MINERAL SPIRITS-BASED MICROEMULSIONS: A NOVEL CLEANING SYSTEM FOR PAINTED SURFACES

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This paper reports further developments emerging from a collaboration between The Dow Chemical Company, Tate, and the Getty Conservation Institute which seeks to explore improved cleaning systems for unvarnished modern painted surfaces. Specifically, the present study describes three novel microemulsion systems based on water and mineral spirits, each formulated with different surfactants, either ionic or non-ionic. Of particular interest in the systems examined is their capacity to form thermodynamically stable water-in-oil (solvent-continuous) microemulsions which are clear, fluid, and simple to prepare. Phase diagrams are presented for each system type. Compared against more conventional aqueous and hydrocarbon solvent cleaning liquids, findings are reported of systematic evaluations of the performance of selected microemulsion formulations in cleaning artificially soiled reference paint films. Summaries are included of case study conservation treatments conducted at Tate in which the mineral spirits-based microemulsions formed part of the surface-cleaning treatment strategy.

KEYWORDS: Acrylic, Paint, Cleaning, Microemulsion, Surfactant, Solvent, Hydrocarbon

1. INTRODUCTION

From the cleaning point of view, conservators understand that modern artists’ paint quite often can be “tricky” paint. Typically not protected by a coat of varnish, modern paints – acrylic, vinyl, oil, and so on – can bind dirt strongly and be very sensitive to many of the common cleaning agents in the conservator’s armoury. The responses and sensitivities of particular kinds of modern artists’ paint to cleaning treatments have received an increasing amount of research attention in recent years, as evidenced, for example, by the various studies on water-sensitive modern oils (Mills et al. 2008; Tempest et al. 2013; Silvester et al. 2014) and on polyvinyl acetate paints (Pereira et al. 2013). But the largest body of recent research into the cleaning of modern paints has focused on artists’ acrylic emulsion (latex) paints and on understanding the risks associated with commonly used wet and dry cleaning systems on the surface and bulk properties (Ormsby and Learner 2009). Once known, steps can be taken by the conservator to minimize those risks in practice. The fact remains, however, that the possibilities for selecting effective liquid cleaning agents for acrylic and other tricky modern paints are often constrained by their intrinsic sensitivity to liquids. Generally speaking, two main approaches tend to be adopted for cleaning with ungelled liquids. One is to harness the dirt-removing power of aqueous solutions, through addition, say, of surfactant and/or chelate/deflocculant, at the same time controlling pH and conductivity to restrict paint swelling, pigment pick-up, and other possibly unwanted effects such as surfactant extraction. The critical influences of solution pH and conductivity on acrylic paint sensitivity have been demonstrated by studies that have explored ways of controlling water-induced swelling and the extraction of surfactant and other constituents from these paint films during aqueous cleaning (Wolbers et al. 2013; Dillon et al. 2014). The other approach is to take an inactive, non-polar organic solvent and try to improve its cleaning performance, especially its ability to pick up and disperse particulate dirt. Typically with the latter approach, aliphatic hydrocarbon solvents like mineral (petroleum) spirits would be selected, but the range of non-polar solvent options has broadened recently by the introduction to conservation practice of linear and cyclic silicone solvents (methicones and

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cyclohexane, cyclohexanol, and cyclomethicone) (Stavroudis 2012). By virtue of their low swelling power and low solvency interaction with acrylic paint media, such non-polar solvents might appear to offer potential for low risk wet-cleaning systems, but their relatively poor cleaning efficacy sometimes limits practical effectiveness.

The idea of trying to combine the respective benefits of aqueous and non-polar solvent systems – that is, exploiting the high cleaning efficacy and adaptability of the aqueous environment and the relatively low risk (low swelling) offered by non-polar solvents – is the root of continuing development work by our group on a class of materials known as microemulsions, particularly the water-in-oil (WiO) type in which the non-polar (solvent) phase is the continuous phase. A pre-existing WiO microemulsion product of The Dow Chemical Company, INVERT™ 5000, featured in the early stages of our evaluations of possible new cleaning agents for artists’ acrylic emulsion paints (Keefe et al. 2011; Ormsby et al. 2013), and while this product did show very good cleaning efficacy, practical trials demonstrated it was generally too aggressive on the type of paint under consideration for safe, controlled use. Accordingly, we started investigations into alternative microemulsion formulations that would be better tailored to the specific application of removing dirt from works of art created in acrylic latex paint, or similarly sensitive media.

For the The Dow Chemical Company, Tate, and the Getty Conservation Institute (Dow/Tate/GCI) collaboration, the focus has been on WiO microemulsions in which the “oil” component is a mineral spirits-type aliphatic hydrocarbon solvent. Keefe et al. (2011) described the process by which an initial series of specific microemulsion formulations (hereafter called Series 1) was determined with the aid of Dow’s high throughput robotic laboratory systems. The Series 1 microemulsions comprised Shellsol D38 solvent as the continuous water-immiscible phase, a linear alkylbenzene sulfonate surfactant (LAS, sodium dodecylbenzene sulfonate), two co-surfactants 1-butanol and 1-hexanol, and water. Since their first presentation in 2011, the Series 1 microemulsions have been evaluated from the practical point of view through a combination of systematic laboratory testing (at Tate), field trials, and subjective assessment during professional development workshops organized by GCI (“Cleaning Acrylic Painted Surfaces” [CAPS]) Los Angeles 2009, New York 2011, London 2012, Washington D.C. 2013, Sydney 2013, and Ottawa 2014.

The various practical evaluations of the Series 1 microemulsions provided constructive feedback on desirable and undesirable characteristics which then guided the formulation of two further types of mineral spirits-based WiO microemulsion, hereafter called Series 2 and Series 3, selected formulations from which have also been evaluated in systematic cleaning trials. The Series 2 microemulsions are prepared from water, an aliphatic mineral spirits (Shellsol D38), with the Dow product ECOSURF™ EH6 Surfactant [note 1] as primary surfactant and 1-butanol and 1-hexanol as co-surfactants. The Series 3 microemulsions were developed with the aim of eliminating the alcohol co-surfactants of the Series 1 and Series 2 formulations, primarily in attempt to reduce the activity on paint. Series 3 microemulsions thus comprise just water, an aliphatic mineral spirits (Shellsol D38), and a single anionic surfactant, sodium dioctylsulfosuccinate (DOSS, the surfactant ingredient of Aerosol OT products). Two different forms of sodium dioctylsulfosuccinate have been used in the preparation of Series 3-type microemulsion systems: Series 3a is based on an existing Dow commercial product TRITON™ GR-7M Surfactant; Series 3b is prepared from laboratory-grade pure sodium dioctylsulfosuccinate.

This paper has several aims: to describe in detail the mineral spirits-based Series 1, 2, and 3 microemulsions, including presentation of their phase diagrams; to report on the systematic trials conducted at Tate on comparative cleaning performance in which the microemulsions were evaluated alongside various other more conventional aqueous and mineral spirit-based cleaning liquids; and to present some case study conservation treatments in which the microemulsions have been evaluated as part of a broader surface-cleaning treatment strategy. Although the new microemulsion systems described here have been developed primarily for removal of dirt from modern unvarnished works, they may also find useful applications in cleaning older works; one such example is presented among the case studies.

