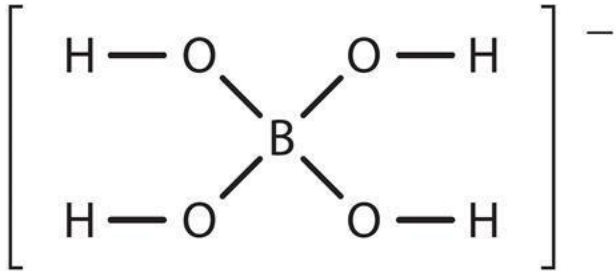
PVOH-Borax Gels: Components



$Na_2B_4O_7 \cdot 10H_2O$



Potential Hazard!

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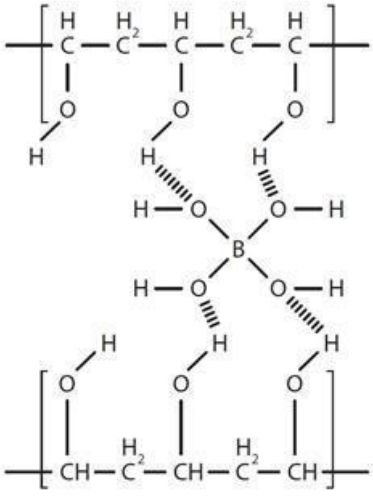
PVOH-Borax Gels: Complexation



Bonds within the complex are weak, transitory arrangements!

This means that the bonds can slip and re-form, allowing the gel to:

- **mold to surfaces**
- **stretch under low stress**
- **break at high stress**
- **remain cohesive**
- **self-heal**

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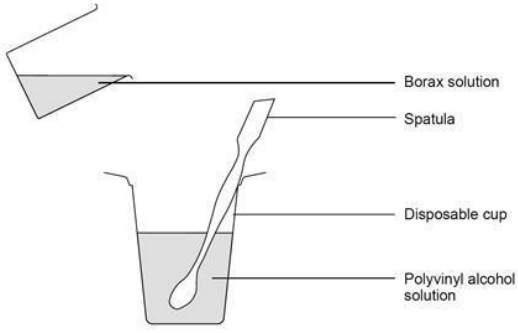
PVOH-Borax Gels: Preparation



Solution 1: PVOH, ≥ 8%

- Heat gently, with mixing, until clear
- Do not boil
- Allow the solution to cool

Solution 2: Borax, 8%

- Heat gently, with mixing, until clear
- Do not boil

Add warm Solution 2 to cool Solution 1. Mix vigorously!

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PVOH-Borax Gels: Preparation

Gel properties determined by:

- PVOH molecular weight
- PVOH concentration
- PVOH/Borax ratio

A good starting point: 4:1 (w/w) 8% PVOH: 8% Borax

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PVOH-Borax Gels: Useful Solvents

Solvents can be added to PVOH solution prior to mixing

- Ethanol
- Isopropanol
- Methyl ethyl ketone
- Immiscible solvents (benzyl alcohol, e.g.) can be stabilized with a surfactant

Additions of 20-30% (v/v) possible
Surfactant additions: 1-2%

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PVOH-Borax Gels: Solvent Effects

Developing conservation practices for cleaning gilded surfaces: Applications for xPVOH-borax organogels to clean two gilded frames

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Keywords
poly(vinyl alcohol)-borax, high viscosity polymeric dispersions (HVPD), organogel, gel cleaning, gilded objects, frames conservation

INTRODUCTION

Interest in high-viscosity polymeric dispersions (HVPDs) of partially hydrolysed poly(vinyl alcohol)/borax (xPVOH-b) for cleaning cultural materials (Carretti et al. 2009; Angelova et al. 2011, 2015, 2016, 2017, and 2018; Angelova 2013; Riedo et al. 2015 and 2017; Duncan 2017; Al-Emam et al. 2019 and 2020; Al-Eman 2021; Lazidou et al. 2019; Baglioni et al. 2021) informed initial studies that showed promise in the removal of overpaint and soiling from gilded surfaces (Sawicki et al. 2019, Parts A and B; Ramiro 2021). These gel-like materials were shown to overcome challenges posed by other cleaning systems, by demonstrating:

Variables:

- PVOH MW
- PVOH Wt%
- Borax Wt%
- Gel age
- Solvent(s)

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PVOH-Borax Gels: Network Modification Ideas

Adding 1% agar, agarose, or gellan

- Should be heated with PVOH solution
- Adds rigidity
- Limits adhesion on cellulosic surfaces

Adding gelatin, high percentages (≥10%)

- Improves particulate pick-up
- Bloom separately; should be added to PVOH solution as it cools
- Creates a double network that resists creep

Adding cellulose powder: poulticing paste

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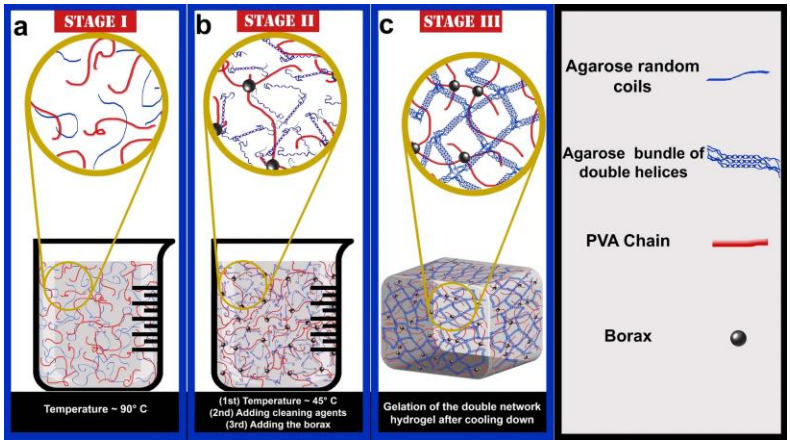
PVOH-Borax Gels: Network Modification Ideas – Agar/ose



Al-Emam, E., Soenen, H., Caen, J. *et al.* Characterization of polyvinyl alcohol-borax /agarose (PVA-B/AG) double network hydrogel utilized for the cleaning of works of art. *Herit Sci* **8**, 106 (2020). https://doi.org/10.1186/s40494-020-00447-3

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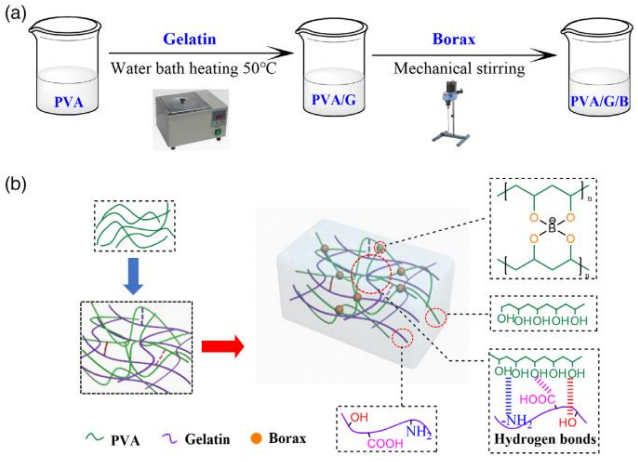
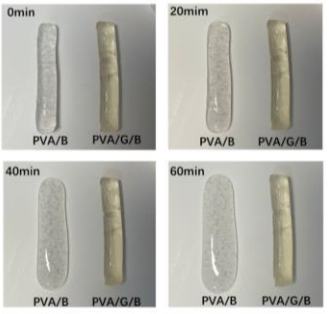
PVOH-Borax Gels: Network Modification Ideas – Gelatin



H. Yu, L. Zhao, L. Wang, J. Appl. Polym. Sci. 2023, 140(20), e53852.

https://doi.org/10.1002/app.53852



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PVOH-Borax Gels: Suggested Applications

- Surface particulate removal
- Coating removal (solvent additions)
- Work on complex topographies
- Glue rehydration & removal
- Cleaning plastics and other sensitive surfaces
- Stain removal

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NANORESTORE® GELS

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Nanorestore® Gels: Dry

Nanorestore Gel Dry

- poly(hydroxyethylmethacrylate)/ poly(vinyl pyrrolidone) [pHEMA/PVP] semi-interpenetrated chemical hydrogels (i.e. covalently bonded)
- Available: 'Medium Water Retention' & 'High Water Retention' (MWR & HWR)
- Highly retentive – in some applications, safe for water-sensitive surfaces

Image: CSGI

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Nanorestore® Gels: Dry

Moisture Retention

Table 1 Compositions (w/w) of the selected semi-IPN hydrogels; HEMA/MBA and HEMA/PVP ratios

	H50	H58	H65
HEMA (%)	25.0	16.8	10.5
MBA (%)	0.2	0.2	0.2
PVP (%)	24.9	25.1	24.4
Water (%)	49.9	57.9	64.9
HEMA/MBA ratio	$1:1 \times 10^{-2}$	$1:1.5 \times 10^{-2}$	$1:2 \times 10^{-2}$
HEMA/PVP ratio	50/50	40/60	30/70

The acronym HXX refers to the XX percentage of water in the reaction mixture

Table 2 Some physicochemical properties of the selected p(HEMA)/PVP, acrylamide [7] and polysaccharide hydrogels

	G (%)	EWC (%)	Water release (mg/cm^2)
H50	90	72	8
H58	78	80	15
H65	74	87	16
Acrylamide "Hard"	95	95	27
Acrylamide "Soft"	88	97	56
AgarArt	-	97	30
Kelcogel	-	97	33

Appl. Phys. A (2014) 114:705–710
DOI 10.1007/s00339-013-8150-0

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Nanorestore® Gels: Dry

Practical Considerations

- **EUR 18.00/150cm² sheet**
- Very consistent processing
- Clear, somewhat brittle gels
- **Can be loaded with aqueous solutions, microemulsions, structured fluids, some polar solvents**
- **Possible to clean and re-use**

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Nanorestore® Gels: Dry

Practical Challenges

- MWR and HWR Dry gels can develop cracks and tears
- Gels become unusable if allowed to dry fully
- Gels can support biological growth; cleaning is difficult
- If loaded with solvent, further use for aqueous delivery is not recommended

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Nanorestore® Gels: Dry Applications

Recommended Applications

- **Use on “flat” surfaces**
- **Humidification, surface cleaning, stain reduction**
- **Controlled delivery on water-sensitive surfaces**
- **Slow swelling and dewetting of adhesive residues and coatings**
- **Cracked/porous surfaces where residues are a concern**

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Nanorestore® Gels: Dry Applications

Images: A. Camp

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Nanorestore® Gels: Peggy

Nanorestore Gel Peggy

- poly(vinyl alcohol) and poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels
- Available: Peggy 5 [poly(vinyl alcohol)] and Peggy 6 [PVA/PVP] as sheets, gums (erasers), and pens
- Flexible, elastic
- Conforms to rough surfaces (Peggy 6 more so than Peggy 5)

