

The removal of aged acrylic coatings from wall paintings using microemulsions

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ABSTRACT

This paper describes experiments designed to remove aged acrylic coatings, such as Paraloid B-72, from lime-based wall paintings using poultices loaded with microemulsions. In the first step, four surfactant-based microemulsions were tested on 60 specimens imitating Paraloid-consolidated

INTRODUCTION

Paraloid B-72 (polyethyl methacrylate), though routinely applied to consolidate poorly bound paint layers on lime-based wall paintings, does change the properties of the original substrate, reducing water capillarity, water vapour permeability and surface wettability (Carretti and Dei 2004). The appearance of paintings is often altered due to changes in light refraction. Furthermore, Paraloid B-72, similar to other fixatives, may contribute to degradation as a result of salt crystallization in the paint below the coating. Therefore, conservators have developed better consolidation methodologies, the most advanced being alcohol-based lime dispersions (Chelazzi et al. 2013). The challenge now faced is the safe removal of the aged consolidants.

Some acrylic fixatives and consolidants can be partially dissolved in organic solvents, even after ageing. Nevertheless, the use of volatile solvents in an enclosed space, such as a church, is difficult and poses health risks. Moreover, the action of liquid organic solvents is poorly controlled when applied directly to porous substrates, and, once the coating is dissolved, the polymer re-deposits inside the pores of the substrate (Baglioni M. et al. 2012, Baglioni P. et al. 2013).

Water-based nanotechnology is now used for removal of polymers. In this approach, solvents are a minimal percentage of the formulation, hence environmental impact and health-related issues are reduced and there is limited spreading of the dissolved polymer. The coating is dispersed in an aqueous medium rather than dissolved (Baglioni P. et al. 2013). FTIR analyses of cross sections taken from consolidated wall paintings treated with this new technique (with multiple scans of the entire sections) show complete removal of Paraloid from the surface and throughout the cross sections below. A great advantage of removing polymers with microemulsions is the absence of polymer dispersion within the bulk.

Microemulsions for the removal of polymers have been tested since the 1990s (Carretti et al. 2007, Carretti et al. 2009, Giorgi et al. 2010, Baglioni M. et al. 2012). In this study, for the first time, a team of conservators and chemists carried out a systematic large-scale assessment of Paraloid B-72 removal. The experiments described here are part of the EU-funded research project NANOFORART (Nanomaterials for the Conservation and Preservation of Movable and Immovable Artworks).

wall paintings to determine which was most effective. In the second step, the best formulation was fine-tuned and tested on six specimens. Among improvements was the replacement of the original surfactant with one that naturally degraded and produced minimal lathering. Successful removal of Paraloid (determined by raking and UV light examination, FTIR analysis and contact angle measurements) was marred by contamination of the specimen by residual cellulose powder (from the poultice), detected with iodine vapour staining. The third experiment was designed to eliminate this contamination. A microemulsion-loaded hydrogel was successfully tested on four specimens. Results indicate that it is possible to extract Paraloid B-72 from wall paintings without contamination.

EXPERIMENTAL

A series of experiments were performed on specimens that represented consolidated lime-based wall paintings. Initial experiments evaluated the efficacy of four surfactant-based microemulsions on a large number of specimens (Experiment 1). Evaluation of treatments and assessment of the results led to improvements in formulations and working methods, which were tested in two subsequent experiments (Experiments 2 and 3).

Specimen preparation

Seventy-four terracotta tiles ($12 \times 12 \times 1.5$ cm) were used to prepare test surfaces for the experiment. They were covered with a 5–8 mm thick layer of slaked lime mortar ($\text{Ca}(\text{OH})_2$) over which two layers of lime-wash were applied. The tiles were placed in a climate chamber with an atmosphere highly enriched in CO_2 (up to 9500 ppm) for 15 days to accelerate the carbonation process (Dheilly et al. 2002). The relative humidity (RH) was held at 90–95% and the temperature (T) at 20°C. After carbonation, a 4×4 cm region at the centre of each tile was brushed with Paraloid B-72 (10% solution in ethyl acetate). This concentration was chosen for visibility. The polymer formed a semi-glossy film that was highly visible after drying. The technique models in-situ surface consolidation, often carried out with several coats of lower concentrations, or where uneven application or absorption results in pooling and dripping, leading to higher local concentrations.