2. Microemulsions

Microemulsions are special combinations of a polar liquid, usually water or a dilute aqueous solution of electrolyte, and an immiscible, hydrophobic liquid that are brought into thermodynamically stable co-existence by means of surfactant and, in some cases, co-surfactant (co-solvent), the combination of which is sufficient to reduce the interfacial tension between the two immiscible phases to ultra-low values (Klier et al. 2000). Microemulsions are optically clear because the size of the domains of dispersed phase is considerably smaller than the wavelength of visible light, typically 10–100 nm. Microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formulation of ordinary emulsions, and typically they are low viscosity fluids. Another feature that distinguishes microemulsions from regular emulsions is that the domains are dynamic in terms of size and

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shape and undergo continuous break-up and reconstitution: the very low interfacial tension allows thermal motions to spontaneously disperse the two immiscible phases. The dynamic nature of these systems allows effective cleaning performance on hydrophobic and hydrophilic components of soils while limiting the degree of contact with the aqueous phase of the cleaner. Considering microemulsions as cleaning agents, a useful property is that the aqueous phase can to some degree accommodate soluble salts and/or other ingredients that might usefully modify performance. Microemulsions are typically described as direct (oil-in-water [OiW] or water-continuous), reversed (WiO or oil-continuous), or bi-continuous. The submicroscopic structures of hypothetical OiW, WiO, and bi-continuous microemulsion systems are illustrated schematically in Figs. 1a, 1b, 1c. These examples include a small molecule co-surfactant (typically an aliphatic alcohol or glycol ether) and a primary surfactant residing at the oil/water interface. The phase behavior of simple microemulsion systems comprising oil, water and surfactant can be studied and described with the aid of ternary phase diagram in which each corner of the diagram represents 100% concentration of the particular component. Where the microemulsion ingredients consist of more than three different substances, as in the case of our Series 1 and Series 2 types, the phase behavior may still be characterized by a “pseudo-ternary” phase diagram in which the total proportion of surfactant and co-surfactant substances is combined on a single axis.

Microemulsions find use in a broad range of industrial and technological applications including enhanced oil recovery, oil removal from contaminated groundwater sites, consumer and industrial cleaning formulations, metal working, catalysis, advanced ceramics processing media, production of nanostructured materials, dyeing, agrochemicals, cosmetics, foods, pharmaceuticals (including controlled delivery), coating formulations, and biotechnology (Klier 2006; Sharma et al. 2012). They are not entirely new to art conservation. Carretti et al. (2007) described two different xylene-in-water microemulsions (also referred to as “nanocontainers”) for different cleaning applications: the removal of acrylic coatings/consolidants and of black crusts from historic wall paintings. Carretti et al. (2009) reported a further development in the use of OiW microemulsions for cleaning works of art in which the microemulsions were embedded in a polymeric network. Cleaning systems described as microemulsions have been reported recently by Brajer et al. (2014) for the removal of acrylic resin (PARALOID™ B72) from wallpaintings: these are water-rich systems consisting of alcohol ethoxylate surfactants and butanone (methyl ethyl ketone), with variants including also other oxygenated solvents. Microemulsion formulations, also intended for the removal of polymer coatings from wallpaintings, are described in Baglioni et al. (2015, 61–82), which contains a comprehensive bibliography on this application.

3. Microemulsion Compositions and Phase Diagrams

As already noted, the Dow/Tate/GCI collaboration has identified three types of microemulsion (Series 1–3) that might serve as useful cleaning liquids for the removal of dirt from artist’s acrylic paint surfaces. The latter two series evolved under influence of feedback from testing at Dow, Tate and from CAPS workshop participants, the essential goal being to achieve lower levels of cleaning activity than the Series 1 systems. Full phase diagrams have been prepared for each type of microemulsion to provide a compositional map showing the combinations of each set of ingredients that form stable WiO microemulsions, those that form OiW microemulsions, and those that have different structure (multi-phase; bicontinuous). The three microemulsion types were all formulated with the same proprietary aliphatic hydrocarbon mineral spirit, Shellsol D38, which in selected cases could be substituted with a similar product, Shellsol D40. The primary surfactants

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**Fig. 1.** Schematic diagram of sub-microscopic structures of microemulsion systems: OiW; bicontinuous phases; WiO.
selected for the three microemulsion classes were chosen on the basis of several criteria: their general cleaning strength in adjacent fields of textile and hard surface cleaning; their cleaning performance in previous studies on soiled acrylic painted surfaces (Keefe et al. 2011); their environmental profile; and their known capacity to form stable WiO microemulsions. In addition to the primary surfactant, Series 1 and 2 microemulsions contain a blend of 1-butanol and 1-hexanol as co-surfactants, inclusion of which was necessary to obtain stable microemulsions. Series 2 and 3 microemulsions have been prepared with both deionized water and adjusted water (pH 6.6, conductivity 6.2 mS/cm) which illustrates how the water phase might be modified to optimize the overall cleaning performance and minimize risks associated with the swelling and extraction of materials from these paints (Dillon et al. 2014).

Dow’s high throughput robotic laboratory systems, as described in Keefe et al. (2011, 42), were utilized to study combinations of ingredients that resulted in stable microemulsions in the Series 1 system. The Series 2 and Series 3 microemulsions have been prepared manually. The microemulsions are easily prepared by hand, as required; typically made up in small batches of 10 g total weight (or multiples of 10 g), amounts of each ingredient by weight are determined using a two decimal place digital balance, and mixing is achieved by simple manual shaking. For microemulsions from Series 2 and Series 3, the ingredients can be combined in any order; for Series 1 emulsions, the LAS surfactant must first be dissolved in the water phase. The recommended order of addition of ingredients for Series 1 is discussed in more detail below.

General observations on each of the Series 1, 2 and 3 microemulsions are provided in table 1. The compositions of each individual microemulsion formulation are presented in tables 2, 4, and 5. Phase diagrams for each series are shown in figs. 2, 3, and 4. Broadly speaking, cleaning efficacy within each microemulsion series varies across the compositional space described by the phase diagram, with greater cleaning performance at higher proportions of water and surfactant. The cleaning activity of a given microemulsion is also governed by a number of other factors, including: the surfactant type and strength (hydrophilic lipophilic balance [HLB] number), the presence and type of co-surfactant(s), modifications to the water phase, etc. For the microemulsion series described here, the strength of surfactant increases in the order TRITON® GR-7M Surfactant < ECOSURF™ EH-6 Surfactant < LAS. In some cases, as briefly described above, the microemulsion systems can accommodate a degree of modification to the water phase, for example by setting a particular pH and conductivity condition, and/or by adding small quantities of a chelating agent, such as citrate, or another surfactant such as ECOSURF™ EH-9 which might allow for fine-tuning of the cleaning activity.

In connection with the practical application of cleaning painted surfaces, the phase diagrams provide a useful graphic framework for exploring possible cleaning options, helping the user to vary the cleaning performance to suit the needs of the particular object under treatment, for example by shifting to higher or lower cleaning activity, or to lower impact on the original paint, as the situation dictates. These fine adjustments may be done by preparation of new batches of microemulsion having the desired proportions, which is a simple matter of weighing out and mixing the necessary amounts of each ingredient. Alternatively, in some cases, depending on the system type and the position in the phase diagram, the cleaning action of a given formulation may be adjusted by “dilution”; that is by addition of small aliquots of mineral spirits or water in amounts appropriate to shift the relative proportions in one or other direction within the appropriate microemulsion territory of the phase diagram. A further option for adjusting microemulsion cleaning performance is mixing of two preparations: if, say, the user has two ready-made stable WiO preparations with quite different relative proportions of ingredients, mixtures of those preparations will provide intermediate combinations in a linearly additive fashion.

Since all of the microemulsion formulations presented here include non-volatile surfactant components, a final “clearance” step is required in the cleaning process to ensure that any residues of surfactant are fully removed from the paint surface. A general rule-of-thumb is that the solvent used for clearance should be the same as, or close in nature to, the continuous phase of the microemulsion.

3.1. SERIES 1 MICROEMULSIONS

The Series 1 microemulsion system comprises linear alkyl benzene sulfonate surfactant (LAS), 1-butanol, 1-hexanol, Shellsol D38 solvent, and water. The phase diagram (fig. 2) shows the respective combinations that result in WiO microemulsions, OiW microemulsions and 2-phase systems. The data on which the phase diagram is based are summarized as table 2. Within this series the LAS/1-butanol/1-hexanol ratio was kept constant (respectively 40:40:20 parts by weight) to allow presentation of a coherent (pseudo-) ternary phase diagram for this five component mixture. Table 2 includes also data on four other water/LAS surfactant/(1-butanol + 1-hexanol)/mineral spirits OiW microemulsion formulations: Sample IDs ME1–26 ME1–27 and ME1–28 were prepared with an LAS/butanol/hexanol ratio of 37.5:42.8:20.6; ME1–29 was prepared with an LAS/butanol/hexanol ratio of 43.7:37.5:18.8. These very closely related systems are included here, as they
featured in early systematic comparative cleaning evaluations carried out at Tate, but strictly they should not be plotted on the Series 1 phase diagram, due to the slightly different surfactant/ co-surfactant blend ratio. The Series 1 microemulsions were prepared by first dissolving the LAS powder in deionized water. Depending on the grade of LAS, this may require gentle heating, for example by placing the bottle under hot tap water, or onto a low-heat hotplate and shaking by hand. The 1-butanol and 1-hexanol are then added to the aqueous solution of LAS, followed by the Shellsol D38 solvent.