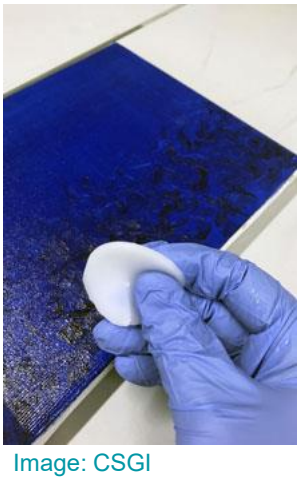

Image: CSGI

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Nanorestore® Gels: Peggy

Practical Considerations

- **EUR 18.00/150cm² sheet**
- Very consistent processing
- Semi-opaque, flexible, elastic gels
- **Can be loaded with aqueous solutions, structured fluids, microemulsions, some polar solvents**
- **Possible to clean and re-use**

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Nanorestore® Gels: Peggy

Practical Challenges

- Peggy gels less retentive than Dry; Peggy 6 less retentive than Peggy 5
- Gels become unusable if allowed to dry fully
- Peggy gels can support biological growth readily
- More limited solvent compatibility than Dry gels
- If loaded with solvent, further use for aqueous delivery is not recommended

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Nanorestore® Gels: Peggy

Recommended Applications

- Use on "flat" or rough surfaces. Peggy 6 conforms better to rough surfaces than Peggy 5
- Humidification, surface cleaning, stain reduction
- Controlled delivery on sensitive surfaces; limiting mechanical action
- Cracked/porous surfaces where residues are a concern
- Tape/adhesive removal
- Adhesive reactivation

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Hydrogel Solvent Compatibility

Because Nanorestore® gels are consistent from batch to batch, their polar solvent compatibility is known:

Gel Dry

Benzyl alcohol
Acetic acid
Ethylene glycol
2-Methoxyethanol
Ethanolamine
Propylene glycol
Ethanol
Methanol
2-Butanol
2-Propanol
Acetone
Butyl acetate
Cyclohexane
Ethyl acetate
Heptane
Methyl ethyl ketone
1-Pentanol
Propylene Carbonate
Xylenes
Toluene

Gel Peggy

Hydroalcoholic solvents (50%)

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Hydrogel Solvent Compatibility

Gel Peggy

Hydroalcoholic solvents (50%)

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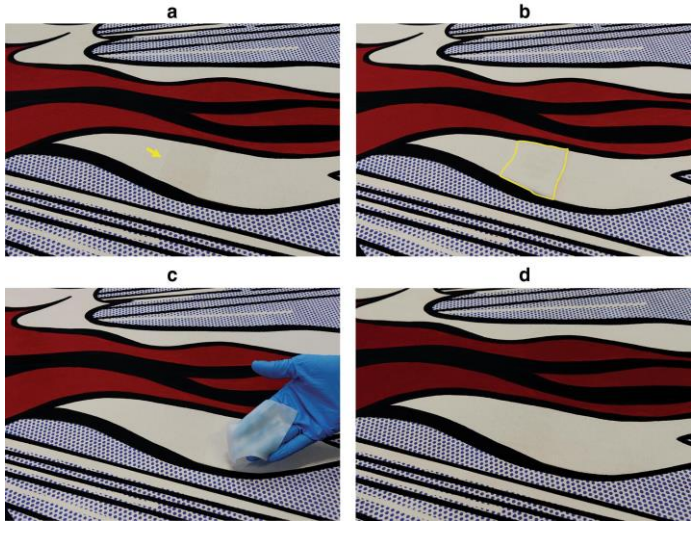
Nanorestore® Gels: Peggy



Bartoletti, A., Barker, R., Chelazzi, D. *et al.* Reviving *WHAAM!* a comparative evaluation of cleaning systems for the conservation treatment of Roy Lichtenstein's iconic painting. *Herit Sci* **8,** 9 (2020). https://doi.org/10.1186/s40494-020-0350-2

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Nanorestore® Gels: Key Decisions

- Surface area to be treated (can be cost prohibitive)
- Improved surface contact (Peggy gels) vs. improved moisture retention (Dry gels)

- *Solvent compatibility*
- *Are other gels feasible?*

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NEW BIOPOLYMER HYDROGEL FORMULATIONS

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Synergistic Polymer Interactions

Coupled gels

- Individual components do not gel on their own
- Interactions between chain backbones, ordering of ionic regions and side chains create physical gels
  - *Exact mechanisms are not well understood*
  - *Often: stereochemical similarities between backbones*

Synergistic effects:

- **Increased solution viscosity**
- **Gel formation**
- **Modification of syneresis behavior**

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Example Culinary Gel Synergies	Agar	Carrageenan (iota)	Carrageenan (kappa)	Gelatin	Gellan (low acyl)	Gellan (high acyl)	Guar gum	Konjac	Locust bean gum	Starch	Xanthan
Agar									■		
Carrageenan (iota)										■	
Carrageenan (kappa)								■	■		
Gelatin											
Gellan (low acyl)											
Gellan (high acyl)											
Guar gum									■		■
Konjac			■						■		■
Locust bean gum	■		■				■	■			■
Starch		■									
Xanthan gum							■	■	■		

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Formulation Inspiration

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Increasing xanthan gum content could enhance the performance of agar/konjac glucomannan-based system

Dongling Qiao [a], Wenjuan Shi [a], Man Luo [a], Wanting Hu [a], Yuchun Huang [a], Fatang Jiang [a], Fengwei Xie [b,*], Binjia Zhang [c,*]

[a] Glyn O. Phillips Hydrocolloid Research Centre at HBUT, National "111" Center for Cellular Regulation and Molecular Pharmaceutics, School of Food and Biological Engineering, Hubei University of Technology, Wuhan, 430068, China
[b] School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom
[c] Group for Cereals and Oils Processing, College of Food Science and Technology, Huazhong Agricultural University, Wuhan, 430070, China

United States Patent [19]
Musson et al.

[11] **Patent Number: 4,894,250**
[45] **Date of Patent: Jan. 16, 1990**

[54] **THERMO-IRREVERSIBLE EDIBLE GELS OF GLUCOMANNAN AND XANTHAN GUMS**

[75] Inventors: **Gary D. Musson; Colin T. Prest,** both of Melton Mowbray, United Kingdom

[73] Assignee: **Mars G.B. Limited,** Berkshire, United Kingdom

[21] Appl. No.: **190,581**

[22] Filed: **May 5, 1988**

[30] **Foreign Application Priority Data**

May 6, 1987 [GB] United Kingdom 8710704

[51] **Int. Cl.**[4] **A23L 1/06**
[52] **U.S. Cl.** **426/573;** 426/575; 426/574
[58] **Field of Search** 426/573, 575, 574

[56] **References Cited**

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2128871	5/1984	United Kingdom .	
2137066	10/1984	United Kingdom .	
2168366	6/1986	United Kingdom .	

Primary Examiner—Jeanette Hunter
Attorney, Agent, or Firm—Curtis, Morris & Safford

[57] **ABSTRACT**

Thermo-irreversible aqueous gels are prepared by subjecting a gellable combination of xanthan gum and a glucomannan gum, preferably from the corms of an Amorphophallus species at a pH above 6 to a heat treatment under conditions of temperature and time to cause the gel to become thermo irreversible. The pH is preferably between 6 and 10 and more especially between 6 and 8. The preferred ratio of xanthan gum to glucomannan is in the range of from 5:95 to 95:5, more especially 1:10 to 10:1 and the preferred concentration of xanthan gum and glucomannan in the aqueous phase is 0.02% to 6%, more preferably 0.5 to 4%, by weight. The thermo irreversible gels of the invention, with the inclusion of food materials, such as minced meat, fruit and vegetables, simulate the texture of natural meat offals and other food structures.

13 Claims, No Drawings

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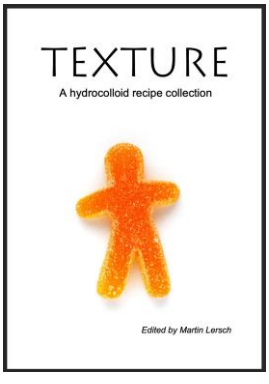
Formulation Inspiration



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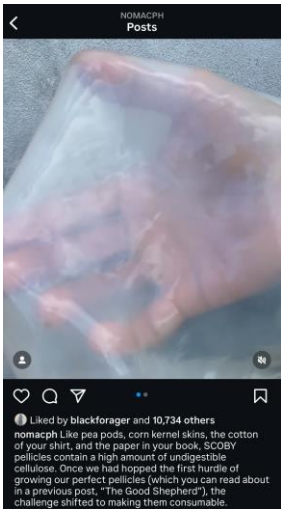
Formulation Inspiration



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XANTHAN/KONJAC-AGAR HYDROGELS

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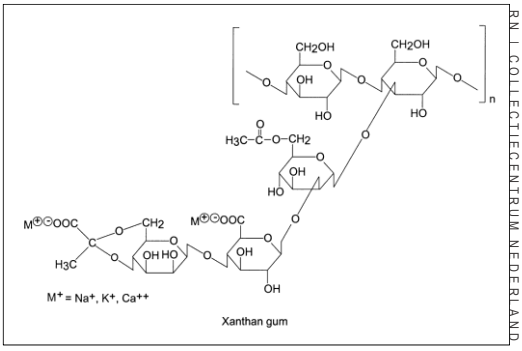
Xanthan Gum



Xanthan gum

Bacterial branched ionic gum

- Cellulose backbone
- Anionic trisaccharide side chains

Practical Considerations

- **Inexpensive (USD 6.80/100g)**
- **Readily hydrates in cold water**
- Typical concentrations: **0.75–1.5%**
- **Very viscous solutions**
- Exceptional **shear thinning**
- **Non-gelling on its own**

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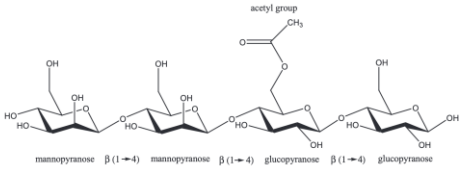
Konjac Glucomannan



Plant polysaccharide

- Root vegetable
- Glucose/mannose backbone
- Acyl substitutions

Practical Considerations

- **Inexpensive (USD 7.00/100g)**
- **Readily hydrates in cold water**
- Typical concentrations: **0.75–1.5%**
- **Very viscous solutions**
- **Shear thinning**
- **Can form a hydrogel by treating with pH 9+ & heating to 90°C**

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Xanthan/Konjac Hydrogels: Exceptional Elasticity

- **Prepared in the same methods as agar/ose, creating a strong, clear, elastic gel**

1% Xanthan gum
1% Konjac glucomannan

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Preparing Xanthan/ Konjac Hydrogels

Recommended: immersion circulator

- Set temperature to maximum.
- Prepare a solution of 1% xanthan and a second solution of 1% konjac. Stir to combine*
- Submerge in the water bath, mixing occasionally until internal temperature exceeds 90C.
- Carefully remove from bath.
- Stir to mix. Pour into mold. Let cool.
- Rinse to remove unentangled polysaccharide at surface.

