A New Approach to Cleaning I: Using Mixtures of Concentrated Stock Solutions and a Database to Arrive at an Optimal Aqueous Cleaning System

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Introduction

The Modular Cleaning Program is a new database system designed to assist the conservator in the cleaning of works of art. The Modular Cleaning Program debuted in September, 2003, at the Verband der Restauratoren (VDR) symposium "Surface Cleaning – Materials and Methods." Version 1.3 of the Modular Cleaning Program was released via Conservation On Line in February of 2004. The Modular Cleaning Program is an interactive computer program that is best understood by demonstration and use. As that option is not available in the context of a written work, we will examine the history of surface cleaning, discuss the features of the cleaning program, and present two case studies.

The Modular Cleaning Program builds upon developments in cleaning theory and extends the theoretical towards the practical. Innovations include the use of pre-mixed, concentrated stock solutions which facilitate the rapid formulation of test cleaning solutions; formulations based on physical constants, equilibrium equations, and other theoretical constructs; and the use of a computerized system to coordinate the mixing and testing of the solutions. While developed from the perspective of paintings conservation, the methodology is universal and applicable to any aqueous cleaning. The first case study will illustrate the removal of a grime layer from an aged varnish. The second, involving the removal of a grime layer from an unvarnished paint surface, demonstrates how the program can expand the repetoire of choices. In this case the conservator found an unexpected solution to the cleaning problem because the program facilitates experimentation.

A Review of Aqueous Surface Cleaning

Historically, in conservation and restoration treatises on paintings, little attention has been paid to surface cleaning in comparison to removing surface coatings. Manuals on the conservation of paintings traditionally have included brief discussions of dry methods of surface cleaning, including the use of dusting brushes and cloths, erasers, and sponges. Foodstuffs, including fresh breadcrumbs, "cakes," potatoes, and onions have also been mentioned (Mora et al. 1984; Keck 1978). Some older published instructions for surface cleaning paintings prove to be quite extraordinary. Theodore De Mayerne's manuscript from the seventeenth century suggests: *"Melt common carpenter's glue, which is quite thick, and pour it, melted over your picture, leave it after it has set... on your picture – then lift it off, all in one piece. This brings with it all the dirt. See if this can come off without damaging the piece (Caley 1990)."*

Water and saliva, used for spit-cleaning, are perhaps the most common materials used for surface cleaning paintings. The addition of materials to water (whether 'de-ionized' or not) has predominantly been limited to the addition of alkalis. Ammonia is perhaps the most common alkali that has been added to water in the twentieth century to adjust the pH of the solution for surface cleaning easel and wall paintings (Mora 1984). The use of methylcellulose gels and paper pulps with water-based systems have also been advocated where prolonged contact with the surface is necessary and/or when mechanical action should be avoided.

Advancements in the petrochemical industry at the end of the nineteenth century led to the development of surfactants and detergents. With these new materials available, the approach to cleaning chemistry became more sophisticated in the twentieth century and commercial, proprietary cleaning products found applications in conservation.

Soaps have long been used in conservation studios even though their exact chemistry may not have been well understood. The use of strong soaps led to a warning against using soaps as a category of cleaning agent in the 1940 *Manual on the Conservation of Paintings*: *"It is perhaps not superfluous to issue a warning against a method of cleaning pictures still in use in recent years in many galleries – washing the painted surface with soap and water. The evil effects of this system are not immediately apparent; but the water may penetrate by capillary attraction through the slightest cracks or fissures in the paint film as far as the priming, which means that sooner or later the film will become detached or swollen, not to mention the bad effects on the varnish (International Institute of Intellectual Co-operation [1940] 1997)."* The addition of "soap" to water-based cleaning systems is sometimes mentioned in cleaning manuals from the twentieth century, however, there is usually no mention of the specific types of soaps nor discussion of their chemical properties.

In the second half of the twentieth century, conservators began using commercial detergents. Detergents found applications in cleaning painted surfaces after having been used in the fields of objects and textile conservation (Plenderleith 1956). For painted surfaces, detergents such as Triton X-100, Synperonic DNB, Igepal, and Vulpex were used (Ramer 1979; Barov 1990; Burnstock 1990). These detergents found wide application since they are soluble in water and/or solvents. Today, Triton XL-80N and Synperonic N are the more commonly used non-ionic surfactants (McCutcheons 2003).

The properties of surfactants have been exploited through the use of proprietary materials such as Photo-flo (developed for use in photography) and even products such as Barbisol, a shaving cream. These types of materials have been used by some conservators as saponifying additives or as additives that help break surface tension in cleaning applications (Rothe 2002).

Alternatives to water-based surface cleaning were also developed, such as those discussed by the paintings conservator Helmut Ruhemann in his description of the proprietary material "Cleaning, Reviving, and Preserving Paste" from C. Robertson in London: *"Alkaline wax emulsions are often used for removing this dirt surface. The widely used mixtures of much diluted wax and varnish have the great disadvantage of removing only part of the dirt and fixing the rest. Moreover they dry so slowly that they collect a great deal of dust before they are hard (Ruhemann 1968)."*

From mid-century onward a number of conservators began publishing their own formulations for surface cleaning systems. Some of the more famous formulations include "AB 57," which was introduced by Philipo and Laura Mora for surface cleaning insoluble salts that compromise inorganic incrustations on wall paintings (Mora 1984).

In the late 1980s Richard Wolbers introduced new approaches to cleaning paintings in a series of five annual workshops conducted at the Getty Conservation Institute (Wolbers 1988). His recent book, *Cleaning Painted Surfaces,* is devoted to the subject of aqueous methods. It is important to note that Wolbers' methodological approach to the subject of surface cleaning may be applied to all types of painted surfaces. Wolbers advocates designing cleaning systems specific to the materials and cleaning challenge presented.

Leslie Carlyle was perhaps the first paintings conservator to find application for chelating agents in surface cleaning painted surfaces (Carlyle 1990). Wolbers incorporated them into his cleaning workshops in the late 1980s. Chelating agents found wider application in conservation in the mid 1980s and were the subject of a number of published research projects (Carlyle 1990; Phenix 1992).

In 1990 the conference "Dirt and Pictures Separated" was held. Papers presented at the conference, and published under the same title, addressed the chemistry of surface cleaning materials as well as the effects of surface cleaning on painted surfaces. Specific surfactants and cleaning agents discussed in the papers included Triton X-100, Synperonic N, di- and tri-ammonium citrate (Hackney 1990).