### Table 1  General observations for each of the Dow/Tate/GCI Series 1, 2 and 3 microemulsion types

|                        | Series 1                  | Series 2                  | Series 3 3a                                      | Series 3 3b                                      |
|------------------------|---------------------------|---------------------------|--------------------------------------------------|--------------------------------------------------|
| **Surfactant type and description** | LAS (sodium salt) Anionic | ECOSURFTM EH-6 Surfactant Surfactant (dioctylsulfosuccinate, sodium salt (in petroleum distillate solvent) Anionic | TRITON™ GR-7M Surfactant Anionic | Diocytlsulfosuccinate, sodium salt in Shellsol D38 + i-PrOH Anionic |
| **General surfactant properties** | Workhorse of the household, industrial and institutional detergent industries. Superior detergent, foaming, wetting and emulsification properties, economical. Purity of different commercially available grades varies. | Superior wetting, excellent oily soil removal, rapid dissolution and good clearance, low odor, readily biodegradable | Excellent emulsifying and dispersing ability, oil soluble, common anionic surfactant used in microemulsions |
| **Co-surfactant required?** | Yes (1-butanol + 1-hexanol) | Yes (1-butanol + 1-hexanol) | No | |
| **Cleaning strength** | Strong 4–24 wt% | Intermediate 12–40 wt% | Mild 14–48 wt% | |
| **Active surfactant level required for microemulsion structures** | WiO and OiW | WiO | WiO | |
| **Types of microemulsion formed** | | | | |
| **Shellsol D38 interchangeable with Shellsol D40?** | Depends on LAS activity and phase diagram position | Yes | Yes | |
| **Interchangeable with DI or pH/ conductivity-adjusted water** | Yes for WiO No for OiW | Yes | Yes | |
The LAS surfactant has the highest surfactant activity of the three systems; thus, of the different systems explored, LAS provides the lowest surfactant levels necessary to form stable microemulsion structures. Lower surfactant levels are beneficial to minimize residual surfactant on the substrate after cleaning treatment and clearance. The LAS surfactant system allows formation both of stable OiW and WiO microemulsion structures depending on the ingredient proportions and the consequent position in the phase diagram. OiW microemulsions are formed when water content is above 50% w/w; WiO microemulsions are formed at water contents of 30% w/w and below. Microemulsions did not form when combined surfactant content was very low (see most of the formulations with 10% w/w combined surfactant) or very high (see the formulations with greater than about 70% w/w combined surfactant). The structure of the microemulsions as either OiW or WiO was determined by conductivity measurements (Kizilbash et al. 2011). Water-continuous (OiW) systems have significantly higher conductivity (of the order of 10×) that of oil-continuous (WiO) systems. The cleaning efficacy of Series 1 microemulsions is generally high due to the LAS surfactant utilized in the system. Furthermore, the water-continuous (OiW) preparations, such as ME1–30, evaluated in the Tate cleaning trials, are expected to have somewhat greater cleaning efficacy than the formulations producing WiO microemulsions. These systems are probably more suited for treatment of objects that have high soiling levels and more tenaciously adhered dirt, as noted for case study 5.1. The WiO options may also have utility for works of art highly sensitive to wet cleaning with water because

| Sample ID | LAS | 1-Butanol | 1-Hexanol | Combined LAS+1-Hexanol | Water Shellsol D38 (or D40) | Samples Evaluated for Cleaning | Conductivity (mS/cm) |
|-----------|-----|-----------|-----------|------------------------|-----------------------------|-------------------------------|---------------------|
| OiW       |     |           |           |                        |                             |                               |                     |
| ME1–1     | 8   | 8         | 4         | 20                     | 70                          |                               | 6.1–6.4             |
| ME1–2     | 12  | 12        | 6         | 30                     | 60                          |                               |                     |
| ME1–3     | 8   | 8         | 4         | 20                     | 60                          |                               |                     |
| ME1–4     | 16  | 16        | 8         | 40                     | 50                          |                               |                     |
| ME1–5     | 12  | 12        | 6         | 30                     | 50                          |                               |                     |
| ME1–6     | 8   | 8         | 4         | 20                     | 50                          |                               |                     |
| ME1–7     | 20  | 20        | 10        | 50                     | 40                          |                               |                     |
| ME1–8     | 16  | 16        | 8         | 40                     | 40                          |                               |                     |
| ME1–9     | 12  | 12        | 6         | 30                     | 40                          |                               |                     |
| ME1–10    | 8   | 8         | 4         | 20                     | 40                          |                               |                     |
| ME1–11    | 24  | 24        | 12        | 60                     | 30                          |                               |                     |
| ME1–12    | 20  | 20        | 10        | 50                     | 30                          |                               |                     |
| ME1–13    | 16  | 16        | 8         | 40                     | 30                          |                               |                     |
| ME1–14    | 12  | 12        | 6         | 30                     | 30                          |                               |                     |
| ME1–15    | 8   | 8         | 4         | 20                     | 30                          |                               |                     |
| WiO       |     |           |           |                        |                             |                               |                     |
| ME1–16    | 24  | 24        | 12        | 60                     | 20                          |                               |                     |
| ME1–17    | 20  | 20        | 10        | 50                     | 20                          |                               |                     |
| ME1–18    | 16  | 16        | 8         | 40                     | 20                          |                               |                     |
| ME1–19    | 12  | 12        | 6         | 30                     | 20                          |                               |                     |
| ME1–20    | 8   | 8         | 4         | 20                     | 20                          |                               |                     |
| ME1–21    | 4   | 4         | 2         | 10                     | 20                          |                               |                     |
| ME1–22    | 20  | 20        | 10        | 50                     | 10                          |                               |                     |
| ME1–23    | 16  | 16        | 8         | 40                     | 10                          |                               |                     |
| ME1–24    | 12  | 12        | 6         | 30                     | 10                          |                               |                     |
| ME1–25    | 8   | 8         | 4         | 20                     | 10                          |                               |                     |
| OiW microemulsions closely related to Series 1 | | | | | | | |
| OiW       |     |           |           |                        |                             |                               |                     |
| ME1–26    | 6   | 6.7       | 3.3       | 16                     | 44                          |                               | 4.5                 |
| ME1–27    | 6   | 6.7       | 3.3       | 16                     | 34                          |                               | 4.7                 |
| ME1–28    | 6   | 6.7       | 3.3       | 16                     | 54                          |                               | n/a                 |
| ME1–29    | 7   | 6         | 3         | 16                     | 54                          |                               | 4.7                 |
| ME1–30    | 4   | 4         | 2         | 10                     | 70a                         |                               | 7.6                 |

Water phase of ME-30 consists of 4 parts of a 5% w/w solution of NaCl and 66 parts deionised water.
the contact time required for effective cleaning is shorter due to the high cleaning efficacy. As with all of the systems described here, cleaning treatments using the Series 1 microemulsions require a clearance step using the appropriate continuous phase solvent depending on the type of system, OiW or WiO; that is, Shellsol D₁₀ or D₁₃ solvent for the WiO systems, and pH- and conductivity-adjusted water for the OiW