Microwave method works well, too.

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Xanthan/Konjac Hydrogels: Notes

Konjac often has a "fishy" odor depending on its source and purification methods. This odor can be diminished by rinsing or by lowering the pH of the solution.

Xanthan/konjac hydrogels can be pushed to conform to surfaces, and the gel will settle into small surface irregularities.

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Xanthan/Konjac Case Study: Iron-Stained Marble, c. 1500

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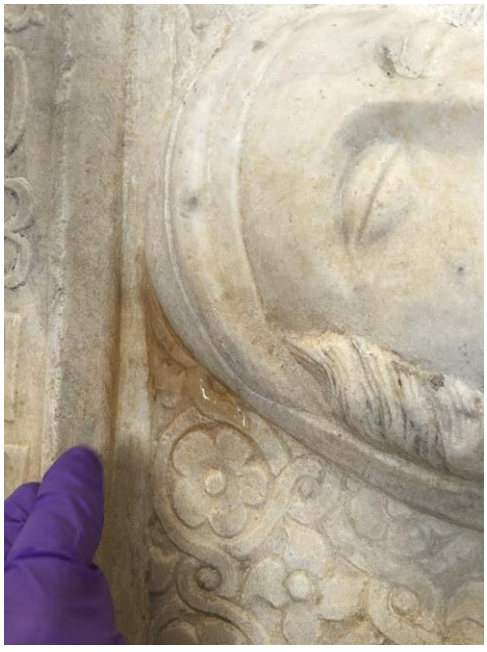

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Xanthan/Konjac Challenges: Adhesion

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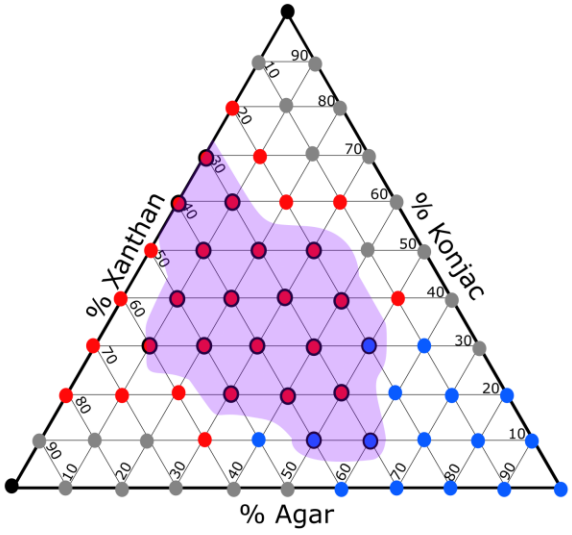
Further Modification: Xanthan/Konjac-Agar Hydrogels



1.5% (w/v) total concentration

- Not a gel - viscous fluid
- Weak gels - poor performance
- Flexible/elastic gel behavior
- Brittle/rigid gel behavior
- Region of interest: "new" gel properties

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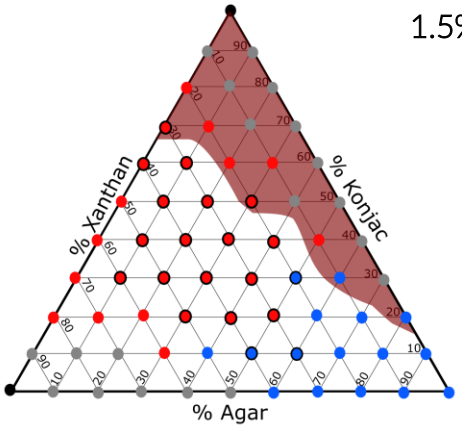
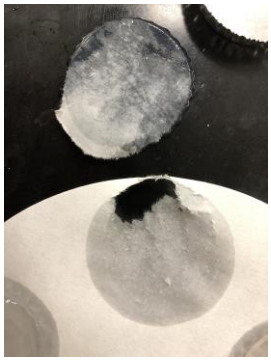
Further Modification: Xanthan/Konjac-Agar Hydrogels



1.5% (w/v) total concentration

- Not a gel - viscous fluid
- Weak gels - poor performance
- Flexible/elastic gel behavior
- Brittle/rigid gel behavior
- Gel adhesion to Whatman filter paper



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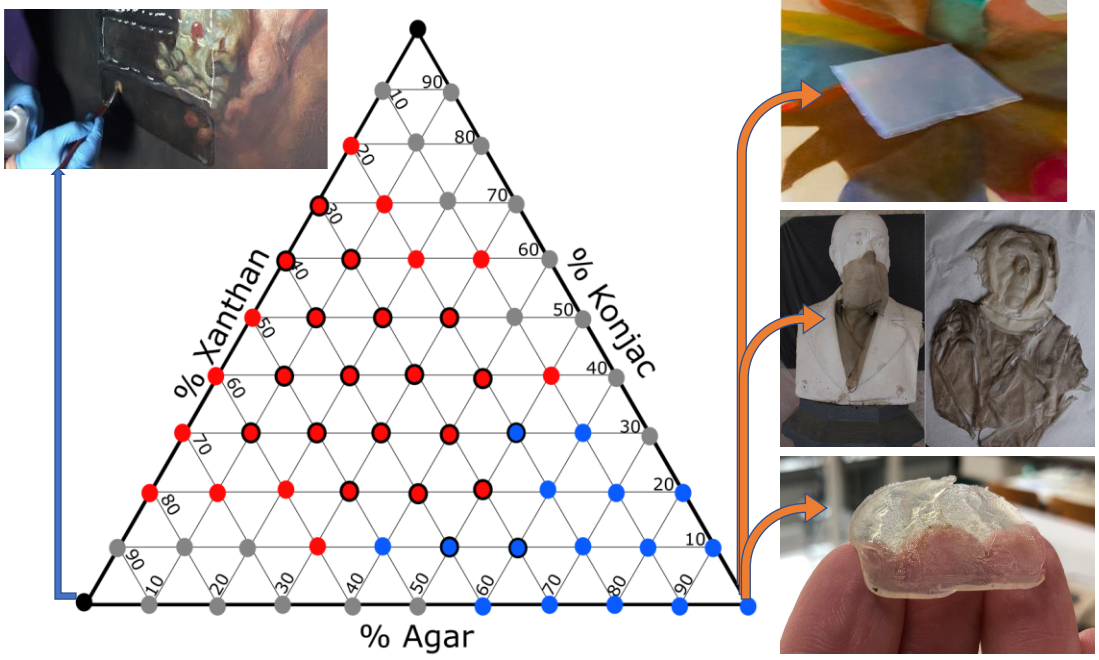

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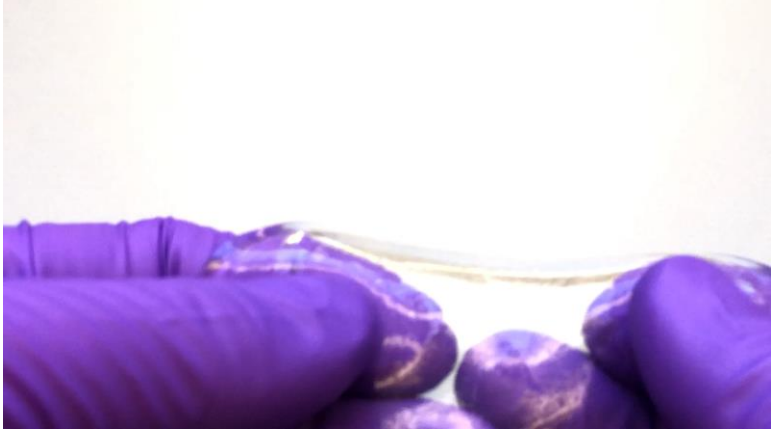
Further Modification: Xanthan/Konjac-Agar Hydrogels



1.5% (w/v) total concentration:
2 parts xanthan
2 parts konjac
1 part agar

- Blend dry ingredients
- SLOW addition to water with mixing (or mix separate solutions)
- Heat > 90°C
- Cast

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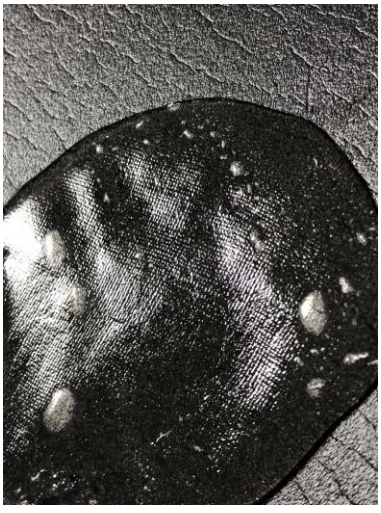
Further Modification: Xanthan-Konjac-Agar Hydrogels



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Further Modification: Xanthan-Konjac-Agar Hydrogels

In this video:
2% (w/v) total concentration:
- 2 parts xanthan
- 2 parts konjac
- 1 part agar

Estimated cost, including power for stirring and operation of immersion circulator bath (4 hours):
$0.87 for 20cm x 25cm x 2mm gel

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Preparation Tips: Xanthan-Konjac-Agar Hydrogels

- Thorough mixing is critical to avoid weak and tough regions
- Insufficient heating will result in a grainy, weepy gel
- XKA gels are able to be reheated several times without loss of mechanical properties
- If the gel isn't good: cut it into pieces and reheat!

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Preparation Tips: Xanthan-Konjac-Agar Hydrogels

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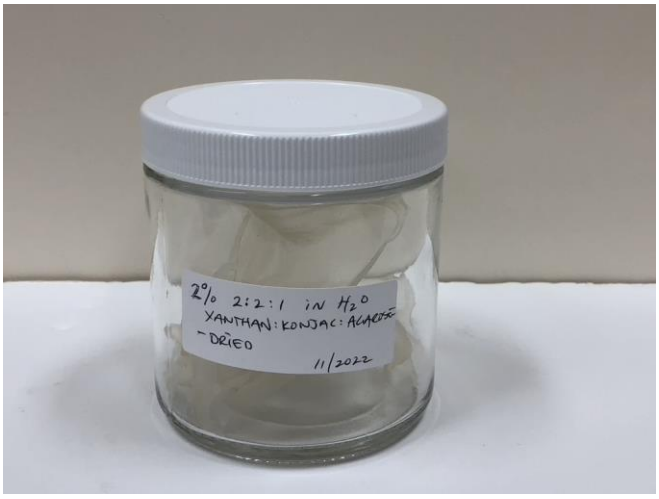
Practical Use: Xanthan-Konjac-Agar Hydrogels



"Loading" a cleaning solution:

- Initial preparation of the gel
- Soaking a freshly prepared gel

Xanthan-konjac-agar(ose) gels **can be dehydrated** and stored.

Dehydrated gels can be rehydrated with aqueous cleaning solutions, with minimal change to gel performance.