The developments in cleaning chemistry have led conservators to understand traditional methods of surface cleaning better. Towards the end of the twentieth century, conservators have tried to imitate the cleaning chemistry and properties of saliva for surface cleaning. Formulations that have been described as "synthetic saliva" have been published (Bellucci 1999; Wolbers 2000).

The Modular Cleaning Program extends and facilitates the development of surface cleaning by use of a computer, much as earlier programs ("TeasTime," Henry 1995; "Triansol: il Triangolo delle solubilità," Cremonesi 1999; "Solvent Solver," Ormsby 2001) assisted conservators in their approach to solvent cleaning. Also like these other programs, the Modular Cleaning Program is shared, at no cost, with the conservation community.

The Basic Principles

From 1997 to 2001 Richard Wolbers collaborated with the Getty Conservation Institute in development of the Gels Research Project to evaluate alternative methods of cleaning (Dorge 2004). An aspect of this project was the discussion of a "logic tree" approach to selecting cleaning systems – intended to be an insight, as it were, into Professor Wolbers' thought process when selecting a cleaning system (Dorge 2004, 141-144). The nascent system, as it applied to water-based cleaning, was modified and built into the Modular Cleaning Program by Chris Stavroudis.

The aqueous cleaning systems introduced by Richard Wolbers can be considered to consist of five orthogonal components (mutually independent components). They are: water, pH buffer, chelating agent, surfactant, and gelling agent. For this reason, the concentrate system is based on a module of five. The test cleaning solutions are made to a total of five parts, which may include some or all of the five components. (If only one or two components are being tested, water is added to make up the total of five parts.) Hence, each stock solution is concentrated five times its normal working concentration. The computer screen has also been divided into five rows. Each row represents one of the five components, or more practically, one milliliter of a concentrated stock solution.

For example, to make a test solution, one mL of water is combined with one mL of a buffer concentrate solution plus, optionally, one mL of concentrated chelating agent solution, and/or one mL of concentrated surfactant solution, and/or one mL of concentrated gelling agent. If necessary, water is added to make up the final total volume of 5 mL.

The Modular Cleaning Program and the use of concentrated stock solutions allows the conservator to test a large range of mixtures in a short period of time. Since the program allows conservators to test far more cleaning options than they would normally have time to test, it is hoped that conservation treatments can continue to move toward more delicate and sensitive cleanings.

The first parameter to consider in formulating an aqueous cleaning system is pH. Control of pH is important in aqueous cleaning systems. As a general rule, as materials age they oxidize. In organic materials, oxidation leads to the formation of acid functional groups on the surface exposed to oxygen in the air. The acid forms of the oxidized molecules tend to be less soluble in water than the deprotonated salt forms. Since acids react with bases, a higher pH will tend to deprotonate the acid and render it more soluble in water. So, as a general rule, higher pHs will assist in the solubilization of the oxidized material while lower pHs will tend to preserve an oxidized surface.

By buffering a cleaning solution, we ensure that the chosen pH of a solution is maintained during the cleaning. Buffers are weak acids or bases that, at certain pH values, minimize changes in the pH of a solution when additional acid or base is added to the mixture. Buffering a cleaning solution prevents the pH of the cleaning solution from changing as the oxidized organic material dissolves in the course of the cleaning.

Buffers are characterized by their pKa, their acid dissociation constant. Analogous to pH, the pKa is the pH of an aqueous solution, which contains equal parts of the acid form of the buffer and its base form. This is also the pH where the buffer will function most effectively at preventing pH changes from small additions of acid or base to the solution. A weak acid or base will function as a buffer within about 1 pH unit of its pKa value.

The Modular Cleaning Program uses the molecular weight of the buffer and its pKa to perform one of its primary functions, the calculation of the desired amounts of reagents to be mixed into concentrated stock solutions. The concentration of the buffer solution is specified by the conservator. Based on measurements by Richard Wolbers, the recommended target buffer concentration for paint surfaces is 0.05M. Therefore the concentration of the concentrated buffer stock solution is 0.25M (since it will be diluted by 5 when incorporated into a test cleaning solution).

On the computer screen each row is divided into three columns (fig. 1). The center column has buttons which allow the properties of the test cleaning solution to be modified. In the case of buffers, the conservator can choose to increase or decrease the pH of the test solution. Changing the pH usually means changing the buffer used (Tris, bicine, MES, etc.) because each weak acid or base has only a limited buffer range.

This correlates with choosing a concentrated stock buffer solution to be used when mixing a test cleaning solution. Above the buttons is the description of the concentrated stock solution. In Figure 1, the pH 7.5 buffer is Tris (2-amino-2-(hydroxymethyl) propane-1,3-diol), neutralized with hydrochloric acid (HCl), the chelating agent is citric acid pH adjusted to 7.5 with sodium hydroxide (NaOH), and the surfactant is Triton XL-80N, a nonionic surfactant.