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**Table 3** CHARACTERIZATION OF DIFFERENT COMMERCIAL LAS PRODUCTS

| LAS Source | MP Biomedics | Stepan | Acros Organic | Sigma-Aldrich |
|------------|--------------|--------|---------------|---------------|
| Product name/number | Dodecylbenzene sulfonic acid sodium salt/Catalog number 157889 | Nacconol 90G surfactant | Dodecylbenzenesulfonic acid, sodium salt, 88%, technical grade/Catalog number 11710 | Sodium dodecylbenzenesulfonate technical grade/Product number 289957 |
| LAS activity (wt %) (actual) | 96.7 | 92.9 | 93.3 | 93.6 |
| Conductivity (µS/cm) of 1% w/w solution | 1212 | 1293 | 1514 | 2660 |
| Structure | Branched | Linear | Linear | Linear |
| Phosphorus content (wt%; by XRF) | Not detected | 0.10 | 0.11 | 0.67 |
| Ability to form microemulsions | Yes Full phase diagram (fig. 2) | Yes Full phase diagram (fig. 2) | Reduced number of stable microemulsions in phase diagram | No stable microemulsions |

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**Table 4** SERIES 2 WiO MICROEMULSIONS: WATER/ECOSURF™ EH-6 SURFACTANT/(1-BUTANOL + 1-HEXANOL) CO-SURFACTANT/ALIPHATIC MINERAL SPIRITS. INGREDIENTS LISTED BY WEIGHT %, AS SUPPLIED(ALL INGREDIENTS ARE 100% ACTIVE)

| Sample ID | ECOSURF™ EH-6 | 1-Butanol | 1-Hexanol | Combined E + H + B | Water | Shellsol D₃₈ (or D₄₀) | Samples Evaluated for Cleaning |
|-----------|----------------|-----------|-----------|--------------------|-------|-----------------------|-----------------------------|
| ME₂⁻¹     | 30             | 7.5       | 22.5      | 60                 | 30    | 10                    | ✓                           |
| ME₂⁻²     | 25             | 6.25      | 18.75     | 50                 | 30    | 20                    |                             |
| ME₂⁻³     | 20             | 5         | 15        | 40                 | 30    | 30                    | ✓                           |
| ME₂⁻⁴     | 35             | 8.75      | 26.25     | 70                 | 20    | 10                    |                             |
| ME₂⁻⁵     | 30             | 7.5       | 22.5      | 60                 | 20    | 20                    |                             |
| ME₂⁻⁶     | 25             | 6.25      | 18.75     | 50                 | 20    | 30                    |                             |
| ME₂⁻⁷     | 20             | 5         | 15        | 40                 | 20    | 40                    |                             |
| ME₂⁻⁸     | 15             | 3.75      | 11.25     | 30                 | 20    | 50                    |                             |
| ME₂⁻⁹     | 40             | 10        | 30        | 80                 | 10    | 10                    |                             |
| ME₂⁻¹₀    | 35             | 8.75      | 26.25     | 70                 | 10    | 20                    |                             |
| ME₂⁻¹₁    | 30             | 7.5       | 22.5      | 60                 | 10    | 30                    | ✓                           |
| ME₂⁻¹₂    | 25             | 6.25      | 18.75     | 50                 | 10    | 40                    | ✓                           |
| ME₂⁻¹₃    | 20             | 5         | 15        | 40                 | 10    | 50                    | ✓                           |
| ME₂⁻¹₄    | 15             | 3.75      | 11.25     | 30                 | 10    | 60                    |                             |
| ME₂⁻¹₅    | 12             | 3         | 9         | 24                 | 8     | 68                    | ✓                           |
Where possible, if the sensitivity of the paint allows, it may prove beneficial to clear with both types of liquid to minimize LAS surfactant residues.

One challenge encountered in the development of the Series 1 microemulsions was that the ability to form comparable microemulsion structures was strongly influenced by the choice of particular LAS product, the variation in microemulsion-forming behavior seemingly being related to product purity. Four different sources of LAS were investigated in this study, as described in Table 5. The phase diagram for the Series 1 system (fig. 2) shows the various formulations that generated WiO or OiW microemulsions, or multi-phase systems with LAS products supplied by the Stepan Company and by MP Biomedics. The LAS surfactant obtained from Acros Organics material formed stable microemulsions only for portions of the phase diagram. The Sigma-Aldrich LAS material did not form stable single-phase microemulsions at all [note 2]. The Stepan Company product Nacconol 90G has been our preferred LAS surfactant for the Series 1 microemulsions. The Series 1 LAS-based systems were all prepared with deionized water. Water adjusted for

![Fig. 2. Phase diagram for Series 1 microemulsion system: water/LAS surfactant/(1-butanol + 1-hexanol) co-surfactant/aliphatic mineral spirits.](image1)

![Fig. 3. Phase diagram for Series 2 microemulsion system: Water/ECOSURF™ EH-6 Surfactant/(1-butanol + 1-hexanol) co-surfactant/aliphatic mineral spirits.](image2)
TRITON systems. This set of constituents does not support
stably in stable WiO microemulsions and two-phase
component mixture. The phase diagram (fig. 4) shows the combinations of these ingredients that result in stable WiO
microemulsions, bi-continuous, or 2-phase systems;
OiW microemulsions are not formed with the set of
ingredients used for Series 3a. The data from which the phase diagram was generated are summarized as
table 5. In table 5 values for the quantities of
TRITON GR-7M Surfactant are given first as
weight proportion as received and, in parentheses, the
net weight proportion of surfactant discounting the
volatile solvent component. In similar fashion to
the Series 1 and 2 systems, these preparations are
made by simple hand-mixing of measured amounts of
each ingredient to give the particular WiO microemulsion
formulation of interest. Series 3a systems have
been prepared with both deionized water and adjusted
water (pH 6; 6 mS/cm), etc. interchangeably, likewise
with Shellsol D38 or D40 solvent interchangeably.
This microemulsion class may be suited for cleaning
treatments that require gentle cleaning due to highly
sensitive pigment or binder systems and/or mild soiling.

One constraint affecting preparation and use of the
Series 3a microemulsions became apparent as a conse-
quence of the GCI’s CAPS training workshops held
outside the USA: TRITON GR-7M Surfactant is
not available in other regions of the world; and since
it contains a flammable solvent the product cannot
easily be shipped internationally. Accordingly, there
was some incentive to identify alternative dioctylsulfo-
succinate surfactant products which would allow for
an analog of TRITON GR-7M Surfactant system to
be prepared from scratch from locally available

pH and conductivity (pH 6.6, conductivity 6.2 mS/cm)
can be used for WiO systems but did not yield stable
OiW microemulsion systems, presumably because of
the effect of enhanced ionic interactions. Shellsol D38
solvent can generally be replaced by Shellsol D40
within the Series 1 phase diagram; for example, ME1–18 (WiO) was stable with both Shellsol products
and both water types, and ME1–3 (OiW) was stable
with both Shellsol products when deionized water
was used for the aqueous phase.

3.2. SERIES 2 MICROEMULSIONS

The Series 2 system is based on water, Shellsol D38
solvent, ECOSURF™ EH-6 Surfactant, and a
co-surfactant that is again a combination of 1-butanol
and 1-hexanol. As in the Series 1 formulations
the ECOSURF™ EH-6 Surfactant/1-butanol/1-hexanol
ratio was held constant (50:12.5:37.5) to allow present-
ation of a ternary phase diagram for this five
component mixture. The phase diagram (fig. 3) shows the
combinations of these constituents that result respect-
vably in stable WiO microemulsions and two-phase
systems. This set of constituents does not support
OiW microemulsions. The data on which the phase
diagram is based are summarized as table 4. The
Series 2 microemulsions are prepared by simply combi-
ing in a small jar or vial the measured amounts of
water, surfactant, 1-butanol, 1-hexanol, and hydro-
carbon solvent to give the particular WiO formulation
of interest, and shaking the mixture by hand. As
described earlier, Series 2 systems may be prepared
with deionized water, water adjusted for pH and con-
ductivity (e.g. pH 6; ~6 mS/Cm) or water with added
chelating agent. Shellsol D38 or Shellsol D40 may be
used interchangeably as the aliphatic mineral spirits

3.3. SERIES 3 MICROEMULSIONS

The Series 3 microemulsion system is the simplest of
the three described here and comprises just water, ali-
phatic mineral spirits (Shellsol D38 or D40), and an
anionic surfactant; no co-surfactants are required. In
the first formulation trials of the Series 3 systems (here-
after called Series 3a) the anionic surfactant employed
was the Dow product TRITON™ GR-7M Surfactant
(which is sodium dioctylsulfosuccinate, supplied as
64% active ingredient in “petroleum distillate” solvent
[note 3]. The phase diagram (fig. 4) shows the combi-
 nations of these ingredients that result in stable WiO
microemulsions, bi-continuous, or 2-phase systems;
OiW microemulsions are not formed with the set of
ingredients used for Series 3a. The data from which
the phase diagram was generated are summarized as
table 5. In table 5 values for the quantities of
TRITON GR-7M Surfactant are given first as
weight proportion as received and, in parentheses, the
net weight proportion of surfactant discounting the
volatile solvent component. In similar fashion to
the Series 1 and 2 systems, these preparations are
made by simple hand-mixing of measured amounts of
each ingredient to give the particular WiO microemulsion
formulation of interest. Series 3a systems have
been prepared with both deionized water and adjusted
water (pH 6; 6 mS/cm), etc. interchangeably, likewise
with Shellsol D38 or D40 solvent interchangeably.