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Practical Use: Xanthan-Konjac-Agar Hydrogels

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Case Study: GACP1293, Deposition with Angels

- Deaccessioned from Harvard Univ.
- Anecdotes: Used for testing varnishes and cleaning, dating to Gettens and Stout.

- At WUDPAC:
  - Microscopy studies
  - Cleaning experimentation

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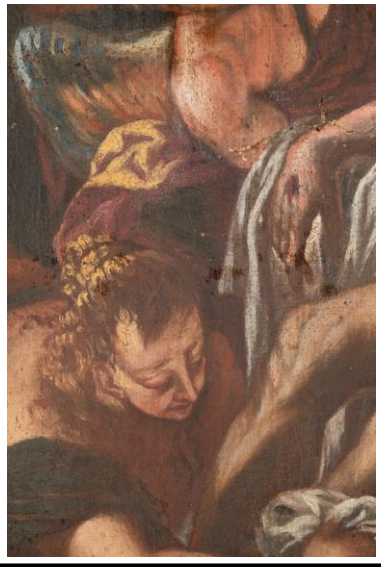
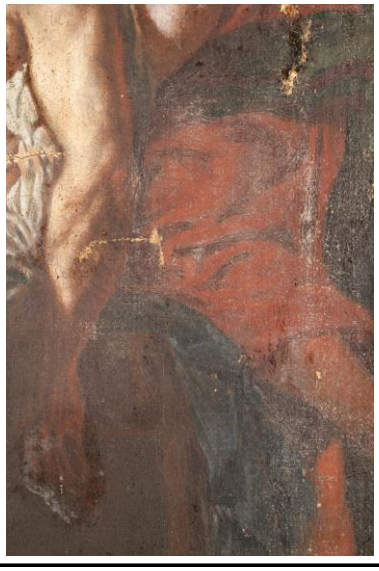
Case Study: Deposition with Angels





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Case Study: Deposition with Angels

- Residual varnish: slight effect with alcohols and ketones
- Pigment pickup with other polar solvents
- Aqueous tests:
  - > pH 8: some coating fractions removed
  - Significant improvement with chelating agents; DTPA most effective
  - Additional improvement with deoxycholic acid
- Goal: reduced mechanical action

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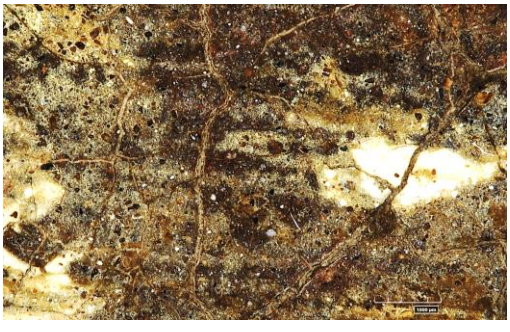
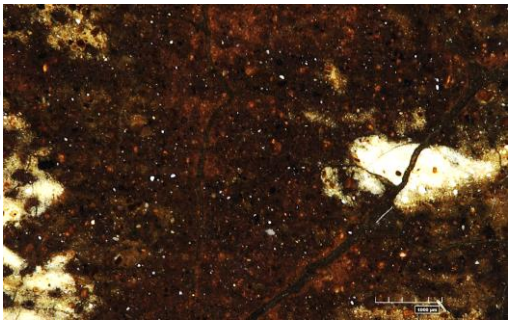
Before Treatment

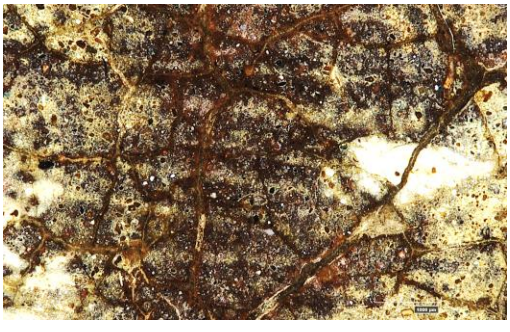


1 exposure, 3 min

15 min total, after clearing/rinsing



9 min total



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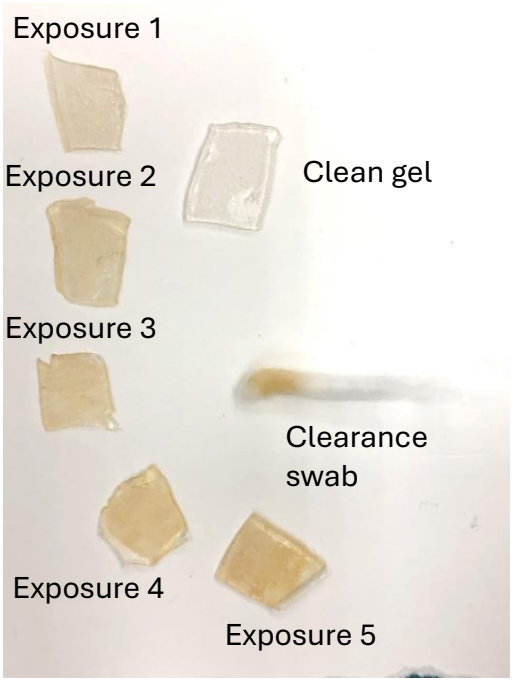

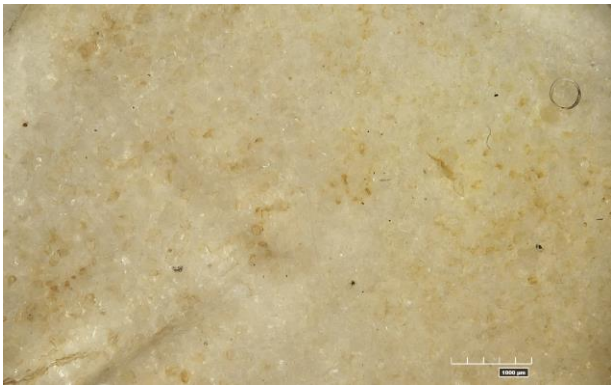

Exposure 5 gel surface after cleaning

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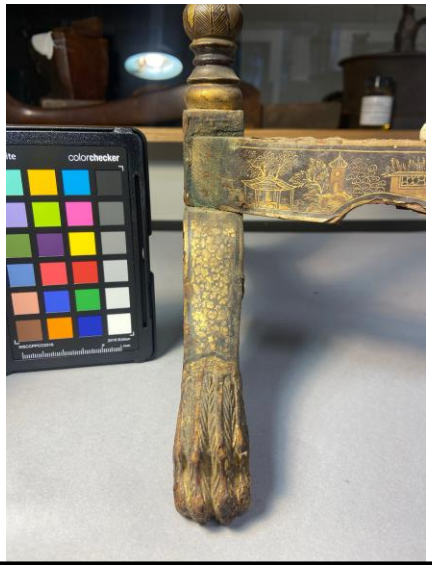
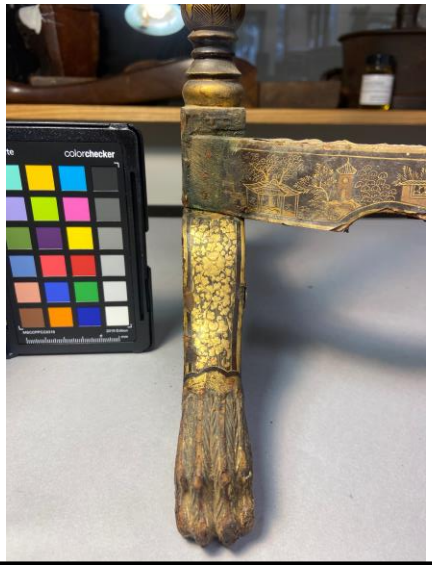
Case Study: Chinese Export Lacquer Nesting Table





1.25% 2:2:1 XKA gel Prepared with 1% EDTA, pH 5.0 buffer

Credit: Caroline Shaver

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Case Study: Tenacious Lining Removal

After many tests requiring 40+ minutes:

2% 2:2:1 XKA, pH 8.5 (bicine) sodium deoxycholate, 1% DTPA, 15 minutes

Credit: Adriana Benavides

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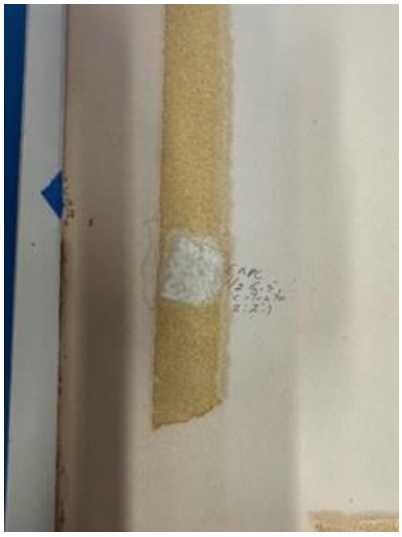
Case Study: Adhesive Tape Removal



Promising tests!

1.5% 2:2:1 XKA
Ethyl acetate/propylene carbonate/SDS microemulsion
0.5% citric acid, pH 6.5

Long exposure, adhesive dewetting

Credit: Chris Stavroudis, Michelle Sullivan

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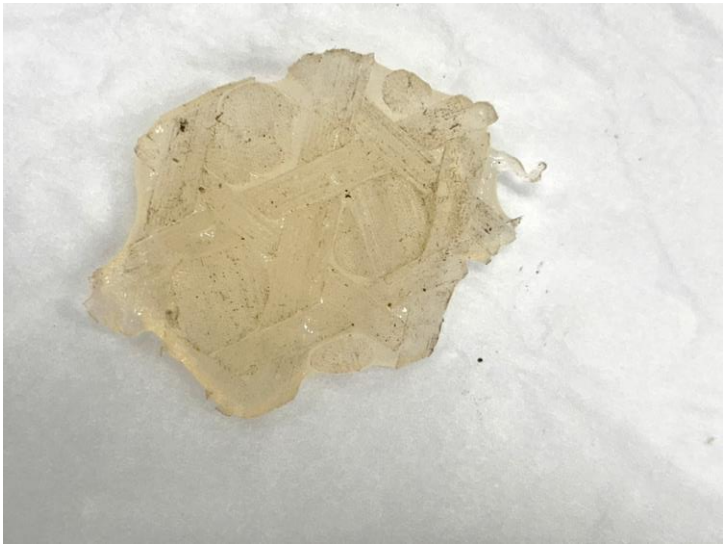
Direct Casting



Must be certain that heating and mixing is adequate.

Poorly heated/mixed/hydrated solution will result in residues!

When direct casting, consider a preparation with a higher agar(ose) ratio: 1:1:1 or 1:1:2?

When heating, do not drive off all of the water, but do not undercook. Do not fail through your own gutlessness.

