Art and Industry:

Novel Approaches to the Evaluation and Development of Cleaning Systems for Artists' Acrylic Latex Paints

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Since their introduction in the mid-1950s, waterborne acrylic latex paints—commonly referred to as acrylic emulsion paints—have been widely adopted by artists.[1] As a class of material, they exhibit great stability, being highly resistant to deterioration, discoloration, embrittlement, and/or mechanical failure. However, new materials present new challenges for those involved in the conservation and restoration of works of art. As renowned British painter David Hockney—one of the pioneers in the artistic use of acrylics—astutely observed:

> *Oil paint has been used by artists for six hundred years, so modern conservators have six centuries of experience to draw on and develop. Acrylics, on the other hand, are little more than half a century old. It is extremely important and very welcome that . . . research into the future conservation of these relatively new materials is being done now to ensure these artworks will be kept in good condition for centuries to come.*[2]

One of the most commonly executed conservation treatments on any work of art is surface cleaning—that is, the removal of dust, dirt, and other accretions and/or deposits that have built up over time. Eventually, the dirt build-up may compromise the painting's appearance to such a degree that a cleaning treatment is warranted. The surface cleaning of acrylic emulsion paintings is, however, not a straightforward procedure, for a number of reasons:

- Acrylic paintings are rarely varnished (unlike traditional oil paintings); as a result, airborne dust and dirt deposit directly onto the paint surface. Acrylic latex paints are generally soft at room temperature, and dirt can become firmly ingrained—in the worst case, permanently embedded in the paint surface. Hence, the margin between successful dirt removal and damage to the paint film can be slim.
- Dirt deposition can be exacerbated by greasy deposits on the surface, such as skin oils resulting from improper handling; indeed, the presence of tenacious dark finger marks is not uncommon with acrylic paintings.
- Artists' acrylic emulsion paints are sensitive to a wide range of liquid agents commonly used for surface cleaning of other works of art, and can be vulnerable to binder swelling and pigment removal during the cleaning process.
- The surfaces of modern and contemporary paintings are often delicately nuanced, with subtle differences in gloss and texture critical to the painting's appearance and coherence, and so even the slightest alteration in surface qualities—by burnishing/roughening or the development of uneven finish—can be highly problematic.
- Surfactant originally present in the paint can migrate and collect at the surface, where it may contribute to the retention of surface dirt, and the removal of surface dirt can also result in the removal of this original surfactant material. Since migrated surfactant could be considered an "original" component of the paint, its possible removal during cleaning treatments is a somewhat contentious issue within conservation: practitioners have not universally agreed whether removal is desirable or acceptable.

One of the key challenges, therefore, is to find cleaning agents which avoid or minimize these risks, but which are also effective at dirt removal. Typically, surface cleaning is done by gently rolling or wiping cotton wool, synthetic fiber, or foam swabs, moistened with a small amount of cleaning liquid, across the surface of the painting (*Figure* 1). In practice, finding a suitable cleaning system for a given painting is normally achieved by ad hoc testing on the object under consideration combined with the expert intuition of conservators; the goal is to try to find a cleaning system that removes dirt at an appropriate speed and with an acceptable level of control over the surface finish. Generally speaking, painting conservators rely on a relatively limited range of chemical ingredients for formulating cleaning systems (surfactants, pH adjusters and regulators, chelates, electrolytes, simple organic solvents) mostly adopted by extension from practices established for the surface cleaning of oil paintings.

Most of the previous cleaning studies on acrylic latex paints, conducted within the conservation profession, have relied on simulating the practical cleaning process by carrying out individual cleaning tests with hand-held swabs laden with cleaning liquid on test paint films (*Figure* 2a).[3] Such approaches to evaluating cleaning performance, while having the advantage of closely replicating the normal cleaning process, are labor-intensive, time-consuming, and difficult to make reproducible. Nevertheless, the few studies of this type that exist have clearly demonstrated that—despite some considerable brand-to-brand variability in terms of paint formulation—use of water-based cleaning agents risks removing migrated surfactant from the surface of the paint, and potentially also from the bulk film.

Other concerns highlighted by research studies include possible pigment removal (especially of organic pigments) and paint swelling by both organic solvent and aqueous systems. Generally speaking, aliphatic (non-aromatic) hydrocarbon solvents have been found to remove less surfactant than aqueous cleaning systems, to cause considerably lower degrees of swelling, and to have minimal effect on bulk film physical properties.[4] However, films pigmented with organic colorants may exhibit an increased tendency for pigment removal when non-polar solvents are used.[5] Although generally more benign in terms of effects on acrylic paints, the cleaning efficacy (i.e., the ability to remove deposited dirt) of simple aliphatic hydrocarbon systems has been found to be appreciably lower than that of aqueous systems.

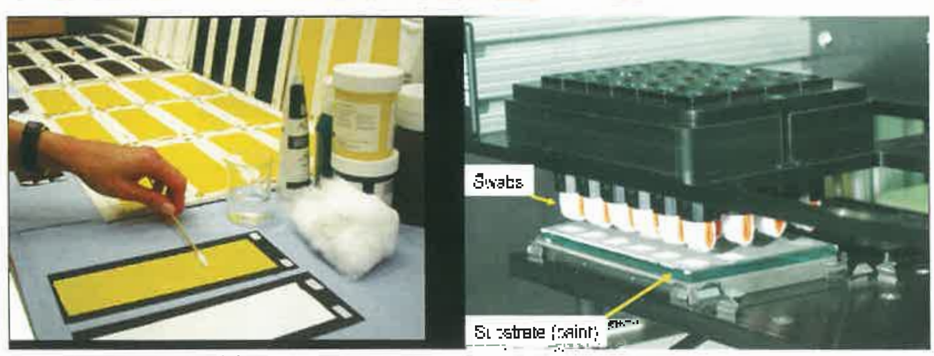
An opportunity to advance research into the cleaning of acrylic paintings arose in early 2008 when scientists in the Coating Materials division at The Dow Chemical Company began a collaboration with the Getty Conservation Institute (GCI) in Los Angeles, and Tate in London, aimed at developing more effective methods for cleaning works of art created with acrylic latex paint. As a leading manufacturer of the base latexes for acrylic house paints, as well as many raw materials used in house paints, cleaning products, fine art acrylic paints, and conservation materials, Dow is applying its expertise in designing and evaluating cleaning systems with art conservators and conservation scientists seeking to preserve important works of art from the last 50 years.

One of the key innovations of this research collaboration has been the application of Dow's high throughput (HTP) automated formulation, testing, and analysis facilities to the problem of evaluating cleaning efficacy of liquids applied in a way that reliably simulates the manual cleaning process typically used by conservators. HTP comprises a sophisticated suite of automated hardware, software, and information research infrastructures that allows for the preparation and analysis of hundreds of samples in a relatively short time period. An integrated set of software programs serves as the backbone for the entire capability to enable complex experimental designs, automated material handling, data collection, data analysis, data storage, and, finally, modeling and mining of large datasets.