This microemulsion class may be suited for cleaning
treatments that require gentle cleaning due to highly
sensitive pigment or binder systems and/or mild soiling.

One constraint affecting preparation and use of the
Series 3a microemulsions became apparent as a conse-
quence of the GCI’s CAPS training workshops held
outside the USA: TRITON™ GR-7M Surfactant is
not available in other regions of the world; and since
it contains a flammable solvent the product cannot
easily be shipped internationally. Accordingly, there
was some incentive to identify alternative dioctylsulfo-
succinate surfactant products which would allow for
an analog of TRITON™ GR-7M Surfactant system to
be prepared from scratch from locally available

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were characterized as non-microemulsions. A number of systems were identified as multi-phase and/or optically anisotropic and could not be reliably distinguished from OiW microemulsions. Formulations lying within the Series 3b microemulsion space tended to have noticeably higher viscosity as the relative proportions of water and surfactant increase.

The solvent suggested for clearance of the Series 3a and 3b microemulsions was Shellsol D38 (or D40) with 2.5% w/w added 2-propanol, which is the continuous phase for the Series 3b systems.

Given the anionic nature of the sodium dioctylsulfosuccinate Series 3-type preparations it might be expected that there is limited scope for adjustment of the chemistry of the water phase, for example, by addition of other ionic additives such as a chelate like triammonium citrate (TAC). Preliminary investigations with the Series 3b type preparations suggest this is indeed the case: inclusion in the water phase of TAC at the 1% w/w level prevents microemulsion formation over most of the compositional space. However, when the TAC was reduced to 0.5% w/w, it was found that some microemulsions could still form (hereafter referred to as Series 3b:TAC), but with a reduced distribution within the phase diagram compared to just water as the aqueous phase (fig. 6). As with the regular Series 3b systems described above, the particular type of microemulsion system formed (WiO, OiW, and bicontinuous) has not yet been determined: we distinguish here only between systems that are demonstrably not microemulsions (multi-phase and/or optically anisotropic) and microemulsions (homogeneous single phase; clear and optically isotropic).

4. Cleaning Test Evaluations

4.1. Cleaning Systems

Selected formulations from each of the three series of mineral spirits-based microemulsions described above were evaluated for cleaning performance in systematic manual cleaning trials conducted at Tate. It was not possible to include every possible microemulsion combination in these trials, hence those selected from within each series represented a range of cleaning efficacies (with respect to removing artificial dirt from acrylic paint films) and were highlighted as promising during initial trials. Selection within each series was also influenced by the desire to trial systems representing a range of water, solvent, and surfactant contents. Those used for the reported study rated highly with respect to cleaning efficacy while also having relatively low impact on paint films. In addition, some had been
used on case study works of art (see section 5), where they had been chosen after a full assessment of surface-cleaning options had been carried out.

For comparative purposes, the mineral spirits-based microemulsions were evaluated alongside other water- and mineral spirits-based cleaning systems. A number of these had been evaluated in previous work by our group (Keefe et al. 2011; Ormsby et al. 2013), however the reported study includes further modifications guided by findings from recent research on the swelling of acrylic paints and concomitant surfactant extraction (Kampasakali et al. 2011; Wolbers et al. 2013; Dillon et al. 2014). Modifications included adjusting aqueous-system pH levels to around 6 and setting ionic strength. All of the surfactants used in the systems tested (see table 1) originate from the Dow/Tate/GCI collaboration and have been introduced elsewhere (Dorman 2012; Stavroudis 2012). Practical experience on works of art has also influenced some of the minor changes to these systems, for example reducing the quantity of surfactants and chelating agents used in simple aqueous mixtures. The final set of preparations tested (table 6) represents the main classes of wet-cleaning systems currently being explored for unvarnished modern paint surfaces; including simple aqueous systems based on deionized water, simple aliphatic hydrocarbon solvent systems (based on Shellsol D40, and the mineral spirits-based microemulsions.

4.2. SAMPLES FOR CLEANING TRIALS

The cleaning performance of the various liquid preparations was evaluated by manual swab cleaning of artificially soiled artists’ acrylic paints and acrylic priming. The paints were prepared by casting onto 10 oz. acrylic primed cotton canvas (Russell and Chapple, UK) using an adjustable film caster (Sheen Instruments, UK), to a dry thickness of ±20 µm. The samples of priming consisted of commercially prepared acrylic primed canvas boards (Atlantis Art Materials, UK). The paint colors (titanium white [PW6]; azo yellow [PY3]) and paint brands (Liquitex Heavy Body Acrylics and Talens Rembrandt Acrylics) were selected to explore the cleaning effects of the preparations on two brands with known surfactant levels, with more or less vulnerable pigment types, and with different inherent gloss levels. Constituents of these paints have been detailed elsewhere (Ormsby et al. 2013, 78). After natural ageing in ambient, dark conditions for 8 months, the paint and priming samples were soiled with an artificial dirt, the composition and application method of which have also been described previously (Ormsby et al. 2013, 79). The cleaning tests were carried out around 2 years later. At the time of testing, the unsoiled control sections of the Talens paint samples (both colors) had substantial amounts of detectable migrated surfactant, and the Liquitex samples varied between trace (PW6) and moderate (PY3) amounts of migrated surfactant. The surface conductivity of the unsoiled control samples varied between 0.22 and 0.35 mS/cm; the priming samples were close to zero.

4.3. METHODOLOGY FOR EVALUATION OF CLEANING SYSTEM PERFORMANCE

To prepare for cleaning tests, the soiled area of each sample was divided into squares and numbered (across the two samples tested per color and brand), leaving one square on each sample as a soiled control, to complement the unsoiled control. Cleaning was carried out according to a specific procedure designed to approximate conservation techniques while maintaining an approach that facilitated direct comparison between cleaning systems, samples and paint brands (Ormsby and von Aderkas 2013). The procedure was slightly modified from that used in a previously reported study (Ormsby et al. 2013).

For each test, a ready-made cotton swab (Dynarex, USA) was dipped into the cleaning solution and rolled once on paper towel to remove excess liquid. The swab was then rolled with consistent light pressure across the soiled surface of the sample until one of the following stopping points was reached: the sample was considered clean (as judged by eye); pigment was removed (visible on the swab); swelling or other change was noted (e.g. paint surface tackiness, abrasion, burnishing); or 50 swab rolls had been applied (i.e. the sample could not be fully cleaned). Aqueous solutions were cleared with water at pH 6
and conductivity $6 \text{mS/cm}$ (adjusted using a volatile acid and alkali); mineral spirit-based solutions and microemulsions were cleared with Alcosol (= Shellsol) $D_{40}$ solvent.

The results of the comparative cleaning tests were quantified using three different descriptors:

(1) The number of swab rolls were recorded until one of the above defined stopping points was reached (where one swab roll was defined as one backward and forward roll). The number of swab rolls to stopping point is effectively an inverse indicator of “cleaning efficacy”: a liquid with a low value for this descriptor reflects rapidity of action and vice versa.