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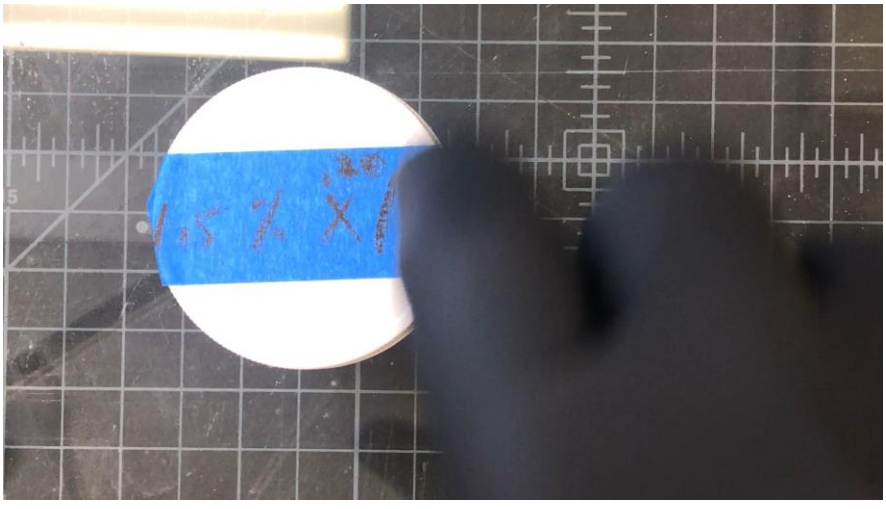
Formulation Substitutions: Xanthan-Locust Bean Gum



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Formulation Substitutions: Xanthan/Salep-Agar

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Formulation Substitutions:

We can substitute several different glucomannans (konjac, salep, e.g.) or galactomannans (locust bean gum, tara gum, e.g.) to produce gels with similar properties!

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Solvent Additions:

We can blend non-miscible (or low miscibility) solvents after heating and before gelation.

2% XKA is capable of stabilizing about 15% (w/w):

- benzyl alcohol
- ethyl acetate
- ethyl lactate
- propylene carbonate
- others

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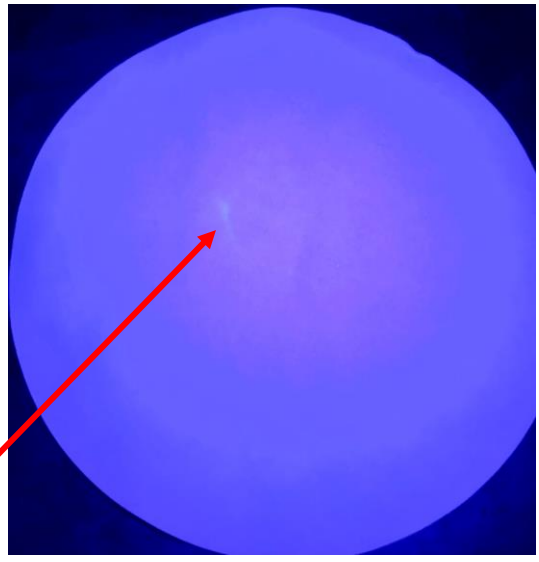
Next Steps: Residue Studies



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Early Mechanical Testing @ UD

Early tests:

- Yield stress increased with the addition of calcium acetate
- Gels can be melted and re-gelled several times without loss of mechanical properties
- XKA gels begin to melt around 55C
- XKA gels can swell 2-3x original size on rehydration
- Mold growth visible after 48-60 hours at ambient conditions with no preservatives

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CURDLAN HYDROGELS

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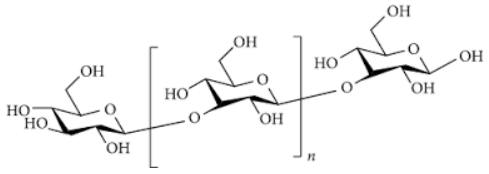
Curdlan



Bacterial beta-glucan

- (1→3)-β-D-glucose polymer, high MW

Practical Considerations

- **Fairly expensive (USD 25.00/100g)**
- Gels upon heating beyond hydration temperature (**heat set**)
- Forms an opaque **elastic, retentive gel** upon heating above 195ºF.
- Thermo-**irreversible; good temperature stability**
- Can form a softer thermo-reversible gel if not heated >150ºF
- **Gel structure, flexibility & toughness depend on solution concentration and solution heating**

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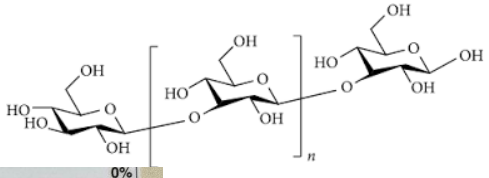
Curdlan



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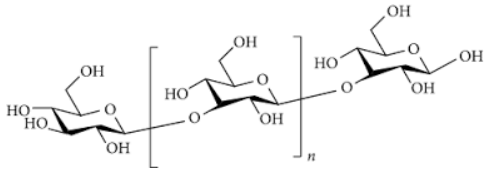
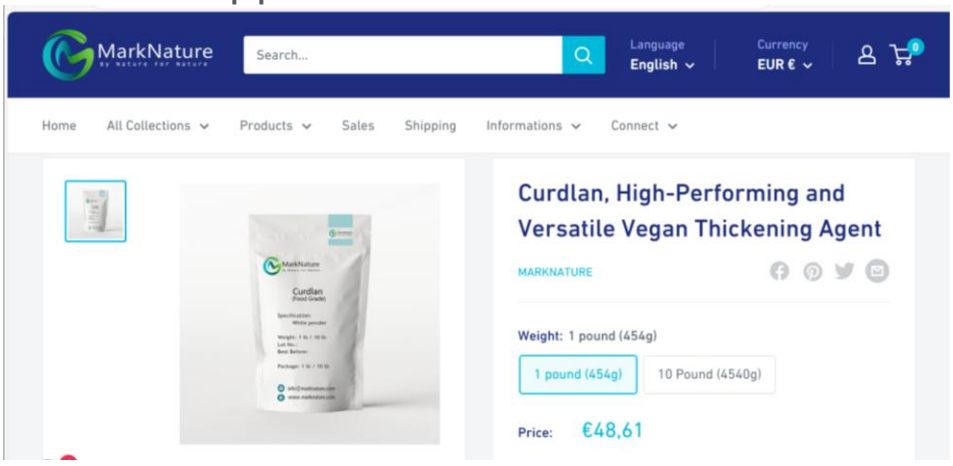
Curdlan



Current supplier: MarkNature



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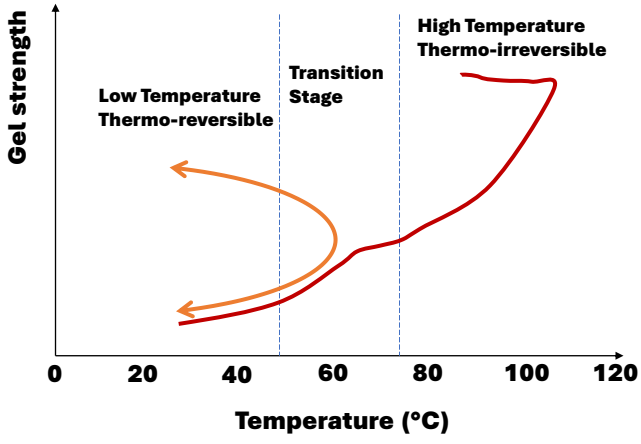
Preparing Curdlan Hydrogels



Heating below 60C: "soft set" gel, thermo-reversible

Heating above 80C: "hard set" gel, thermo-irreversible

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Curdlan Gel Strength: Concentration and Temperature

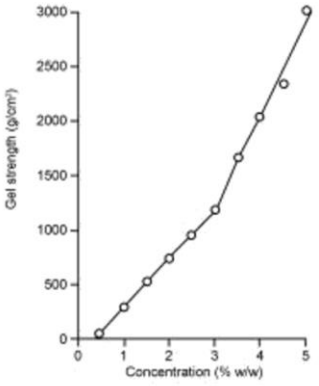

Fig. 20.7 Concentration dependence of gel strength for curdlan at 30 °C[2] (curdlan gel was obtained by heating at 90 °C for 10 min).

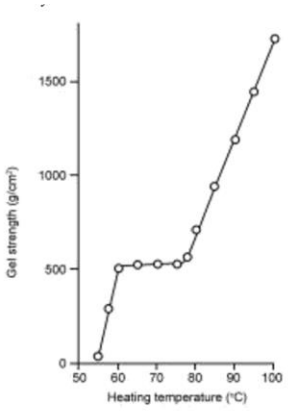

Fig. 20.8 Effect of heating temperature on gel strength of curdlan at a concentration of 3%.[2]

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Preparing Curdlan Hydrogels

Recommended: hot water bath

- Set temperature to 195ºF
- Prepare a curdlan slurry, 5-25% (w/v) in distilled water, in a small plastic zip-top baggie. Shake and manipulate to achieve even dispersion.
- Pour a thin layer (~2-3 mm) of the slurry into a flat-bottomed beaker or jar, or suspend the baggie in the water bath.
- Suspend the container in the water bath for at least 5 minutes, up to 1 hour.
- Allow the curdlan gel to cool. Remove from container.
- Rinse to remove unentangled polysaccharide

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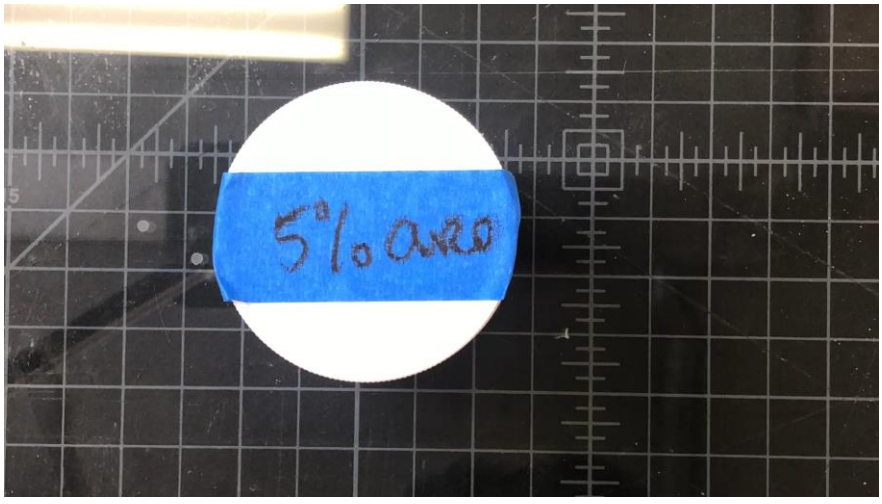
Preparing Curdlan Hydrogels



