

Super-Absorbent Polymer Gels for Oil and Grease Removal from Metal and Non-Metal Surfaces

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Presentation Outline

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Technical Objectives
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Motivation

Development of environmentally friendly non-aqueous cleaners for use on Department of Defense (DoD) weapons systems and platforms are required to meet increasingly stringent environmental regulations.

The cleaners need to be free of hazardous air pollutants (HAPs) and contain low amounts of volatile organic compounds (VOCs) or are VOC-exempt (i.e., compounds that are developed explicitly exempted from regulation such as VOCs).



Background



- Currently, cold solvent cleaners (MIL-PRF-680/P-D-680) containing volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) are used to remove oil and grease from aircraft and engine components and from ground support equipment, posing an environmental risk
- Recent advances in the design and synthesis of wet-swelling polymers, such as hydrogels suggest that intrinsic characteristics can be engineered for practical applications. Hydrogels can undergo a dramatic but reversible volume change by absorbing large quantities of water, and have found applications in diapers, inks and display devices.
- In 2007, Sada (co-PI) and colleagues reported a novel class of lipophilic polyelectrolyte gels bearing positively charged repeating units (substituted tetraalkylammonium with long alkyl chains) and negatively charged counter-ions (substituted tetraphenylborate; TFPB⁻) that swell reversibly by absorbing organic solvents having various polarities ($\epsilon = 1.9\text{-}46$; the lower the dielectric constant (ϵ), the less polar the solvent).

Technical Objectives

- a. **The objective of this project is to develop a new surface cleaning technology for removal of oil, grease and particulate matters from metal and non-metal surfaces.**
- b. **Develop and evaluate novel lipophilic super-absorbent swelling gels as a disruptive solid-state cleaning technology that will facilitate the DoD) in overcoming limitations of currently employed cleaning techniques.**
- c. **Demonstrate that developed gel will have necessary mechanical forces to remove particulate contaminants upon absorbing oils and grease on metal and non-metal surfaces without causing abrasion.**
- c. **Demonstrate that after the cleaning operation, cleaning media can be safely collected and recycled.**



Gel Synthesis

Designing Lipophilic Polyelectrolyte Gels for Improved Surface Cleaning

- For organic solvents having extremely low dielectric constants, such as hydrocarbon oils, more lipophilic polymer chains will improve the absorbency and swelling capacity of the lipophilic gel.
- Enhance mechanical strength of the polymer to improve the cleaning capacity, especially for the removal of particulate contaminants by incorporating (1) double-network structure and (2) polyrotaxane-based freely mobile junctions.
- Synthesized gels will be characterized for the swelling degree, morphological and mechanical properties, and for the cleaning ability. Best lipophilic polymer chains, cross-linkers, and double-network gel components will be screened to achieve maximum cleaning efficiency.

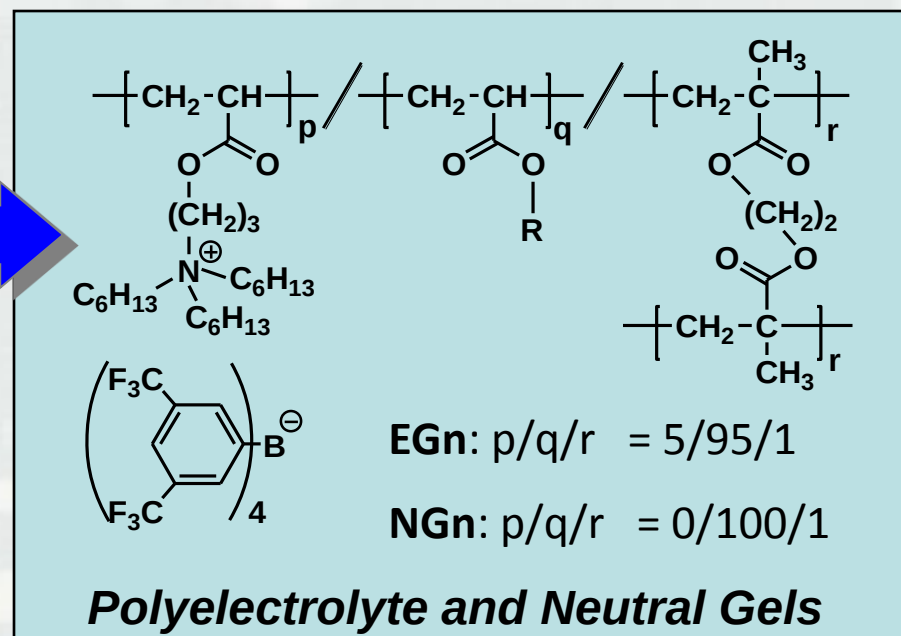
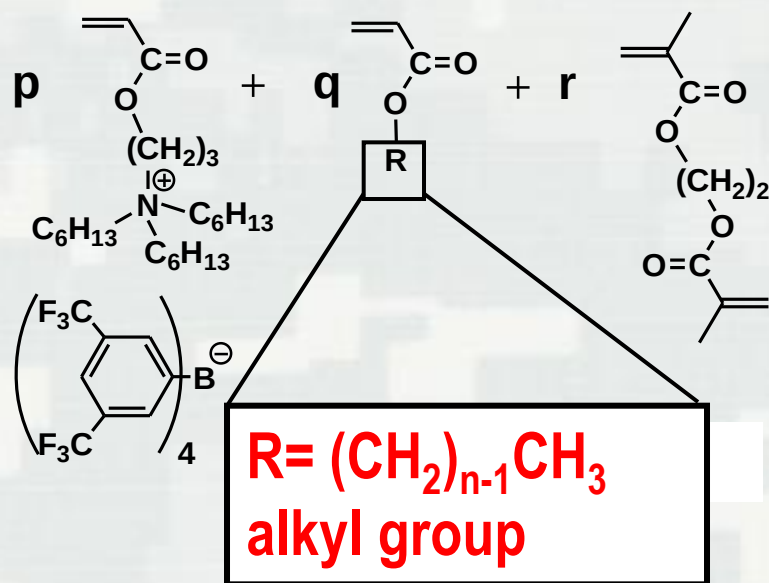
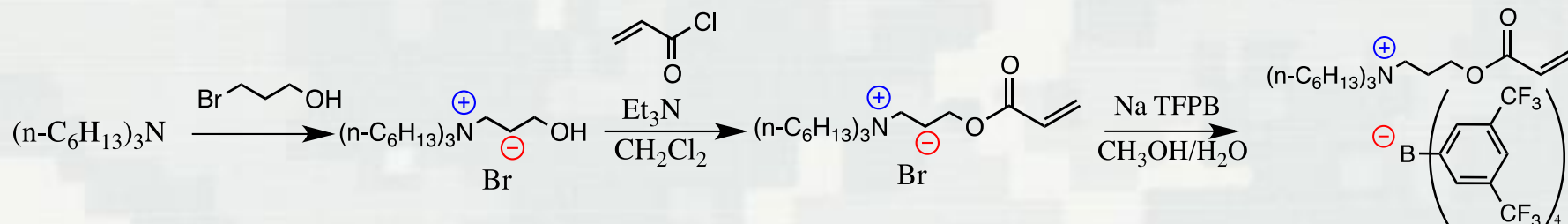
Key Gel Design Concepts

- 1. Incorporation of Miscible in Organic Solvents into Polymer Gels**
- 2. Recyclability via some mechanism with some stimuli responsive**