In this collaboration, HTP tools from the coatings and consumer products workflows were modified to prepare and screen hundreds of cleaning formulations for the application of surface cleaning fine art acrylic paints. A key element of this work was the adaptation of one of Dow's HTP cleaning robots to closely simulate the process of manual swab cleaning (*Figure* 2b). The leading candidates in each class of cleaning formulation were then evaluated in parallel via manual testing trials by conservators, with guidance and feedback coordinated by researchers at Tate.

Three classes of cleaning solutions were formulated and tested: aqueous, aliphatic hydrocarbon solvents, and water-in-oil microemulsions. The goal for both the aqueous and aliphatic hydrocarbon solvent-based options was to formulate systems with optimum cleaning efficacy, so that contact time with the paint surface could be minimized during cleaning procedures. Ideally, only volatile components

Figure 1—Dr. Bronwyn Ormsby, senior conservation scientist, Tate, London, surface cleaning Alexander Liberman's acrylic painting *Andromeda*, 1962 (Tate T00650). Photo: Tate, 2008. © Liberman Art partners.



(a) (b)

Figure 2—(a): Typical approach to evaluation of performance of cleaning systems on artists' acrylic paints: manual swab application on reference paint films. Image © Tate, 2004. (b): HTP robotic cleaning device adapted to simulate manual swab cleaning of artists' acrylic paints.

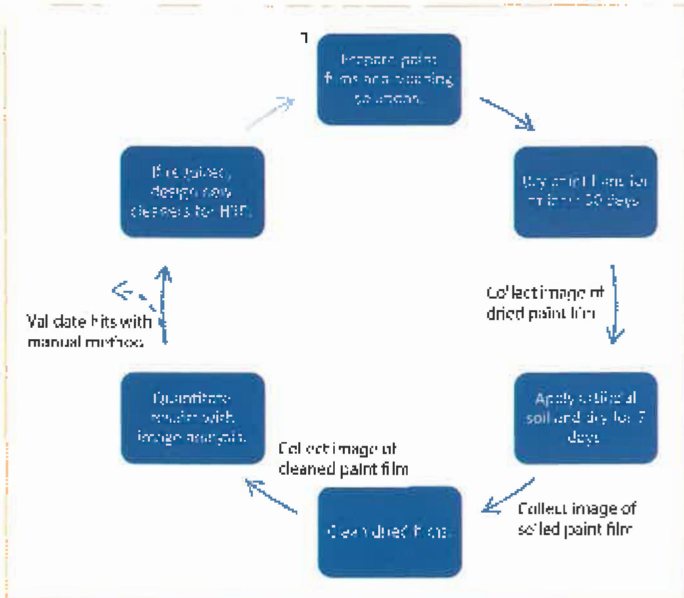


Figure 3—Schematic of general workflow for HTP cleaning method.

Table 1—Composition of the Artificial Soil Used in the HTP and Subjective Tests of Cleaning Performance

Component	% (w/w)
Carbon black	0.2
Iron oxide (ochre)	0.1
Silica	0.2
Kaolin	2.4
Gelatine powder	1.2
Soluble starch	1.2
Cement (type I)	2.1
Olive oil	1.2
Mineral oil	1.9
VM&P naphtha	89.6

would be used to ensure their complete evaporation from the paint surface after cleaning. However, in practice, conservators often rely on the addition of nonvolatile components in cleaning systems and then attempt to completely clear any residues of that formulation after use. In addition, the impact of additive concentrations and solution conductivity on cleaning efficacy was systematically explored via experiments designed to minimize system residue and potential damage to the dried paint films.

Water-in-oil microemulsions are a relatively new material class to the painting conservation field. They consist of a fluid, thermodynamically stable dispersion of oil (in this case, aliphatic hydrocarbon solvent) and water, with domain sizes in the hundreds of angstroms range, and, as such, tend to form clear systems. They typically contain surfactant and co-solvents to help compatibilize the solvent and water sub-phases. Microemulsions were identified as a group of materials that could address the deficiencies of water-based and aliphatic hydrocarbon solvent systems. In traditional cleaning solutions, aqueous systems have more powerful cleaning efficacy but also potentially pose more risk to paint films. As discussed earlier, it is known that aqueous systems are particularly prone to remove original material from the paint surface. Exposure to water will also temporarily change the physical properties of the paint film and the long-term implications of water exposure and removal of the surfactant from the paint matrix remain unknown. Aliphatic hydrocarbon solvent-based systems are believed to have less impact on the original paint film, but demonstrate poorer cleaning efficacy.

To produce a microemulsion, the correct combination of surfactant type, co-solvent type, and solvent must be found and tailored to specific applications. In the initial screening, a commercial microemulsion tailored for industrial cleaning, INVERT™ 5000, was investigated.[6] This system demonstrated high cleaning efficacy, but poor clearance from the paint film due to low volatility. In addition, it was noted as causing pigment removal on some of the manually evaluated samples. A series of water-in-oil microemulsions was then formulated and tested using the HTP equipment. The aim of these new materials is to provide art conservators an improved and/or alternative approach to cleaning modern works of art, and particularly those works that are sensitive to water.

In this article, an overview of this research collaboration is given, outlining a method to quantify and differentiate the cleaning efficacy of aqueous, aliphatic hydrocarbon solvent, and water-in-oil microemulsion-based cleaning solutions for soiled acrylic paint films using the HTP tools and software.

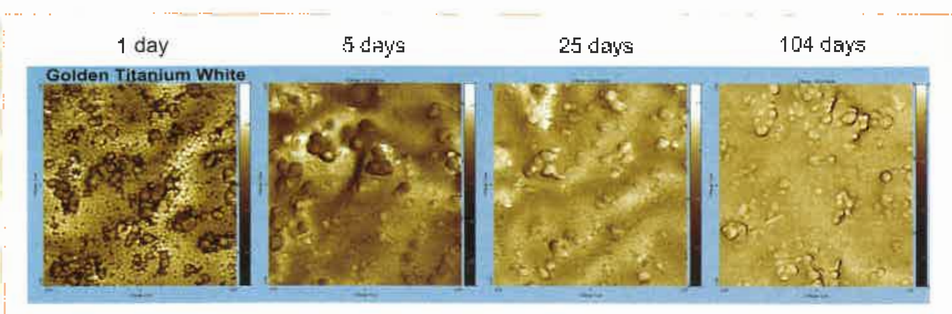


Figure 4—Drying and stabilization of Golden Heavy Body Acrylic titanium white artists' paint. Tapping Mode AFM images of paints at intervals of 1, 5, 25, and 104 days after application.

This is followed by an outline of the manual evaluations carried out to further test these systems under more realistic conservation treatment conditions.

EXPERIMENTAL

High Throughput Evaluation of Cleaning Efficacy

The overall goal of the HTP approach was to devise a method that reliably simulated the manual swab cleaning of a painted surface, which was reproducible, quantitative, and allowed for rapid screening of a large number of cleaning solutions. The general HTP workflow is outlined in the schematic in *Figure* 3.