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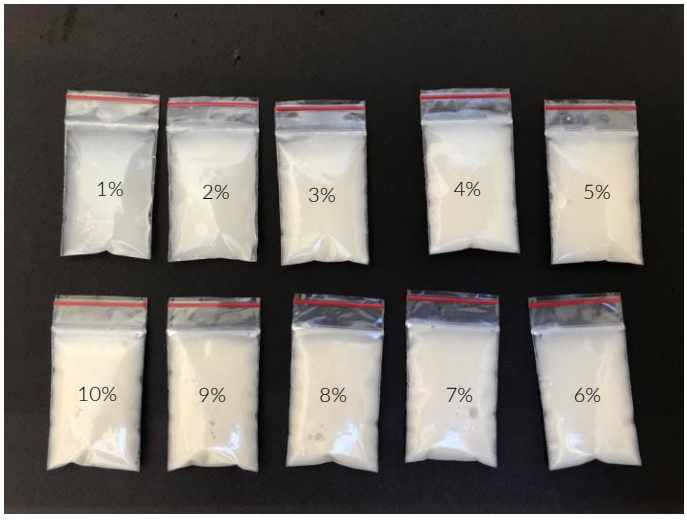
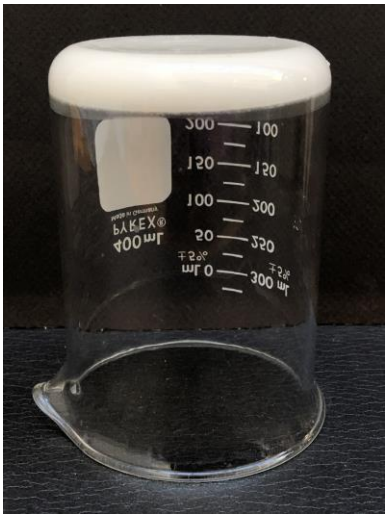
Preparing Curdlan Hydrogels





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Preparing Curdlan Hydrogels

Curdlan gels will take on the shape of any form once the dispersion reaches the heat setting temperature.

Ideas:

- blocks
- sheets
- “noodles”
- lozenges/pointed erasers

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Preparing Curdlan Hydrogels

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Curdlan Gels: Useful Properties

- Heat setting – additional options for gel preparation
- Subsequent temperature stability
  - Can be warmed/heated
  - Can be frozen!
- Impressive water retention
- Very high gel strength & cohesion:
  Good for mechanical techniques

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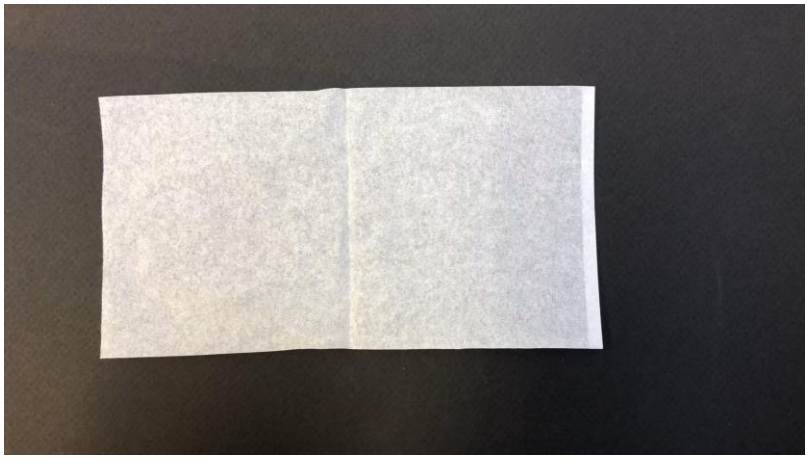
Comparing Curdlan & Peggy Gels



Time-lapse: 30s, water transfer to KimWipe. 10% Curdlan (left) and Peggy 5 Gum (right), both loaded with the same aqueous solution.

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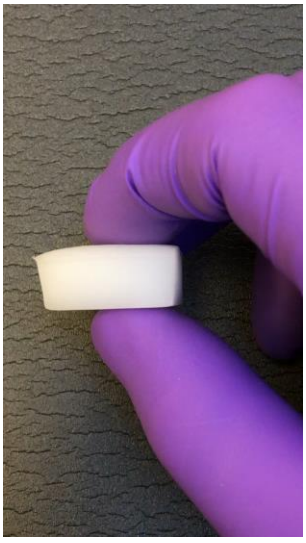
Comparing Curdlan & Peggy Gels



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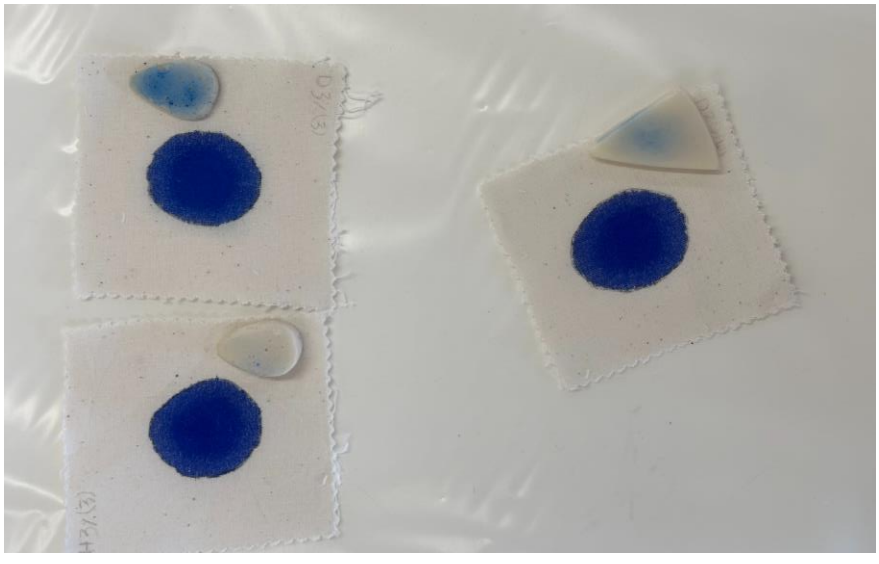
Testing Curdlan with Chelators



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Curdlan Hydrogels: Notes

Curdlan gels will promote biological growth after just a few days; limit air exposure

Curdlan gels can be warmed to increase the activity of diffused moisture

Gel strength decreases with increased inorganic salt concentration and/or solvent in initial formulation; recommended to prepare a gel first and then load it with a cleaning solution

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Curdlan Hydrogels: Recommended Uses

Controlled humidification:

- *Cast sheets for overall humidification*
- *"Noodles" for humidifying individual creases*

Dampened eraser:

- *Cut/cast blocks*

Delivery of aqueous cleaning preparations

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Curdlan Hydrogels: Recommended Uses

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SOLVENT COMPATIBILITY

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Hydrogel Solvent Compatibility

Remember that hydrogels are generally 90%+ water by mass, and that the gel structures are often stabilized by hydrogen bonding and the ionic environment.

Changing the solubility parameters of the liquid phase can cause gel instability, densification, and phase separation.

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Hydrogel Solvent Compatibility

Water-miscible solvents can be tolerated by most hydrogels in small proportions. Solvents with high hydrogen bonding (alcohols, especially) are expected to be tolerated up to 50% v/v in some cases.

High dipole solvents and solvents with a high dielectric constant (able to separate charges) can cause some gels to tighten and become more dense,

but they may be tolerated at upwards of 5-10% mixed into the initial formulation prior to gelation

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Key Properties – Polar Solvents

Solvent	Formula	Density	Water Solubility	Dipole Moment	Dielectric Constant	Viscosity	Notes
		g/mL	g/100g	(D)		mPa•s	
Acetone	C3H6O	0.786	M	2.85	21	0.30	
Acetyl acetone	C5H8O2	0.975	16	3.0	23	0.60	Hazardous material! Interesting ability to act as a chelating agent
Benzyl alcohol	C7H8O	1.042	3.5	1.7	13	5.47	
1-butanol	C4H10O	0.81	7.7	1.7	17.5	2.59	
Dimethyl sulfoxide	C2H6OS	1.092	M	3.9	46.7	2.00	
Ethanol	CH2O6	0.789	M	1.7	24	1.08	
Ethyl acetate	C4H8O2	0.894	8.7	1.78	6.0	0.43	
Ethyl lactate	C5H10O3	1.03	M	3.46	13.1	2.71	
Methyl ethyl ketone	C4H10O	0.805	25.6	2.8	18.6	0.41	
N-methyl-2-pyrolidinone (NMP)	C5H9NO	1.028	M	4.1	33	1.65	
2-propanol	C3H8O	0.785	M	1.66	19	2.07	
Propylene carbonate	C4H6O3	1.205	24	4.9	64	2.47	
Water	H2O	0.998	M	1.85	80.1	0.89	

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Hydrogel Solvent Compatibility

Because Nanorestore® gels are consistent from batch to batch, their polar solvent compatibility is known:

Gel Dry

- Benzyl alcohol
- Acetic acid
- Ethylene glycol
- 2-Methoxyethanol
- Ethanolamine
- Propylene glycol
- Ethanol
- Methanol
- 2-Butanol
- 2-Propanol
- Acetone
- Butyl acetate
- Cyclohexane
- Ethyl acetate
- Heptane
- Methyl ethyl ketone
- 1-Pentanol
- Propylene Carbonate
- Xylenes
- Toluene

Gel Peggy

- Hydroalcoholic solvents (50%)

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PVOH-Borax Gels: Useful Solvents

Solvents can be added to PVOH solution prior to mixing

- Ethanol
- Isopropanol
- Methyl ethyl ketone
- Immiscible solvents (benzyl alcohol, e.g.) can be stabilized with a surfactant

Additions of 20-30% (v/v) possible
Surfactant additions: 1-2%

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PVOH-Borax Gels: Solvent Effects

Developing conservation practices for cleaning gilded surfaces: Applications for xPVOH-borax organogels to clean two gilded frames

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Keywords
poly(vinyl alcohol)-borax, high viscosity polymeric dispersions (HVPD), organogel, gel cleaning, gilded objects, frames conservation

INTRODUCTION

Interest in high-viscosity polymeric dispersions (HVPDs) of partially hydrolysed poly(vinyl alcohol)/borax (xPVOH-b) for cleaning cultural materials (Carretti et al. 2009; Angelova et al. 2011, 2015, 2016, 2017, and 2018; Angelova 2013; Riedo et al. 2015 and 2017; Duncan 2017; Al-Emam et al. 2019 and 2020; Al-Eman 2021; Lazidou et al. 2019; Baglioni et al. 2021) informed initial studies that showed promise in the removal of overpaint and soiling from gilded surfaces (Sawicki et al. 2019, Parts A and B; Ramiro 2021). These gel-like materials were shown to overcome challenges posed by other cleaning systems, by demonstrating:

Variables:

- PVOH MW
- PVOH Wt%
- Borax Wt%
- Gel age
- Solvent(s)

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Microemulsion Compatibility

Oil-in-water microemulsions may be compatible with hydrogels, particularly if:

- The water phase makes up the vast majority of the mixture
- The microemulsion is thermodynamically stable at the operating temperature

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Hydrogel Solvent Compatibility

For self-prepared hydrogels, testing for solvent compatibility is critical.