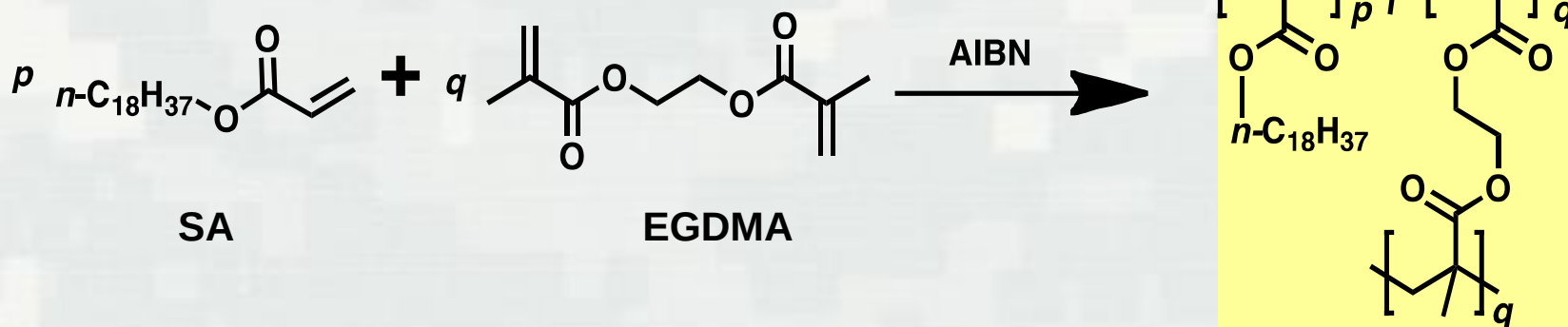
Gel Synthesis

Syntheses of Polyelectrolyte (G1) and Neutral Gels



Gel Synthesis

Lipophilic gel (SA-EGDMA) can be accomplished via the following scheme



Yields: NG-18-1% : 84.7 %
NG-18-0.5%: 79.1 %
NG-18-0.2%: 68.9 %
NG-18-0.1%: 83.6 %

NG-18-x% (x=0.1, 0.2, 0.5, 1)

x: ratio of EGDMA

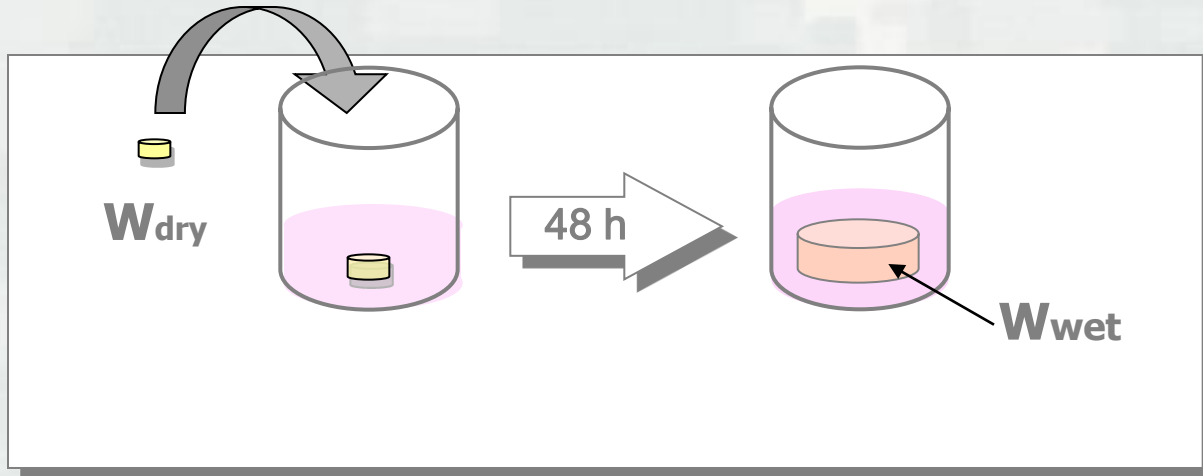
Lipophilic Neutral Gels



Gel Characterization

Swelling Degree

Swelling degrees in oils and organic solvents



Swelling Degrees(Q) are defined by the following equation using dry weight (W_{dry}) and wet weight (W_{wet}) of the gel.

$$Q = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}}$$

W_{dry} : weight of dry gel

W_{wet} : weight of wet gel

$W_{\text{wet}} - W_{\text{dry}}$: weight of absorbed solvents



Swelling Degree, Mechanical Force, Morphology and Functional Group Characterization

Polymer Characterization

Characterize the size, morphology, phase transition, and functional groups of the synthesized polymers before the cleaning tests using:

Infrared spectrometer (FTIR), UV-visible spectrophotometer, thermogravimetry analyzer (TGA), and differential scanning calorimeter (DSC).

Mechanical properties

Mechanical properties are determined by compression (Instron 5000) of synthesized gels at a constant deformation rate to obtain force-deformation, force-time, stress-strain, and stress-time relationships.

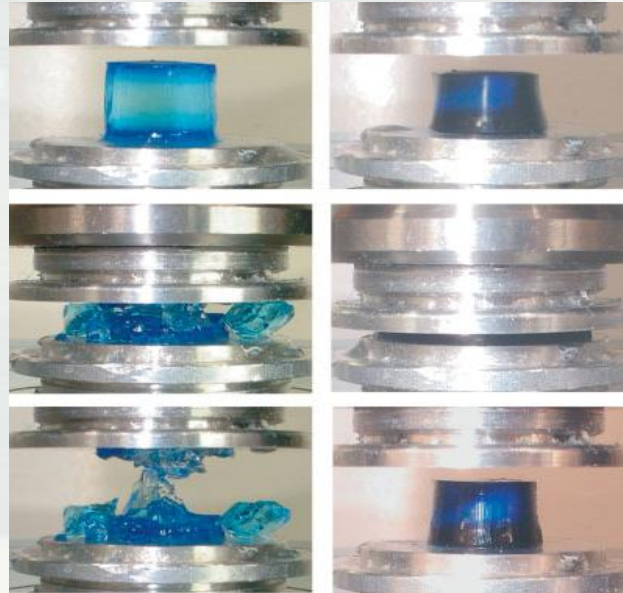


Compress & Tensile Tester



Lipophilic Polyelectrolyte Gels –Mechanical Properties

Enhancement of mechanical strength



Double Network gel (RIGHT) sustains a high compression compared to a single network gel (LEFT).

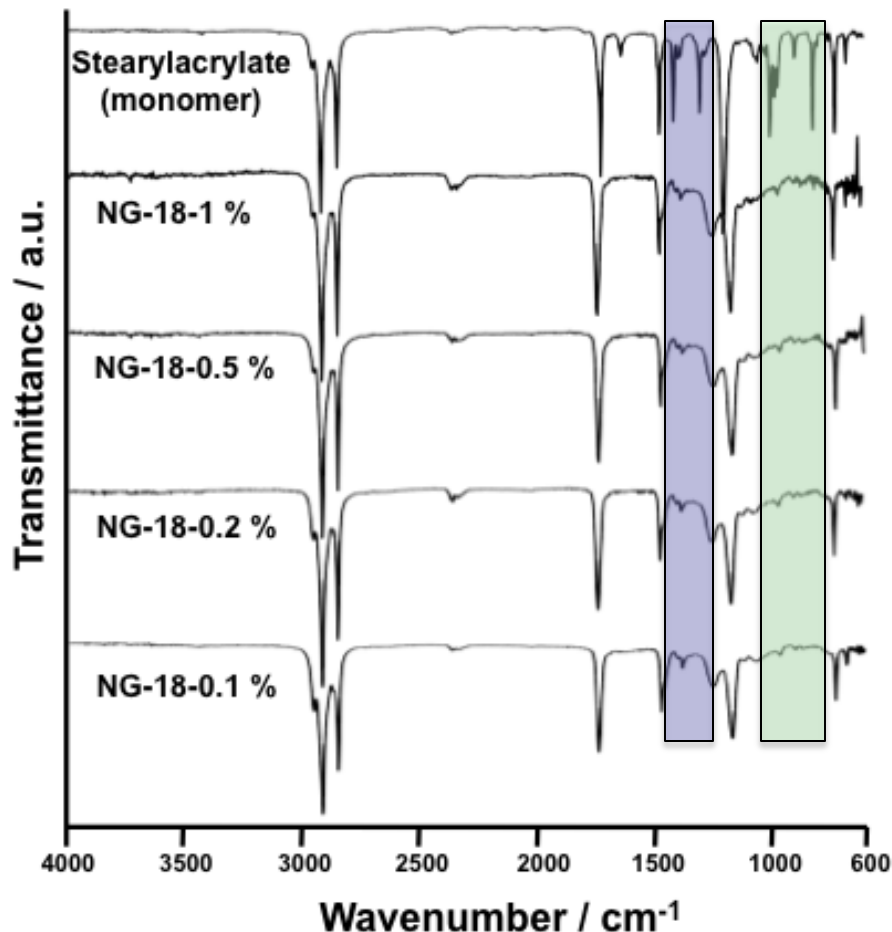
The fracture stress: 0.42 MPa (LEFT)
17.2 MPa (RIGHT)