Sample Preparation for HTP Cleaning Evaluations

All of the HTP cleaning evaluations were carried out on films prepared from Golden Heavy Body Acrylic titanium white paint, cast onto glass slides to a dry film thickness of ~200 µm. The cast paint films were dried in a controlled environment of 25°C/50% RH for at least 30 days prior to coating with an artificial soil mixture prepared according to a formulation developed in earlier studies (*Table* 1).[7] The artificial soil mixture was prepared by blending together the solid and liquid constituents and then brushed onto the dried paint films using a foam applicator. Two applications of soil were applied to provide a medium-to-heavy coating. The soiled films were then dried for seven days prior to the HTP cleaning evaluation.

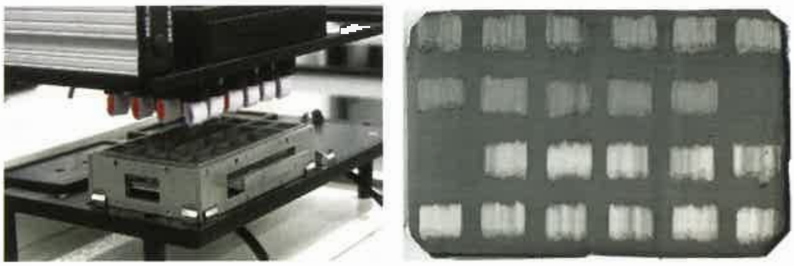
In developing the methodology for the preparation of samples for HTP cleaning evaluations, it was important to determine the time taken for the applied test paint films to dry (i.e., coalesce) completely, since this factor governed the time periods between paint film preparation, application of the artificial soil, and HTP testing. Also of interest was the migration and deposition of surfactant at the paint surface.[8,3] Accordingly, in the development phase of the HTP project, changes in the test paint films over time during the initial period of drying were monitored using atomic force microscopy (AFM) (*Figure* 4). Details of the AFM method and selected results for the Golden Heavy Body Acrylic titanium white paint are given in the *Appendix*.

Cleaning Liquids

A range of aqueous and aliphatic hydrocarbon solvent based cleaning solutions were tested for cleaning efficacy using the HTP method. In addition, one commercial and a series of newly formulated water-in-oil microemulsions were examined. The formulations were prepared either manually or using robotic liquid handlers that are part of the HTP work process. The formulations tested were based on raw materials that included both chemicals currently used in art conservation and materials new to the conservation field (*Table* 2).

Table 2—Raw Materials Used in Cleaning Formulations Tested with the HTP Method

Surfactants	
SatinFX™	ethylene oxide/butylene oxide block copolymer (EOBO)
TRITON™ CG-110	alkyl polyglucoside
TRITON X-100	alkyl phenol ethoxylate
ECOSURF™ EH6	alcohol alkoxylate (nonionic)
ECOSURF EH9	alcohol alkoxylate (nonionic)
ECOSURF SA9	alcohol alkoxylate (nonionic)
LAS	linear alkyl sulfonate
Solvents	
Water	
Ethanol	
VM&P naphtha	aliphatic hydrocarbon blend
Shellsol D38	aliphatic hydrocarbon blend
1-Hexanol	
1-Butanol	
DOWANOL™ DPnB	dipropylene glycol n-butyl ether major isomer: $C_4H_9O[CH_2CH(CH_3)O]_2H$
DOWANOL EPh	ethylene glycol phenyl ether $Ph-OCH_2CH_2OH$
Hexyl CARBITOL™	diethylene glycol monohexyl ether $C_6H_{13}(OCH_2CH_2)_2OH$
Butyl CELLOSOLVE™	ethylene glycol monobutyl ether $C_4H_9OCH_2CH_2OH$
Salts and Chelates	
VERSENE™ NA$_2$	EDTA disodium salt
Triammonium citrate	citric acid, tri-ammonium salt
NaCl	sodium chloride
Commercial Microemulsion	
INVERT™ 5000	water-in-oil microemulsion



(a) (b)

Figure 5—(a) HTP cleaning device. (b) Artificially soiled paint film cleaned with HTP device. Top 11 locations cleaned with water, bottom 11 locations cleaned with a formulated aqueous cleaning solution. The greater efficacy of the formulated cleaning liquid is clearly evident. Two locations in rows 2 and 3 were left uncleaned as reference controls.

HTP Cleaning Device

The HTP cleaning device used in this work (*Figure* 5) consists of a movable head-piece fitted with up to 24 "brushes," which can be brought into gentle contact with the substrate to be cleaned (in

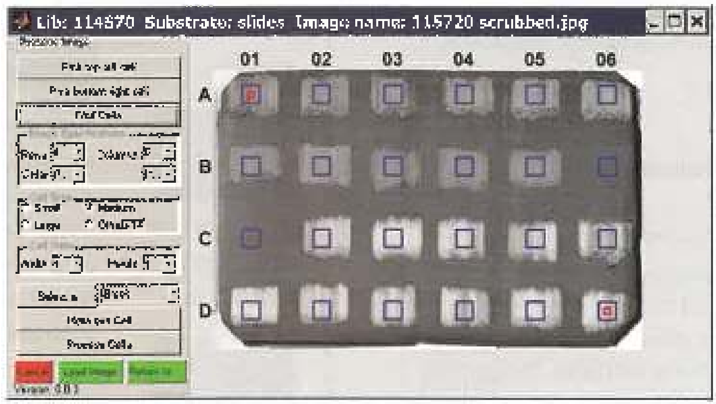


Figure 6—Screenshot of image analysis software in operation for quantification of change in color of cleaned areas.

this case, the artificially soiled acrylic paint films). The soiled paint film is clamped at the base of a jig that forms 24 non-communicable cells, each capable of receiving a small quantity of cleaning liquid delivered via an automated pipette. The device is programmed so that, as soon as cleaning liquid is delivered to the cells, the head (with the brushes in contact with the soiled paint surface) oscillates gently in the y direction for a specified number of cycles. The cleaning robot thus allows for 24 locations on each test paint film to be cleaned simultaneously under near identical physical conditions: each location was treated with the same amount of cleaning solution, the same applied pressure, the same speed, and for the same number of cleaning cycles.

The "brushes" used here were chosen so as to be similar in composition and stiffness to the cotton swabs typically used by painting conservators. They consisted of a foam interior (to provide stiffness) covered with cotton batting. Again, in order to closely simulate the practical process of cleaning works of art in which low liquid volumes are typically used, the quantity of cleaning solution was standardized at 50 µl per cell. The speed of the robotic cleaning strokes was one second per stroke. For the evaluation of aqueous-based cleaning solutions, four strokes (two passes back and forth) were used, and for aliphatic hydrocarbon solvent-based systems which were generally less active than aqueous formulations—24 strokes (12 passes back and forth) were used. New cleaning swabs were used for each cleaning trial.

Figure 7—Initial development of the HTP cleaning method. Raw images of paint samples cleaned with aqueous liquids (top) and VM&P naphtha based systems (bottom).