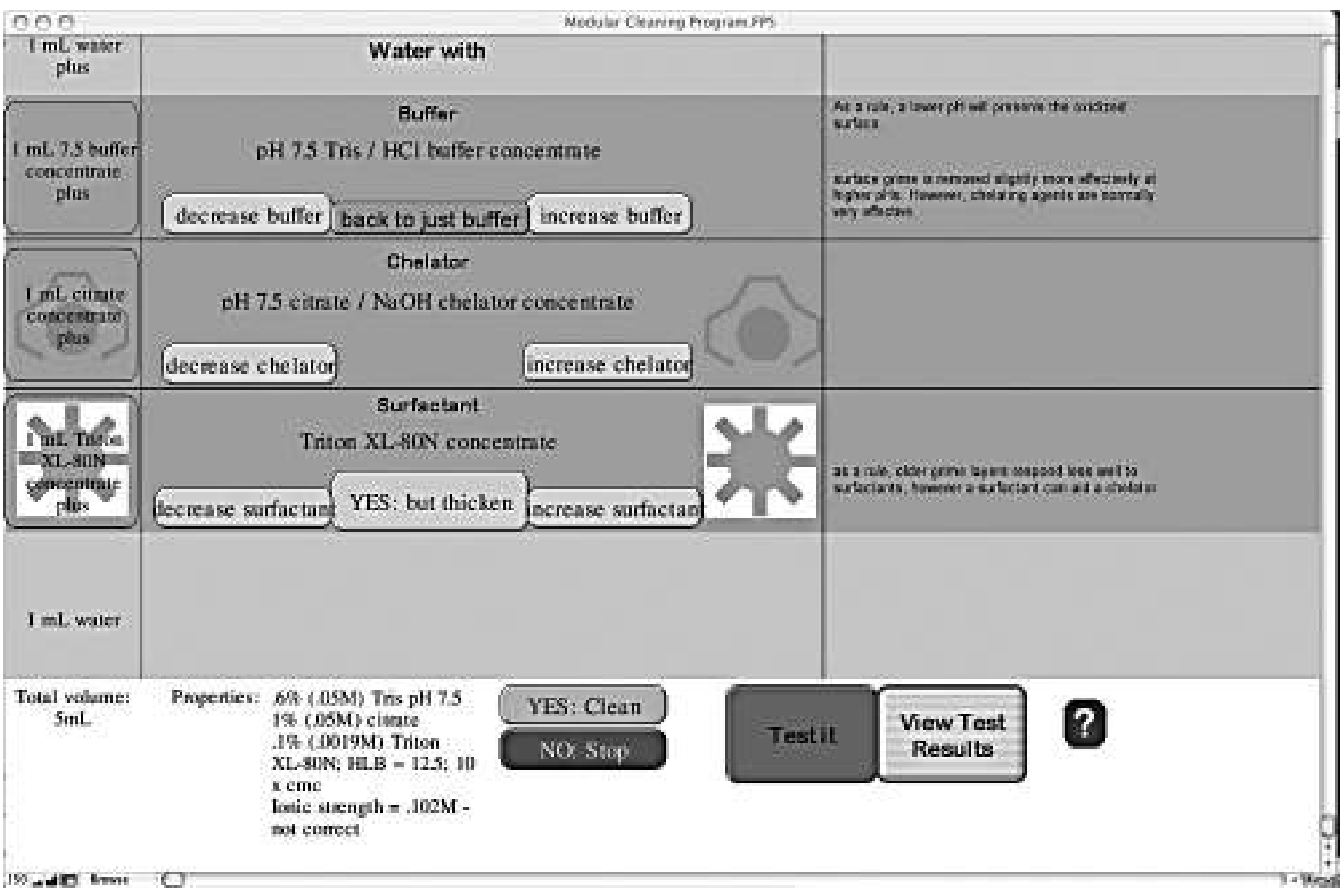
The left column shows the amount of the concentrated stock solution to be added to the test cleaning solution and a logo that is used to distinguish each solution. The logo also appears on the concentrated stock solution's label. Clicking on the logo takes the conservator from the "Modular Cleaning Program" database to the "solutions" database, described later.

The right column shows hints or comments pertinent to the type of work being treated, such as how pH will affect an aged varnish layer or how pH influences the removal of the aged surface grime. Hints have been built into the database for some of the materials to be found on paintings. As the program is used by more conservators, hints will be added and expanded. The comments are not by any means a suggestion as to how the work of art should be cleaned, but rather a reminder of how each component of a cleaning system might affect what is to be removed and how it might affect the substrate.

The background color of the rows in the Modular Cleaning Program change to indicate the pH of the test cleaning solution. (The colors were chosen to resemble those of pH test papers.)

In addition to water and a pH buffer, test cleaning solutions can be mixed to include surfactants, chelating agents, and gelling agents. When using the system, the conservator would choose to add these components based on the progress of the test cleaning. They can be added to the testing scheme in any order. The following paragraphs will discuss each of these agents and how they are integrated into the Modular Cleaning Program.

Figure 1. The Modular Cleaning Program's aqueous test cleaning screen. Shown is a test cleaning solution consisting of water and Tris buffered to pH 7.5 with citrate added as a chelator and Triton XL-80N added as the surfactant. No gelling agent has been specified so the 5th component, an additional 1mL of water, indicated by the lower band brings the final volume of the test cleaning solution to 5mL.



The term surfactant is derived from "surface active agent" and is an encompassing term that refers to detergents, soaps, emulsifiers, wetting agents, and resin soaps. The first property we need to know about a surfactant is whether it is ionic or nonionic. A nonionic surfactant is a neutral species in solution, neither an acid nor a base. In practical terms, this means it can be used predictably at any pH. Ionic surfactants can be anionic (the surfactant molecule is an acid), cationic (a base), or zwitterionic (where the molecule consists of both acidic and basic functional groups). If a surfactant is anionic or cationic, being an acid or a base, it is further characterized by a pKa. The pKa and, if known, the solubility of the fatty, undisassociated molecule in water determine the minimum pH at which the surfactant can be used. If these values cannot be found in the literature, the database also accepts an ad hoc measurement of the pH at which the ionic surfactant solution separates into two phases, water and an oily or solid phase.

The other parameters that describe a surfactant are HLB, CMC, and aggregation number (plus its molecular weight). HLB is the hydrophilic lipophilic balance number, a measure of the relative size of the water-soluble portion of the surfactant in relation to the fatty portion of the molecule. Anionic surfactants can have HLB values as high as 40 (like sodium lauryl sulfate – Orvus), but non-ionics have a maximum HLB value of 20.

CMC stands for the critical micelle concentration. Detergency occurs when a critical amount of a surfactant in solution is reached and the surfactant molecules group into micelles. In an aqueous solution, the surfactant molecules orient themselves with their fatty ends to the inside and the water soluble ends to the outside of the micelles. Micelles can form around fatty, non-polar material and aid its being carried away in water. The concentration where micelles just begin to form is termed the critical micelle concentration. When formulating a detergent, you want to have surfactant present in excess of the CMC, so it can carry grime away, but not too much of an excess because that will have a tendency to leave excess detergent behind, complicating rinsing and clearance.

The aggregation number is the average number of surfactant molecules that form into a micelle. The aggregation number is characteristic for each surfactant. The larger the number the more surfactant you will have to put into solution in excess of the CMC to get a given concentration of micelles. A lower aggregation number means you can use a bit less surfactant.

The Modular Cleaning Program allows the surfactant to be specified either as a simple concentration or as a multiple of the CMC. A typical value is to have the working concentration of the surfactant at 5x the CMC, which means that the concentrated stock solution is at 25x the CMC. When both the CMC and aggregation numbers are known, the program also calculates the micelle concentration.

Surfactants are added to the test cleaning solution in the database by clicking on the "Yes, But Modify" button. As with the buffer, the surfactant can be increased or decreased by clicking on the buttons in the center column, selecting higher or lower HLB surfactants. The computer will not recommend an ionic surfactant below its critical pH.