(Gong et al., *Adv. Mater.* 2003)



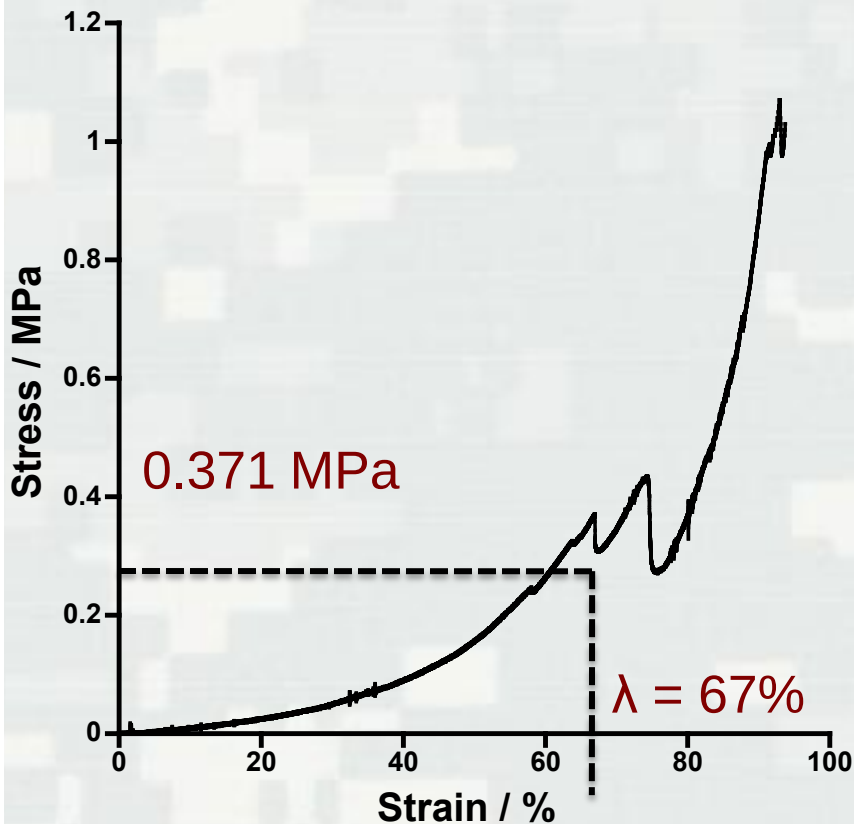
Results: Characterization of NG-18 Gels

(a) FT-IR spectroscopy



Disappearance of the peaks from C=C bond

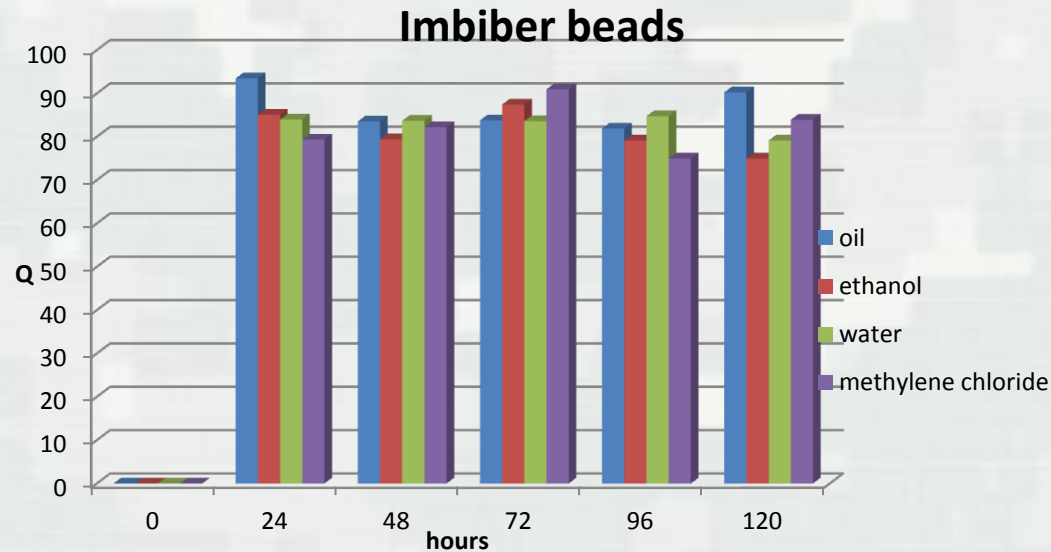
(b) Compression test



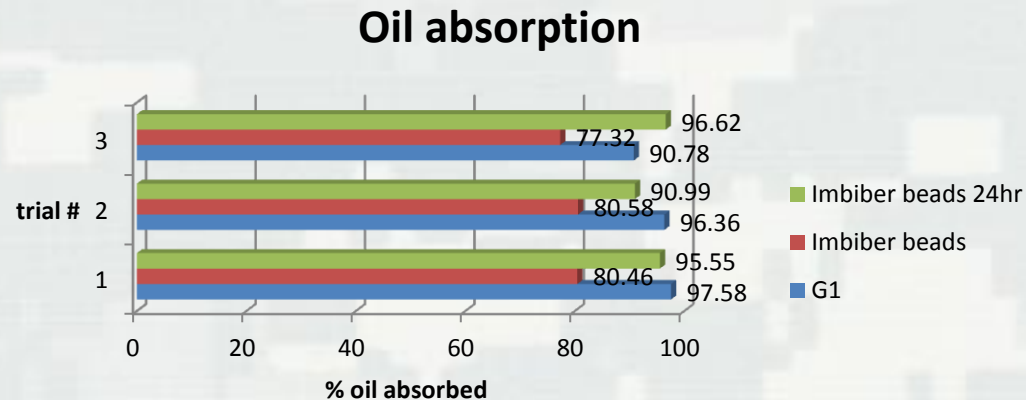
Withstand similar degree of compression to general polyacrylamide gel



Results



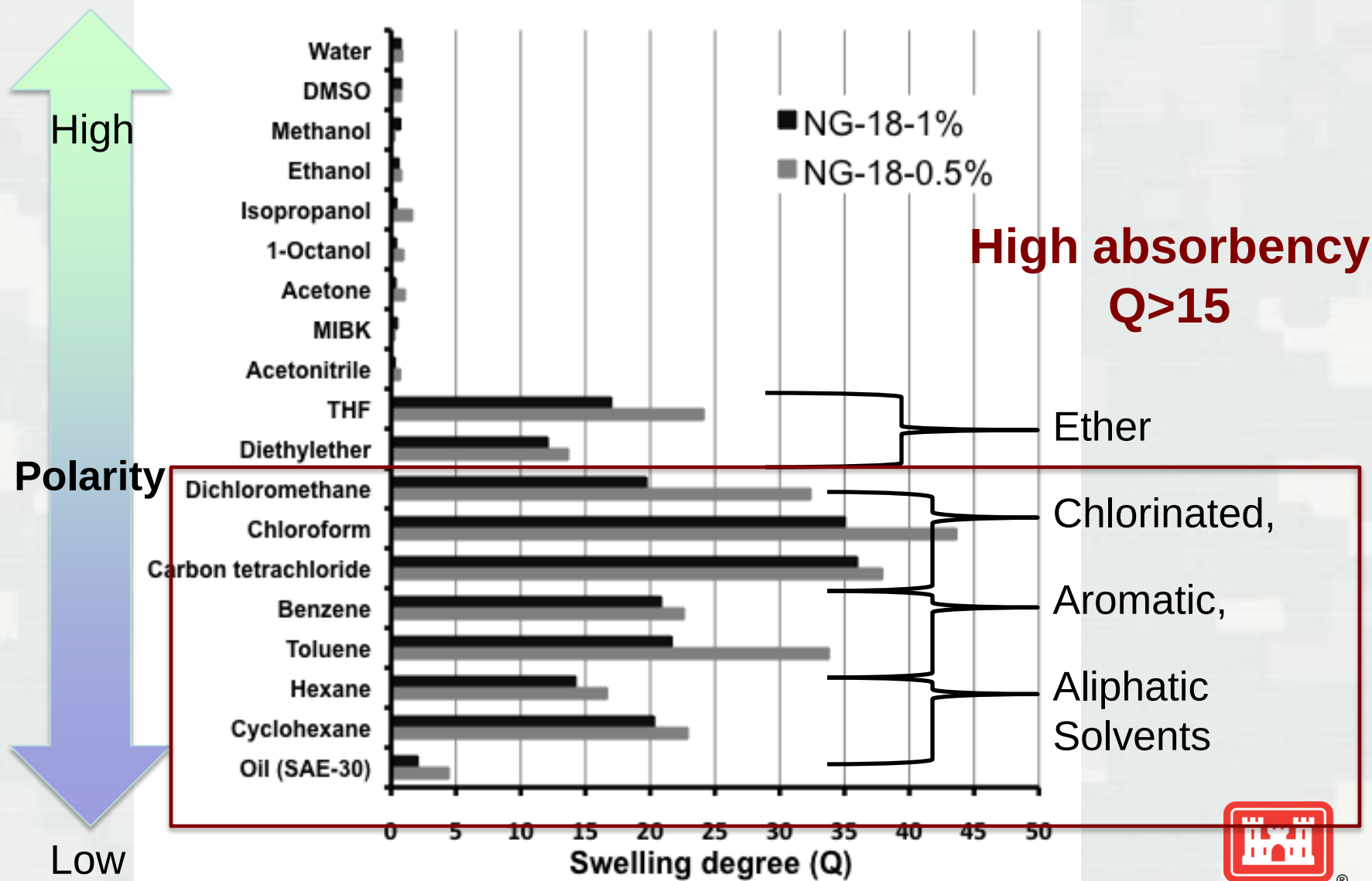
Swelling ratios, Q , for the gel alkyl styrene based imbiber beads in various solvents