Quantification of Cleaning Efficacy

The cleaning efficacy of each test liquid was quantified via measurement of differences in color appearance between the original dried (unsoiled) paint, the soiled paint, and the cleaned paint. Color differences were calculated from CIE L*a*b* measurements derived from digital images of the paint films at each condition. Cleaning efficacy was defined as the ratio ($\Delta E_2/\Delta E_1$) of two color difference values:

ΔE_1—color difference between initial state and soiled (uncleaned) state:

ΔE_2—color difference between soiled state and cleaned state.

The color measurements were generated by analysis of scanned images using dedicated Matlab-based software developed by the Information Research group at Dow. A screen capture from the software (*Figure* 6) illustrates the process by which cleaning efficacy data is obtained for each cell within a single test matrix. For this type of analysis, the software allows the user to select the color space (XYZ, L*a*b*) and the specific regions of the sample to be analyzed. In the example shown in *Figure* 6, color values are being measured for the area within each blue box. The overall cleaning efficacy (*% clean*) determined for any given liquid was taken as the average of the results obtained for a series (usually between 3 and 12) of replicate cells.

Sample Preparation for Manual Evaluation of Cleaning Efficacy by Conservators

The test paint films used for the subjective evaluations by conservators differed from those used for the HTP study in terms of substrate, number of brands tested, age, and the soiling method used. These samples were developed independently and were designed to approximate painting surfaces as closely as possible. This sample group consisted of four brands of professional artists' quality acrylic paints (Winsor & Newton, Liquitex, Talens, and Golden Artist Colors) cast onto a Fredrix 10 oz double-acrylic dispersion primed cotton duck canvas using a Sheen instruments adjustable film caster to a dry film thickness of ~110 µm. In total, a group of 23 samples—14 titanium white (PW6) and 9 azo yellow (PY3)—were evaluated. All samples were cast in 2003; some were thermally aged prior to soiling in a Fisons 185 HWC environmental oven (60°C: 55% RH) for 16 weeks; others were light aged at 15,000 lux for 16 weeks under Philips TLD 58W/840 daylight fluorescent tubes with the UV component filtered by acrylic sheet. Assuming reciprocity, this is equivalent to ~50 years' exposure under normal museum conditions. All samples were soiled via spraying rather than brushing in 2006, after the initial period of natural or accelerated aging. After soiling, all samples had a further three years' natural aging in dark conditions prior to serving in the cleaning efficacy tests. The same artificial soil mixture was used for the subjective tests at Tate as in the HTP tests at Dow (*Table* 1). The relative cleaning performance of a range of liquids was evaluated by manual testing and visual observations, as outlined in the Results section.

RESULTS

Initial Development of the HTP Cleaning Method

The reproducibility of the HTP cleaning method was determined in a series of 11 replicate cleaning trials using four cleaning liquids expected to vary quite significantly in performance (see *Table* 3). Typical raw data from those trials (i.e., digital images of the soiled samples cleaned by the HTP robot) are shown in *Figure* 7. The standard deviation of the method ranged from ±5–10%. This level of noise was sufficient to differentiate the performance of the large number of cleaning solutions investigated. The goal of the HTP method was to screen a large number of cleaning solutions and identify a smaller

Table 3—Initial Development of the HTP Cleaning Method. Values for % Clean and Standard Deviations for % Clean of Selected Cleaning Liquids

Cleaning Liquid	% Clean	Std. Dev. % Clean
Water	13	5
Water + TRITON™ X-100 Surfactant + triammonium citrate (98 : 1 : 1 by weight)	54	7
VM&P naphtha	44	7
VM&P naphtha + 1% LAS + 3% FOBO	53	11

group of potential candidates. These potential candidates were then evaluated using more traditional and often more rigorous methods prior to commercialization or, in this case, recommendations to the art conservation field. The *% clean* values for the formulated aqueous cleaning solution and the formulated aliphatic hydrocarbon solvent-based cleaning solution systems were the same. However, significantly more cleaning strokes were required to achieve this performance with the VM&P naphtha (aliphatic hydrocarbon) formulation. As noted in the Experimental section, the conditions for the aqueous and aliphatic hydrocarbon solvent-based systems were adjusted to allow for differentiated performance in each class: tests with aqueous systems employed four strokes of the automated cleaning brushes, whereas tests with naphtha-based systems used 24 strokes.

Also investigated were the influences of various additives (surfactants types, solvents, chelating agents, etc.) on the cleaning efficacy of aqueous and naphtha-based cleaning preparations. A subset of the aqueous cleaning solutions tested in the initial trials is listed in *Table* 4 with the corresponding *% clean* values. Cleaning efficacy ranged from approximately 10% to 80% for the aqueous formulations. The highest performing aqueous formulation of this group consisted of 1% triammonium citrate and 1% ECOSURF™ EH9, the latter substance being an alcohol alkoxylate non-APE surfactant manufactured by Dow. In a later stage of the project, further, focused studies (reported as follows) were executed with this combination of ingredients in order to examine the impact of surfactant concentration, solution pH, and conductivity on cleaning efficacy.

The automated instrumentation used in HTP research projects at Dow is supported by an integrated set of software programs to allow complex experimental design, automated material handling, data collection, data analysis, data storage, and finally modeling and mining of large datasets. Data visualization software is routinely used to aid in data analysis and mining. An example of the output from this type of analysis is shown in *Figure* 8. In this plot, generated using a commercial software package, Miner3D,[10] the respective cleaning performance of each of the group of formulations is demonstrated visually. The cleaning efficacy of each solution is represented by the color and size of the circles: large blue circles represent high cleaning efficacy and small red circles represent poor cleaning efficacy. The variability in cleaning performance of each cleaning solution within a set of replicates is indicated by the multiple entries along the x-axis which represent cleaning trials of the same formulation at different locations on the soiled substrate. The actual cleaning efficacy for each replicate in a set is listed at the top right corner of each circle. Finally, the software allows for the area of the original, soiled, and cleaned images used in the ΔE color difference calculations to be viewed alongside the measured performance results. This type of data analysis allows the HTP user to quickly review large volumes of data.

Influence of pH on Cleaning Efficacy

The influence of pH on the efficacy of an aqueous cleaning system was studied with a series of aqueous solutions formulated with 0.1 wt% ECOSURF™ EH9 surfactant titrated with dilute HCl or NaOH to integer values within the pH range 4 to 10. The results are summarized in *Figure* 9, from which it can be seen that for this simple water/surfactant system the cleaning efficacy was significantly lower for the solutions at pH 6 and pH 7 compared to the solutions above and below that pH range.

Influence of Surfactant and Chelate Concentrations

A study designed to explore the influence on cleaning efficacy of surfactant and triammonium citrate concentrations was also executed using the HTP cleaning method. A full factorial design was executed in order to look at the main effects of the independent variables or factors (surfactant level and triammonium citrate level) on cleaning performance in addition to identifying any interaction effects that exist between the factors. An interaction effect exists when differences in one factor depend on the level of another factor.