A chelating agent, is a molecule capable of binding to a metal ion and bringing the metal ion into solution. The chelating agents conservators commonly use for surface cleaning are citric acid (as various citrates) and EDTA (ethylenediaminetetraacetic acid). Chelating agents have multiple coordination sites, which allow the molecule to envelop and bind to a metal ion.

Many of the coordination sites on a chelating agent are carboxylic acid groups, so chelating agents are specified by multiple pKa values – citric acid has three acid groups, EDTA has four, and DTPA (diethylenetriaminepentaacetic acid) has five carboxylic acid groups, each having a different pKa value. At any given pH, the chelating solution will contain molecules with various combinations of disassociated acid groups. The amount of each species in solution is calculated by the computer at each concentrated stock solution's pH.

The effect of pH on chelating agents is very complex, and a thorough discussion of the topic is beyond the scope of this paper. One consequence of the complexity is that while some concentrated stock solutions can function at any pH, for instance you only need one bottle of a concentrated nonionic surfactant stock solution which can be added to any test cleaning solution, a separate concentrated chelating agent stock solution must be mixed for each pH.

Chelating agents are also characterized by their affinities (formation constants) for different metal ions. These formation constants will be used in a future version of the database to calculate the necessary concentrations of metal ion buffers to be added to a cleaning solution to minimize solubilization of a desirable ion, i.e. one that is part of the work of art. In this current version of the Modular Cleaning Program the formation constant for the calcium ion is used as the indication of strength of the chelating agent. Clicking the increase or decrease buttons for chelating agents in the database selects chelating agents with higher or lower values of the calcium formation constant.

Test cleaning solutions may also be gelled by adding a concentrated gelling agent. The database supports nonionic (cellulose ethers) and cationic (Carbopol) gelling agents. In practice, using the gelling agents is difficult because the concentrates, being five times the gel's working concentration, are very stiff and difficult to disperse in the test solution. The gelling agents are ranked by their viscosity at a given concentration.

There exist many other ways to modify an aqueous cleaning system, and many of these will be incorporated into future versions of the Program. These modifications can be made by the conservator now, but are not supported by the database. The addition of co-solvents (small amounts of organic solvents), ionic buffers (soluble salts to modify the ionic strength of the test cleaning solution), enzymes, and multiple surfactants are all possibilities.

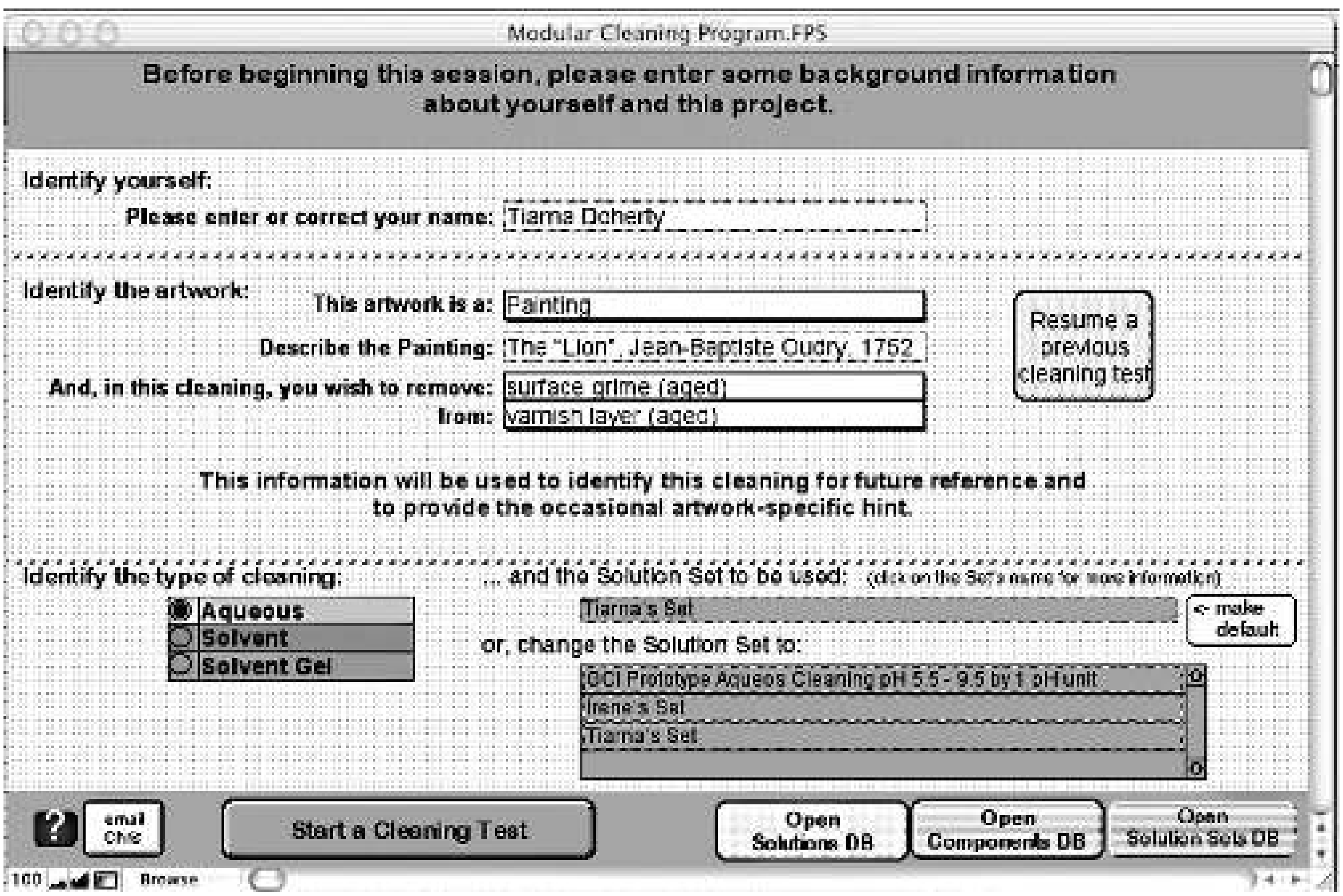
The Modular Cleaning Database is comprised of 19 interrelated databases. However, from the user's perspective, the system is made of five main parts. When the Modular Cleaning Program is started, after the "welcome" screen, the conservator is taken to the "background" page (fig. 2), where the parameters of the cleaning are established. This is where the work of art and conservator are identified, and the material being removed and the substrate from which it will be removed are entered. There are buttons on the "background" page to take the conservator to the "components" database, the "solutions" database, and the "solution sets" database.