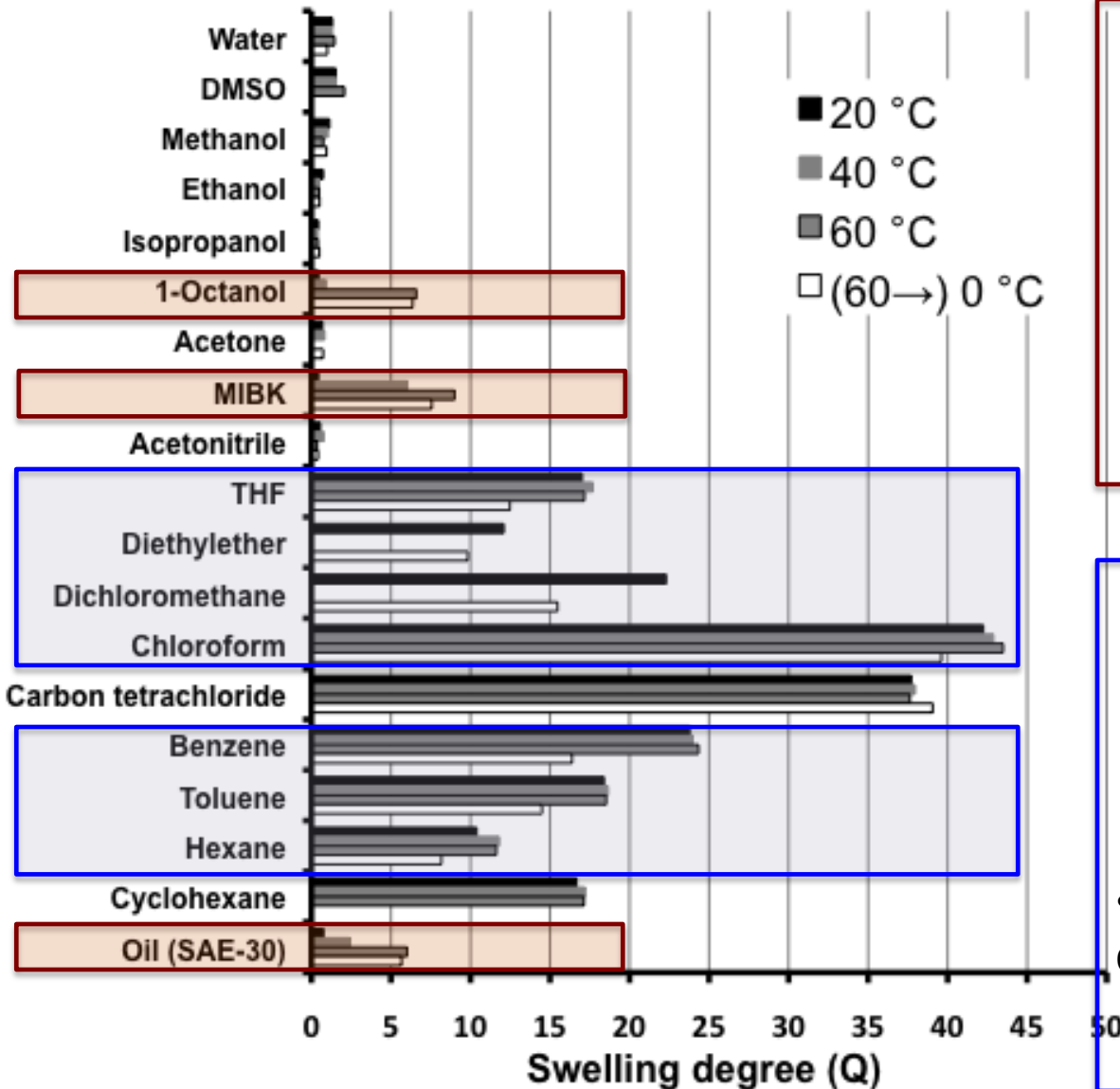
Absorption of SAE 30 oil by polymer gels G1 and the imbiber beads



Results. Swelling Degree in Various Solvents



Results: Temperature Dependence on Swelling Degree

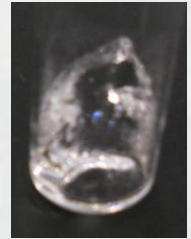


Red region

25-40 °C



40-60 °C



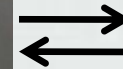
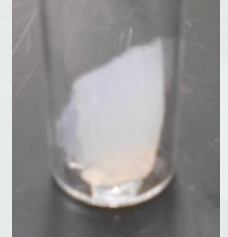
- Increment of compatibility by heating
- Irreversible change

Blue region

25-60 °C



0 °C



- Volume transition via crystallization of long alkyl chain
- Reversible change



Cleaning Tests

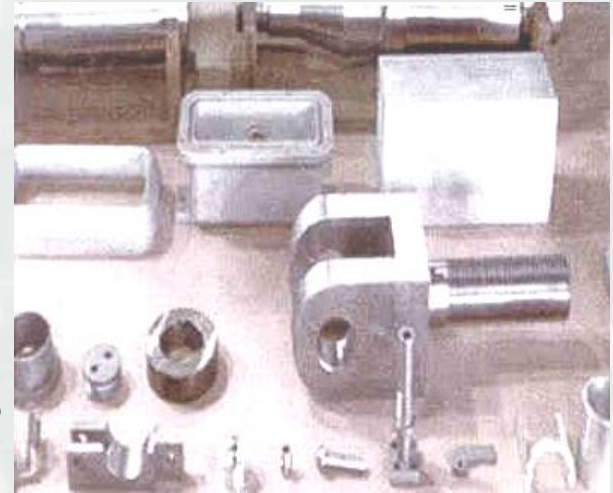
- All cleaning tests are designed and performed based on American Society for Testing and Materials (ASTM) and Military standards.
- Industrial metal (e.g., stainless steel, aluminum) and non-metal surfaces (e.g., plastic, rubber) having a wide variety of shape, size, and elemental compositions are used to test the application of the gel cleaner on complex geometries such as in crevices and blind holes.