The composition of cleaning solutions tested (shown in *Table* 5) were trialed in replicates of three. The number of cleaning strokes was lowered

Table 4—Initial Development of the HTP Cleaning Method. Cleaning Performance of Aqueous Systems Evaluated Using the HTP Method[a]

Cleaning System	% Clean	Std. Dev. (%)	Tukey-Kramer Classification					
1% ECOSURF™ EH9 + 1% triammonium citrate	78.6	2.6	A					
2.5% Hexyl CARBITOL™ + 1% LAS +2.5% VERSENE™ Na_2	73.4	9.0	A	B				
1% ECOSURF EH9 + 0.25% triammonium citrate	69.4	7.4	A	B	C			
1% TRITON™ X-100 + 0.25% triammonium citrate	68.6	6.9	A	B	C			
1% TRITON X-100 + 1% triammonium citrate	68.4	7.3	A	B	C			
1% TRITON CG-110 + 1% triammonium citrate	61.8	7.7		B	C	D		
2.5% DOWANOL™ DPnB + 1% LAS + 0.25% VERSENE Na_2	56.8	6.5			C	D		
2.5% DOWANOL EPh + 1% LAS + 2.5% VERSENE Na_2	55.6	8.5			C	D	E	
2.5% DOWANOL DPnB + 1% LAS + 2.5% VERSENE Na_2	55.2	5.5			C	D	E	
1% LAS + 0.25% VERSENE Na_2	40.3	13.3					E	
1% Ethanol	14.0	11.4						F
5% Ethanol	13.0	9.1						F
Water	12.5	5.1						F

(a) The Tukey-Kramer HSD (honestly significant difference) statistical test was applied to the dataset; cleaning formulations not connected by the same letter are significantly different in terms of performance.

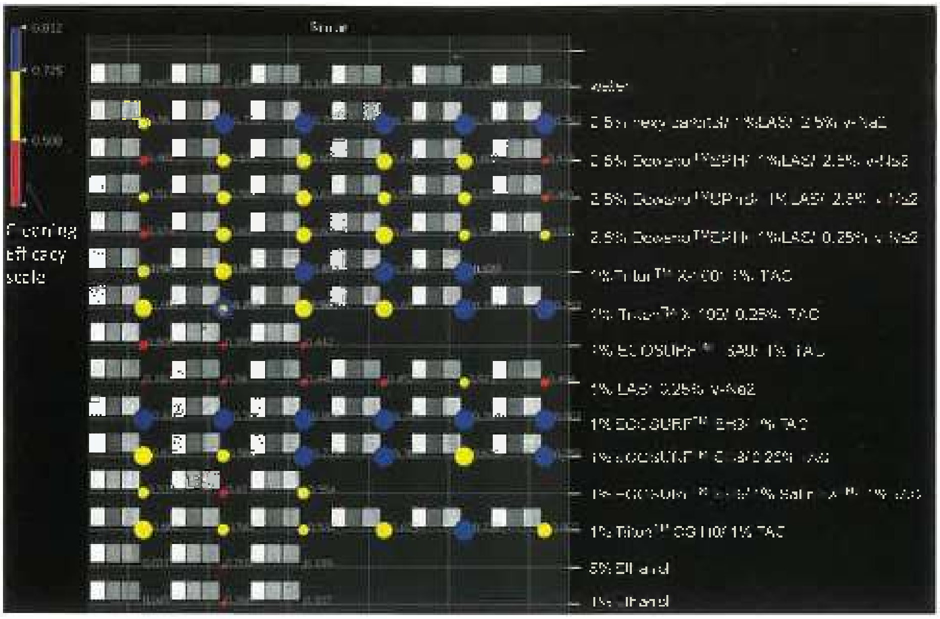


Figure 8—Cleaning performance of a series of formulations. The size and color of the circles represent the cleaning efficacy. Large blue circles correlate with high cleaning efficacy. Small red circles correlate with poor cleaning efficacy. The x-axis shows the variability of the method with replicate cleaning trials of the same formulation at different locations on the soiled substrates. The images of the original, soiled, and cleaned films used to calculate the % clean using the image analysis software are shown for each trial. The cleaning efficacy value is listed to the right of the images.

from four to two for this study to increase the resolution between cleaning solutions with relatively high cleaning efficacy.

A model based on the concentrations of ECOSURF™ EH9 surfactant and triammonium citrate was developed with an R square value of 77%. Both the surfactant level and triammonium citrate level were significant in the model developed for cleaning efficacy. In addition, the cross-product of the independent variables was also significant in the model. This indicates that an interaction effect does exist between the surfactant level and triammonium citrate level on cleaning efficacy. This can be seen visually in the plot of predicted performance based on level of surfactant and triammonium citrate (shown in *Figure* 10) where the cleaning efficacy is poor when either additive is present at low levels regardless of the level of the other factor. The level of triammonium citrate was directly correlated to the conductivity of the cleaning solutions. This correlation allowed for a second model of the concentration of ECOSURF EH9 surfactant and solution conductivity. This model had the same quality and significant factors as the first model. The plot in *Figure* 10 also shows the predicted performance of the cleaning solutions based on conductivity. The formulation space with the highest predicted clean ing performance was with 1 wt% ECOSURF EH9 surfactant and 0.75–1 wt% triammonium citrate and 7.5–10 mS/cm in solution conductivity. The clean efficacy model predictions were validated in subsequent cleaning trials. This type of analysis across a broad formulation space provides the practitioner with information about the trade offs between the surfactant loading, solution conductivity, and overall cleaning performance.

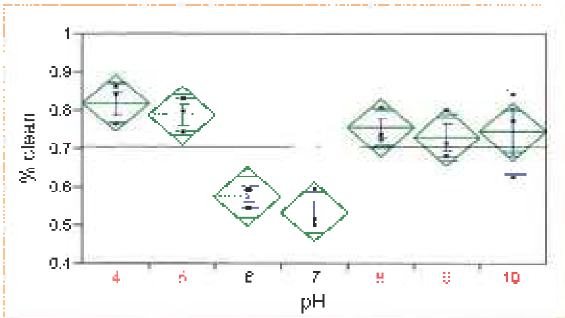


Figure 9—Cleaning performance of a series of aqueous solutions formulated with 0.1 wt% ECOSURF EH9 Surfactant at pH ranging from 4 to 10. The formulations with pH levels below 6 and above 7 were more effective cleaning agents.