(2) The relative degree of cleaning (dirt removal) was rated, after both the cleaning and clearance steps were performed and the surface had dried, across a scale from $0$ to $5$. This was done by visually comparing the cleaned area to the control areas by eye, with a rating of $5$ considered clean (i.e. as clean as the unsoiled control). This indicator reflects ultimate capacity for cleaning.

(3) An overall rating was used to describe (on a scale from $1$ to $12$) the relative magnitude of overall change to the paint surface, incorporating both the amounts of dirt removed and any perceived alteration to the paint (see Appendix).

Additional notes were recorded on other aspects of the cleaning process, such as the consistency of swabbing action, degree of control over the cleaning solution, surface wetting behavior and any clearance issues encountered.

4.4. Summary of Cleaning Test Results

4.4.1. Average Swab Roll Numbers Across All Paint Samples and Cleaning Systems

As shown in fig. 7, the average number of swab rolls required to clean the samples with the microemulsions was considerably fewer than most of the aqueous systems and all of the simple mineral spirits systems. The aqueous systems with added ECOSURFTM EH-9 Surfactant and/or TAC resulted in a useful reduction of the numbers of swab rolls required to reach the cleaning end point. However in general, the aqueous systems required higher numbers of rolls than the microemulsion systems (with the exception of the $0.5\%$ ECOSURFTM EH-9 Surfactant and $0.5\%$ TAC blend which equalled the Series 3 microemulsion results). The enhanced efficacy of the microemulsions may be beneficial when paint surfaces are fragile or heavily soiled and/or where there is a risk of driving soiling into the paint surface with prolonged contact.

The different series of the mineral spirits-based microemulsions showed slight differences in soiling removal efficacy. The slightly lower efficacy of Series 2 and Series 3 microemulsions reflects the deliberate design and modification of these systems outlined in section 3. The addition of water into ME$2-12$ and ME$3-9$ increased the efficacy of soil removal (due to the higher water content), however due to the error margins noted, it was not possible to assess whether the addition of TAC to the water phase of the Series 2 and 3 microemulsions had any beneficial effect. For the same reason it was not possible to draw conclusions about differences in cleaning efficacy (soiling removal) within each microemulsion series. Using the same samples and assessment criteria as described in section 4.3, additional tests carried out at Tate with four different microemulsion formulations from Series 2 [table 3] – ME$2-1$ (high water/high surfactant); ME$2-3$ (high water/low surfactant); ME$2-13$ (low water/low surfactant); and ME$2-11$ (low water/high surfactant) – confirmed that preparations with higher water content cleaned more efficiently, and that options containing high surfactant levels also increased the rate of soiling removal.

4.4.2. Average Relative Degree of Cleaning Across All Paint Samples and Cleaning Systems

Figure 8 shows the rating scale from $0$ to $5$ where the cleaning systems were ranked in terms of cleaning efficacy based on a visual judgement of the cleaned area after drying. A value of $5$ was considered as clean as the unsoiled control area of each sample. The data presented in fig. 8 indicates that the microemulsions (and some of the TAC and surfactant-containing adjusted aqueous systems) cleaned the samples to the greatest degree. It was also noted, however, that none of the cleaning systems achieved a rating of $5$. For the microemulsions, it appeared that Series 1 resulted in a slightly more clean paint surface than either Series 2 or 3.

4.4.3. Assessing Change During and After Cleaning

Change to the test samples during and after cleaning could be attributed to two primary effects: the removal of dirt (to varying degrees), and a permanent, perceived, undesirable alteration to the paint. Possibilities for unwanted change or effect on the paint consisted of: pigment removal (i.e. color on the swab); swelling/abrasion noted at the paint surface during cleaning; significant gloss change noted after cleaning; or issues connected with clearance of the non-volatile components of the cleaning system, which are currently being explored.

Using the classification scheme and the numerical $1–12$ rating scale described in section 4.3 and Appendix 1, the respective effects of each cleaning system on the four test paints and the acrylic priming were tallied. The tally of observations provided a general idea of how often unwanted change occurred with each system (Ormsby and von Aderkas 2013).
It suffices here to make some general, qualitative observations on the occurrences of unwanted change to the test paints as a consequence of the various cleaning systems under test. The simple aqueous systems provided a useful benchmark in terms of activity on the paint: virtually no incidences of unwanted change occurred with any of the simple water solutions (D.I. water; pH/conductivity-adjusted water; water with either TAC or ECOSURF™ EH-9), with one exception in the case of water plus both TAC and ECOSURF™ EH-9. The simple mineral spirit systems, on the other hand, exhibited more variable activity and sometimes resulted in rapid paint degradation.

### Table 6: Wet-Cleaning Systems Evaluated for Cleaning Performance in Systematic Manual Cleaning Trials Conducted at Tate. Amounts of Each Ingredient Quantified by Weight Proportion

| Preparation Type/Base Solvent | No. | Cleaning Solution |
|-------------------------------|-----|-------------------|
| Aqueous                       |     |                   |
| 1 Deionized water             |     |                   |
| 2 Water, pH 6, 1 mS/cm^b       |     |                   |
| 3 Water, pH 6, 6 mS/cm^b      |     |                   |
| 4 Water, pH 6, 20 mS/cm^b     |     |                   |
| 5 Deionized water + 0.5% w/w ECOSURF™ EH-9 Surfactant | | |
| 6 Deionized water + 0.5% w/w TAC | | |
| 7 Deionized water + 0.5% w/w ECOSURF™ EH-9 Surfactant + 0.5% w/w TAC | | |
| Mineral spirits               |     |                   |
| 8 Shellsol D₄₀ solvent         |     |                   |
| 9 1% w/w ECOSURF™ EH-3 in Shellsol D₄₀ | | |
| 10 0.5% w/w TRITON™ GR-7M Surfactant in Shellsol D₄₀ | | |
| Mineral spirits microemulsion: Series 1 | | |
| 11 ME₁–26                     | 40  | 44                | 6.7  | 3.3  | 6   |
| 12 ME₁–27                     | 50  | 34                | 6.7  | 3.3  | 6   |
| 13 ME₁–30                     | 20  | 70 (including 4 parts NaCl as 5% w/w solution) | 4.2  | 2.1  | 4   |
| Mineral spirits microemulsion: Series 2 | | |
| 14 ME₂–15                     | 68  | 8                 | 3    | 9    | 12  |
| 15 ME₂–15 + TAC               | 68  | 8 (+ 1.2 TAC^a)  | 3    | 9    | 12  |
| 16 ME₂–12                     | 40  | 10                | 6.25 | 18.75| 25  |
| 17 ME₂–12 (water dilution 10:1 v/v) | 40  | 20                | 6.25 | 18.75| 25  |
| 18 ME₂–12 + TAC               | 40  | 10 (+ 1.2 TAC)   | 6.25 | 18.75| 25  |
| Mineral spirits microemulsion: Series 3 | | |
| 19 ME₃–13                     | 63  | 10                | 27   |     |     |
| 20 ME₃–13 + TAC               | 63  | 10 (+ 1.2 TAC^a) | 27   |     |     |
| 21 ME₃–9                      | 36  | 10                | 54   |     |     |
| 22 ME₃–9 (water dilution 10:2 v/v) | 63  | 30                | 27   |     |     |
| 23 ME₃–9 + TAC                | 63  | 10 (+ 1.2 TAC^a) | 27   |     |     |

^aTAC was added in stated proportion as a 5% w/w solution in deionized water.  
^b pH and conductivity set by dil. acetic acid and dil. ammonium hydroxide.
EH9 at 0.5%. The aqueous solutions containing TAC and ECOSURF™ EH-9 Surfactant were almost free of unwanted change (observed at the macro scale) while remaining competitive in terms of cleaning performance.

In similar fashion to the simple aqueous systems, there were few occurrences of unwanted change associated with the set of simple mineral spirit preparations: Shellsol D40 alone, and with added ECOSURF™ EH3 or TRITON™ GR-7M surfactant. However, some dissatisfaction was expressed at the handling properties of these systems and the level of dirt removal they achieved. It was also noted that these systems were “pushing dirt around” and leaving a “haze”. This haze may at least in part be associated with the disturbance of the migrated surfactant layer, causing some scattering of light (Kampasakali et al. 2011), in addition to any soil remaining on the paint surface.