Procedure

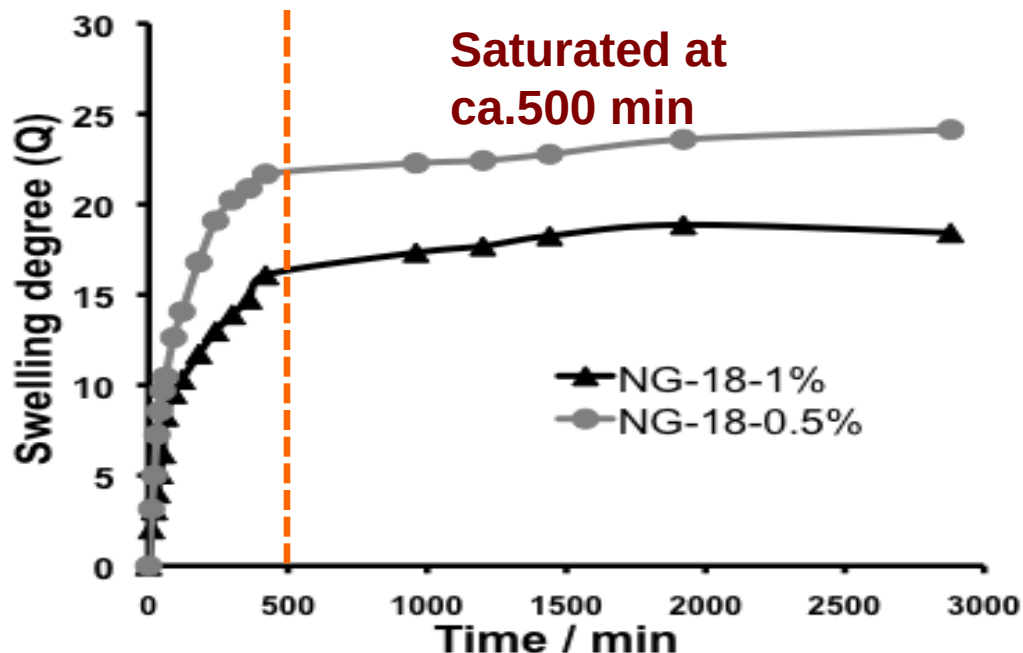
(1) Prepare model contaminants in the laboratory:

- i. Mixture of motor oil, and alumina on steel coupons
- ii. A diverse mixture of contaminants prepared with additional components such as tar, asphalt, and sand.

(2) Cleaning tests using field samples of contaminated metal surfaces provided by Naval Facilities Engineering Service Center.



Results: Swelling Degree with Time in THF



Lagergren pseudo-first (1)
pseudo-second (2) order
kinetics equations

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

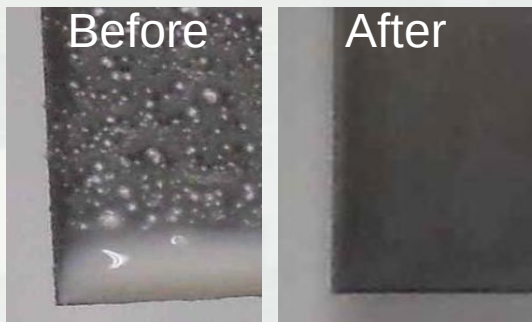
$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

	First order		Second order	
Sample	k_1, min^{-1}	R^2	k_2, min^{-1}	R^2
NG-18-1%	4.38×10^{-3}	0.971	5.55×10^{-4}	0.998
NG-18-0.5%	5.30×10^{-3}	0.985	5.72×10^{-4}	0.999



Results: Cleaning Test with NG-18 gel swollen in THF

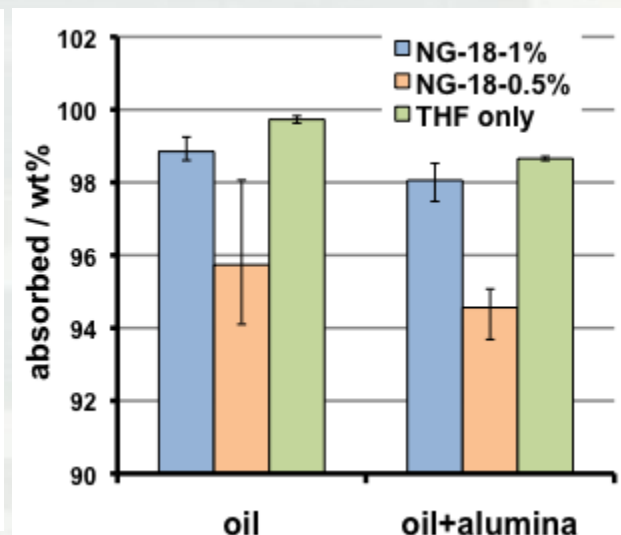
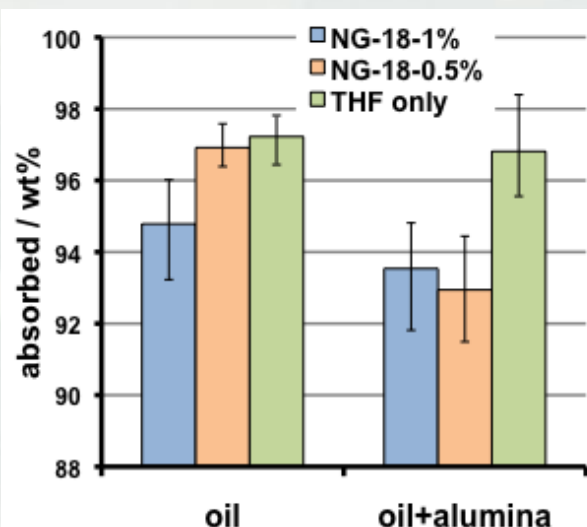
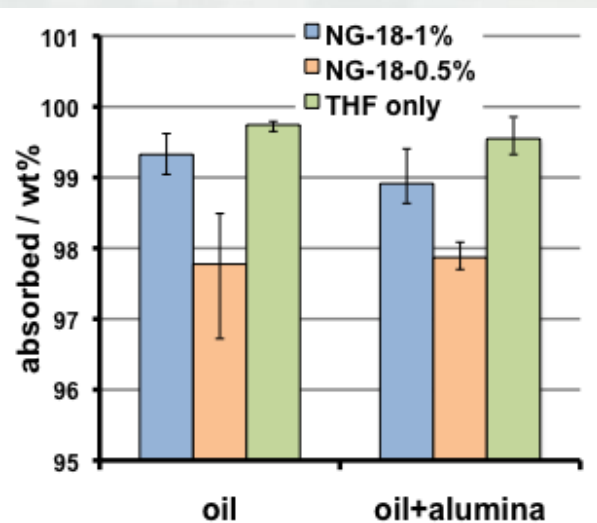
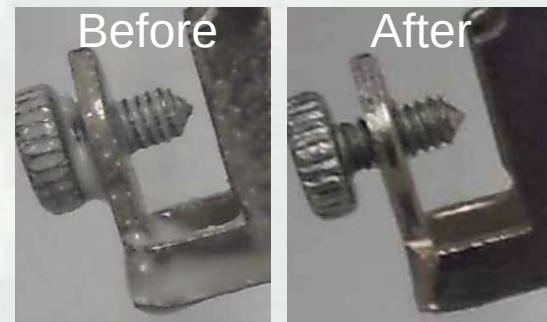
Stainless steel coupon