Solution formulation, ionic stabilization, polymer concentration, and other factors determine a solvent's compatibility with the gel structure.

Qualitative tests: Place a small amount of gel in a solvent/water mixture.

- Does the gel shrink, swell, or stay the same size?
- Does the gel change opacity?

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TESTING!

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Variables to Test

Properties to tailor

- **pH**
- **Conductivity**
- **Use of chelating agents**
- **Use of surfactants**
- *Viscosity/rheological agents → gels*
- *Reactive additives: enzymes, redox reagents*

Additional factors:

- Time
- Mechanical action
- Temperature
- Addition of non-aqueous solvents

AND:

- Gel type
- Gel concentration
- Processing
- Clearing procedure

INTRODUCTION TO HYDROGELS IN CONSERVATION CLEANING
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General Testing Strategy

1. Determine safe aqueous parameters for original
2. Test for effective solution parameters, targeting the soiling/grime/stain, etc.
3. Determine which gel structure is most beneficial
   - How retentive? Cohesive? How rough is the surface? Do you need optical clarity? Etc.
4. Test methods of loading solution/solvent into the selected hydrogel
5. Determine effective dwell time
6. Test appropriate clearance measures

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RESIDUES AND RINSING

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Residues

- **Increased likelihood of residues:**
  - "Fresh" gels – *rinse with distilled water to remove unentangled polysaccharides*
  - Lower concentration gels
  - Softer gels
  - Cracked, porous surfaces

- **Reduced incidence of residues:**
  - Tissue barrier *but with altered capillary action*
  - Temporary hydrophobization
  - Clear using appropriate rinsing solution* loaded into gel

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Residues Visualization

- **Qualitative examination:**
  - UV-induced visible luminescence
  - Particularly useful for absorbent surfaces
    - See: Sullivan (2017)
  - Optical microscopy

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Practical Considerations: Rinsing/Clearing

Questions to consider:

- How porous is the substrate/structure?
- Are there any sensitivities to moisture to anticipate?
- Does the delivery method work well with the structure and condition of the surface?
- How likely is clearance? Are you willing to leave material behind as part of your treatment?

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Clearing Aqueous Solutions

- Goal 1: prevent precipitation of solubilized constituents
- Goal 2: prevent new solubilization of preserved materials
- Sub-goal: continue/slow down cleaning

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Clearing Aqueous Solutions

“pH-Adjusted Water”

- **dilute mixtures of acetic acid and ammonium hydroxide**
- **both components volatile**
- **buffered between 3.8-5.6 and 8.3-10.1**
- **ionic strength determined by concentration**
- **formulate according to pH used and estimated conductivity of surface**

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COMPARING GEL TYPES

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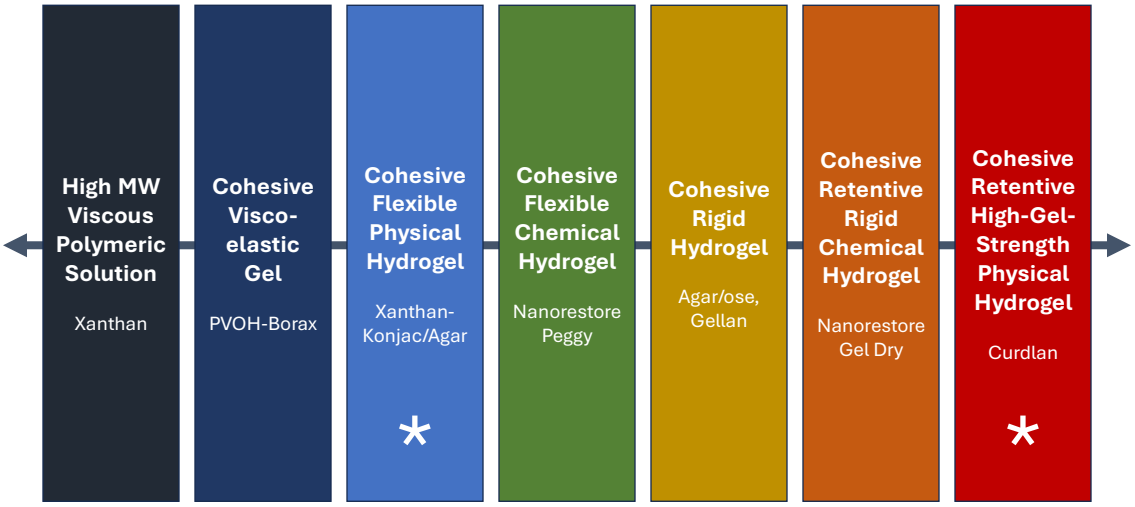
Advantages of Material Diversity



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Risk of Residues

LOW	MEDIUM	HIGH
Nanorestore Dry	Agarose*	
Nanorestore Peggy	Agar*	
PVOH-Borax*	Gellan*	
Curdlan*	XKA*	

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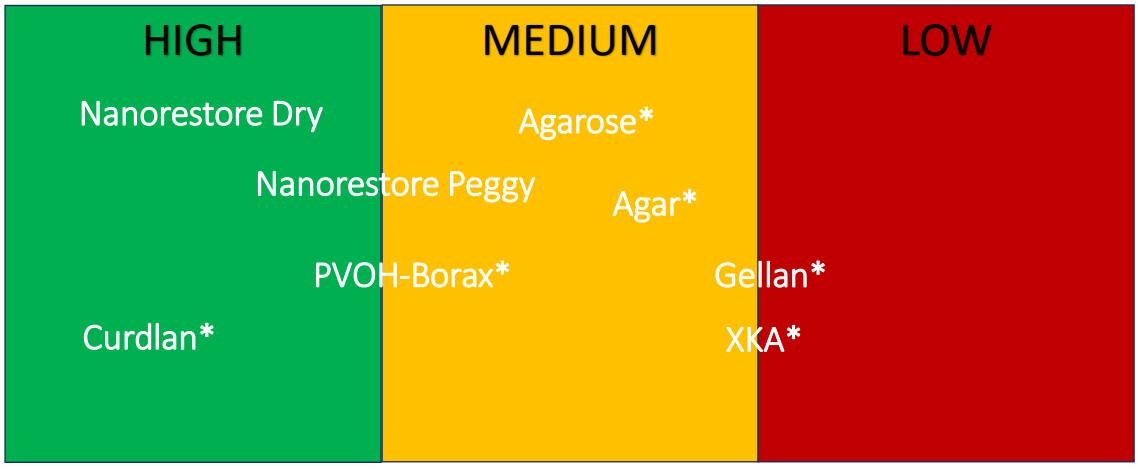
Moisture Retention



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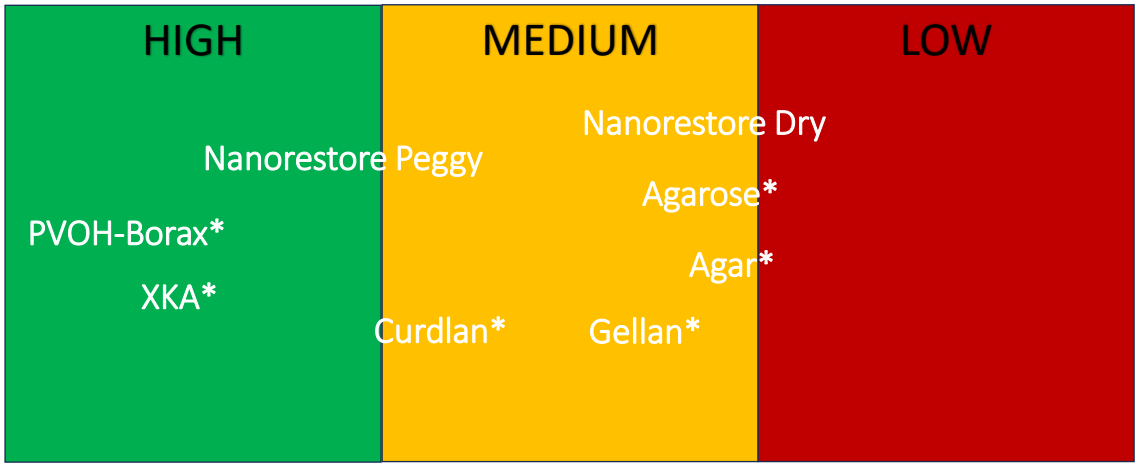
Softness/Conformability



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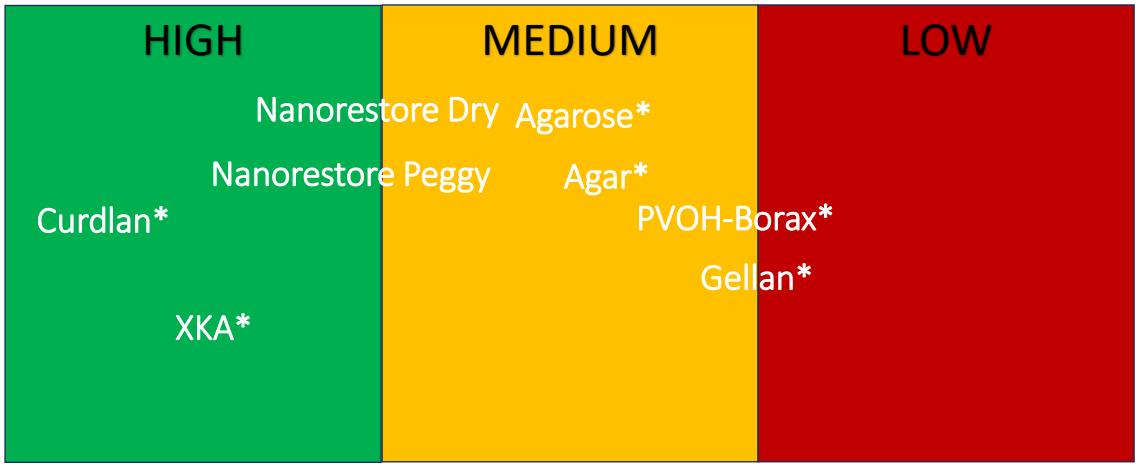
Gel Strength



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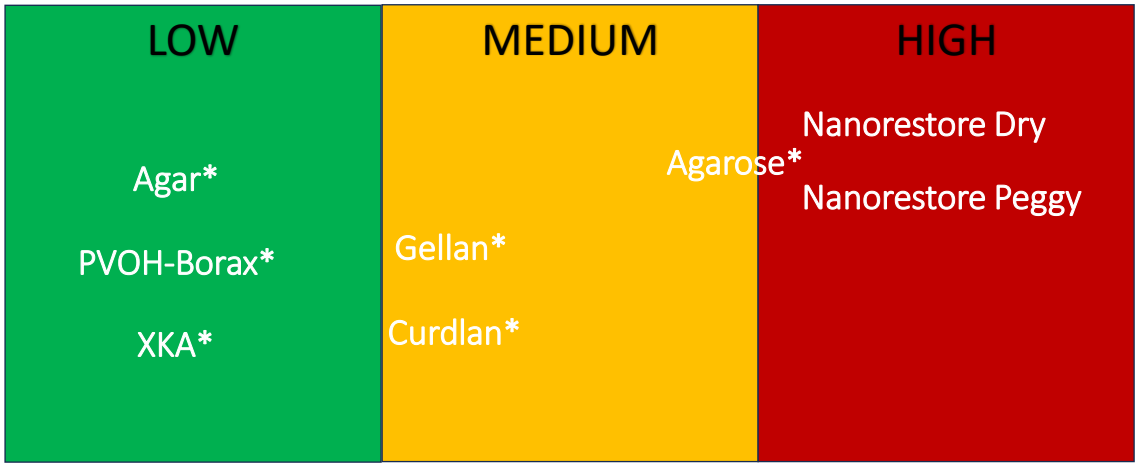
Cost