Compared to the simple aqueous solutions and simple mineral spirit preparations, rather more instances of unwanted change to the paint films occurred with the new microemulsion systems, which presumably reflects the enhanced activity of these multi-component formulations. The main cause of the change noted was pigment transfer from the PY3 samples. Exceptions to this general pattern included some of the Series 3 microemulsions (ME3–13 and [ME3–13 + TAC], that is, the lowest surfactant-containing option tested for Series 3) which produced very few instances of unwanted change and offered high cleaning efficacy (see fig. 8).

Overall, of the group of mineral spirits-based microemulsions, the Series 1 options caused slightly fewer occurrences of unwanted change. This may be due to the speed at which the systems removed soiling, thereby reducing mechanical action and contact with the paint surface. The Series 2 microemulsions had a lower cleaning efficacy than Series 1, and caused more unwanted change in the form of pigment transfer, gloss change and surface tackiness, which is presumably at least partially due to the slower cleaning action of this series. The Series 3 microemulsions had the lowest cleaning efficacy of the three series, but had a more controllable action and caused fewer incidences of unwanted change than Series 2. Within Series 3, ME3–13 + TAC did not cause any unwanted change, while ME3–13 resulted in unwanted change for only one sample. Conservators testing the three microemulsion series at Tate and in CAPS workshops also reported that the Series 1 systems tended to act too quickly and were not able to be controlled in a satisfactory way. This may be related to the fact that many of the initial microemulsions tested from Series 1 were primarily water-continuous (OiW) systems.

4.4.4. Samples of Acrylic Priming

Samples of commercial acrylic priming were included in the systematic cleaning trials as they are inherently rougher than the artists’ paint films and represent a more challenging cleaning situation. On the whole, the samples of acrylic priming were resistant to cleaning. None of the simple aqueous and mineral spirit-based solutions cleaned the samples to a significant degree (all reached the 50 swab roll stopping point) and had a degree of cleaning rating ranging from 0 to 2 (of a possible 5). However, the mineral spirit microemulsions (particularly the Series 1 and Series 2 options) proved to be relatively effective on this sample type, requiring between 10–30 swab rolls to reach a stopping point, with an average degree of cleaning rating between 3 and 4. It was also noted that it was particularly difficult to judge unwanted change for these samples, and that due to the roughness and greater surface area inherent to these films, none of the cleaned areas resembled the white unsoiled control. Applying microemulsion systems using a brush, in gelled form or through tissue may be useful options to explore.

5. Treatment Case Studies

Since 2011, the mineral spirits-based microemulsion series have been adopted, where appropriate, as part of the surface-cleaning system testing strategy for unvarnished painted works of art in Tate’s collection. Although the cleaning systems were originally designed and modified for use on acrylic paint substrates, they have also been used on aged oil- and polyvinyl acetate (PVAc)-based painted surfaces, as briefly summarized below, thus demonstrating their applicability to a wider range painted surfaces. It is important to note: that the microemulsion systems were used in combination with more established surface-cleaning methods; that the treatments were evaluated subjectively, not fully scientifically; and that in one case (see 5.1) the evaluation and treatment were not completed due to competing program demands.

5.1. EVA HESSE ADDENDUM (1967). TATE TO2394

This modern sculpture consists of a gray, titanium white-based acrylic dispersion copolymer polyethylene-acrylate/methylmethacrylate paint layer with an additional unpigmented PVAc coating on the rope sections. Several attempts had been made to remove the unwanted soiling from this work in the past, to no avail. During a treatment preparation campaign in 2012–2013, it was established that the paint on the upper portion of the work was neither water nor mineral spirits sensitive and that the bulk of the soiling could be removed using water adjusted to pH
6 and 6 mS/cm conductivity. However, the soiling on the coated rope sections did not respond to a range of adjusted aqueous or simple mineral spirit systems. In addition, the PVAc coating and white paint proved to be sensitive to polar solvents. In light of these constraints, the three series of mineral spirits-based microemulsions were tested on the rope sections. The Series 1 and 2 systems proved effective at removing soiling while leaving the PVAc coating intact. After extensive testing however, the Series 2 microemulsion ME2–15 was chosen as the most appropriate preparation to clean the coated rope surfaces, as it removed the bulk of the soiling while maintaining the integrity of the coating. The microemulsion tests were cleared with Shellsol D40 solvent and the treatment supplemented in some areas, with modified aqueous systems. As mentioned, due to time constraints, this treatment was not completed prior to loan, and may be revisited with a full scientific evaluation in the near future. Figure 9 is a detail of Addendum, showing some of the cleaning tests carried out on one of the rope sections from this work.

5.2. Richard Smith, Piano (1961). Tate TO2003

Richard Smith’s Piano (1961) is a three-dimensional painting constructed from cotton duck on plywood. It is painted in PVAc and possibly oil media. In recent preparations for display, it required treatment in-situ to reduce fingerprints and accumulated soiling resulting from inherent difficulties associated with the handling of this large work. Previous attempts at surface cleaning had been abandoned due to the sensitivity of the yellow paint layer. After brush vacuuming and dry cleaning with sponges, testing for the removal of stubborn fingerprints was carried out using a group of fifteen aqueous and solvent-based systems. To summarize, the soiling on the white passages was successfully reduced using an aqueous system consisting of 0.5% v/v ECOSURF™ EH-9 Surfactant and 0.5% w/v TAC, cleared with pH and conductivity-adjusted water. The scuffs and fingerprints on the water-sensitive yellow passages were successfully reduced using Series 3 microemulsion ME3–9. This system offered controlled, effective dirt removal with no yellow pigment transfer, and clearance using Shellsol D40 solvent posed minimal risk to this water-sensitive passage. The aim of the treatment was to reduce the fingerprints and scuffs so that they no longer drew the eye towards
them; for this, the Series 3 microemulsion proved valuable by facilitating the incremental reduction of finger-marks without compromising the surrounding paint layer through creating over-cleaned areas and/or pigment transfer. Figure 10 shows details of Piano where the scuffs and marks have been reduced.

5.3. J.M.W. TURNER, TWO RECUMBENT NUDE FIGURES (1828). TATE NO. 5517

Turner’s Two Recumbent Nude Figures was conserved in 2011-2012 as preparation for display at Tate Britain. At that point in the collaboration the first series of mineral spirit microemulsions were tested alongside other cleaning systems to remove a very stubborn, aged, multi-layered soil deposit from an aged oil paint film. The painting was initially lightly dry cleaned with sponges, then a series of aqueous-system cleaning tests revealed that the paint layer was slightly water sensitive and prone to blanching. After partial cleaning was achieved using established systems, some of the early Series 1 microemulsions (specifically ME1-27, 28, 29, 30) were tested and found to remove the soiling successfully, at a similar controllable efficacy, apart from the ME1-30 (the highest water content variant) which worked more slowly, presumably due to the predominantly oily nature of the soiling layers. According to our current understanding of this series, all of the microemulsions tested on this painting were OiW compositions (table 2). The background of the painting was cleaned with ME1-27, 28 and 29 using large swabs, the central figure was cleaned with ME1-27 and 28 using smaller swabs and by working through tissue and/or removing the soil-containing microemulsion with

Fig. 9. Detail of cleaning tests (small white areas towards the lower portion, close to the end of the rope) using ME2-15 on Eva Hesse’s Addendum. This treatment was not completed, as the work was required for loan. © Tate, 2013.

Fig. 10. Details from Richard Smith’s Piano; (a) before cleaning and (b) after localized cleaning, as photographed and carried out in the gallery space. The Series 3 microemulsions facilitated the subtle, localized cleaning of unwanted scuffs and marks from this water-sensitive paint, most visible in the area just above the lower black line. © Tate, 2013.
brushes. Shellsol D38 solvent was used to clear the systems, followed by deionized water which was applied to clear possible LAS surfactant residues. Figure 11 shows a detail of the dirt removal process from the damaged, heavily soiled, face and neck area of Two Recumbent Nude Figures.