The Paraloid-treated tiles were placed in a ventilated dark climate chamber for 12 days with 12-hour periods at $70 \pm 5^\circ\text{C}$ and $10 \pm 2\%$ RH alternating with 20°C and 50% RH. A pilot trial indicated that this regime induced maximum polymer degradation within the timescale of the project. Ten tiles, which were used in Experiments 2 and 3, were subsequently aged for a further 10 days the following year. Calculations based on the Arrhenius equation suggest that ageing polymeric conservation materials at 70°C for 30 days induces chemical and physical changes approximating those achieved after 50 years in real time (Shashoua 1995). All tiles remained in an ambient atmosphere the night before the experiments. Before proceeding with Experiment 1, four tiles were selected to test the effect of ageing on the polymer, versus non-aged samples. On each of the paired tiles, a poultice containing one of the four microemulsions to be tested was applied for two hours. There was a noticeable difference in polymer removal on the aged and non-aged tiles.

Experiment 1 – Evaluation of microemulsions

Sixty specimens were used in an initial experiment, in which four microemulsion formulations were tested (Table 1), with 15 tiles for each. The four detergent systems were selected based on authors' experience with microemulsions. The organic solvents used were low-toxicity, low-polarity liquids capable of dissolving or swelling acrylic polymers. They included ethyl acetate, 2-butanone (methyl ethyl ketone), butyl acetate and 2-butanol.

In the MEB system, a mixture of ethyl acetate, 2-butanone and butyl acetate (1:1:1 w/w) was stabilised in water using a Brij C10 alcohol

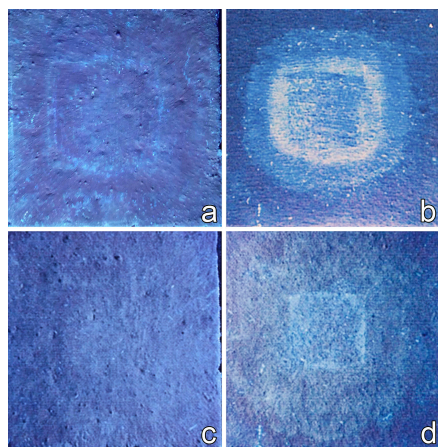


Figure 1

Reduction of UV light-induced fluorescence on specimens, comparing more successful removal of Paraloid (left column) with less successful removal (right): (a) and (b) after first cleaning; (c) and (d) after second cleaning

Figure 2

Contact angle of a drop of water on the specimen surface: (a) before removal of Paraloid; (b) Paraloid partially removed; (c) after complete removal

Table 1

Microemulsion formulations targeting Paraloid B-72 in Experiment 1

	M3: MEB	M4: MEK1	M5: MEK/ BuOH	M6: MEK2
water	85	82.10	65.9	82.10
surfactant	(Brij C10 ^a) 6	(Brij C10 ^a) 4.35	(Brij C10 ^a) 3.5	(Brij O10 ^a) 4.35
2-butanone	3	13.55	20.9	13.55
ethyl acetate	3	-	-	-
propylene carbonate	3	-	-	-
2-butanol	-	-	9.7	-

^aAlcohol ethoxylates

ethoxylate, which has high detergency, good emulsifying properties and is biodegradable.

Systems MEK1 and MEK2 were based on ternary mixtures of water, 2-butanone and two different alcohol ethoxylate surfactants, i.e. a Brij C10 and a Brij O10.

System MEK/BuOH was a variation of the MEK1 system, in which 2-butanol was added to the formulation as a co-surfactant in order to increase the amount of the active organic phase.

The microemulsions were mixed in the ratio 1: 0.75 (v/v) with cellulose powders Arbocel BC200 and Arbocel BWW40 (1:1 v/v). This poultice was applied to the square of Paraloid in a ca. 5 mm thick layer using Japanese tissue (9.6 g/m²) as an intervention layer. The poultice remained on the surface, uncovered, for 4–6 hours, after which it was removed and replaced with a water poultice, which remained until it was almost dry (ca. 6–8 hours). Upon poultice removal, the surface was thoroughly washed with water and a brush. The procedure was performed twice on all tiles.