Table 5—Relationship between Composition, Conductivity, and Performance of Aqueous Cleaning Systems Based on Nonionic Surfactant (ECOSURF EH9) and Chelate (Triammonium Citrate)

ECOSURF EH9 (wt%)	Triammonium Citrate (wt%)	Conductivity (mS/cm)	% Clean
0.1	1.0	8.47	17
0.1	0.1	1.62	16
0.55	0.55	5.95	31
1.0	1.0	10.3	60
1.0	0.55	5.19	37
1.0	0.1	1.2	25

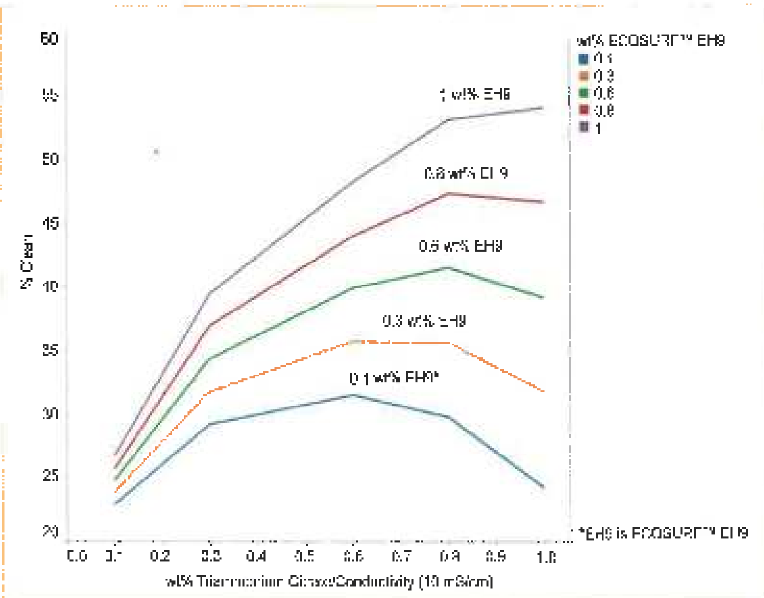


Figure 10—Predicted cleaning performance based on concentrations of ECOSURF™ EH9 surfactant, triammonium citrate, and solution conductivity (x10 mS/cm).

Performance of Naphtha-Based Cleaning Systems

The identification of effective aliphatic hydrocarbon solvent-based cleaning solutions proved to be a greater challenge than for the aqueous systems. Generally speaking, additions of conventional surfactants and oxygenated solvents to VM&P naphtha resulted in systems that had relatively poor cleaning performance. However, formulations composed of VM&P naphtha with additions of a novel nonionic poly(ethylene oxide)/co-poly(butylene oxide) surfactant (EOBO) in combination with Linear Alkyl Sulfonate (LAS) were found by the HTP trials to have improved performance (*Table* 6). Both experimental and commercial grades of the EOBO material were found to have similar performance: optimal proportions (%wt) according to the HTP test results were 1% LAS + 3% EOBO. (Note: the experimental grade of the nonionic surfactant is here denoted by EOBO; the commercial grade has the trade name SatinFX™).

Water-in-Oil Microemulsions

Given the limited enhancements to cleaning performance generally achieved by simple additions of surfactant to an aliphatic hydrocarbon solvent (naphtha), alternative approaches to developing naphtha-based cleaning systems were explored, including water-in-oil microemulsions. Initial attention focused on an existing Dow microemulsion product, INVERT™ 5000, developed in the mid-1990s.[12] Like all true microemulsions, INVERT 5000 is a thermodynamically stable and optically clear formulation; it is formulated from water, naphtha-type aliphatic hydrocarbon solvent, ionic surfactants, glycol ether co-solvents, and other minor ingredients.

The performance of the microemulsion product was evaluated against the most effective aqueous and mineral spirit systems identified in the HTP method. In this comparison study, the number of cleaning strokes was kept constant at 24 for both the aqueous and hydrocarbon solvent based systems. The results (*Table* 7) demonstrate that the cleaning efficacy of the microemulsion system was significantly higher than neat VM&P naphtha and a VM&P naphtha + EOBO surfactant formulation as discussed in the previous section. In addition, in statistical terms, the cleaning performance achieved the same level as the highest efficacy aqueous systems.

Subjective Evaluation of Cleaning Efficacy

As discussed, the HTP testing method was designed to screen a large number of cleaning solutions rapidly. The high scoring HTP cleaning systems were then further assessed through initial field trials at Tate using established conservation swab rolling techniques. This stage is important in the development of new products for conservation as the factors that influence success naturally increase in number and complexity as the evaluations more closely approximate the processes involved in conserving and restoring works of art.

For this study, the systematic application of a range of cleaning systems using uniform size cotton swabs provided complementary information to the HTP trials through information gained from the following assessments:

1. Visual assessment of relative degree of cleaning (soil removal efficacy) after 8 x swab rolls—this correlates most directly to the HTP results.
2. Number of swab rolls required to clean paint films to a chosen stopping point—i.e., the "complete clean" stage—determined as either when: the sample was acceptably clean/pigment was removed from the underlying paint film/swelling of the paint film was noted/surface change/damage was noted/100 swab rolls had been applied.
3. Visual assessment of the relative degree of soiling removal at the "complete clean" stage.
4. Application of a relative degree of "change/damage" score to the paint film: e.g., combining the effects of pigment removal, gloss change, swelling, and/or abrasion of the paint surface.
5. Assessment of cleaning solution handling properties: consistency of swabbing action, control, surface wetting, and clearance after application.

Table 8 contains the results from all of the subjective cleaning evaluations. The first assessment approximated the cleaning efficacy achieved with the HTP system at ~8 swab rolls (consisting of 8 x 1 forward and back swab rolls). Each cleaning solution was applied to the 23 soiled test paint canvas samples and the results judged by eye and expressed in a scale ranging from 1 to 10, where 10 was the most effective system at removing soiling (Column A). Eight swab rolls did not clean many of the samples to a significant degree; hence, the maximum rating was rated as 5/10. Nonetheless, the solutions rated highest in terms of cleaning efficacy were the neat and diluted INVERT™ 5000 microemulsions. The next most efficient cleaning solutions included the surfactant and chelating agent combinations, followed by various simple aqueous systems, with the nonpolar aliphatic-based solutions consistently rating poorly. The performance of the different cleaning solutions in this evaluation had good agreement with the reported HTP system results.

When the "complete" clean results were judged by eye (Column D), the mineral spirit-based solutions remained the least successful at removing soiling and the INVERT 5000 microemulsion was the most successful alongside the aqueous surfactant and chelating agent combinations. The group of simple aqueous systems also cleaned moderately well. While still rating relatively poorly, the SatinFX™/LAS mineral spirit combinations offered an improvement in cleaning efficacy over the pure mineral spirit solvent option. It was also noted that cleaning efficacy appears to partly depend on the wetting power of each cleaning solution and that the paint film surface texture also affected the relative ease of cleaning, i.e., samples with regular, flat surfaces tended to clean more easily.