6. CONCLUSIONS AND FURTHER WORK

The microemulsion systems described here are intended to provide practising conservators with new tools and options for the surface cleaning of artists’ acrylic paints and other water- and solvent-sensitive paint surfaces. The WiO microemulsion formulations, especially, offer possibilities for exploiting positive aspects of water-based cleaning systems (good pick-up and dispersion of soils; control over the conductivity and pH; use of adjuvants such as chelates, etc.) while limiting, to a degree, the risks associated with exposure to aqueous cleaners. The preparations reported here introduce some new surfactant products to conservation, but these microemulsions are intentionally formulated around familiar ingredients, principally mineral spirits and proprietary grades thereof. They are easy to prepare, requiring simple weighing out of the ingredients and minimal shaking by hand. In addition to showing the ranges of proportions that form WiO microemulsions, OiW microemulsions, or other types of mixture, the phase diagrams presented here also provide a graphic framework that can guide the user in fine adjustments of the ingredient proportions in pursuit of optimal cleaning performance.

The preparations under consideration here all involve non-volatile surfactants, and all the usual concerns about such substances apply, foremost of which are the matters of clearance and of the possible risks associated with any non-cleared residues. Scientific studies (including X-ray photoelectron spectroscopy, X-ray absorption near-edge spectroscopy), and Time-of-Flight Secondary Ion Mass Spectrometry are presently under way which seek to assess the effectiveness of the clearance procedures that have been suggested for each of the three microemulsion system types presented, the main principle of which is dilution rinsing with the solvent of the continuous phase. Findings of those studies will be reported in due course (Ormsby et al. in press). One hypothetical advantage of the WiO microemulsions over conventional aqueous cleaning systems is reduced levels of swelling of the paint during exposure to the cleaning liquid; further studies are also envisaged that will examine the validity of this hypothesis in comparative studies of the swelling action on artists’ acrylic paints of these classes of microemulsion compared to common aqueous cleaning solutions.

The new microemulsion preparations described here will continue to be evaluated from the practical point of view by the project members, through continuing systematic cleaning trials on simulated soiled artists’ acrylic paint, through testing in relation to actual conservation treatments, and through inclusion in further iterations of the GCI/Tate CAPS professional development workshops. All of these vehicles for practical testing have provided useful feedback that has guided the technical and scientific development work, and they remain important ancillary activities for our group. The different modes of practical testing have already highlighted some lines of enquiry for further research activity beyond the clearance and swelling issues just noted, for example: determination of the tolerance, especially, of the Series 2 and Series 3 microemulsion systems to adjustment of the conditions (in terms of pH, conductivity, and chelate content) of the water phase; and viability of non-ionic alternatives to sodium dioctylsulfosuccinate in the Series 3-type systems. Additional microemulsion systems prepared from non-ionic surfactants and without higher alcohol co-surfactant may offer advantages in terms of clearance, reduced paint sensitivity, and the possibilities for fine-tuning cleaning action. We hope that this preliminary report on mineral spirits-based microemulsions provides the foundation for further research on and practice with this novel and interesting class of cleaning liquid in which two very dissimilar substances – hydrocarbon solvent and water - are helped through mediation to achieve a compatible, stable relationship.

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APPENDIX

The overall cleaning system ratings used to describe the relative magnitude of overall change to the sample surfaces, incorporating both removed dirt and any perceived alteration to the paint (as judged by eye), were assigned according to the following criteria:

This scheme effectively divides cleaning systems into two classes in terms of their tendency to cause perceptible changes in the paint or not. Cleaning systems rated with even numbers 2–10 produced no perceived alteration to the paint; and within this class higher number ratings reflect greater degree of cleaning. Similarly, cleaning systems rated with odd numbers 1–9 produced some perceived alteration to the paint; and, again, within this class higher number ratings reflect greater degree of cleaning.

Ratings 11 or 12 were adopted for effects of cleaning systems that did not fall clearly into the two classes just mentioned.

| Description of Overall Effect (For Each Rating) | Rating |
|-----------------------------------------------|--------|
| Class: degree of dirt removal with some perceived alteration to paint surface (abrasion/burnishing/pigment loss/swelling/gloss/clearance concerns). | 1 Remove little or no dirt + some change to paint film |
| | 2 Remove little or no dirt + no visual change to paint film |
| | 3 Remove minor amounts of dirt + some change to paint film |
| | 4 Remove minor amounts of dirt + no visual change to paint film |
| | 5 Remove moderate amounts of dirt + some change to paint film |
| | 6 Remove moderate amounts of dirt + no visual change to paint film |
| | 7 Remove majority of dirt + some change to paint film |
| | 8 Remove majority of dirt + no visual change to paint film |
| | 9 Remove all dirt + some visual change to paint film |
| | 10 Remove all dirt + no visual change to paint film |
| | 11 Remove all dirt + no concerns other than clearance |
| | 12 Other |

NOTES

1. The ECOSURF™ EH Non-ionic Surfactants (EH13, EH6, and EH9) are ethoxylated/propoxylated branched alcohol (2-ethyl hexanol) products varying essentially in their degree of ethoxylation/propoxylation and hence HLB value. The ECOSURF™ Surfactant products emerged from earlier studies by the Dow/Tate/GCI collaboration (see Ormsby et al. 2015) as possible alternatives to alkyl phenol ethoxylate (APEO) non-ionic surfactants like TRITON™ X-100. For technical information on the ECOSURF™ Surfactants, see http://www.dow.com/products.

2. Ion chromatography, phosphorous NMR, and conductivity measurements of the four LAS sources indicated that the ionic content of the Sigma-Aldrich grade of LAS was twice that of the other LAS sources (see Table 3). This material also had more total phosphorous content coupled with a higher ratio of pyro-phosphate relative to ortho-phosphate. In general anionic surfactant-based microemulsions can be very sensitive to inorganic electrolytes because the electrolytes can screen electrostatic interactions between the anionic head groups making them less soluble in water (Kizilbash et al. 2011). We believe that the higher ionic content of the Sigma-Aldrich material is preventing the formation of 1-phase microemulsions.

3. The product’s MSDS sheet describes the solvent composition as:

Solvent naphtha (petroleum) light aromatic naphtha CAS# 64742–95–6 ~11% (Medium aliphatic solvent naphtha (petroleum) CAS# 64742–94–5 ~6%)

Heavy aromatic naphtha CAS# 64742–88–7 ~11%

2-ethylhexanol CAS# 104–76–7 ~5%

The presence of a moderate proportion of aromatic naphtha in the petroleum distillate solvent of TRITON™ GR-7M Surfactant gives the product some odor.

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**Further Reading**

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**Sources of Materials**

**TRITON™ GR-7M Surfactant; ECOSURF™ EH Surfactant Series**: Chemical Marketing Concepts, 200 Pickett District Road, New Milford, CT 06776–4416. [http://www.chemicalmarketing.com](http://www.chemicalmarketing.com).

**ECOSURF™ EH-9**: also at Conservation Resources International LLC. [http://www.conservationresources.com](http://www.conservationresources.com). Globally Harmonized System [GHS] (in accordance with United States OSHA Hazard Communication Standard 29CFR 1910) classification for ECOSURF™
EH-9 is: ‘H310: Causes eye irritation (Category 2A); Signal word – Warning’.

Dioctyl sulfosuccinate, sodium salt: Sigma-Aldrich. http://www.sigmaaldrich.com/united-states.html

Globally Harmonized System [GHS] (in accordance with United States OSHA Hazard Communication Standard 29CFR 1910) classifications for dioctyl sulfosuccinate, sodium salt are: ‘H315: Causes skin irritation (Category 2); H318: Causes serious eye damage (Category 1); H402: Harmful to aquatic life (Category 3); Signal word – Danger’.

Nacconol 90G (LAS/sodium dodecylbenzene sulfonate): Stepan. http://www.stepan.com.

Shellsol D38: Talas, 330 Morgan Ave., Brooklyn, NY 11211. www.talasonline.com.

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