The tiles were examined and photographed in raking white light and in UV radiation (UVA-Spot 400/T, Deffner & Johann, emitting wavelengths from 320 to 380 nm) prior to treatment and after each of the two treatments. A reduction of gloss was observed in raking light after each treatment. Similarly, strong UV light-induced fluorescence was reduced with each treatment. The number of repetitions for each formulation provided a clear indication of how effective each microemulsion was at removing Paraloid (Figure 1). Most effective was the MEK/BuOH formulation.

Polymer removal was also investigated by measuring the change in contact angle of a drop of distilled water on the surface of tiles. Use of these data with the Young equation allows determination of the wettability. A microscope with 400× magnification, a USB interface and accompanying software were used to measure the angle (Figure 2).

Paraloid B-72 within the bulk of specimens was shown by infrared spectrometry in microreflectance mode (Figure 3). Samples cleaned with microemulsion were cross-sectioned perpendicularly to the surface. A non-cleaned sample (i.e. with Paraloid present) was also cross-sectioned and used as a reference. Analysis was performed by collecting spectra from the surface throughout the entire thickness of the plaster. The IR beam spot-size is about 20 microns. A Thermo Nicolet Nexus 870 FTIR spectrometer with a 0.5% w/w sensitivity and resolution of 2 cm⁻¹, equipped

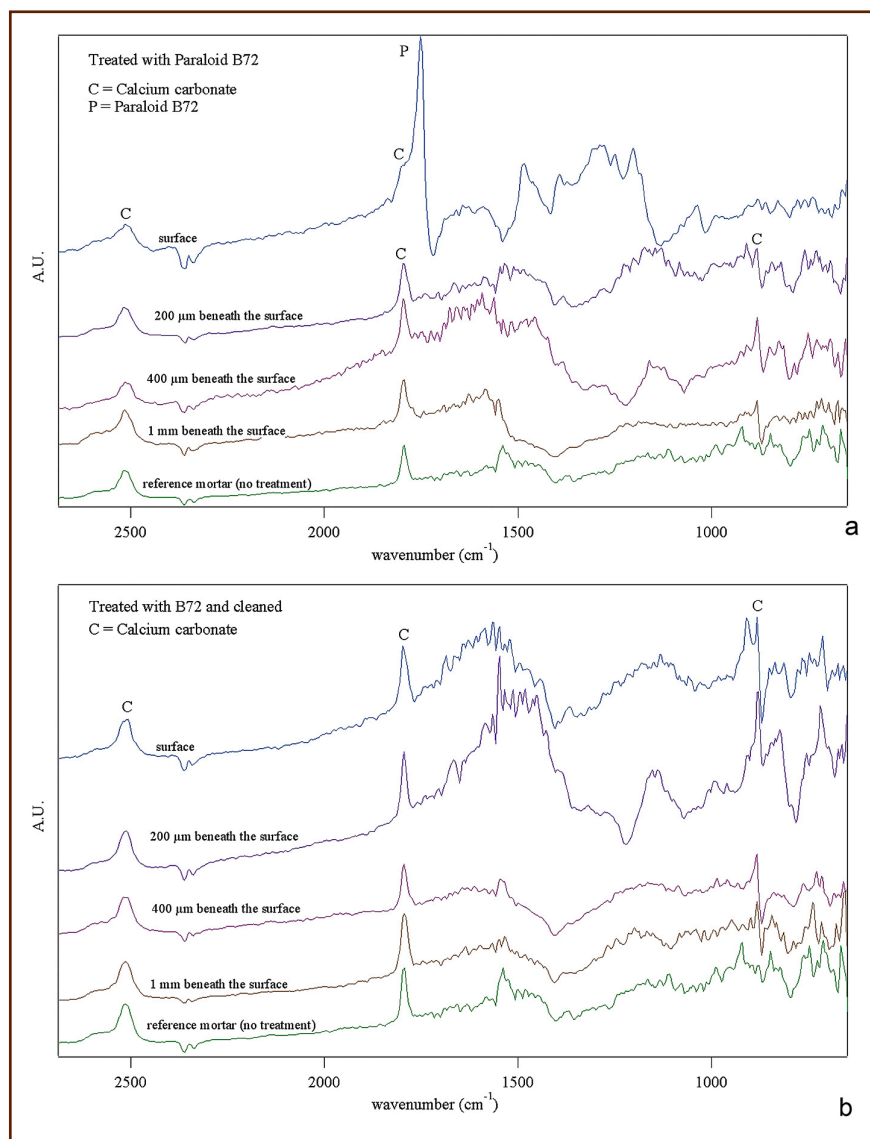


Figure 3

FTIR spectra (microreflectance) of specimens treated with Paraloid B-72 (a), and cleaned with microemulsion M5 (b). The region between 2700–650⁻¹ cm is shown in absorption units (AU) after normalisation based on the band at 2516⁻¹ cm attributed to calcium carbonate