The "components" database is the most conventional database with which the conservator will interact. It contains information on hundreds of chemicals used in conservation: buffers, chelating agents, surfactants, gelling agents, acids, and bases from which the concentrated stock solutions are mixed. It also includes solvents, which will be used in future versions of the software, and even some polymers and resins. It lists chemical composition, physical properties, and may list health and safety information, the MSDS, and include a link to the information in the most current NIOSH (the US National Institute for Occupational Safety and Health) Pocket Guide to Chemical Hazards. (Not all chemicals in the database have NIOSH listings.) The MSDS information in the database is taken from Internet sources and is listed as an information-only reference. Conservators should always consult the MSDS sheet provided by their chemical supplier.

The physical chemical constants included in the "components" database in most cases include a reference to the publication from which they were taken. Numerous sources were consulted (Freiser & Fernando 1963; Weast 1972; Freiser 1992; Huibers 1996; Wolbers 2000; Lide 2002; Harris 2003; McCutcheon's 2003). In the case of surfactants, finding the necessary physical properties and physical constants has been challenging since many of these properties seem never to have been quantified as they are so complicated to measure precisely.

The "solutions" database is where components are mixed together to make the concentrated stock solutions. The database performs numerous calculations based on the physical constants located in the "components" database. Because the pH values of the concentrated solutions are known (having been chosen by the conservator and been set with a pH meter) the complex ionic equilibrium equations can be solved exactly. The "solutions" database also calculates recipes and mixing directions for the concentrated stock solutions and formats the appropriate labels that can be printed to identify the concentrated stock solution containers.

Figure 2. The "background" page where the parameters of a cleaning are selected by the conservator.



The "Modular Cleaning Program" database combines the concentrated stock solutions from the "solutions" database to make the test cleaning solutions. This database calculates the solution properties of all the components in the test cleaning solution. Though it only ever possesses one record, that is, the test cleaning solution that is being evaluated, the database combines information from almost all of the other databases to allow the conservator to orchestrate the testing process. When the optimal cleaning solution has been determined by testing, it calculates the formula of and recipe for the cleaning solution.

The "solution sets" database organizes and builds families of the concentrated stock solutions into sets that can be chosen by the conservator at the start of a treatment. In the future, customized sets of concentrated stock solutions may be developed for special cleaning problems like the cleaning of acrylic paint surfaces or stain removal from marble. There is also a database that keeps track of the testing process. When the "Test it" button is clicked, that Modular Cleaning Program database copies the relevant information about the current test cleaning solution into the "test it" database. The conservator is prompted to enter information about the test cleaning solution's effect on the material being removed and on the substrate, which should be preserved. This information is retained and can be viewed (by clicking on the "view test results" button) or printed out (by clicking the "print" button from the view test results page) to document the testing process that led to an optimal cleaning solution. It also allows testing to be resumed in cases where the testing is interrupted.

Navigation through the databases is simple and intuitive. All navigation is via mouse clicks, either on buttons or on key words on the screen. Specific knowledge of FileMaker Pro is not necessary to use the program. During a cleaning test, clicking on the left, logo column of a cleaning component will take the conservator to the information in the "solutions" database for that concentrated stock solution (fig. 3).

From the "solutions" database, clicking on the button bars for any of the ingredients that comprise the concentrate takes the conservator to the information on that material in the "components" database (fig. 4).

From the "components" database, clicking on the "Properties" button takes the conservator to the physical and chemical information that is specific for that material (fig. 5) (The kind of information presented for a chelating agent is different from that for a surfactant.)

Figure 3. The specification of the pH 7.5 Tris buffer concentrated stock solution as displayed in the "solutions" database.