During the complete clean stage, observations were also made on any visible risks associated with each of the cleaning systems. This included assessing issues critical to art conservation such as pigment loss, swelling, and changes to the paint surface. For this, a rating system was developed to indicate the level of "change/damage" caused (Column E). The solutions with the lowest number posed the highest risk—where combined pigment

Table 6—Performance of Naphtha-Based Cleaning Systems Evaluated Using the HTP Method

VM&P Naphtha-Based Cleaning Systems								
Additives and Proportion	**% Clean**	**Std. Dev. (%)**	**Tukey-Kramer Class**					
1% LAS 3% EOBO	74.5	17.5	A					
1% LAS 3% SatinFX™	73.4	7.1	A	B				
0.5% LAS 1.5% EOBO	60.2	5.3	A	B	C			
VM&P Naphtha	38.7	13.8			C	D		
2.5% Hexyl CARBITOL™ 2.5% DOWANOL™ DPnB 1% LAS	33.2	6.2			C	D		
2.5% Butyl CELLOSOLVE™ 2.5% DOWANOL DPnB 1% LAS	19.5	4.5				D		

Table 7—Performance of INVERT 5000 Microemulsion Compared with Selected Aqueous and Aliphatic Hydrocarbon Solvent-Based Cleaning Systems

Cleaning System	% Clean	Std. Dev. (%)	Tukey-Kramer Class	
1% ECOSURF™ EH9 0.25% triammonium citrate	93.2	1.2	A	
1% TRITON™ X-100 0.25% triammonium citrate	92.6	5.6	A	
INVERT 5000	84.3	3.1	A	
VM&P naphtha 1% LAS 3% SatinFX	63.0	6.0		B
VM&P naphtha	41.2	4.1		C

Table 8—Combined Results for Swab-Roll Tests on 23 Different Paint Films on Acrylic Primed Canvas

	Material/Solution (Concentration)					
	A. Clean Rating after 8 Swab Rolls: 1-10, 10=clean	B. Number of Swab Rolls to Fully Clean	Std. Dev. B. Number of Swab Rolls to Fully Clean	C. Rating for Speed of Cleaning: 1-10, 10=fastest	D. Clean Rating Final Clean: 1-10, 10=clean	E. Relative "Change/Damage" Rating: 1=worst, 10=best
Water +						
Carbonated water (syphon)	3	58	29	6	7	8
Saliva	3	58	25	6	7	8
Deionized water (DI)	3	62	29	5	7	10
Tap water	3	67	26	5	6	10
DI water, pH 5.0 (with acetic acid)	3	69	27	5	6	10
1% v/v ethanol in DI water	3	66	25	5	6	10
Water + Surfactant and/or Chelate						
1% w/v TAC + 1% v/v TRITON™ XL-80N in DI water	4	42	23	7	8	7
1% ECOSURF™ EH9 + 1% TAC in DI water	4	44	25	7	8	7
1% ECOSURF EH9 + 0.5% TAC in DI water	4	44	24	7	8	7
1% w/v TAC solution in DI water	3	57	27	6	7	8
Microemulsion						
INVERT™ 5000	5	15	12	10	8	1
INVERT 5000 (diluted 1:1 with 120-160°C petroleum spirit)	5	23	14	9	8	3
Aliphatic Hydrocarbon Solvent + Surfactant						
2% SatinFX™ + 0.5% LAS in 80-100°C petroleum spirit	1	82	26	3	5	10
1% SatinFX + 0.5% LAS in 80-100°C petroleum spirit	1	81	23	3	5	10

loss, paint loss, gloss alteration, and surface abrasion were noted. The highest ranking (10) was attributed to solutions where no damage/change was noted either during or after cleaning. Differences were further refined according to the number of samples affected; hence, if a particular solution caused change/damage to only one sample, the rating was lower than one that had repeatedly caused change/damage.

Not surprisingly, these "risk" observations had a dramatic effect on the rating of some systems. For example, INVERT 5000, which rated highest in terms of cleaning efficacy, rated relatively poorly with regard to change/damage. With this system, pigment transfer was noted with 17 of the 23 samples tested, subsequently reducing to six samples when using the diluted system. The aqueous surfactant and chelating agent combinations also rated highly in terms of cleaning efficacy. However, they were often affected by foaming at the paint surface which resulted in poor visibility during the cleaning process and prompted concerns about adequate clearance from the paint surface. The simple aqueous systems did not appear to cause any visible damage/change during or after treatment. Of the mineral spirits systems tested, the SatinFX/LAS mixture rated well in terms of low damage potential, and therefore may be of some use in situations where aqueous systems and water-in-oil microemulsions are not suitable. It was noted that, in all cases, migrated surfactant was removed to some extent. However, the amounts removed by the solvent-based systems tended to be less than all of the systems that contained water, including the INVERT 5000 microemulsion.

Custom-Formulated Microemulsion Systems

Based on the overall performance of the first microemulsion tested, which was originally designed for industrial cleaning applications, a range of new, tailored microemulsions have been formulated with the aim of maintaining a high level of cleaning efficacy while minimizing the potential deficiencies of pigment transfer and swelling of the acrylic polymer noted during the subjective testing trials. To achieve this, the DOWANOL™ PnBGE and DOWANOL DPnP GE co-solvents present in the initial microemulsion were replaced with 1-butanol and 1-hexanol, which have lower boiling points, faster evaporation rates, and lower solubility in acrylic polymers. The higher volatility of the alcohols is also advantageous as this will help minimize the need for a clearance step of the cleaning solution. The aliphatic hydrocarbon solvent-based continuous phase was also changed from VM&P naphtha to Shellsol™ D38, which has a lower evaporation rate and will provide conservators with more time to execute the cleaning procedure.

The software application Library Studio (Accelrys)[13] was used to design the microemulsion formulations that were prepared using the HTP robotic liquid handler (Hamilton Microlab Star).[14] Formulations were prepared at a small scale, using 1.2 ml glass vials in a 96-well format, arranged in an 8 row by 12 column array. Each group of 96-well vials is referred to within as a plate. *Figure* 11 is a visual representation of how the composition of the microemulsions varied across the 96-well plate design. The concentration of Shellsol D38 was kept constant for each plate and multiple plates were prepared to test different amounts of Shellsol D38. The concentration of surfactant, co-solvent (alcohol), and salt was varied across each plate. A mixture of 1-butanol and 1-hexanol was used as a co-solvent blend, and the ratio between the two was varied across each level of surfactant to assess the effect of hydrophobicity on formation of stable microemulsions. Water was added to each vial to keep the total weight constant. The factors of surfactant concentration, salt concentration, Shellsol D38 concentration, total co-solvent concentration, and the co-solvent blend ratio were investigated. This resulted in a total of 432 different microemulsion compositions. The formulation components, order of addition, and concentration levels of each component are listed in *Table* 9.