with a microreflectance microscope, was used. 128 scans were collected for each spectrum. As highlighted in Figure 3, spectra showed removal of the Paraloid layer to below detection limits. The strong carbonyl IR absorptions shown by acrylics were used as a marker and indicated Paraloid B-72. No Paraloid was detected below the surfaces.

Tidemarks were observed in UV light on many specimens (see Figure 1). None of the surfactants included in the microemulsions fluoresced, but cellulose powder did, which indicated that residual cellulose powder was migrating from the wet phase (area covered by poultice) to the dry phase and collecting at the interfaces. This was confirmed by the increasing weight of the specimens after each treatment (not, decreasing, as expected with the removal of polymer).

Profuse lathering was noticed during the washing process, which indicated the presence of residual surfactant. Therefore, a surfactant leaving less residue was sought in the next stage, which focused on minimising residual contamination.

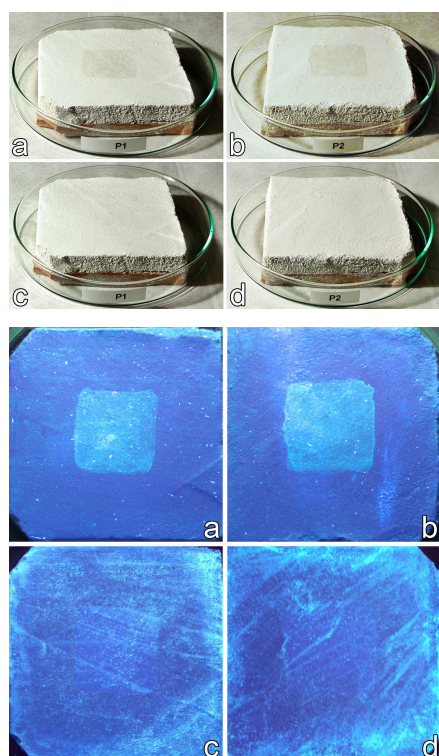


Figure 4
Specimens examined in raking light: (a) and (b) before treatment; (c) and (d) after treatment with microemulsion (M5 NR)

Figure 5
Specimens examined in UV light: (a) and (b) before treatment; (c) and (d) after treatment with microemulsion M5 266

Table 2
Screen analysis for Arbocel BC200 and BWW40 (according to datasheet provided by J. Rettenmaier & Söhne GmbH + Co KG)

	>300 μm	>100 μm	>32 μm
Arbocel BC200	max. 0.5%	max. 15%	40–80%
Arbocel BWW40	max. 0.2%	max. 20%	40–70%

Table 3
Possible residual materials and their responses to UV light and iodine vapour

residual material	UV light-induced fluorescence	staining with iodine vapour
Paraloid B-72 ^a	yes	no
surfactant	no	yes ^a
cellulose powder	yes	yes

^a diminishing over time

Experiment 2 – Improving the formulation

Based on the findings of Experiment 1, a new microemulsion was formulated to limit any surfactant residue. The aim was to use a surfactant whose residues degraded naturally over time if left on cleaned wall paintings. A narrow range (NR) ethoxylated alcohol surfactant was chosen for this. This surfactant is known to be dermatologically benign, rapidly biodegradable with alcohol as a by-product, and non-toxic to aquatic organisms (Baglioni M. et al. 2014). The by-product has no activity as a surface tension modifier and does not change the physicochemical properties of the surface. NR has a lower cloud point (temperature where the mixture starts to phase separate) than the surfactant used in the previous MEK/BuOH formulation. At room temperature, therefore, the MEK/BuOH-NR system is closer to its cloud point. It is known that surfactant-based formulations display maximal detergency in this condition (Holmberg et al. 2003).