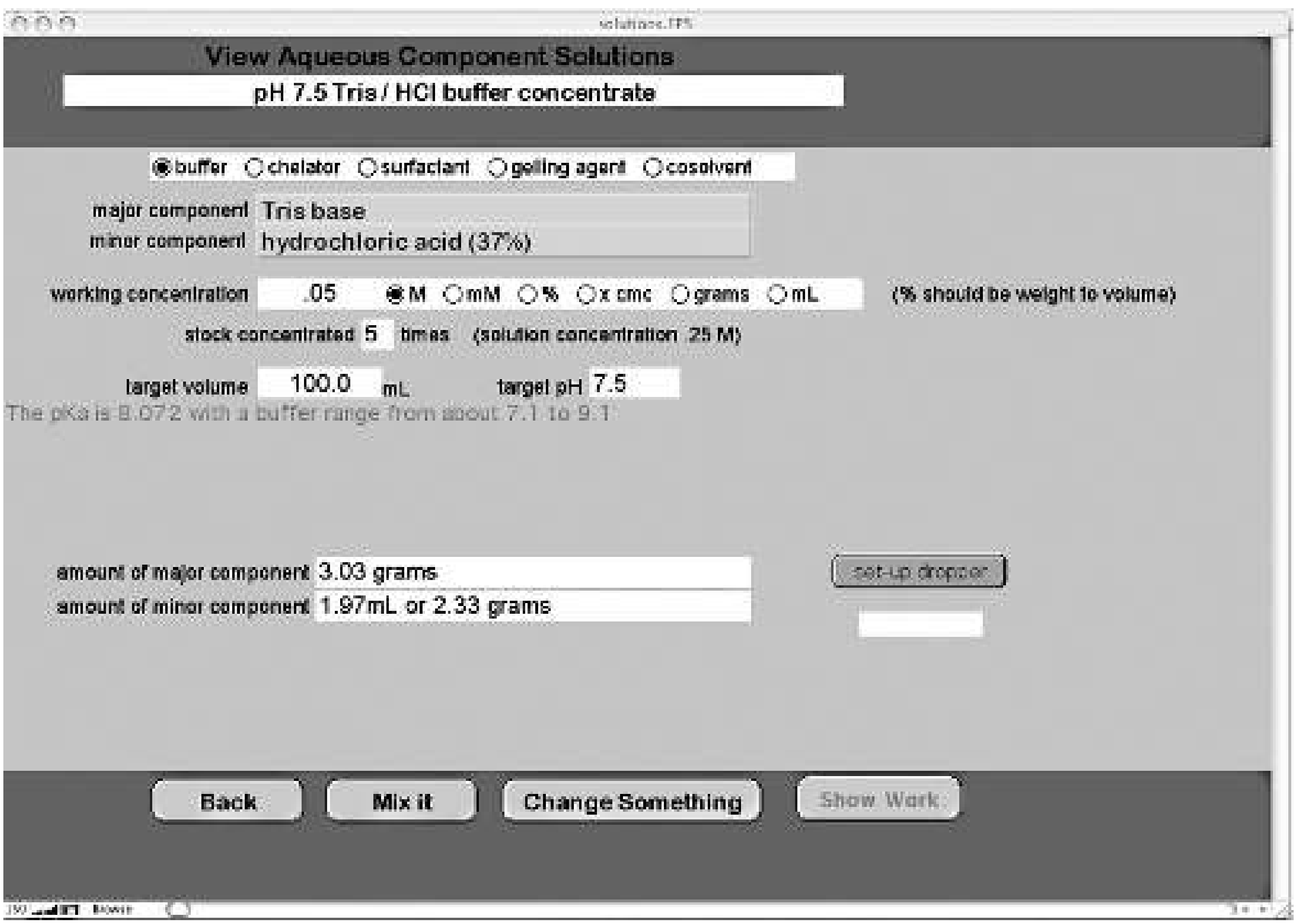


Figure 4. The information on Tris displayed in the "components" database.

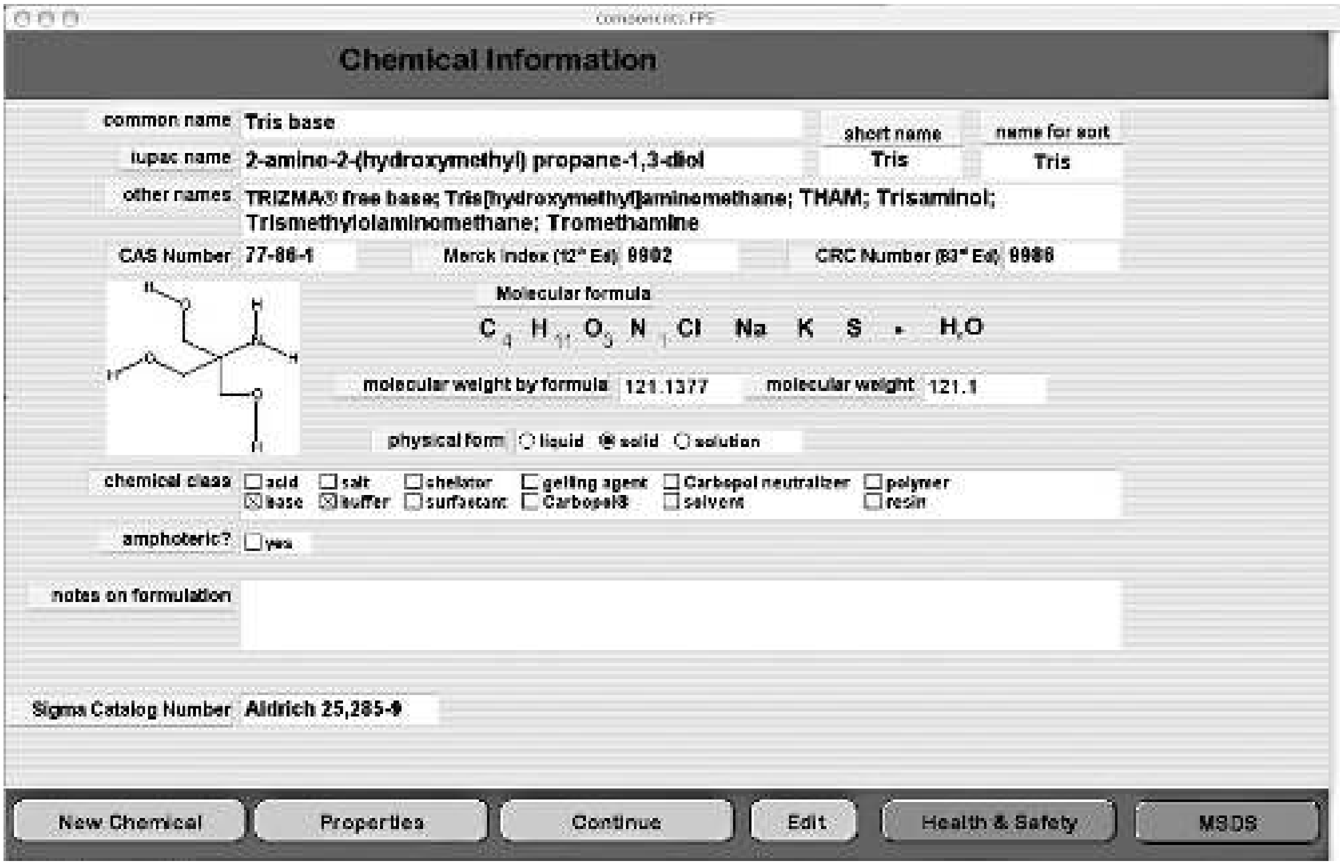
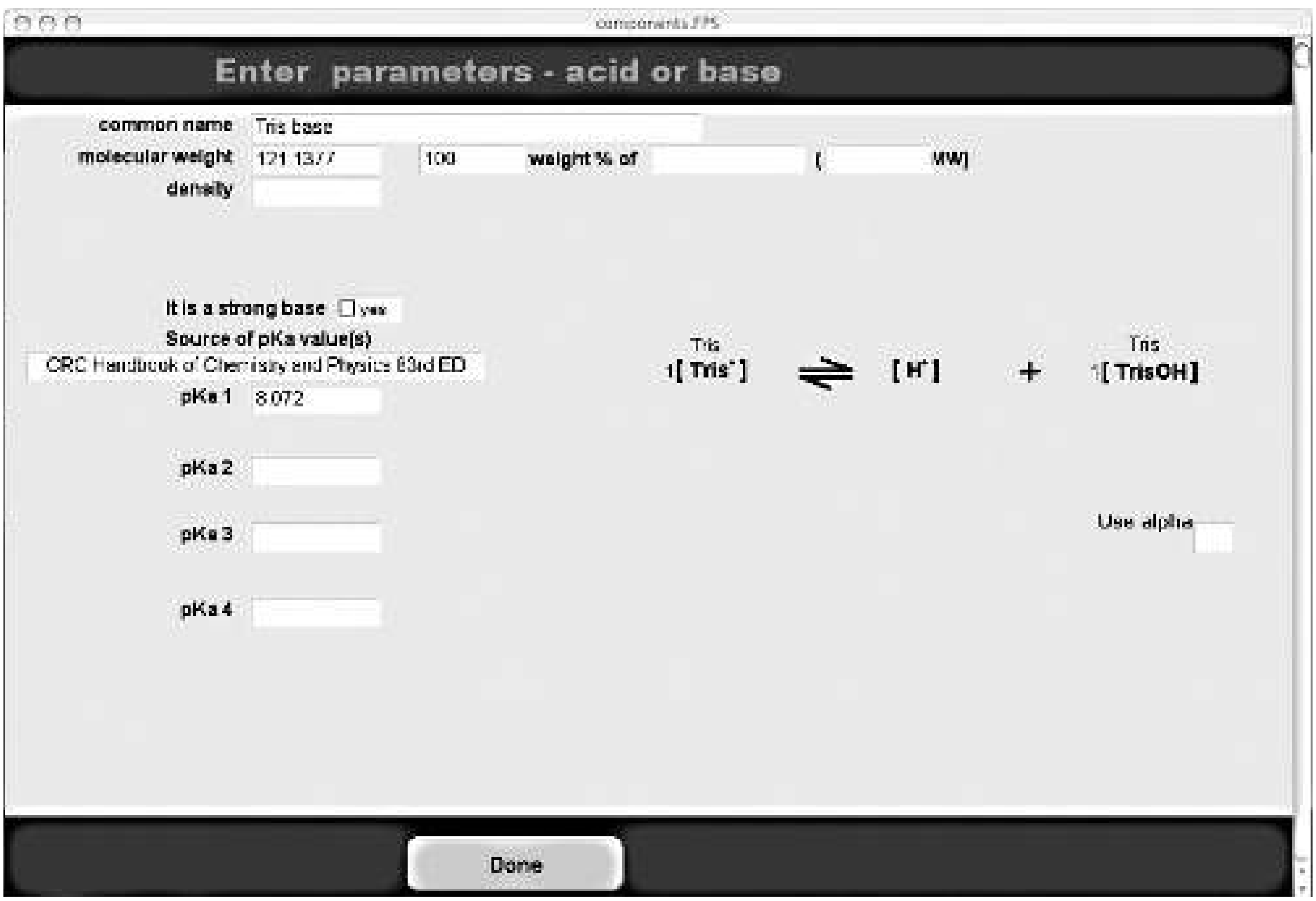