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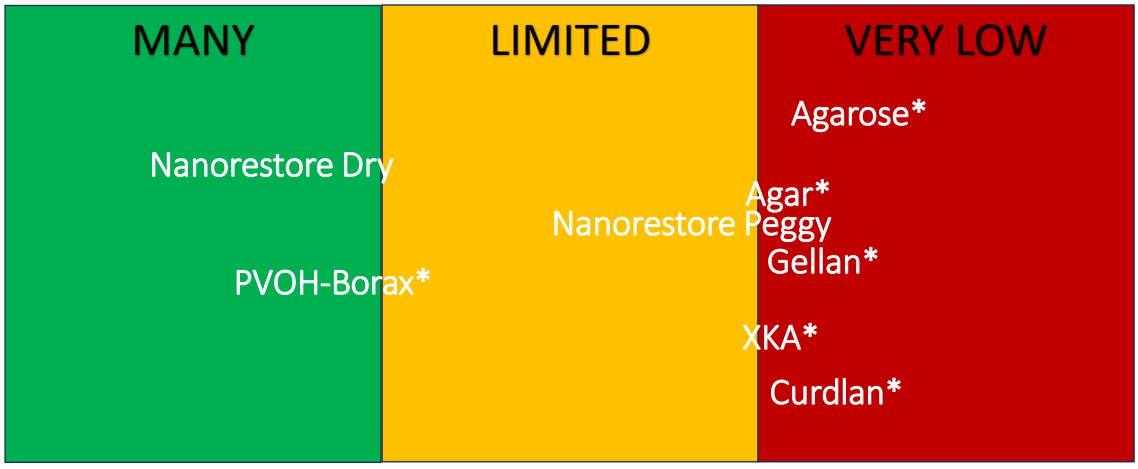
Solvent Compatibility



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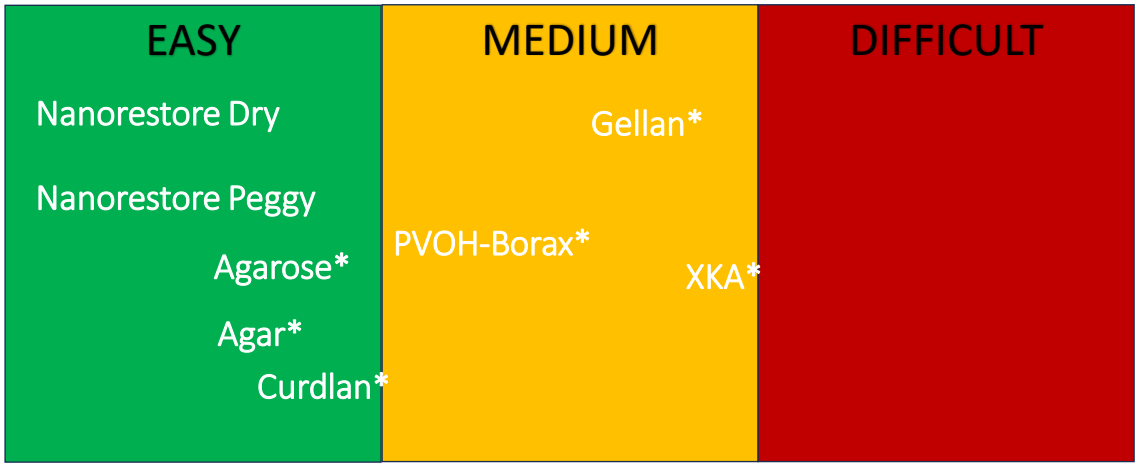
Ease of Preparation



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Availability

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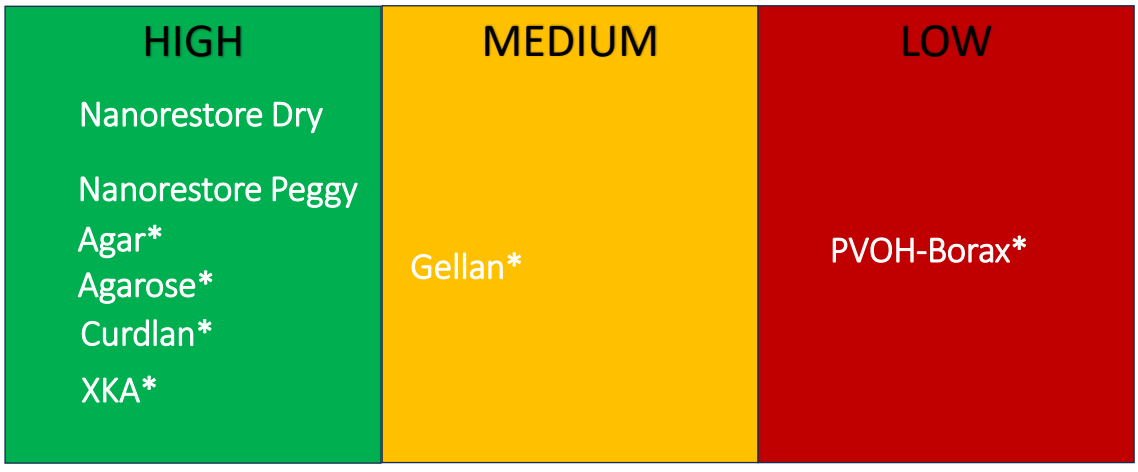
pH Stability



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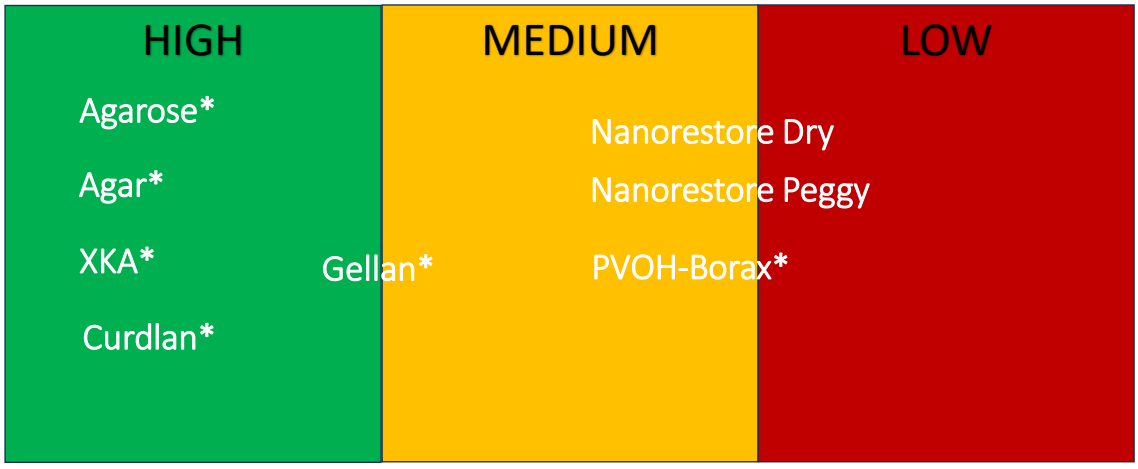
Chelator Compatibility



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Recommended Uses

	Agar/Agarose	Gellan	Xanthan-Konjac-Agar/ose	Curdlan	Nanorestore®	PVOH-Borax
Water-sensitive	Very high concentration				Dry Gel: Best option!	Very brief exposures
Stain/Tideline Reduction	Very high concentration					
Fragmented Gels/Pastes					Dry Gel possible	
Warm Pours/Sprays			Sprays not recommended			
Mechanical						
Dewetting/ Long exposure						

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Q&A and WRAP-UP

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Course Goals

1. Consider alternative modes of delivery for humidification and cleaning
2. Develop a sense for identifying useful gel properties
3. Describe methods of formulating and manipulating hydrogels to match desired effects

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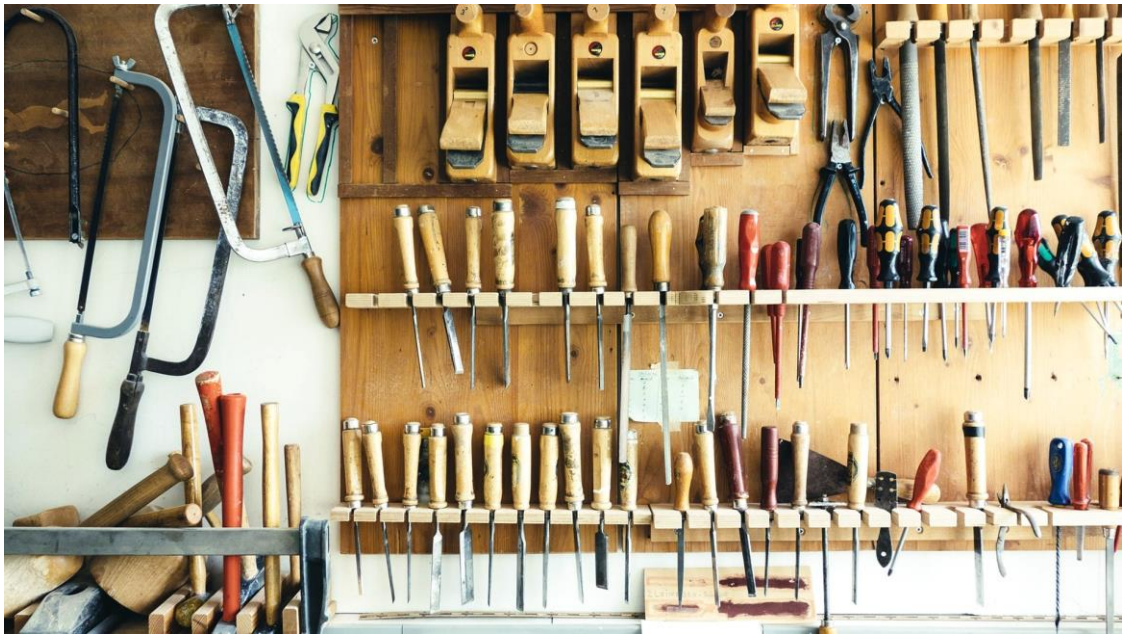

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Thank you for your attention.

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