The new formulation (MEK/BuOH-NR) replaced the surfactant in MEK/BuOH with BuOH-NR without altering the other components. The microemulsion was mixed with cellulose powder and applied to Paraloid B-72 on six specimens using the same protocol as in Experiment 1. A denser Japanese tissue was used as the intervention layer (11 g/m²) in an attempt to prevent migration of cellulose powder. One of the improvements in the new formulation was evident during the washing process; there was a noticeable reduction in lathering.

Examination of test surfaces in raking light with the naked eye after treatment showed no trace of polymer (Figure 4). However, examination in UV light showed residual material (Figure 5) similar to that seen in Experiment 1. Examination with a stereo microscope showed that a large part of the residual material was cellulose powder, which had migrated through the denser Japanese tissue. The interstices between tissue fibres showed numerous openings of ca. 0.20 mm, which allowed access to both Arbocel BC200 and BWW40 (Table 2). However, contamination could also have been a result of residual surfactant, and its quantification after cleaning and determining its rate of degradation was a challenge.

Because the surfactant could not be detected using UV light, staining by iodine vapour was adopted. Iodine staining has long been used to increase the visibility of marker compounds on thin layer chromatography plates (Sherman and Fried 1991). Iodine vapour reacts reversibly with many functional groups, particularly with unsaturated compounds, to give red-brown stains. After drying, the tiles were exposed for 5 minutes to vapour from 1 g iodine crystals placed on the bottom of a glass chamber (distance to specimen surface was 5 cm). Since reaction with iodine is weak and reversible (the stain fades after several minutes), samples could be re-tested at a later stage without changing the components chemically.

The differences in the characteristics of the organic materials introduced onto the specimens were used to assess the results of the experiment (Table 3). The study of patterns obtained by iodine vapour staining (performed three times, each separated by an interval of two months) compared to UV light-induced fluorescence and raking light contributed information about the efficacy of the cleaning and the nature and amount

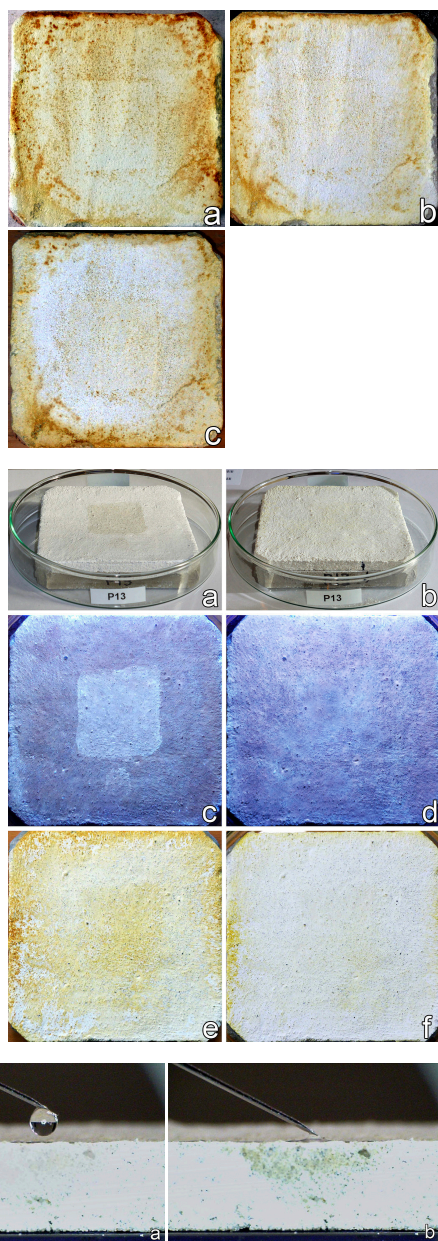


Figure 6
Iodine staining performed directly after treatment (a), two months after treatment (b) and four months after treatment (c)

Figure 7
Specimen cleaned with microemulsion-loaded hydrogel examined with: raking light before (a) and after (b) treatment; UV light before (c) and after (d) treatment; iodine stain directly after (e) and two months after (f) treatment

Figure 8
Wettability of surface tested after removal of Paraloid with hydrogel: a) prior to water application; b) water absorbed when drop touches surface

of residual contamination. Absence of fluorescence in the areas containing Paraloid indicated that it had indeed been removed from the surfaces. The UV-induced fluorescence along the perimeters of the specimens could not be attributed to migrated Paraloid since there was no difference in surface wettability compared to that of the clean surfaces. The patterns of UV light-induced fluorescence were similar to those produced by the iodine vapour stain. A reduction in the intensity of the stain after two months marked the degradation of the surfactant. Thereafter, the level of discolouration remained stable and could be attributed to residual cellulose (Figure 6). An assessment of all six specimens led to the conclusion that contamination with cellulose powder from the poultice was a major problem in the treatment.