Figure 5. The properties of Tris as displayed in the "components" database.



Clicking on buttons takes the conservator deeper into the database. To return to the previous screens, the conservator need only click on buttons labeled "Back," "Done," or "Continue," depending on the context.

The Modular Cleaning Program is designed for the conservator to modify and extend. Because all of the calculations are based on physical properties, you can integrate a new material into your testing by simply entering it in the components database, adding the required physical properties, building the cleaning solutions, and adding the solutions to an existing solution set or creating a new solution set.

While the inner workings of the database are intricate and complex, using the system is easy and fast. A test cleaning solution can be made in less than a minute from the stock concentrate solutions. It is possible and appropriate to test numerous combinations of the stock concentrate solutions to arrive at the optimum cleaning result.

The Modular Cleaning Program in Use

Case Study I

To demonstrate the cleaning system in use, the surface cleaning of the *Lion* by Jean-Baptiste Oudry (fig. 6) will be described here. The *Lion* (signed and dated 1752), along with eleven other portraits of animals painted by Jean-Baptiste Oudry, was bought by the Duke of Mecklenberg-Schwerin in the mid-eighteenth century and remains in the collection of the Staatliches Museum Schwerin. The *Lion* measures 310 x 256.5 centimeters (122 x 101 inches). There is very little documentation regarding the display and conservation history of this painting. One of the largest paintings in the collection, the *Lion* has been in storage since the mid to late 19th century (Michels 2002). The smaller paintings in the collection appear to have been on display continuously and have thus been part of conservation and restoration campaigns. The painting is being conserved at the Getty Museum in consultation with conservators and curators at the Staatliches Museum Schwerin, Germany. Tiarna Doherty, Assistant Conservator of Paintings at the J. Paul Getty Museum, is cleaning the painting.

Figure 6. The *Lion* by Jean-Baptise Oudry seen on a temporary stretcher in the paintings conservation studio of the J. Paul Getty Museum in 2002.

When examined in 2001, the *Lion* had a very uneven surface due to the effects of aged varnish and a considerable amount of surface grime. It was decided that the approach to cleaning the *Lion* was to be two-fold: surface cleaning would be done before the varnish would be thinned or removed. This meant that the cleaning tests would be narrowly targeted to distinguish between the solubilities of the different layers. After removal of the dirt layer it would be easier to control the thinning or removal of varnish, thus allowing for a slow and balanced aesthetic cleaning.

In the preliminary examination of the painting, water and spit-cleaning tests were performed to see how much dirt could be removed from the surface. While it was evident that the painting was very dirty, little could be removed using water or saliva alone. It was anticipated that surface cleaning would require a modified water-based system. Fortuitously, the treatment of the Oudry painting coincided with the development of the Modular Cleaning Program.

After verifying that the paint and substrate were not adversely affected by water, the surface grime was tested with pH buffered water. Disposable polyethylene pipettes were used to measure the concentrated stock solutions (fig . 7)

Figure 7. Picture of cart with laptop computer and concentrated stock solutions in front of the *Lion*.

Figure 8. Detail of pipettes and measuring cups used with the concentrated stock solutions.

into small, polyethylene "weighing" cups, which were used to hold the test mixtures (fig . 8).

The beginning step was to take 1 mL of distilled water, 1 mL of the concentrated buffer stock solution, and three additional mLs of distilled water and mix them in a numbered weighing cup. Five mLs of test solution are sufficient to evaluate the cleaning potential of the test cleaning solution in a number of areas on a painting.

The surface cleaning tests at pHs 5.5 and 6.5 were not substantially more effective than water alone. Water buffered to pH 7.5 was able to remove some surface grime.

At pHs above 6.5 with citrate chelating agent (in addition to the buffer and a surfactant), some yellow-colored material was observed on the swab. It was surmised that the yellow material was degraded varnish removed from the surface. As the goal of the cleaning was to leave the varnish entirely intact, testing was continued without chelating agents.

Ultimately, water buffered to pH 8.5 with the addition of Triton XL-80N was found to remove the dirt effectively without seeming to disturb the degraded varnish layer. This solution was cleared by rinsing the surface with water buffered to pH 8.5.

The cleaning tests for the Oudry progressed through 35 solutions. There were often subtle differences in both the handling and the cleaning effect of the solutions. An advantage to using the computer to assist in the testing is that it keeps track of the testing progress. By numbering the polyethylene cups to match the tests, and entering the conservator's observations for each test into the computer, a detailed record of the testing process is produced.