Painted coupon



Metal parts with bolt



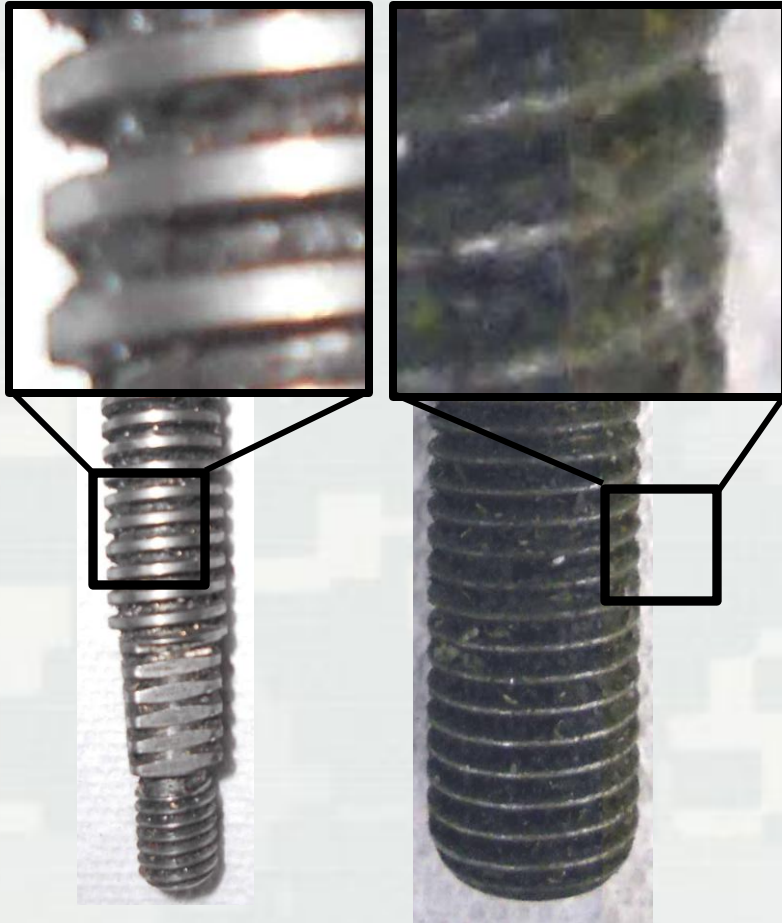
Oil: SAE-30 motor oil
Alumina: sumicorundum AA-04

High Cleaning Ability >95 wt%

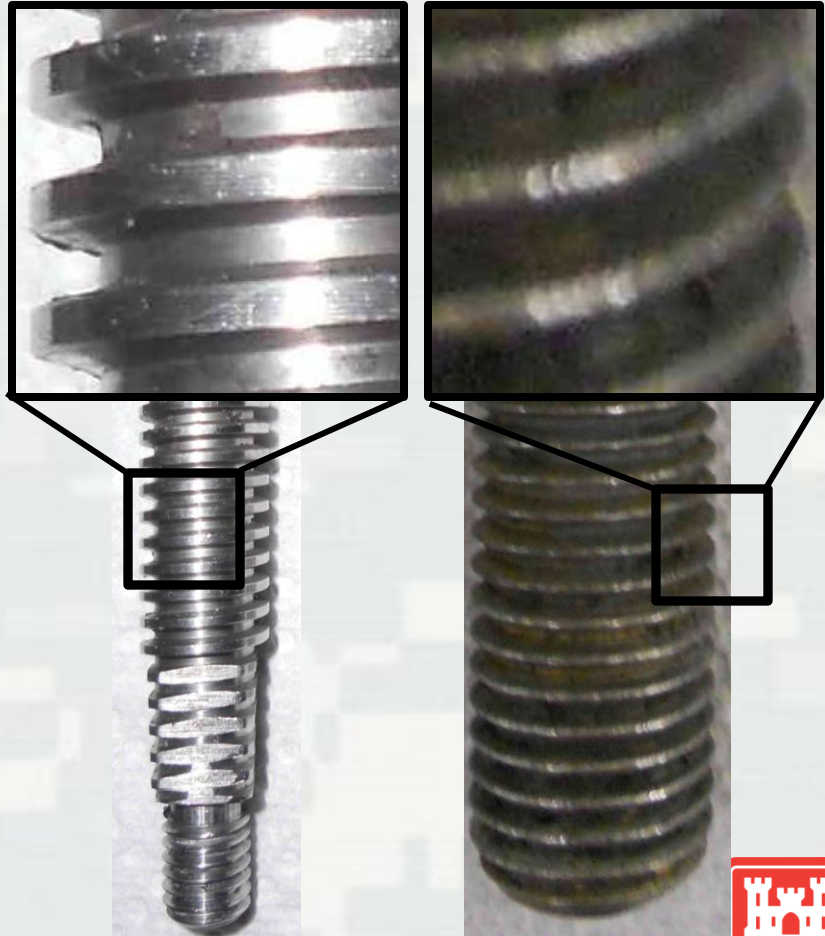


Results: Cleaning Test with NG-18 gel swollen in THF

Before

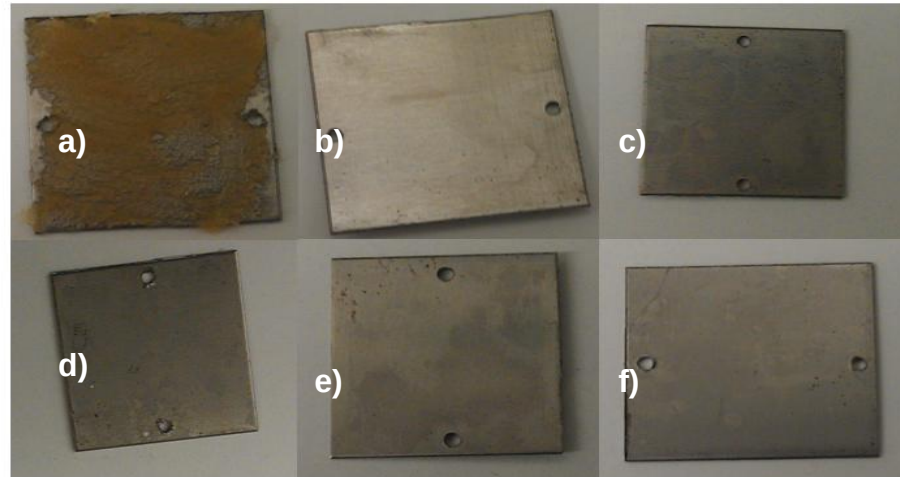


After

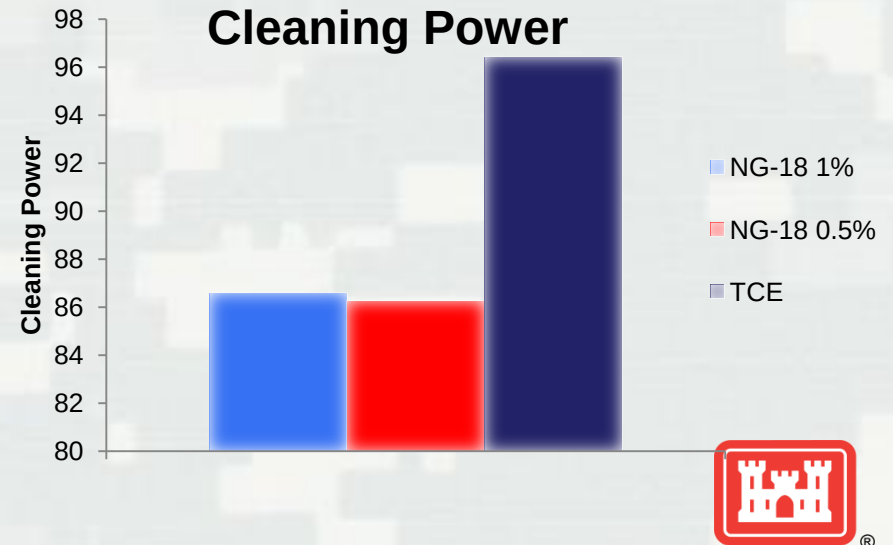
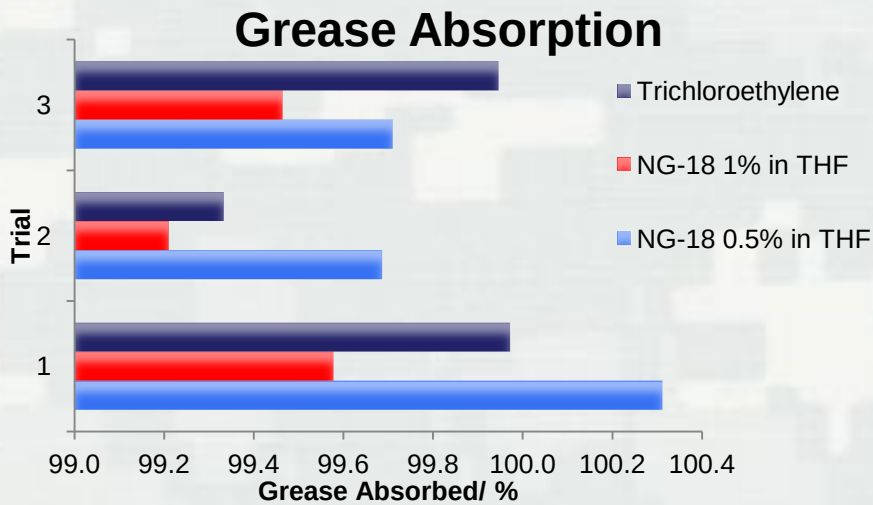