Table 9—Formulation Components: Their Levels and Order of Addition

Component	Order of Addition	Concentrations Tested
Water	1	Balance
Sodium dodecylbenzene sulfonate (LAS)	2	5, 6, and 7 wt%
Sodium chloride (NaCl)	3	0, 0.1, 0.2, and 0.4 wt%
Total co-solvent (alcohol)	—	10, 15, and 20 wt%
1-Butanol : 1-hexanol ratio (for each total alcohol level)	4 and 5	0 : 1 0.33 : 0.67 0.67 : 0.33 1 : 0
Shellsol D38	6	30, 40, and 50 wt%

To prepare the formulations, stock solutions of LAS and NaCl in water were made using The Hamilton Microlab Star liquid handling robot to the required concentrations. For each material, calibrations were performed to correlate the amount of each volume dispensed with the desired mass. This was accomplished using a weighing robot by dispensing known volumes of liquids into tared glass vials and re-weighing the vials. Each calibration volume set was repeated in triplicate to estimate the calibration error. The relationship between target volumes and actual weight for the materials used here was linear in the range of the dispense amounts used. The robot heating stage was used at 50°C to facilitate dispensing of the concentrated LAS stock solutions (25–35 wt%). Prepared formulations were shaken vigorously by hand, and allowed to equilibrate at room temperature overnight. Samples that appeared visually clear and a single-phase were then tested for cleaning using the HTP system.

Images of the formulations were collected using a proprietary high throughput phase identification and characterization robot (PICA II). Photos of each formulation were collected at least 24 hours after preparation. A representative set of such images is shown in *Figure* 12. Fourteen of the 432 formulations prepared formed stable water-in-oil microemulsions (examples of the clear, stable formulations are circled). The microemulsions formulated with the lowest total co-solvent level with a blend ratio of 3.3% 1-hexanol and 6.7% 1-butanol formed stable microemulsions. In addition, formulations prepared with the high level of 1-butanol and no 1-hexanol also formed stable microemulsions. In general, the presence of NaCl in the formulations did not lead to stable microemulsion structures. The level of surfactant (LAS) and level of Shellsol D38 seemingly did not influence the microemulsion stability. This result demonstrates the difficulty of identifying stable microemulsion structures by more traditional bench methods where the number of possible experimental samples is limited.

Preliminary testing of the 14 new microemulsions using the HTP cleaning method indicates that they have excellent cleaning efficacy. A complete evaluation of these new microemulsions via the manual testing protocol is currently in progress at Tate. As per the outlined trials, this multifaceted evaluation will identify if these cleaning solutions demonstrate the full balance of properties required for use in treatment of acrylic emulsion painted works of art. The results from this manual testing will be reported in a separate communication.

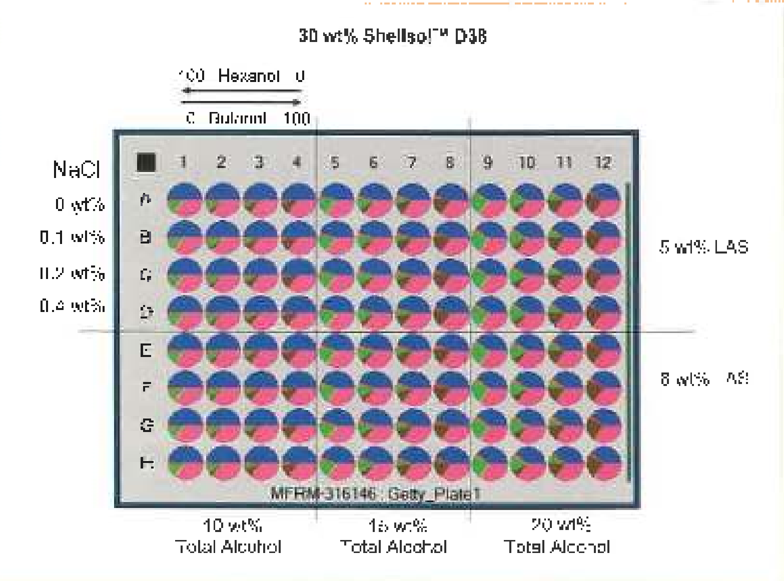


Figure 11—Visual representation of the experimental approach to formulating the new range of microemulsions using a full factorial design of experiments. The full design included 432 formulations. The composition of 96 of the formulations is shown as follows: (Blue=water, red=LAS, green=1-Hexanol, brown=n Butanol, pink=Shellsol D38, yellow=NaCl).

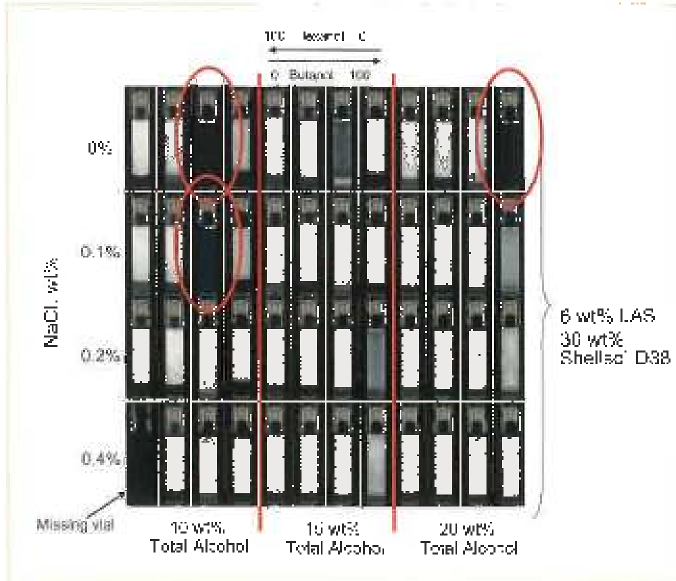


Figure 12—HTP formulation of water-in-oil microemulsions. Stable, clear single-phase formulations are identified by automated image analysis. The 48 formulations shown are the bottom half of the 96 array represented in Figure 11. Clear, colorless formulations (circled in red) indicate a stable microemulsion state.

CONCLUSIONS

A method has been developed to quantify and differentiate the cleaning efficacies of traditional and novel aqueous, aliphatic hydrocarbon solvent, and water-in-oil microemulsion-based cleaning systems using the high throughput tools and methodology at The Dow Chemical Company. Cleaning solutions with good cleaning efficacy were identified from all three classes of formulations by screening hundreds of formulations on the high throughput tools. The results from the high throughput method were validated by established conservation cleaning treatments at Tate, London where the performance of the different cleaning solutions was in very good agreement with the results generated on the high throughput equipment.

One significant finding from this initial work was the identification of water-in-oil microemulsions as a potential new type of cleaning formulation for art conservation that provides high cleaning efficacy with a naphtha-based continuous phase. During manual testing trials at Tate, the cleaning formulations were evaluated for potential risk to the acrylic paint films in addition to the ability to remove soil. The original microemulsion trialed (INVERT™ 5000) demonstrated high risk to the test acrylic paints due to pigment removal and changes in surface gloss. New microemulsions were formulated that aimed to meet all the required performance criteria of high cleaning efficacy and low potential risk. These new microemulsions were found to have outstanding cleaning efficacy from the HTP testing and are currently being evaluated at Tate for a more complete assessment of their cleaning performance.

Overall, the collaboration of the three institutions (Dow, Tate, GCI) was a unique combination of skill sets that is providing critical solutions to the art conservation community. This work demonstrated the use of high throughput methodology for an art conservation science application. Finally, it identified promising new collaborative approaches and materials for cleaning in conservation.

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