Once the optimal cleaning system is determined one can choose the "Yes: Clean" button, which will calculate the amount of materials in the solution for a specified volume and provide mixing instructions so the conservator can prepare a larger batch of the cleaning solution.

Figure 9. *Portrait of Elisha Caleb Dean*, 1854, by Solomon Nunes Carvalho. Photograph before treatment in specular light showing the uneven, leathery surface.

The Modular Cleaning Program in Use

Case Study II

The treatment of *Portrait of Elisha Caleb Dean*, 1854, by Solomon Nunes Carvalho demonstrates how the Modular Cleaning Program can allow the conservator to find a cleaning solution that otherwise wouldn't have even been tested. The painting belongs to a private party and was treated by Chris Stavroudis, Conservator in Private Practice.

The Carvalho portrait is an oil (est.) painting on canvas. It is stretched over a wooden panel and measures 11" x 10" (fig. 9). The painting was framed in an oval frame, protecting the corners of the painted surface. It appeared that the painting had never been removed from the frame. While it had been abused, it did not seem to have ever been abused by a conservator. The painting was unvarnished.

The surface of the painting was leathery and uneven. Because it had never been varnished or treated before, it was assumed that the surface grime was strongly adsorbed and that the surface had oxidized to a considerable extent. Therefore, to minimize the risk of dissolving original material, test cleanings were started at a low pH.

Testing with the Modular Cleaning System, buffers alone were not effective (neither was water or "spit cleaning"). Higher pHs were observed to cause blanching. Testing with surfactants added to buffers was not particularly helpful, although they did remove slightly more grime. This is to be expected. Research on soiling has demonstrated that fresh grime is readily removed by surfactants, but aged grime requires a chelating agent (Wolbers 1992; Phenix & Burnstock 1992).

Tests with citrate as a chelating agent (along with the buffer and surfactant) were found to work much better, but left the surface dull and cloudy. Upon Richard Wolbers' recommendations for the original "logic tree," an EDTA stock solution had been incorporated into the stock solution set. The conservator was unfamiliar with cleaning with EDTA and presumed it to be too strong a chelating agent to use on a painted surface, however tested it nonetheless. When applied to a small area, the recovered surface was beautiful.

The painting was cleaned with a solution mixed from the Modular Cleaning System – pH 5.5 (MES buffer) with Brij 700 and 0.05M EDTA and a small amount of HPMC to thicken the solution slightly. It was cleared with carbonated distilled water (acidic itself), and the whole surface was rolled with xylene. Establishing the optimum cleaning solution required the mixing of 12 test solutions, taking perhaps 20 minutes.

The recovered surface was almost presentable as it was, although it was a bit dry and under-saturated. In this case, the unexposed corners of the painting were a reference to the degree of saturation appropriate for the painting. The surface was lightly misted with a tiny amount of dammar varnish, which was brushed out with a dry brush (fig. 10).

Figure 10. Carvalho painting after treatment installed in its original oval-matted frame.

Conclusion

The Modular Cleaning System and the use of concentrated stock solutions allows the conservator to test a large range of cleaning solutions in a short period of time. By testing far more cleaning options than can normally be mixed and tested, the conservator can continue to move toward more delicate and sensitive cleanings. The database and the design of the modular concentrated stock solutions allow the conservator to concentrate on the aesthetics of a cleaning rather than on the mechanics of mixing cleaning solutions.

The Modular Cleaning Program calculates the formulations of both the concentrated stock solutions and the test cleaning solutions based on physical constants. This brings a rationality to the cleaning of works of art that historically was based on an almost ritual reliance on formulas. The availability of physical constants with references to their sources as well as health and safety information just a few mouse clicks away saves the conservator numerous trips to reference books.

Once the conservator has prepared the concentrated stock solutions they may be kept at-hand in the studio. Nearly all have excellent shelf lives and since such small volumes are used for testing, the set will last for a good number of test cleanings. For smaller works of art, the final cleaning solution can actually be made from the concentrates. The entire testing process minimizes waste.

By allowing conservators to correlate the effectiveness of a cleaning with the modular components, the Program reinforces the understanding of modern cleaning theory. The system may also find application in conservation training programs.

The Modular Cleaning System is evolving. In the planning for future versions are:

- A discussion of test solution clearance (rinsing) and recommendations for clearance of each test solution.
- The ability to use two surfactants in the same test solution.
- The ability to add co-solvents, small amounts of organic solvents that extend the capabilities of an aqueous cleaning system.
- The ability to add ionic strength buffers.
- The ability to add metal ion buffers to minimize solubilization of desirable metal ions from the substrate.
- A comprehensive help system.

The system has some problems and limitations:

- It will never adequately handle emulsion based cleaning systems.
- FileMaker Pro does not support extremely complex mathematics or the generation of dynamic charts or graphs.

And a final limitation, The Modular Cleaning System is a tool to assist conservators in their decision making. Computers cannot clean works of art. A database will never replace the intelligence and "eye" of the conservator.

The Modular Cleaning System is being distributed to professional conservators and may be downloaded from CoOL (Conservation On Line) at http://palimpsest.stanford.edu/byauth/stavroudis/mcp/. There are versions of the software for Windows and Macintosh operating systems. The 19 interrelated databases can be downloaded by conservators who already own FileMaker Pro (version 5.0 through version 6.0). Conservators who do not own FileMaker can download the databases bundled with a runtime version of FileMaker Pro. There are runtime versions for Macintosh System 9, Macintosh OS-X, and Windows 98 and higher.

To prevent its use by amateurs, the Modular Cleaning Program requires a serial number before it can be opened for the first time. Professional conservators may register with Chris Stavroudis to obtain a serial number. Registered users will also be notified when updated versions of the software is available.

Please note: No technical support will be provided. The software is under copyright and may not be sold or distributed. Modifications made by other parties must be shared with the user community.

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Sources of Materials

Software:

FileMaker® Pro Developer 5.5 and FileMaker® Pro 6.0
FileMaker, Inc.
5201 Patrick Henry Dr.
Santa Clara, CA 95054
(408) 987-7000

Supplies:

Disposable Polyethylene Pipette (1/2 mL. graduation. 3 mL draw. 7 mL Capacity)

Weighing Cups (Polyethylene, graduated. Total capacity is 30cc)

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Chemicals frequently used in stock solution sets (acids, bases, buffers, chelating agents, co-solvents, surfactants):

Sigma catalog:

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