Results: Cleaning Test with NG-18 gel swollen in THF

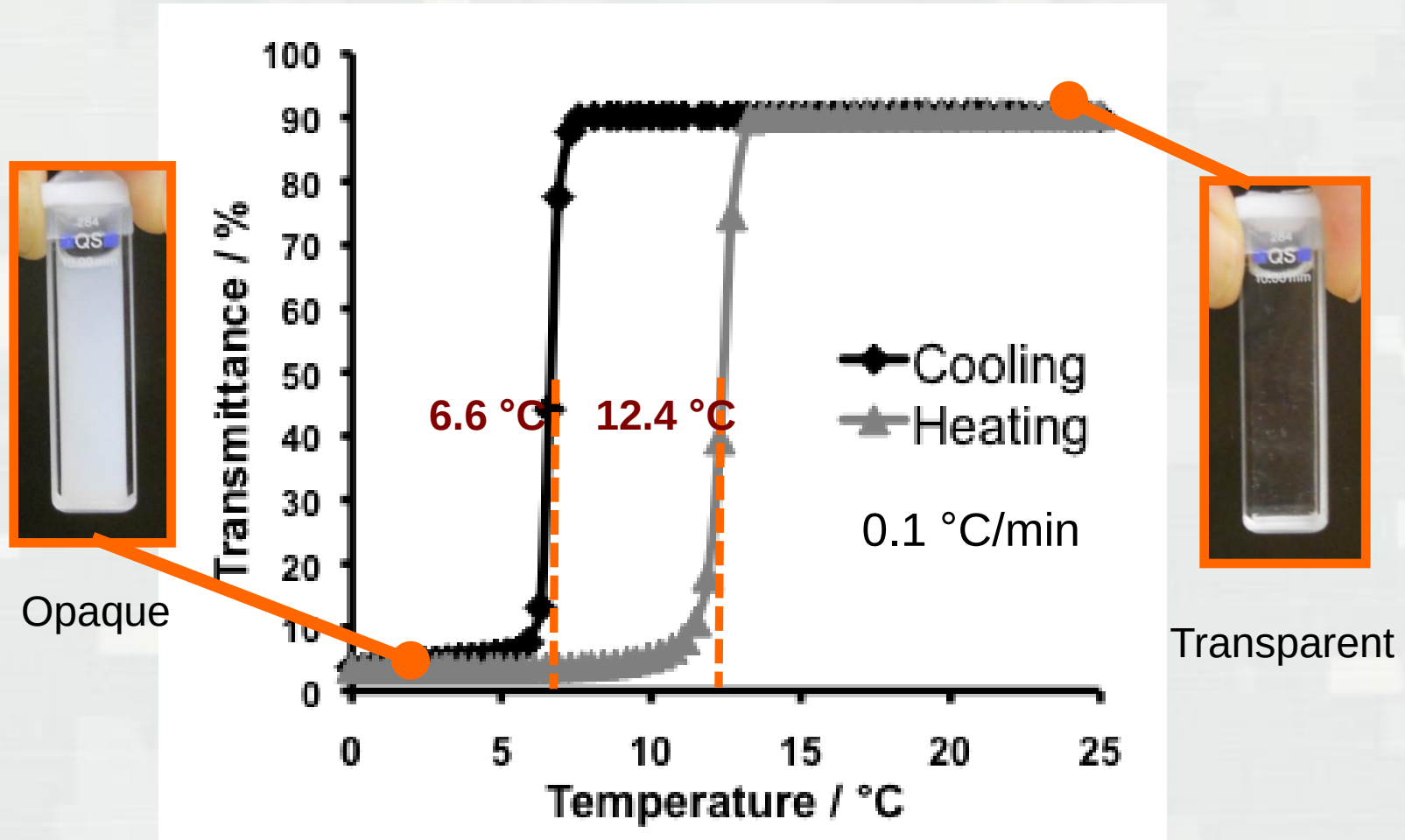
- a) Greased (contaminated) metal coupon
- b) Uncontaminated metal coupon
- c) Metal Coupon cleaned with NG-18 0.5% swollen in THF for 13.5 minutes



- d) Metal coupon cleaned with NG-18 0.5% swollen in THF
- e) Metal coupon cleaned with NG-18 1% swollen in THF
- f) Metal coupon cleaned with trichloroethylene



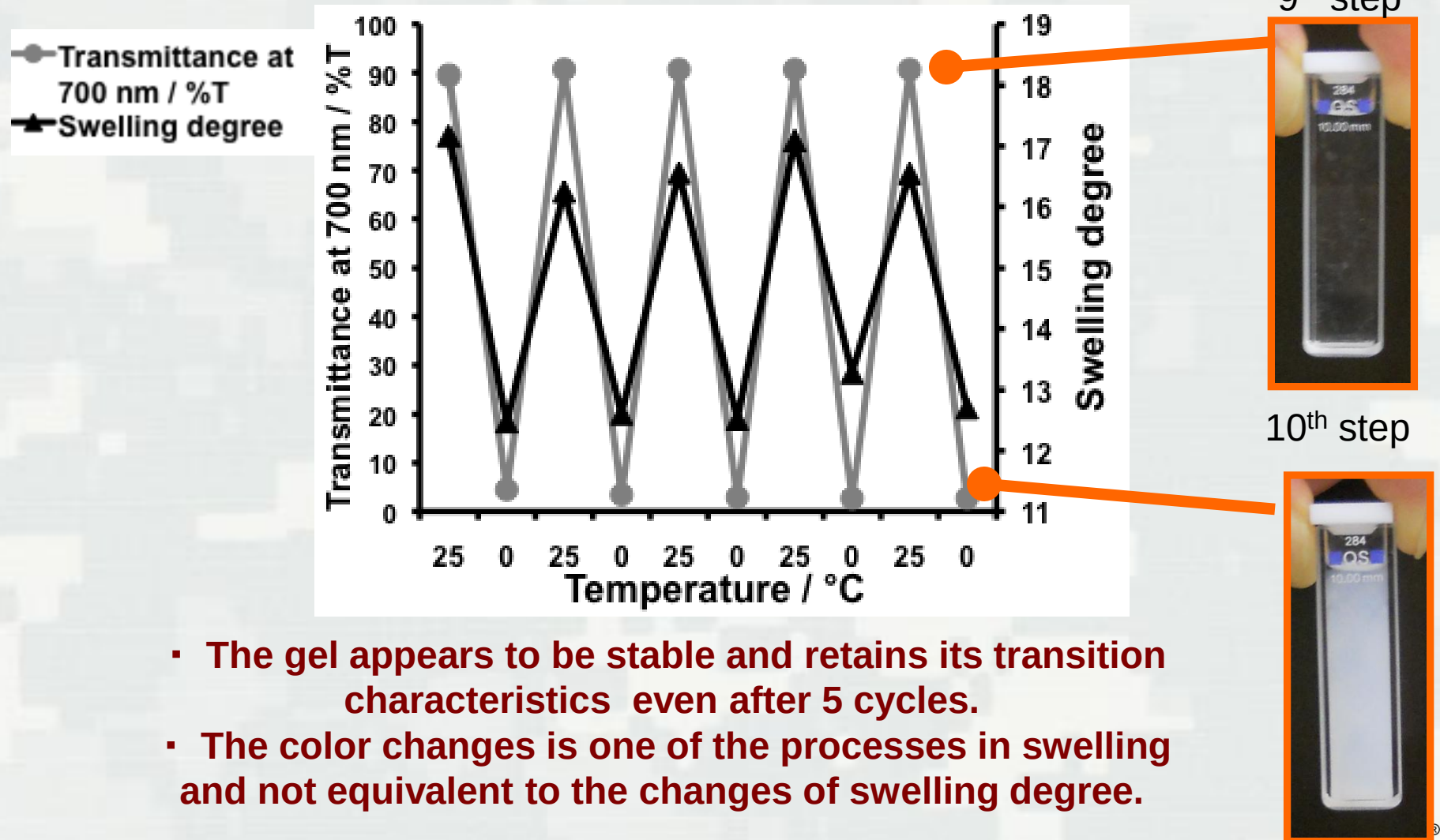
Results: Changes of Transmittance at 700 nm with Temperature