Experiment 3 – Preventing contamination

Based on the results of Experiment 2, the research focussed on developing a cleaning system that could prevent cellulose powder contamination. A chemical hydrogel composed of poly(hydroxy ethyl methacrylate)/poly(vinyl pyrrolidone) abbreviated to pHEMA/pVP was substituted for the cellulose poultice. In chemical gels, a network is built by the formation of covalent bonds between polymer chains. Hydrogels allow easy handling and removal from the treated substrate without leaving solid residues.¹ Water-based cleaning fluids can be applied to a sheet of hydrogel cut to the required dimensions. The cleaning fluids are released gradually when the gel is applied to the substrate. Hydrogels based on pHEMA/pVP have proven highly effective in the selective and safe removal of dirt on water-sensitive surfaces (Domingues et al. 2013), but they have yet to be used for cleaning wall paintings.

The gel was tested on four specimens. It was loaded with the microemulsion (MEK/BuOH-NR) overnight. A 5 × 5 cm square of gel was placed over the 4 × 4 cm Paraloid square in direct contact with the surface, without an intervention layer. A microemulsion/Arbocel poultice (5 mm thick) placed over the gel functioned as a ‘reservoir’ replenishing microemulsion as it was absorbed by the Paraloid. The specimen was covered and left overnight. After removal of gel and poultice, the surfaces were washed with water and a brush, as previously.

Comparison of raking- and UV-light photographs indicated that Paraloid was removed using the hydrogel (Figure 7). Intense UV-induced fluorescence along the periphery of the specimens, observed in the first two experiments, was absent in the third. Iodine staining was more evenly distributed than staining in Experiment 2, and was almost gone when repeated two months later, indicating some residual degrading surfactant.

It was not possible to measure the contact angle on the surface because the water was immediately absorbed by the lime-wash and plaster upon application. Compared with the contact angle before treatment, it was clear that the Paraloid had been removed (Figure 8).

CONCLUSION

The removal of aged Paraloid B-72 from lime-based wall paintings without contaminating surfaces is possible using microemulsions. Observations

in raking and UV light, supplemented with measuring the contact angle of water on a cleaned surface indicated whether removal of acrylic was successful. On cleaned specimens, FTIR spectra revealed that there was no dispersed Paraloid within the bulk of the specimens. However, initial experiments showed that contamination was occurring from materials used in the cleaning process. Iodine staining, a reversible technique, revealed residual surfactants and cellulose powder.

The use of a chemical hydrogel made it possible to completely avoid any solid residue. Moreover, a new microemulsion MEK/BuOH-NR with naturally degrading surfactant was used, and any surfactant residue disappeared rapidly from surfaces. The proposed methodology is feasible, harmless for the wall painting and reduces the safety risks associated with organic solvents.

PERSPECTIVES IN THE USE OF GELS FOR CLEANING WALL PAINTINGS

The use of hydrogels in conservation has been limited to the cleaning of easel paintings or other works of art which are particularly sensitive to the action of water or solvents. However, hydrogels can also be used for the detergent systems in the cleaning of wall paintings. Hydrogels could represent an advance since they replace traditional sorbents, including cellulose powder, which is shown to leave residues on surfaces.

Initial investigations performed with microemulsion-loaded hydrogels show this is a promising method. Further improvements include making higher density gels to allow the elimination of the ‘microemulsion reservoir’ provided by cellulose poultice. For this purpose, the rheological properties of the gel will have to be fine-tuned to obtain a gel with the appropriate tensile properties to be easily manipulated and, at the same time, be flexible enough to contact surfaces effectively while allowing optimal release of the liquid detergent system.

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NOTES

¹ The methods described in this paper are not related to the methodology developed by Wolbers, which is based on physical gels. For the differences between these two systems, see Carretti 2008.

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MATERIALS LIST

Hydrogels

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Surfactant NR

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