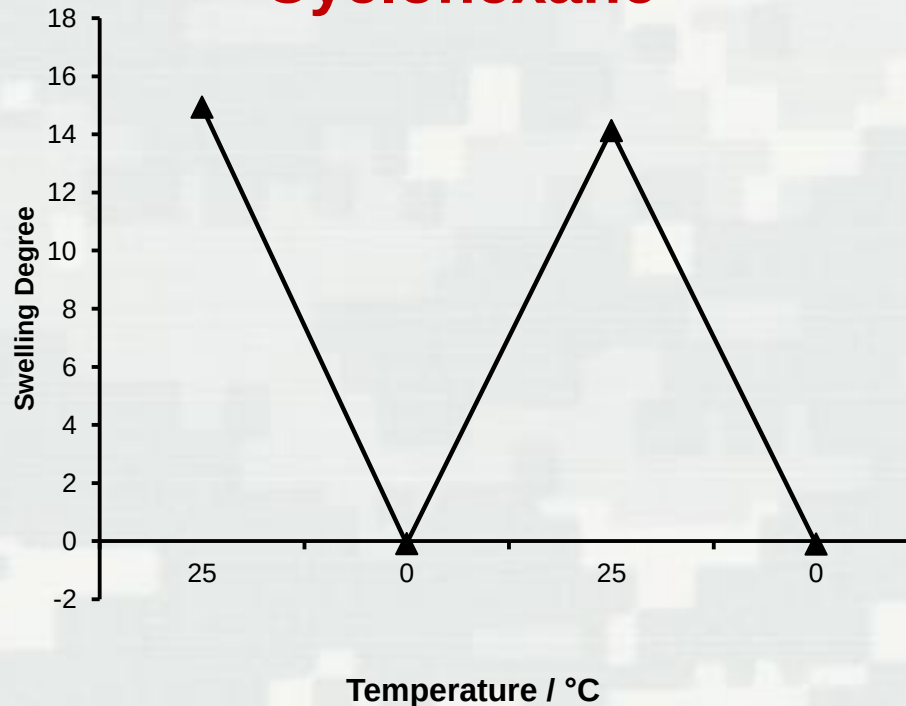
This hysteresis behavior was due to supercooling phenomenon on the cooling process.



Results: Cyclic Temperature Changes Test - THF



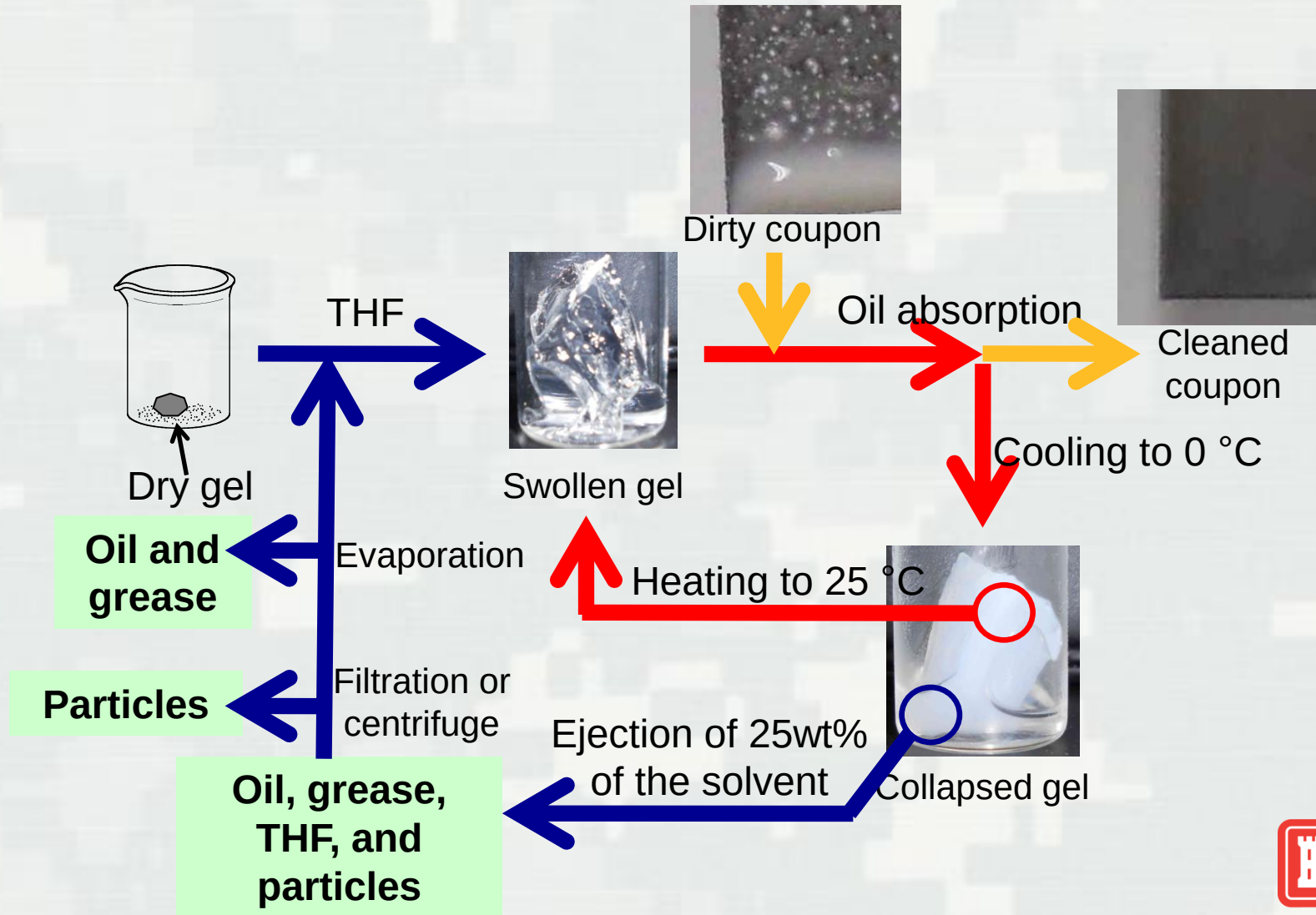
Results: Cyclic Temperature Changes Test - Cyclohexane



- The gel appears to be stable after two cycles, though the kinetics are slower than with THF
- The color changes is one of the processes in swelling and not equivalent to the changes of swelling degree.



Results: A Cyclic Surface Cleaning Procedure with NG-18 Gel System



Summary and Conclusions

- We demonstrated the synthesis and characterization of poly(SA-co-EGDMA) (NG-18) gels. The swelling characteristics of the gels were studied as a function of the solvent polarity and temperature, and the kinetics of swelling were also examined. Volume transition via crystallization of the long alkyl chain was investigated by transmittance at 700 nm light with controlling temperature. These properties suggested the utility of NG-18 gels as recyclable VOCs absorbent materials.
- The gel cleaning was compared with TCE cleaning for removing ASTM test grease. TCE cleans in about 6 min, gel cleaning takes about 13 min. Since gel is a recyclable system, the total cleaning costs are much less compared to TCE cleaning. The cleaning process reduces environmental emissions (VOCs and HAPs)
- Further design of the gel and studies of additional solvents would lead to increased swelling, mechanical strength and increased cleaning capabilities, while additional solvent evaluation would lead to lower toxicity, VOCs and HAPs
- **Publication:** Polym. Bull. (2011) 67:915–926;
Thermal response and recyclability of poly(stearylacrylate-co-ethylene glycol dimethacrylate) gel as a VOCs absorbent.
- **Patent:** (In Preparation)
Oil and Grease Sorbing Polymer Gel Based Low VOC Cleaning Process for Metal and Non-metal Surface Cleaning

